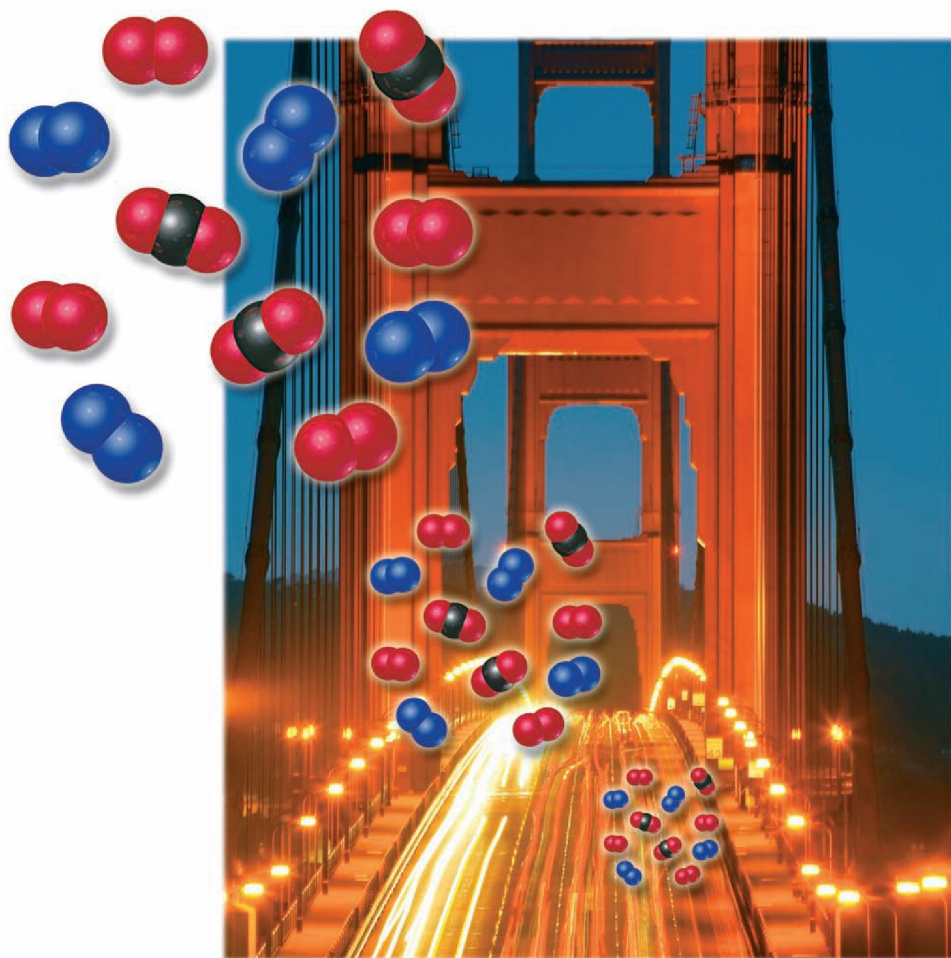


CHAPTER
15

CHEMICAL
EQUILIBRIUM



TRAFFIC ENTERING AND LEAVING San Francisco over the Golden Gate Bridge in the early morning.

15.1 The Concept of Equilibrium

We begin by examining the concept of equilibrium.

15.2 The Equilibrium Constant

We then define the *equilibrium constant* and learn how to write *equilibrium-constant expressions* for homogeneous reactions.

15.3 Interpreting and Working with Equilibrium Constants

We also learn how to interpret the magnitude of an equilibrium constant and how to determine the way in which its value is affected when the chemical equation is reversed or changed in some other fashion.

15.4 Heterogeneous Equilibria

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

15.5 Calculating Equilibrium Constants

We will see that the value of an equilibrium constant can be calculated using equilibrium concentrations of reactants and products.

15.6 Applications of Equilibrium Constants

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

15.7 Le Châtelier's Principle

We conclude the chapter with a discussion of *Le Châtelier's principle*, which predicts how a system at equilibrium responds to changes in concentration, volume, pressure, and temperature.

TO BE IN EQUILIBRIUM IS TO BE IN A STATE OF BALANCE. A tug of war in which the two sides are pulling with equal force so that the rope does not move is an example of a *static* equilibrium, one in which an object is at rest. Equilibria can also be *dynamic*, as illustrated in the

chapter-opening photograph, which shows cars traveling in both directions over a bridge that serves as an entranceway to a city. If the rate at which cars leave the city equals the rate at which they enter, the two opposing processes are in balance, and the net number of cars in the city is constant.

We have already encountered several instances of dynamic equilibrium. For example, the vapor above a liquid is in equilibrium with the liquid phase. ∞ (Section 11.5) The rate at which molecules escape from the liquid into the gas phase equals the rate at which molecules in the gas phase strike the surface and become part of the liquid. Similarly, in a saturated solution of sodium chloride the solid sodium chloride is in equilibrium with the ions dispersed in water. ∞ (Section 13.2) The rate at which ions leave the solid surface equals the rate at which other ions are removed from the liquid to become part of the solid. Both of these examples involve a pair of opposing processes. At equilibrium these opposing processes are occurring at the same rate.

In this chapter we will consider yet another type of dynamic equilibrium, one involving chemical reactions. **Chemical equilibrium** occurs when opposing reactions are proceeding at equal rates: The rate at which the products are formed from the reactants equals the rate at which the reactants are formed from the products. As a result, concentrations cease to change, making the reaction appear to be stopped. How fast a reaction reaches equilibrium is a matter of kinetics.

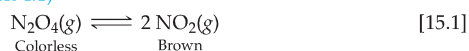
Chemical equilibria are involved in a great many natural phenomena, and they play important roles in many industrial processes. In this and the next two chapters, we will explore chemical equilibrium in some detail. Here we will learn how to express the equilibrium position of a reaction in quantitative terms. We will also study the factors that determine the relative concentrations of reactants and products in equilibrium mixtures.

15.1 THE CONCEPT OF EQUILIBRIUM

Let's examine a simple reaction to see how it reaches an *equilibrium state*—a mixture of reactants and products whose concentrations no longer change with time. We begin with N_2O_4 , a colorless substance that dissociates to form NO_2 , which is brown. Figure 15.1 shows a sample of frozen N_2O_4 inside a sealed tube resting in a beaker. Because the chemical reaction occurs in a closed system, the reaction will eventually reach equilibrium.

The solid N_2O_4 vaporizes as it is warmed above its boiling point (21.2 °C), and the gas turns progressively darker as the colorless N_2O_4 gas dissociates into brown NO_2 gas (Figure 15.1). Eventually, even though there is still N_2O_4 in the tube, the color stops getting darker because the system reaches equilibrium. We are left with an *equilibrium mixture* of N_2O_4 and NO_2 in which the concentrations of the gases no longer change as time passes.

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



We can analyze this equilibrium using our knowledge of kinetics. Let's call the decomposition of N_2O_4 to form NO_2 the forward reaction and the reaction of NO_2 to re-form N_2O_4 the reverse reaction. In this case both the forward reaction and the reverse reaction are elementary reactions. As we learned in Section 14.6, the rate laws for elementary reactions can be written from their chemical equations:



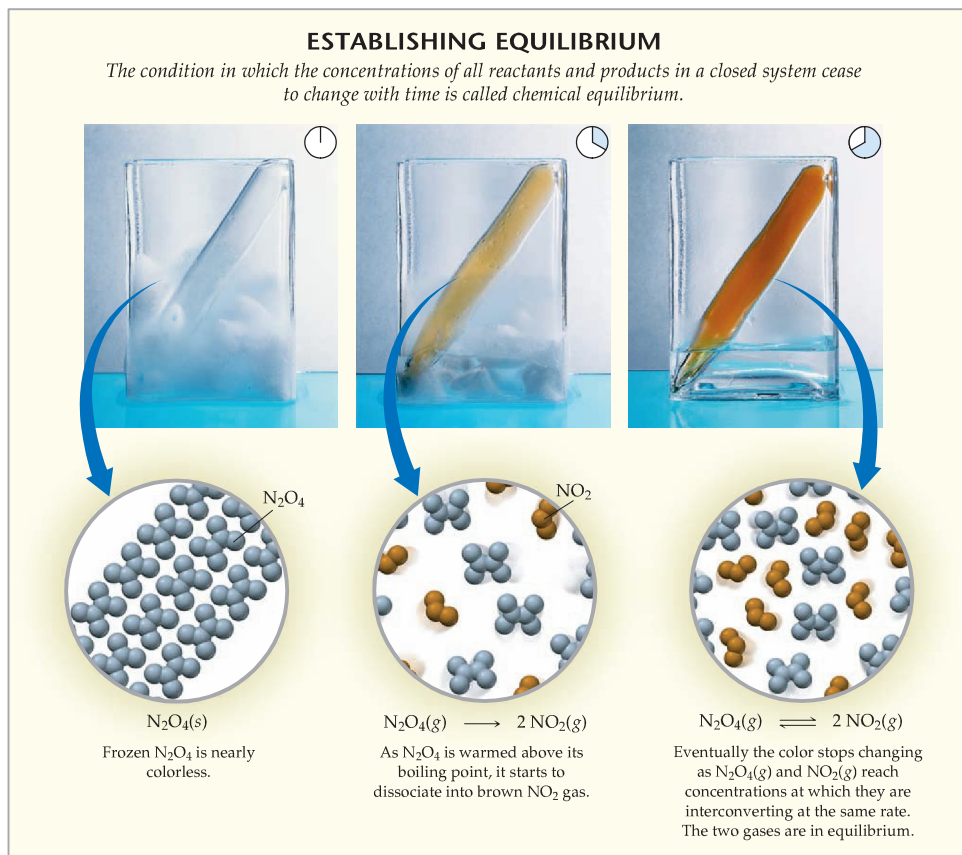
where k_f and k_r are the rate constants for the forward and reverse reactions, respectively. At equilibrium the rate at which products are produced from reactants equals the rate at which reactants are produced from products:

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

Rearranging this equation gives

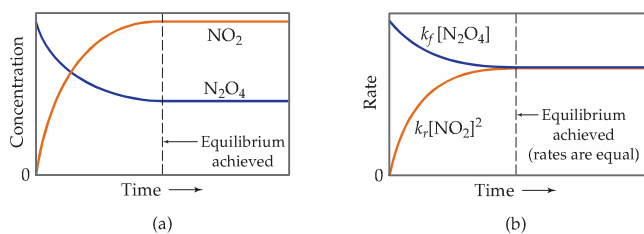
$$\frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{k_f}{k_r} = \text{a constant} \quad [15.5]$$

As shown in Equation 15.5, the quotient of two constants, such as k_f and k_r , is itself a constant. Thus, at equilibrium the ratio of the concentration terms involving N_2O_4 and NO_2 equals a constant. (We will consider this constant, called the *equilibrium constant*, in Section 15.2.) It makes no difference whether we start with N_2O_4 or with NO_2 , or even with some mixture of the two. At equilibrium the ratio equals a specific value. Thus, there is an important constraint on the proportions of N_2O_4 and NO_2 at equilibrium.



▲ **Figure 15.1** The $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$ equilibrium.

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



◀ **Figure 15.2** Achieving chemical equilibrium for $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$. (a) The concentration of N_2O_4 decreases while the concentration of NO_2 increases during the course of the reaction. Equilibrium is indicated when the concentrations no longer change with time. (b) The rate of disappearance of N_2O_4 decreases with time as the concentration of N_2O_4 decreases. At the same time, the rate of formation of NO_2 also decreases with time. Equilibrium occurs when these two rates are equal.

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.

We will examine the last of these facts in the next section.

GIVE IT SOME THOUGHT

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

15.2 THE EQUILIBRIUM CONSTANT

Opposing reactions naturally lead to an equilibrium, regardless of how complicated the reaction might be 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, in the presence of a catalyst, combines N_2 and H_2 at a pressure of several hundred atmospheres and a temperature of several hundred degrees Celsius. The two gases react to form ammonia under these conditions, but in a closed system the reaction does not lead to complete consumption of the N_2 and H_2 . Rather, at some point the reaction appears to stop, with all three components of the reaction mixture present at the same time.

The manner in which the concentrations of H_2 , N_2 , and NH_3 vary with time is shown in Figure 15.3(a). Notice that an equilibrium mixture is obtained regardless of whether we begin with N_2 and H_2 or only with NH_3 . *The equilibrium condition can be reached from either direction.*

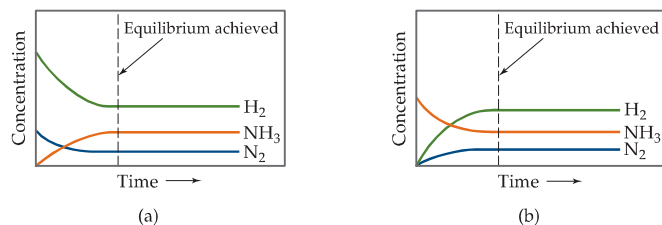
GIVE IT SOME THOUGHT

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

Earlier, we saw that when the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$ reaches equilibrium, a ratio based on the equilibrium concentrations of N_2O_4 and NO_2 has a constant value (Equation 15.5). A similar relationship governs the concentrations of N_2 , H_2 , and NH_3 at equilibrium. If we were to systematically change the relative amounts of the three gases in the starting mixture and then analyze each equilibrium mixture, we could determine the relationship among the equilibrium concentrations.

► **Figure 15.3 Concentration changes approaching equilibrium.**

(a) Equilibrium for the reaction $\text{N}_2 + 3 \text{H}_2 \rightleftharpoons 2 \text{NH}_3$ is approached beginning with H_2 and N_2 present in the ratio 3:1 and no NH_3 present.
(b) Equilibrium for the same reaction is approached beginning with only NH_3 in the reaction vessel.



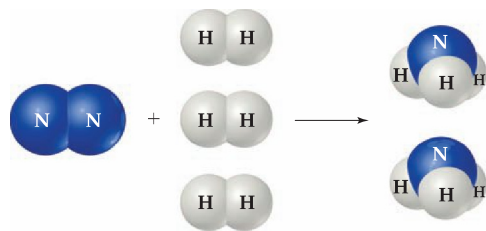
Chemistry Put to Work

THE HABER PROCESS

We presented a “Chemistry and Life” box in Section 14.7 that discussed *nitrogen fixation*, the processes that convert N_2 gas into ammonia, which can then be incorporated into living organisms. We learned that the enzyme nitrogenase is responsible for generating most of the fixed nitrogen essential for plant growth. However, the quantity of food required to feed the ever-increasing human population far exceeds that provided by nitrogen-fixing plants, so human agriculture requires substantial amounts of ammonia-based fertilizers that can be applied directly to croplands. Thus, of all the chemical reactions that humans have learned to carry out and 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 a process for synthesizing ammonia directly from nitrogen and hydrogen (Figure 15.4). The process is sometimes called the *Haber–Bosch process* to also honor Karl Bosch, the engineer who developed the equipment for the industrial production of ammonia. The engineering needed to implement the Haber process requires the use of temperatures and pressures (approximately 500°C and 200 atm) that were difficult to achieve at that time.

The Haber process provides a historically interesting example of the complex impact of chemistry on our lives. At the start of World War I, in 1914, Germany depended on nitrate deposits in Chile for the nitrogen-containing compounds needed to manufacture explosives. During the war the Allied naval



▲ **Figure 15.4 The Haber process.** Used to convert $N_2(g)$ and $H_2(g)$ to $NH_3(g)$, this process, although exothermic, requires breaking the very strong triple bond in N_2 .



▲ **Figure 15.5 Liquid ammonia used as fertilizer.** Ammonia, produced by the Haber process, can be added directly to the soil as a fertilizer. Agricultural use is the largest single application of manufactured NH_3 .

blockade of South America cut off this supply. However, by fixing nitrogen from air, Germany was able to continue to produce explosives. Experts have estimated that World War I would have ended before 1918 had it not been for the Haber process.

From these unhappy beginnings as a major factor in international warfare, the Haber process has become the world’s principal source of fixed nitrogen. The same process that prolonged World War I has enabled the manufacture of fertilizers that have increased crop yields, thereby saving millions of people from starvation. About 40 billion pounds of ammonia are manufactured annually in the United States, mostly by the Haber process. The ammonia can be applied directly to the soil as fertilizer (Figure 15.5). It can also be converted into ammonium salts—for example, ammonium sulfate, $(NH_4)_2SO_4$, and ammonium hydrogen phosphate, $(NH_4)_2HPO_4$ —which, in turn, are 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 for 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: 15.38 and 15.64

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 following 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 expressed by the expression

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

We call this relationship the **equilibrium-constant expression** (or merely the equilibrium expression) for the reaction. The constant K_c , which we call the **equilibrium constant**, is the numerical value obtained when we substitute equilibrium concentrations into the equilibrium-constant expression. The subscript c on the K indicates that concentrations expressed in molarity are used to evaluate the constant.

In general, the numerator of the equilibrium-constant expression is the product of the concentrations of all substances on the product side of the equilibrium equation, each raised to a power equal to its coefficient in the balanced equation. The denominator is similarly derived from the reactant side of the equilibrium equation. (Remember, the convention is to write the substances on the *product* side in the *numerator* and the substances on the *reactant* side in the *denominator*.) Thus, for the Haber process, $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$, the equilibrium-constant expression is

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

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

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

■ SAMPLE EXERCISE 15.1 | Writing Equilibrium-Constant Expressions

Write the equilibrium expression for K_c for the following reactions:

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

■ SOLUTION

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

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

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

■ PRACTICE EXERCISE

Write the equilibrium-constant expression K_c for (a) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$, (b) $\text{Cd}^{2+}(\text{aq}) + 4 \text{Br}^-(\text{aq}) \rightleftharpoons \text{CdBr}_4^{2-}(\text{aq})$

Answers: (a) $K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$; (b) $K_c = \frac{[\text{CdBr}_4^{2-}]}{[\text{Cd}^{2+}][\text{Br}^-]^4}$

Evaluating K_c

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

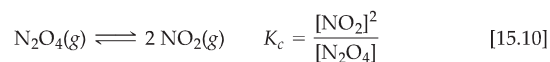


TABLE 15.1 ■ Initial and Equilibrium Concentrations of N_2O_4 and NO_2 in the Gas Phase at 100°C

Experiment	Initial $[\text{N}_2\text{O}_4]$ (M)	Initial $[\text{NO}_2]$ (M)	Equilibrium $[\text{N}_2\text{O}_4]$ (M)	Equilibrium $[\text{NO}_2]$ (M)	K_c
1	0.0	0.0200	0.00140	0.0172	0.211
2	0.0	0.0300	0.00280	0.0243	0.211
3	0.0	0.0400	0.00452	0.0310	0.213
4	0.0200	0.0	0.00452	0.0310	0.213

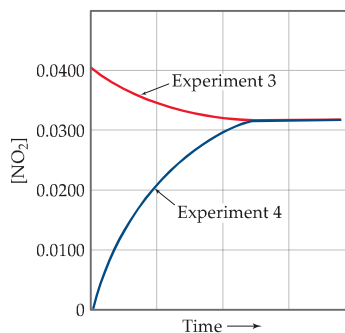
We start with several sealed tubes containing different concentrations of NO_2 and N_2O_4 . The tubes are kept at 100°C until equilibrium is reached. We then analyze the mixtures and determine the equilibrium concentrations of NO_2 and N_2O_4 , as shown in Table 15.1 ▲.

To evaluate the equilibrium constant, K_c , we insert the equilibrium concentrations into the equilibrium-constant expression. For example, using the 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 were calculated, as listed in Table 15.1. Note that the value for K_c is constant ($K_c = 0.212$, within the limits of experimental error) even though the initial concentrations vary. Furthermore, the results of Experiment 4 show that equilibrium can be achieved beginning with N_2O_4 rather than with NO_2 . That is, equilibrium can be approached from either direction. Figure 15.6 ► shows how both Experiments 3 and 4 result in the same equilibrium mixture even though one begins with 0.0400 M NO_2 and the other with $0.0200\text{ M N}_2\text{O}_4$.

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



▲ Figure 15.6 Concentration changes approaching equilibrium. As seen in Table 15.1, the same equilibrium mixture is produced starting with either 0.0400 M NO_2 (Experiment 3) or $0.0200\text{ M N}_2\text{O}_4$ (Experiment 4).

GIVE IT SOME THOUGHT

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

Equilibrium Constants in Terms of Pressure, K_p

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

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

where P_A is the partial pressure of A in atmospheres, and so forth. For example, for $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ we have

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

GIVE IT SOME THOUGHT

What do the symbols K_c and K_p represent?

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 a subscript c or p , which of these equilibrium constants we are using. It is possible, however, to calculate one from the other using the ideal-gas equation (Section 10.4) to convert between concentration (in molarity, M) and pressure (in atm):

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

The usual units for n/V are mol/L, which equals molarity, M . For substance A 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 the expression for K_p (Equation 15.11), we obtain a general expression relating K_p and K_c .

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

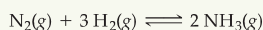
The quantity Δn is the change in the number of moles of gas in the chemical equation for the reaction. It equals the sum of the coefficients of the gaseous products minus the sum of the coefficients of the gaseous reactants:

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

For example, in the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$, there are two moles of the product NO_2 (the coefficient in the balanced equation) and one mole of the reactant N_2O_4 . Therefore, $\Delta n = 2 - 1 = 1$, and $K_p = K_c(RT)$ for this reaction. From Equation 15.14, we see that $K_p = K_c$ only when the same number of moles of gas appears on both sides of the balanced chemical equation, which means that $\Delta n = 0$.

SAMPLE EXERCISE 15.2 | Converting between K_c and K_p

In the synthesis of ammonia from nitrogen and hydrogen,



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

SOLUTION

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

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

Solve: There are two moles of gaseous products (2NH_3) and four moles of gaseous reactants ($1\text{N}_2 + 3\text{H}_2$). Therefore, $\Delta n = 2 - 4 = -2$. (Remember that Δ functions are always based on products minus reactants.) The temperature, T , is $273 + 300 = 573\text{ K}$. The value for the ideal-gas constant, R , is $0.0821\text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}$. Using $K_c = 9.60$, we therefore have

$$K_p = K_c(RT)^{\Delta n} = (9.60)(0.0821 \times 573)^{-2} = \frac{(9.60)}{(0.0821 \times 573)^2} = 4.34 \times 10^{-3}$$

PRACTICE EXERCISE

For the equilibrium $2\text{SO}_3(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$, K_c is 4.08×10^{-3} at 1000 K . Calculate the value for K_p .

Answer: 0.335

Equilibrium Constants and Units

You may wonder why equilibrium constants are reported without units. The equilibrium constant is related to the kinetics of a reaction as well as to the thermodynamics of the process. (We will 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 to a reference concentration (1 *M*) or a reference pressure (1 atm). For example, if the concentration of a substance in an equilibrium mixture is 0.010 *M*, its activity is 0.010 *M*/1 *M* = 0.010. The units of such ratios always cancel, and consequently, activities have no units. Furthermore, the numerical value of the activity equals the concentration. For pure solids and pure liquids, the situation is even simpler because the activities then merely equal 1 (again with no units).

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



GIVE IT SOME THOUGHT

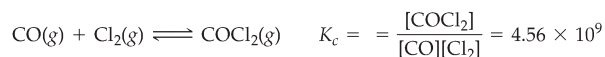
If the concentration of N_2O_4 in an equilibrium mixture is 0.00140 *M*, what is its activity? (Assume the solution is ideal.)

15.3 INTERPRETING AND WORKING WITH EQUILIBRIUM CONSTANTS

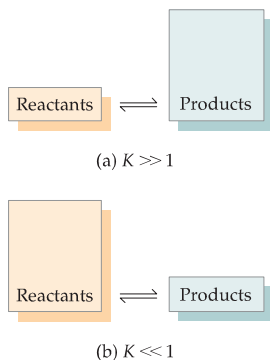
In this section we explore two important ideas. Before doing calculations with equilibrium constants, it is valuable to understand what the magnitude of an equilibrium constant can tell us about the relative concentrations of reactants and products in an equilibrium mixture. It is also useful to consider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

The Magnitude of Equilibrium Constants

Equilibrium constants can vary from very large to very small. The magnitude of the constant provides us with important information about the composition of an equilibrium mixture. For example, consider the reaction of carbon monoxide gas and chlorine gas at 100 °C to form phosgene (COCl_2), a toxic gas used in the manufacture of certain polymers and insecticides:



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



▲ Figure 15.7 K and the composition of the equilibrium mixture. The equilibrium expression has products in the numerator and reactants in the denominator. (a) When $K \gg 1$, there are more products than reactants at equilibrium, and the equilibrium is said to lie to the right. (b) When $K \ll 1$, there are more reactants than products at equilibrium, and the equilibrium is said to lie to the left.

We then say that the equilibrium *lies to the left*. In general,

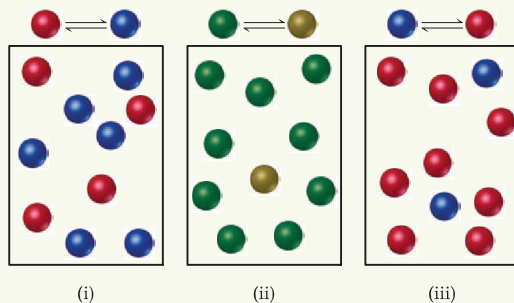
If $K \gg 1$ (that is, large K): Equilibrium lies to the right; products predominate.

If $K \ll 1$ (that is, small K): Equilibrium lies to the left; reactants predominate.

These situations are summarized in Figure 15.7. Remember, opposing rates, not concentrations, are equal at equilibrium. Thus, equilibrium constants for different reactions can span a very wide range.

SAMPLE EXERCISE 15.3 Interpreting the Magnitude of an Equilibrium Constant

The following diagrams represent three different systems at equilibrium, all in the same size containers. (a) Without doing any calculations, rank the three systems in order of increasing equilibrium constant, 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 first asked to judge the relative magnitudes of three equilibrium constants and then to calculate them.

Plan: (a) The more product that is present at equilibrium, relative to the reactant, the greater the equilibrium constant. (b) The equilibrium constant is given by the concentrations of products over reactants.

Solve:

(a) Each box contains 10 spheres. The amount of product in each varies as follows: (i) 6, (ii) 1, (iii) 8. Thus, the equilibrium constant varies in the order (ii) $<$ (i) $<$ (iii).

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

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

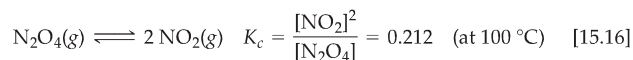
PRACTICE EXERCISE

For the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$, $K_p = 794$ at 298 K and $K_p = 54$ at 700 K. Is the formation of HI favored more at the higher or lower temperature?

Answer: The formation of product, HI, is favored at the lower temperature because K_p is larger at the lower temperature.

The Direction of the Chemical Equation and K

Because an equilibrium can be approached from either direction, the direction in which we write the chemical equation for an equilibrium is arbitrary. For example, we have seen that we can represent the $\text{N}_2\text{O}_4 - \text{NO}_2$ equilibrium as



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



The equilibrium expression is then

$$K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{1}{0.212} = 4.72 \quad (\text{at } 100^\circ\text{C}) \quad [15.17]$$

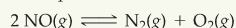
Equation 15.17 is just the reciprocal of the equilibrium-constant expression in Equation 15.16. *The equilibrium-constant expression for a reaction written in one direction is the reciprocal of the one for the reaction written in the reverse direction.* Consequently, the numerical value of the equilibrium constant for the reaction written in one direction is the reciprocal of that for the reverse reaction. Both expressions are equally valid, but it is meaningless to say that the equilibrium constant for the equilibrium between NO_2 and N_2O_4 is 0.212 or 4.72 unless we indicate how the equilibrium reaction is written and specify the temperature.

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

The equilibrium constant for the reaction of N_2 with O_2 to form NO equals $K_c = 1 \times 10^{-30}$ at 25°C :



Using this information, write the equilibrium constant expression and calculate the equilibrium constant for the following reaction:



SOLUTION

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

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

Solve:

Writing products over reactants, we have

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

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

$$K_c = \frac{[\text{N}_2][\text{O}_2]}{[\text{NO}]^2} = \frac{1}{1 \times 10^{-30}} = 1 \times 10^{30}$$

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

PRACTICE EXERCISE

For the formation of NH_3 from N_2 and H_2 , $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$, $K_p = 4.34 \times 10^{-3}$ at 300°C . What is the value of K_p for the reverse reaction?

Answer: 2.30×10^2

Relating Chemical Equations and Equilibrium Constants

Just as the equilibrium constants of forward and reverse reactions are reciprocals of each other, the equilibrium constants of reactions associated in other ways are also related. For example, if we were to multiply our original $\text{N}_2\text{O}_4 - \text{NO}_2$ equilibrium by 2, we would have



The equilibrium-constant expression, K_c , for this equation is

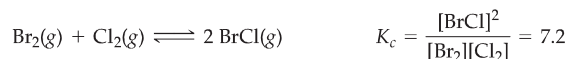
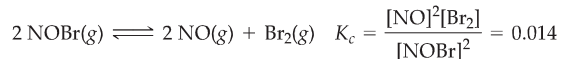
$$K_c = \frac{[\text{NO}_2]^4}{[\text{N}_2\text{O}_4]^2}$$

which is simply the square of the equilibrium-constant expression for the original equation, given in Equation 15.10. Because the new equilibrium-constant expression equals the original expression squared, the new equilibrium constant equals the original constant squared: in this case $0.212^2 = 0.0449$ (at 100°C).

GIVE IT SOME THOUGHT

How does the magnitude of the equilibrium constant K_p for the reaction $2 \text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$ change if the equilibrium is written $6 \text{HI}(g) \rightleftharpoons 3 \text{H}_2(g) + 3 \text{I}_2(g)$?

Sometimes, as in problems that utilize Hess's law (Section 5.6), we must use equations made up of two or more steps in the overall process. We obtain the net equation by adding the individual equations and canceling identical terms. Consider the following two reactions, their equilibrium-constant expressions, and their equilibrium constants at 100 °C:



The net sum of these two equations is



and the equilibrium-constant expression for the net equation is the product of the expressions for the individual steps:

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

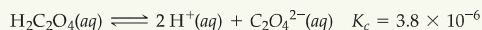
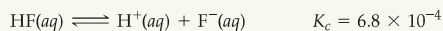
Because the equilibrium-constant expression for the net equation is the product of two equilibrium-constant expressions, the equilibrium constant for the net equation is the product of the two individual equilibrium constants: $K_c = 0.014 \times 7.2 = 0.10$.

To summarize:

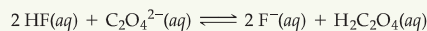
1. The equilibrium constant of a reaction in the *reverse* direction is the *inverse* of the equilibrium constant of the reaction in the forward direction.
2. The equilibrium constant of a reaction that has been *multiplied* by a number is the equilibrium constant raised to a *power* equal to that number.
3. The equilibrium constant for a net reaction made up of *two or more steps* is the *product* of the equilibrium constants for the individual steps.

SAMPLE EXERCISE 15.5 | Combining Equilibrium Expressions

Given the following information,



determine the value of K_c for the reaction

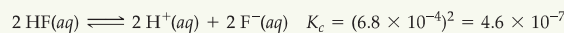


SOLUTION

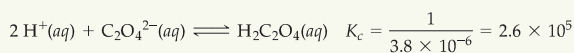
Analyze: We are given two equilibrium equations and the corresponding equilibrium constants and are asked to determine the equilibrium constant for a third equation, which is related to the first two.

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

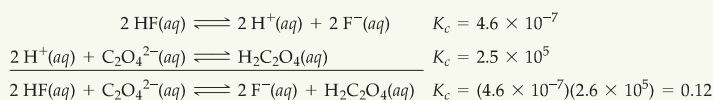
Solve: If we multiply the first equation by 2 and make the corresponding change to its equilibrium constant (raising to the power 2), we get



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.



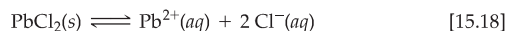
■ PRACTICE EXERCISE

Given that, at 700 K, $K_p = 54.0$ for the reaction $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{HI}(g)$ and $K_p = 1.04 \times 10^{-4}$ for the reaction $\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g)$, determine the value of K_p for the reaction $2 \text{NH}_3(g) + 3 \text{I}_2(g) \rightleftharpoons 6 \text{HI}(g) + \text{N}_2(g)$ at 700 K.

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

15.4 HETEROGENEOUS EQUILIBRIA

Many equilibria, such as the hydrogen-nitrogen-ammonia system, involve substances all in the same phase. Such equilibria are called **homogeneous equilibria**. In other cases the substances in equilibrium are in different phases, giving rise to **heterogeneous equilibria**. As an example, consider the equilibrium that occurs when solid lead(II) chloride (PbCl_2) dissolves in water to form a saturated solution:



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

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

Even though $\text{PbCl}_2(s)$ does not appear in the equilibrium-constant expression, it must be present for equilibrium to occur.

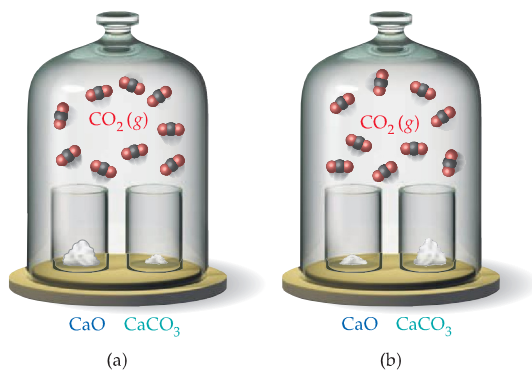
The fact that pure solids and pure liquids are excluded from equilibrium-constant expressions can be explained in two ways. First, the concentration of a pure solid or liquid has a constant value. If the mass of a solid is doubled, its volume also doubles. Thus, its concentration, which relates to the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

The omission of pure solids and liquids from equilibrium-constant expressions can also be rationalized in a second way. Recall from the last section that what is substituted into a thermodynamic equilibrium expression is the activity of each substance, which is a ratio of the concentration to a reference value. For a pure substance, the reference value is the concentration of the pure substance itself, so that the activity of any pure solid or liquid is always simply 1.

▲ GIVE IT SOME THOUGHT

Write the equilibrium-constant expression for the evaporation of water, $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g)$, in terms of partial pressures, K_p .

► **Figure 15.8 A heterogeneous equilibrium.** The equilibrium involving CaCO_3 , CaO , and CO_2 is a heterogeneous equilibrium. The equilibrium pressure of CO_2 is the same in the two bell jars as long as the two systems are at the same temperature, even though the relative amounts of pure CaCO_3 and CaO differ greatly. The equilibrium-constant expression for the reaction is $K_p = P_{\text{CO}_2}$.



As a further example of a heterogeneous reaction, consider the decomposition of calcium carbonate:



Omitting the concentrations of solids from the equilibrium-constant 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 CaCO_3 , CaO , and CO_2 will always lead to the same partial pressure of CO_2 as long as all three components are present. As shown in Figure 15.8▲, we would have the same pressure of CO_2 regardless of the relative amounts of CaO and CaCO_3 .

■ SAMPLE EXERCISE 15.6 | Writing Equilibrium-Constant Expressions for Heterogeneous Reactions

Write the equilibrium-constant expression for K_c for each of the following reactions:

- (a) $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{l})$
 (b) $\text{SnO}_2(\text{s}) + 2 \text{CO}(\text{g}) \rightleftharpoons \text{Sn}(\text{s}) + 2 \text{CO}_2(\text{g})$

SOLUTION

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

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

Solve:

- (a) The equilibrium-constant expression is

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

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

- (b) The equilibrium-constant expression is

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

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

■ PRACTICE EXERCISE

Write the following equilibrium-constant expressions:

- (a) K_c for $\text{Cr}(\text{s}) + 3 \text{Ag}^+(\text{aq}) \rightleftharpoons \text{Cr}^{3+}(\text{aq}) + 3 \text{Ag}(\text{s})$
 (b) K_p for $3 \text{Fe}(\text{s}) + 4 \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{Fe}_3\text{O}_4(\text{s}) + 4 \text{H}_2(\text{g})$

Answers: (a) $K_c = \frac{[\text{Cr}^{3+}]}{[\text{Ag}^+]^3}$, (b) $K_p = \frac{(P_{\text{H}_2})^4}{(P_{\text{H}_2\text{O}})^4}$

SAMPLE EXERCISE 15.7 Analyzing a Heterogeneous Equilibrium

Each of the following mixtures was placed in a closed container and allowed to stand. Which is capable of attaining the equilibrium $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$: (a) pure CaCO_3 , (b) CaO and a CO_2 pressure greater than the value of K_p , (c) some CaCO_3 and a CO_2 pressure greater than the value of K_p , (d) CaCO_3 and CaO ?

SOLUTION

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

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

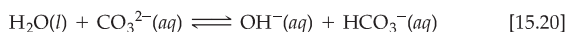
Solve: Equilibrium can be reached in all cases except (c) as long as sufficient quantities of solids are present. (a) CaCO_3 simply decomposes, forming $\text{CaO}(s)$ and $\text{CO}_2(g)$ until the equilibrium pressure of CO_2 is attained. There must be enough CaCO_3 , however, to allow the CO_2 pressure to reach equilibrium. (b) CO_2 continues to combine with CaO until the partial pressure of the CO_2 decreases to the equilibrium value. (c) There is no CaO present, so equilibrium cannot be attained because there is no way the CO_2 pressure can decrease to its equilibrium value (which would require some of the CO_2 to react with CaO). (d) The situation is essentially the same as in (a): CaCO_3 decomposes until equilibrium is attained. The presence of CaO initially makes no difference.

PRACTICE EXERCISE

When added to $\text{Fe}_3\text{O}_4(s)$ in a closed container, which one of the following substances— $\text{H}_2(g)$, $\text{H}_2\text{O}(g)$, $\text{O}_2(g)$ —will allow equilibrium to be established in the reaction $3 \text{Fe}(s) + 4 \text{H}_2\text{O}(g) \rightleftharpoons \text{Fe}_3\text{O}_4(s) + 4 \text{H}_2(g)$?

Answer: only $\text{H}_2(g)$

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



gives an equilibrium-constant expression in which $[\text{H}_2\text{O}]$ is excluded:

$$K_c = \frac{[\text{OH}^-][\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} \quad [15.21]$$

GIVE IT SOME THOUGHT

Write the equilibrium-constant expression for the following reaction: $\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$

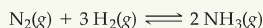
15.5 CALCULATING EQUILIBRIUM CONSTANTS

One of the first tasks confronting Haber when he approached the problem of ammonia synthesis was finding the magnitude of the equilibrium constant for the synthesis of NH_3 at various temperatures. If the value of K for Equation 15.6 was very small, the amount of NH_3 in an equilibrium mixture would be small relative to the amounts of N_2 and H_2 . That is, if the equilibrium lies too far to the left, it would be impossible to develop a satisfactory synthesis process for ammonia.

Haber and his coworkers therefore evaluated the equilibrium constants for this reaction at various temperatures. The method they employed is analogous to that described in constructing Table 15.1: They started with various mixtures of N_2 , H_2 , and NH_3 , allowed the mixtures to achieve equilibrium at a specific temperature, and measured the concentrations of all three gases at equilibrium. Because the equilibrium concentrations of all products and reactants were known, the equilibrium constant could be calculated directly from the equilibrium-constant expression.

■ SAMPLE EXERCISE 15.8 | Calculating K When All Equilibrium Concentrations Are Known

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



■ SOLUTION

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

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

Solve:

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

■ PRACTICE EXERCISE

An aqueous solution of acetic acid is found to have the following equilibrium concentrations at 25 °C: $[HC_2H_3O_2] = 1.65 \times 10^{-2} M$; $[H^+] = 5.44 \times 10^{-4} M$; and $[C_2H_3O_2^-] = 5.44 \times 10^{-4} M$. Calculate the equilibrium constant K_c for the ionization of acetic acid at 25 °C. The reaction is



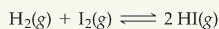
Answer: 1.79×10^{-5}

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

1. Tabulate all the known initial and equilibrium concentrations of the species that appear in the equilibrium-constant expression.
2. For those species for which both the 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, use the coefficients in the balanced chemical equation) to calculate the changes in concentration for all the other species in the equilibrium.
4. From the initial concentrations and the changes in concentration, calculate the equilibrium concentrations. These are then used to evaluate the equilibrium constant.

SAMPLE EXERCISE 15.9 | Calculating K from Initial and Equilibrium Concentrations

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

**SOLUTION**

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Finally, now that we know the equilibrium concentration of each reactant and product, we can 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.

PRACTICE EXERCISE

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

Answer: 0.338

15.6 APPLICATIONS OF EQUILIBRIUM CONSTANTS

We have seen that the magnitude of K indicates the extent to which a reaction will proceed. If K is very large, the equilibrium mixture will contain mostly substances on the product side of the equation. (That is, the reaction will tend to proceed far to the right.) If K is very small (that is, much less than 1), the equilibrium mixture will contain mainly reactants. The equilibrium constant also allows us to (1) predict the direction in which a reaction mixture will proceed to achieve equilibrium and (2) calculate the concentrations of reactants and products when equilibrium has been reached.

Predicting the Direction of Reaction

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

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

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

To reach equilibrium, the quotient $[\text{NH}_3]^2/[\text{N}_2][\text{H}_2]^3$ will need to 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 the concentration of NH_3 decreases and the concentrations of N_2 and H_2 increase. Thus, the reaction proceeds toward equilibrium by forming N_2 and H_2 from NH_3 ; that is, the reaction proceeds from right to left.

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



the reaction quotient is defined as

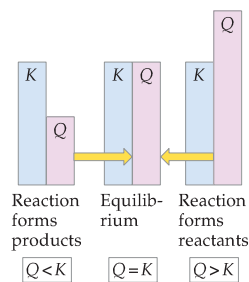
$$Q_c = \frac{[\text{D}]^d[\text{E}]^e}{[\text{A}]^a[\text{B}]^b} \quad [15.22]$$

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

Although we use the equilibrium-constant expression to calculate the reaction quotient, the concentrations that we use are not restricted to the equilibrium state. Thus, in our earlier example, when we substituted the starting concentrations into the equilibrium-constant expression, 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.

To determine the direction in which a reaction will proceed to achieve equilibrium, we compare the values of Q_c and K_c or Q_p and K_p . Three possible situations arise:

- $Q = K$: The reaction quotient will equal the equilibrium constant only if the system is already at equilibrium.
- $Q > K$: The concentration of products is too large and that of reactants too small. Thus, substances on the right side of the chemical equation will react to form substances on the left; the reaction moves from right to left in approaching equilibrium.



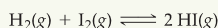
◀ **Figure 15.9 Predicting the direction of a reaction by comparing Q and K .** The relative magnitudes of the reaction quotient Q and the equilibrium constant K indicate how the reaction mixture changes as it moves toward equilibrium. If Q is smaller than K , the reaction proceeds from left to right until $Q = K$. When $Q = K$, the reaction is at equilibrium and has no tendency to change. If Q is larger than K , the reaction proceeds from right to left until $Q = K$.

- $Q < K$: The concentration of products is too small and that of reactants too large. Thus, the reaction will achieve equilibrium by forming more products; it moves from left to right.

These relationships are summarized in Figure 15.9 ▲.

■ SAMPLE EXERCISE 15.10 | 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 will proceed to reach equilibrium at 448 °C if we start with 2.0×10^{-2} mol of HI, 1.0×10^{-2} mol of H_2 , and 3.0×10^{-2} mol of I_2 in a 2.00-L container.

SOLUTION

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

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

Solve: The initial concentrations are

$$[\text{HI}] = 2.0 \times 10^{-2} \text{ mol}/2.00 \text{ L} = 1.0 \times 10^{-2} \text{ M}$$

$$[\text{H}_2] = 1.0 \times 10^{-2} \text{ mol}/2.00 \text{ L} = 5.0 \times 10^{-3} \text{ M}$$

$$[\text{I}_2] = 3.0 \times 10^{-2} \text{ mol}/2.00 \text{ L} = 1.5 \times 10^{-2} \text{ M}$$

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_2 and I_2 must decrease to reach equilibrium; the reaction will proceed from left to right as it moves toward equilibrium.

■ PRACTICE EXERCISE

At 1000 K the value of K_p for the reaction $2 \text{SO}_3(\text{g}) \rightleftharpoons 2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g})$ is 0.338. Calculate the value for Q_p , and predict the direction in which the reaction will proceed toward equilibrium if the initial partial pressures are $P_{\text{SO}_3} = 0.16 \text{ atm}$; $P_{\text{SO}_2} = 0.41 \text{ atm}$; $P_{\text{O}_2} = 2.5 \text{ atm}$.

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

Calculating Equilibrium Concentrations

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

SAMPLE EXERCISE 15.11 | Calculating Equilibrium Concentrations

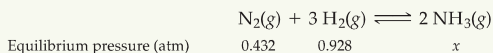
For the Haber process, $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$, $K_p = 1.45 \times 10^{-5}$ at 500 °C. In an equilibrium mixture of the three gases at 500 °C, the partial pressure of H_2 is 0.928 atm and that of N_2 is 0.432 atm. What is the partial pressure of NH_3 in this equilibrium mixture?

SOLUTION

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

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

Solve: We tabulate the equilibrium pressures as follows:



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

$$K_p = \frac{(P_{\text{NH}_3})^2}{P_{\text{N}_2}(P_{\text{H}_2})^3} = \frac{x^2}{(0.432)(0.928)^3} = 1.45 \times 10^{-5}$$

We now rearrange the equation to solve for x :

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

$$x = \sqrt{5.01 \times 10^{-6}} = 2.24 \times 10^{-3} \text{ atm} = P_{\text{NH}_3}$$

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

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

PRACTICE EXERCISE

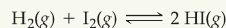
At 500 K the reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ has $K_p = 0.497$. In an equilibrium mixture at 500 K, the partial pressure of PCl_5 is 0.860 atm and that of PCl_3 is 0.350 atm. What is the partial pressure of Cl_2 in the equilibrium mixture?

Answer: 1.22 atm

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

SAMPLE EXERCISE 15.12 | Calculating Equilibrium Concentrations from Initial Concentrations

A 1.000-L flask is filled with 1.000 mol of H_2 and 2.000 mol of I_2 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 H_2 , I_2 , and HI in moles per liter?

SOLUTION

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

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

Solve: First, we note the initial concentrations of H_2 and I_2 in the 1.000-L flask:

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

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

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

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

For each x mol of H_2 that reacts, x mol of I_2 are consumed and $2x$ mol of HI are produced:

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

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

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

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

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

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

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

$$x = \frac{-(-151.5) \pm \sqrt{1(-151.5)^2 - 4(46.5)(101.0)}}{2(46.5)} = 2.323 \text{ or } 0.935$$

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

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

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

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

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

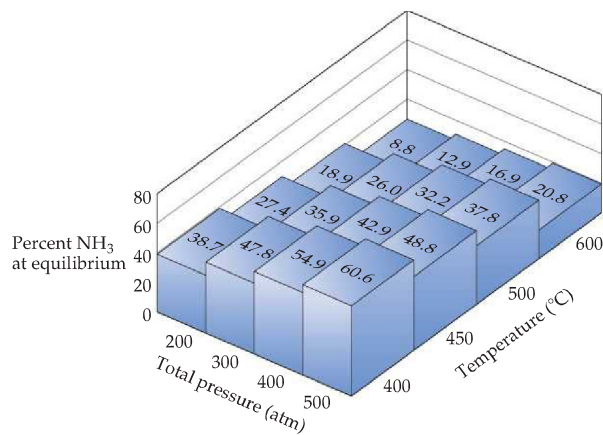
$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(1.87)^2}{(0.065)(1.065)} = 51$$

Comment: Whenever you use a quadratic equation to solve an equilibrium problem, one of the solutions will not be chemically meaningful and should be rejected.

■ PRACTICE EXERCISE

For the equilibrium $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$, the equilibrium constant K_p has the value 0.497 at 500 K. A gas cylinder at 500 K is charged with $\text{PCl}_5(\text{g})$ at an initial pressure of 1.66 atm. What are the equilibrium pressures of PCl_5 , PCl_3 , and Cl_2 at this temperature?

Answer: $P_{\text{PCl}_5} = 0.967 \text{ atm}$; $P_{\text{PCl}_3} = P_{\text{Cl}_2} = 0.693 \text{ atm}$



▲ **Figure 15.10** Effect of temperature and pressure on the percentage of NH_3 in an equilibrium mixture of N_2 , H_2 , and NH_3 . Each mixture was produced by starting with a 3:1 molar mixture of H_2 and N_2 . The yield of NH_3 is greatest at the lowest temperature and at the highest pressure.

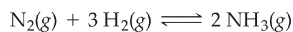
by a change in temperature, pressure, or the concentration of one of the components, the system will shift its equilibrium position so as to counteract the effect of the disturbance.

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

Change in Reactant or Product Concentrations

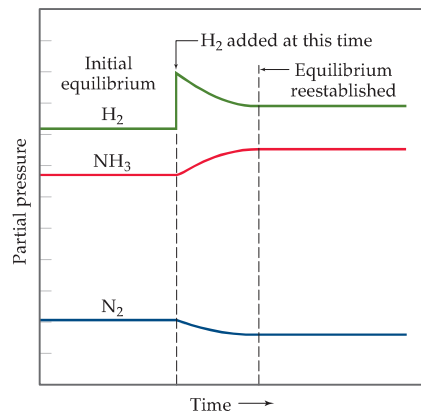
A system at equilibrium is in a dynamic state of balance. When the conditions of the equilibrium are altered, the equilibrium shifts until a new state of balance is attained. Le Châtelier's principle states that the shift will be in the direction that minimizes or reduces the effect of the change. Therefore, *if a chemical system is at equilibrium and we increase the concentration of a substance (either a reactant or a product), the system reacts to consume some of the substance. Conversely, if we decrease the concentration of a substance, the system reacts to produce some of the substance.*

As an example, consider an equilibrium mixture of N_2 , H_2 , and NH_3 :



Adding H_2 would cause the system to shift so as to reduce the newly increased concentration of H_2 . This change can occur only by consuming H_2 and simultaneously consuming N_2 to form more NH_3 . This situation is illustrated in Figure 15.11. Adding more N_2 to the equilibrium mixture would likewise cause the direction of the reaction to shift toward forming more NH_3 . Removing NH_3 would also cause a shift toward producing more NH_3 , whereas *adding* NH_3 to the system at equilibrium would cause the concentrations to shift in the direction that reduces the newly increased NH_3 concentration. Some of the added ammonia would decompose to form N_2 and H_2 .

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

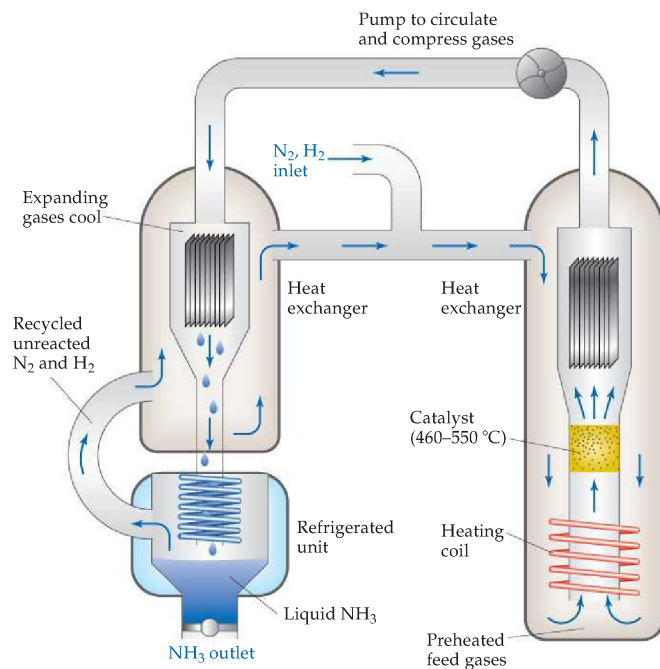


▲ **Figure 15.11** Effect of adding H_2 to an equilibrium mixture of N_2 , H_2 , and NH_3 . When H_2 is added, a portion of the H_2 reacts with N_2 to form NH_3 , thereby establishing a new equilibrium position that has the same equilibrium constant. The results shown are in accordance with Le Châtelier's principle.

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

15.7 LE CHÂTELIER'S PRINCIPLE

When Haber developed his process for making ammonia from N_2 and H_2 , he sought the factors that might be varied to increase the yield of NH_3 . Using the values of the equilibrium constant at various temperatures, he calculated the equilibrium amounts of NH_3 formed under a variety of conditions. Some of Haber's results are shown in Figure 15.10. Notice that the percent of NH_3 present at equilibrium decreases with increasing temperature and increases with increasing pressure. We can understand these effects in terms of a principle first put forward by Henri-Louis Le Châtelier* (1850–1936), a French industrial chemist. **Le Châtelier's principle** can be stated as follows: *If a system at equilibrium is disturbed*



◀ **Figure 15.12 Schematic diagram summarizing the industrial production of ammonia.** Incoming N_2 and H_2 gases are heated to approximately $500\text{ }^\circ\text{C}$ and passed over a catalyst. The resultant gas mixture is allowed to expand and cool, causing NH_3 to liquefy. Unreacted N_2 and H_2 gases are recycled.

removed by selectively liquefying it; the boiling point of NH_3 ($-33\text{ }^\circ\text{C}$) is much higher than that of N_2 ($-196\text{ }^\circ\text{C}$) and H_2 ($-253\text{ }^\circ\text{C}$). The liquid NH_3 is removed, and the N_2 and H_2 are recycled to form more NH_3 , as diagrammed in Figure 15.12▲. By continuously removing the product, the reaction is driven essentially to completion.

GIVE IT SOME THOUGHT

What happens to the equilibrium $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ if (a) O_2 is added to the system, (b) NO is removed?

Effects of Volume and Pressure Changes

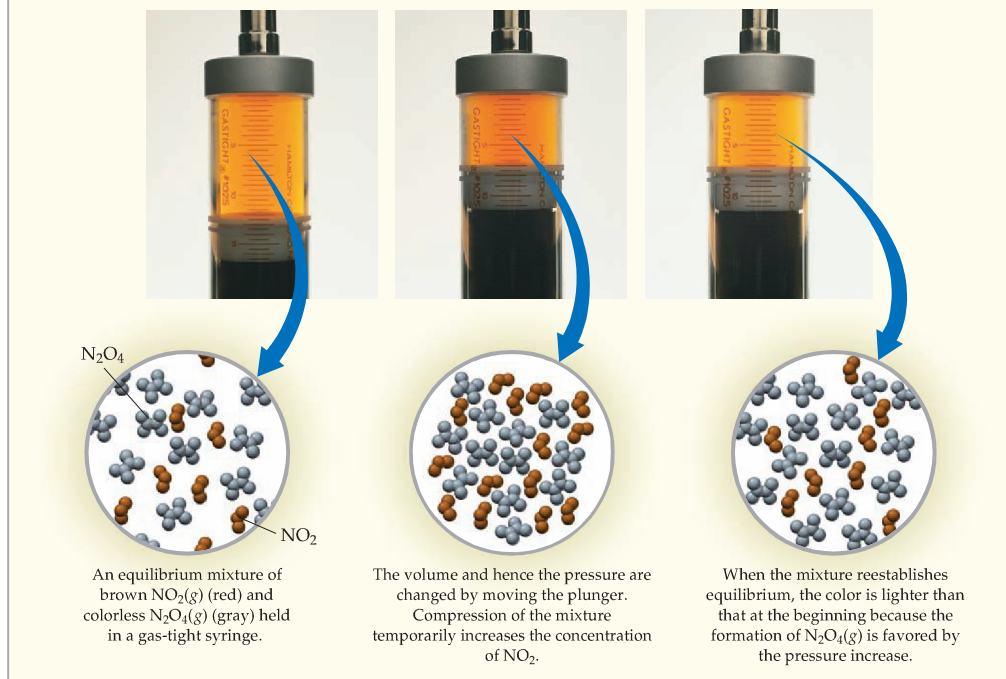
If a system is at equilibrium and its volume is decreased, thereby increasing its total pressure, Le Châtelier's principle indicates that the system will respond by shifting its equilibrium position to reduce the pressure. A system can reduce its pressure by reducing the total number of gas molecules (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.* Conversely, increasing the volume causes a shift in the direction that produces more gas molecules.

For example, let's again consider the equilibrium $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$. What happens if the total pressure of an equilibrium mixture is increased by decreasing the volume as shown in the sequential photos in Figure 15.13▼? According to Le Châtelier's principle, we expect the equilibrium to shift to the side that reduces the total number of moles of gas, which is the reactant side in this case. (Notice the coefficients in the chemical equation; 1 mol of N_2O_4 appears on the reactant side and 2 mol NO_2 appears on the product side.) We therefore expect the equilibrium to shift to the left, so that NO_2 is

LE CHÂTELIER'S PRINCIPLE

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

The equilibrium shown is $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$.



▲ **Figure 15.13** Effect of pressure on an equilibrium. (The equilibrium shown is $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$.)

converted into N_2O_4 as equilibrium is reestablished. In Figure 15.13, compressing the gas mixture initially causes the color to darken as the concentration of NO_2 increases. The color then fades as equilibrium is reestablished. The color fades because the pressure increase causes the equilibrium to shift in favor of colorless N_2O_4 .

GIVE IT SOME THOUGHT

What happens to the equilibrium $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$ if the volume of the system is increased?

For the reaction $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$, four molecules of reactant are consumed for every two molecules of product produced. Consequently, an increase in pressure (decrease in volume) causes a shift toward the side with fewer gas molecules, which leads to the formation of more NH_3 , as indicated in Figure 15.10. In the case of the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$, the number of molecules of gaseous products (two) equals the number of molecules of gaseous reactants; therefore, changing the pressure will not influence the position of the equilibrium.

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

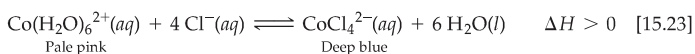
$$Q_p = \frac{(P_{NH_3})^2}{P_{N_2}(P_{H_2})^3} = \frac{(0.332)^2}{(4.92)(14.76)^3} = 6.97 \times 10^{-6} \neq K_p$$

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

It is possible to change the total pressure of the system without changing its volume. For example, pressure increases if additional amounts of any of the reacting components are added to the system. We have already seen how to deal with a change in concentration of a reactant or product. The total pressure within 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 cause shifts in equilibrium without changing the value of the equilibrium constant. In contrast, almost every equilibrium constant changes in value as the temperature changes. For example, consider the equilibrium established when cobalt(II) chloride ($CoCl_2$) is dissolved in hydrochloric acid, $HCl(aq)$:



The formation of $CoCl_4^{2-}$ from $Co(H_2O)_6^{2+}$ is an endothermic process. We will discuss the significance of this enthalpy change shortly. Because $Co(H_2O)_6^{2+}$ is pink and $CoCl_4^{2-}$ is blue, the position of this equilibrium is readily apparent from the color of the solution. Figure 15.14(left) shows a room-temperature solution of $CoCl_2$ in $HCl(aq)$. Both $Co(H_2O)_6^{2+}$ and $CoCl_4^{2-}$ are present in significant amounts in the solution; the violet color results from the presence of both the pink and blue ions. When the solution is heated [Figure 15.14(middle)], it becomes intensely blue in color, indicating that the equilibrium has shifted to form more $CoCl_4^{2-}$. Cooling the solution, as in Figure 15.14(right), leads to a pink solution, indicating that the equilibrium has shifted to produce more $Co(H_2O)_6^{2+}$. How can we explain the dependence of this equilibrium on temperature?

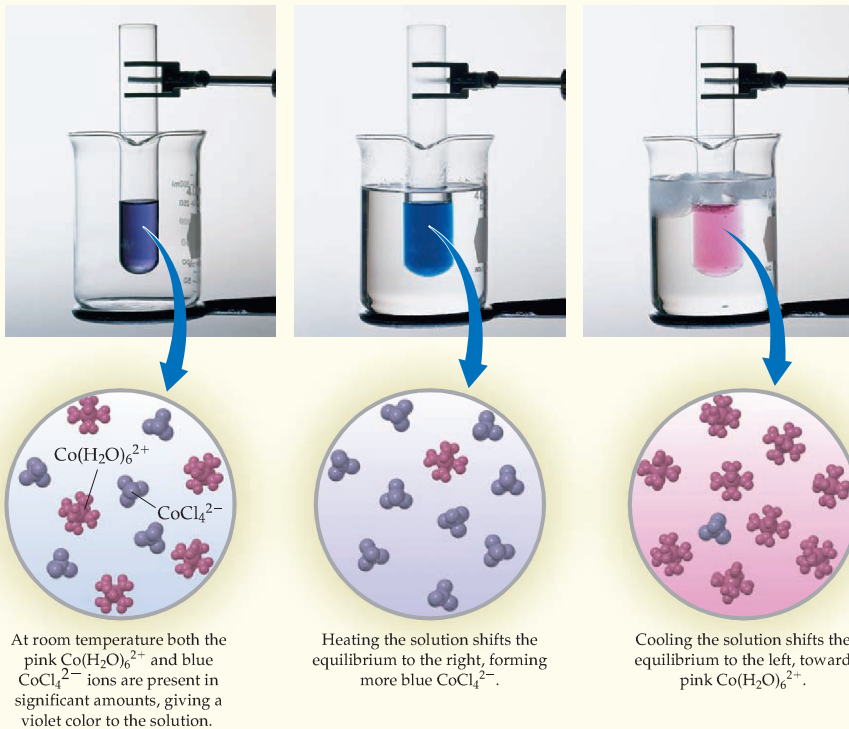
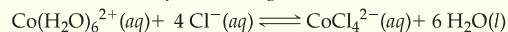
We can deduce the rules for the temperature dependence of the equilibrium constant by applying Le Châtelier's principle. A simple way to do this is to treat heat as if it were a chemical reagent. In an *endothermic* (heat-absorbing) reaction we can consider heat as a *reactant*, whereas in an *exothermic* (heat-releasing) reaction we can consider heat as 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.

EFFECT OF TEMPERATURE CHANGES

Almost every equilibrium constant changes in value as the temperature changes. In an endothermic reaction, such as the one shown, heat is absorbed as reactants are converted to products. Increasing the temperature causes the equilibrium to shift to the right and K to increase. Lowering the temperature shifts the equilibrium in the direction that produces heat, to the left, decreasing K .



▲ **Figure 15.14 Temperature and equilibrium.** (The reaction shown is $\text{Co}(\text{H}_2\text{O})_6^{2+}(\text{aq}) + 4 \text{Cl}^{-}(\text{aq}) \rightleftharpoons \text{CoCl}_4^{2-}(\text{aq}) + 6 \text{H}_2\text{O}(\text{l})$.)

GIVE IT SOME THOUGHT

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

In an endothermic reaction, such as Equation 15.23, 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 products, and K increases. For Equation 15.23, increasing the temperature leads to the formation of more CoCl_4^{2-} , as observed in Figure 15.14(b).

In an exothermic reaction the opposite occurs. Heat is absorbed as products are converted to reactants; therefore the equilibrium shifts to the left and K decreases. We can summarize these results as follows:

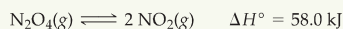
Endothermic: Increasing T results in an increase in K .

Exothermic: Increasing T results in a decrease in K .

Cooling a reaction has the opposite effect. As we lower the temperature, the equilibrium shifts to the side that produces heat. Thus, cooling an endothermic reaction shifts the equilibrium to the left, decreasing K . We observed this effect in Figure 15.14(c). Cooling an exothermic reaction shifts the equilibrium to the right, increasing K .

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

Consider the equilibrium



In which direction will the equilibrium shift when (a) N_2O_4 is added, (b) NO_2 is removed, (c) the total pressure is increased by addition of $\text{N}_2(\text{g})$, (d) the volume is increased, (e) the temperature is decreased?

SOLUTION

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

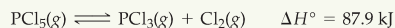
Plan: Le Châtelier's principle can be used to determine the effects of each of these changes.

Solve:

- (a) The system will adjust to decrease the concentration of the added N_2O_4 , so the equilibrium shifts to the right, in the direction of products.
 (b) The system will adjust to the removal of NO_2 by shifting to the side that produces more NO_2 ; thus, the equilibrium shifts to the right.
 (c) Adding N_2 will increase the total pressure of the system, but N_2 is not involved in the reaction. The partial pressures of NO_2 and N_2O_4 are therefore unchanged, and there is no shift in the position of the equilibrium.
 (d) If the volume is increased, the system will shift in the direction that occupies a larger volume (more gas molecules); thus, the equilibrium shifts to the right. (This is the opposite of the effect observed in Figure 15.13, where the volume was decreased.)
 (e) The reaction is endothermic, so we can imagine heat as a reagent on the reactant side of the equation. Decreasing the temperature will shift the equilibrium in the direction that produces heat, so the equilibrium shifts to the left, toward the formation of more N_2O_4 . Note that only this last change also affects the value of the equilibrium constant, K .

■ PRACTICE EXERCISE

For the reaction

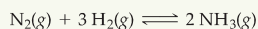


in which direction will the equilibrium shift when (a) $\text{Cl}_2(\text{g})$ is removed, (b) the temperature is decreased, (c) the volume of the reaction system is increased, (d) $\text{PCl}_3(\text{g})$ is added?

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

■ SAMPLE EXERCISE 15.14 | Predicting the Effect of Temperature on K

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



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

SOLUTION

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

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

TABLE 15.2 Variation in K_p for the Equilibrium $\text{N}_2 + 3 \text{H}_2 \rightleftharpoons 2 \text{NH}_3$ as a Function of Temperature

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

Solve:

(a) Recall that the standard enthalpy change for a reaction is given by the sum of the standard molar enthalpies of formation of the products, each multiplied by its coefficient in the balanced chemical equation, less the same quantities for the reactants. At 25 °C, ΔH_f° for $\text{NH}_3(\text{g})$ is -46.19 kJ/mol . The ΔH_f° values for $\text{H}_2(\text{g})$ and $\text{N}_2(\text{g})$ are zero by definition because the enthalpies of formation of the elements in their normal states at 25 °C are defined as zero (Section 5.7). Because 2 mol of NH_3 is formed, the total enthalpy change is

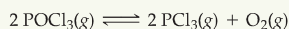
$$(2 \text{ mol})(-46.19 \text{ kJ/mol}) - 0 = -92.38 \text{ kJ}$$

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

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

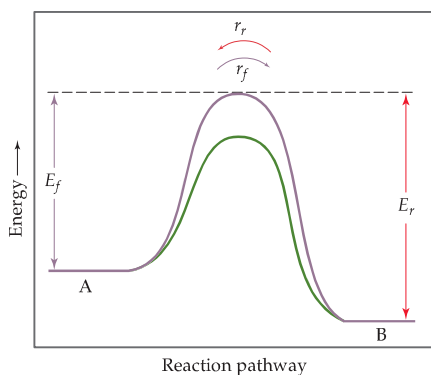
PRACTICE EXERCISE

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



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

Answer: $\Delta H^\circ = 508.3 \text{ kJ}$; the equilibrium constant will increase with increasing temperature



▲ Figure 15.15 Effect of a catalyst on equilibrium. At equilibrium for the hypothetical reaction $\text{A} \rightleftharpoons \text{B}$, the forward reaction rate, r_f , equals the reverse reaction rate, r_r . The violet curve represents the path over the transition state in the absence of a catalyst. A catalyst lowers the energy of the transition state, as shown by the green curve. Thus, the activation energy is lowered for both the forward and the reverse reactions. As a result, the rates of forward and reverse reactions in the catalyzed reaction are increased.

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 the reactants and products. The activation energy of the forward reaction is lowered to the same extent as that for the reverse reaction. The catalyst thereby increases the rates of both the forward and reverse reactions. As a result, a catalyst increases the rate at which equilibrium is achieved, but it does not change the composition of the equilibrium mixture. The value of the equilibrium constant for a reaction is not affected by the presence of a catalyst.

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 a process for ammonia synthesis, Haber had to deal with a rapid decrease in the equilibrium constant with increasing temperature, as shown in 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 was still 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, Haber finally settled on iron mixed with metal oxides. Variants of the original catalyst formulations are still used. These catalysts make it possible to obtain a reasonably rapid approach to equilibrium at temperatures around 400 °C to 500 °C and with gas pressures of 200 to 600 atm. The high pressures are needed to obtain a satisfactory degree of conversion at equilibrium. You can see from

Figure 15.10 that if an improved catalyst could be found—one that would lead to sufficiently rapid reaction at temperatures lower than 400 °C to 500 °C—it would be possible to obtain the same degree of equilibrium conversion at much lower pressures. This would result in great savings in the cost of equipment for ammonia synthesis. In view of the growing need for nitrogen as fertilizer, the fixation of nitrogen is a process of ever-increasing importance.

GIVE IT SOME THOUGHT

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

SAMPLE INTEGRATIVE EXERCISE | Putting Concepts Together

At temperatures near 800 °C, steam passed over hot coke (a form of carbon obtained from coal) reacts to form CO and H₂:



The mixture of gases that results is an important industrial fuel called *water gas*. (a) At 800 °C the equilibrium constant for this reaction is $K_p = 14.1$. What are the equilibrium partial pressures of H₂O, CO, and H₂ in the equilibrium mixture at this temperature if we start with solid carbon and 0.100 mol of H₂O in a 1.00-L vessel? (b) What is the minimum amount of carbon required to achieve equilibrium under these conditions? (c) What is the total pressure in the vessel at equilibrium? (d) At 25 °C the value of K_p for this reaction is 1.7×10^{-21} . Is the reaction exothermic or endothermic? (e) To produce the maximum amount of CO and H₂ at equilibrium, should the pressure of the system be increased or decreased?

SOLUTION

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

$$P_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}RT}{V} = \frac{(0.100 \text{ mol})(0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(1073 \text{ K})}{1.00 \text{ L}} = 8.81 \text{ atm}$$

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

C(s)	+	H ₂ O(g)	\rightleftharpoons	CO(g)	+	H ₂ (g)
Initial		8.81 atm		0 atm		0 atm
Change		-x		+x		+x
Equilibrium		8.81 - x atm		x atm		x atm

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

$$K_p = \frac{P_{\text{CO}}P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} = \frac{(x)(x)}{(8.81 - x)} = 14.1$$

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

$$x^2 = (14.1)(8.81 - x)$$

$$x^2 + 14.1x - 124.22 = 0$$

Solving this equation for x using the quadratic formula yields $x = 6.14$ atm. Hence, the equilibrium partial pressures are $P_{\text{CO}} = x = 6.14$ atm, $P_{\text{H}_2} = x = 6.14$ atm, and $P_{\text{H}_2\text{O}} = (8.81 - x) = 2.67$ atm.

(b) Part (a) shows that $x = 6.14$ atm of H₂O must react for the system to achieve equilibrium. We can use the ideal-gas equation to convert this partial pressure into a mole amount.

$$n = \frac{PV}{RT} = \frac{(6.14 \text{ atm})(1.00 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(1073 \text{ K})} = 0.0697 \text{ mol}$$

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

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

$$P_{\text{total}} = P_{\text{H}_2\text{O}} + P_{\text{CO}} + P_{\text{H}_2} = 2.67 \text{ atm} + 6.14 \text{ atm} + 6.14 \text{ atm} = 14.95 \text{ atm}$$

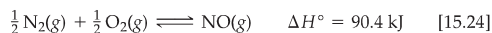
(d) In discussing Le Châtelier's principle, we saw that endothermic reactions exhibit an increase in K_p with increasing temperature. Because the equilibrium constant for this reaction increases as temperature increases, the reaction must be endothermic. From the enthalpies of formation given in Appendix C, we can verify our prediction by calculating the enthalpy change for the reaction, $\Delta H^\circ = \Delta H_f^\circ(\text{CO}) + \Delta H_f^\circ(\text{H}_2) - \Delta H_f^\circ(\text{C}) - \Delta H_f^\circ(\text{H}_2\text{O}) = +131.3 \text{ kJ}$. The positive sign for ΔH° indicates that the reaction is endothermic.

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

Chemistry Put to Work

CONTROLLING NITRIC OXIDE EMISSIONS

The formation of NO from N_2 and O_2 provides another interesting example of the practical importance of changes in the equilibrium constant and reaction rate with temperature. The equilibrium equation and the standard enthalpy change for the reaction are

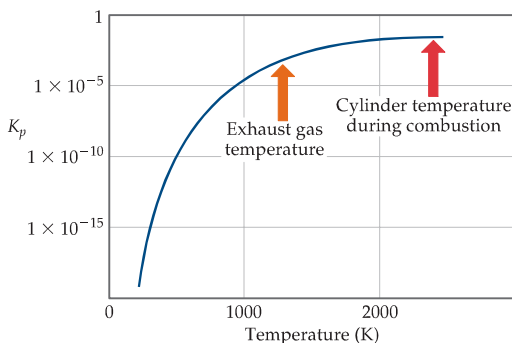


The reaction is endothermic; that is, heat is absorbed when NO is formed from the elements. By applying Le Châtelier's principle, we deduce that an increase in temperature will shift the equilibrium in the direction of more NO. The equilibrium constant K_p for formation of 1 mol of NO from the elements at 300 K is only about 10^{-15} . In contrast, at a much higher temperature of about 2400 K the equilibrium constant is 10^{13} times as large, about 0.05. The manner in which K_p for Equation 15.24 varies with temperature is shown in Figure 15.16.

This graph helps to explain why NO is a pollution problem. In the cylinder of a modern high-compression auto engine, the temperatures during the fuel-burning part of the cycle may be approximately 2400 K. Also, there is a fairly large excess of air in the cylinder. These conditions favor the formation of some NO. After the combustion, however, the gases are quickly cooled. As the temperature drops, the equilibrium in Equation 15.24 shifts strongly to the left (that is, in the direction of N_2 and O_2). The lower temperatures also mean that the rate of the reaction is decreased, however, so the NO formed at high temperatures is essentially "frozen" in that form as the gas cools.

The gases exhausting from the cylinder are still quite hot, perhaps 1200 K. At this temperature, as shown in Figure 15.16, the equilibrium constant for formation of NO is much smaller. However, the rate of conversion of NO to N_2 and O_2 is too slow to permit much loss of NO before the gases are cooled still 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 the rapid conversion of NO to N_2 and O_2 at the temperature of the exhaust gas. Some catalysts for this reaction have been developed that are reasonably effective under the grueling conditions found in automotive exhaust systems. Nevertheless, scientists and engineers are continually searching for new materials that provide even more effective catalysis of the decomposition of nitrogen oxides.



▲ Figure 15.16 Equilibrium and temperature. The graph shows how the equilibrium constant for the reaction $\frac{1}{2} \text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightleftharpoons \text{NO}(\text{g})$ varies as a function of 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 REVIEW

SUMMARY AND KEY TERMS

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

Section 15.2 An equilibrium that is used throughout this chapter is the reaction $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$. 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-constant expression** is written as

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

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

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

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

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

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

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

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

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

KEY SKILLS

- Understand what is meant by chemical equilibrium and how it relates to reaction rates.
- Write the equilibrium-constant expression for any reaction.
- Relate K_c and K_p .
- 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.

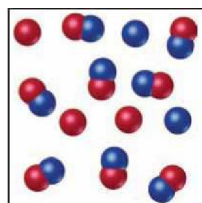
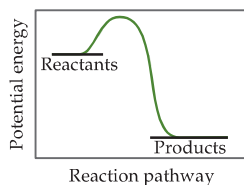
- Write the equilibrium-constant expression for a heterogeneous reaction.
- Calculate an equilibrium constant from concentration measurements.
- Predict the direction of a reaction given the equilibrium constant and the concentrations of reactants and products.
- Calculate equilibrium concentrations given the equilibrium constant and all but one equilibrium concentration.
- Calculate equilibrium concentrations given the equilibrium constant and the starting concentrations.
- Understand how changing the concentrations, volume, or temperature of a system at equilibrium affects the equilibrium position.

KEY EQUATIONS

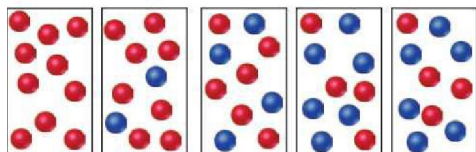
- $K_c = \frac{[D]^d[E]^e}{[A]^a[B]^b}$ [15.8] The equilibrium-constant expression for a general reaction of the type $a A + b B \rightleftharpoons d D + e E$; the concentrations are equilibrium concentrations only
- $K_p = \frac{(P_D)^d(P_E)^e}{(P_A)^a(P_B)^b}$ [15.11] The equilibrium-constant expression in terms of equilibrium partial pressures
- $K_p = K_c(RT)^{\Delta n}$ [15.14] Relating the equilibrium constant based on pressures to the equilibrium constant based on concentration
- $Q_c = \frac{[D]^d[E]^e}{[A]^a[B]^b}$ [15.22] The reaction quotient. The concentrations are for any time during a reaction. If the concentrations are equilibrium concentrations, then $Q_c = K_c$.

VISUALIZING CONCEPTS

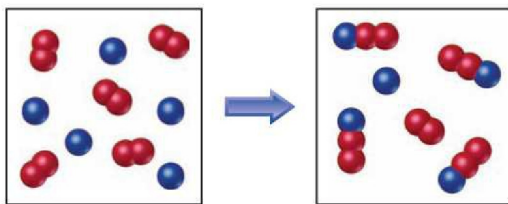
- 15.1 (a) Based on the following energy profile, predict whether $k_f > k_r$ or $k_f < k_r$. (b) Using Equation 15.5, predict whether the equilibrium constant for the process is greater than 1 or less than 1. [Section 15.1]



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

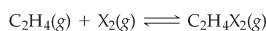


- 15.4 The following diagram represents a reaction shown going to completion. (a) Letting A = red spheres and B = blue spheres, write a balanced equation for the reaction. (b) Write the equilibrium-constant expression for the reaction. (c) Assuming that all of the molecules are in the gas phase, calculate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

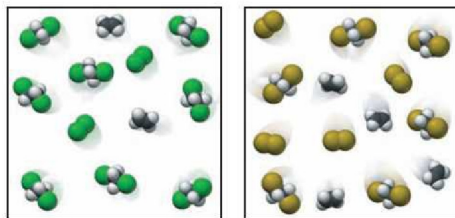


- 15.3 The following diagram represents an equilibrium mixture produced for a reaction of the type $A + X \rightleftharpoons AX$. If the volume is 1 L, is K greater or smaller than 1? [Section 15.2]

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

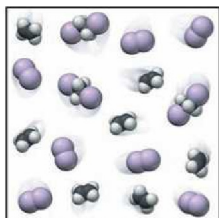


The following figures represent the concentrations at equilibrium at the same temperature when X_2 is Cl_2 (green), Br_2 (brown), and I_2 (purple). List the equilibria from smallest to largest equilibrium constant. [Section 15.3]



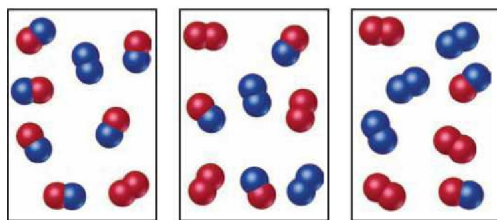
(a)

(b)



(c)

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

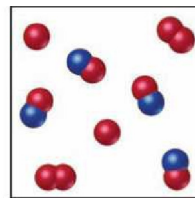


(i)

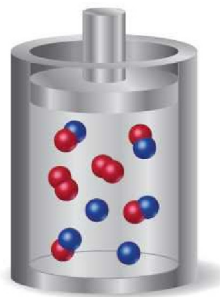
(ii)

(iii)

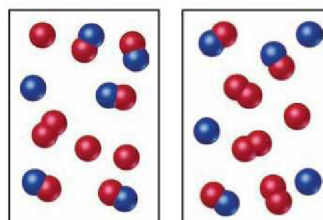
- 15.7 The reaction $A_2(g) + B(g) \rightleftharpoons A(g) + AB(g)$ has an equilibrium constant of $K_p = 2$. The accompanying diagram shows a mixture containing A atoms (red), A_2 molecules, and AB molecules (red and blue). How many B atoms should be added to the diagram to illustrate an equilibrium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



- 15.8 The following diagram represents the equilibrium state for the reaction $A_2(g) + 2 B(g) \rightleftharpoons 2 AB(g)$. (a) Assuming the volume is 1 L, calculate the equilibrium constant, K_c , for the reaction. (b) If the volume of the equilibrium mixture is decreased, will the number of AB molecules increase or decrease? [Sections 15.5 and 15.7]



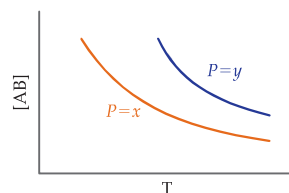
- 15.9 The following diagrams represent equilibrium mixtures for the reaction $A_2 + B \rightleftharpoons A + AB$ at (1) 300 K and (2) 500 K. The A atoms are red, and the B atoms are blue. Is the reaction exothermic or endothermic? [Section 15.7]



(a)

(b)

- 15.10 The following graph represents the yield of the compound AB at equilibrium in the reaction $A(g) + B(g) \rightleftharpoons AB(g)$.



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

EXERCISES

Equilibrium; The Equilibrium Constant

- 15.11** Suppose that the gas-phase reactions $A \longrightarrow B$ and $B \longrightarrow A$ are both elementary processes with rate constants of $3.8 \times 10^{-2} \text{ s}^{-1}$ and $3.1 \times 10^{-1} \text{ s}^{-1}$, respectively. (a) What is the value of the equilibrium constant for the equilibrium $A(g) \rightleftharpoons B(g)$? (b) Which is greater at equilibrium, the partial pressure of A or the partial pressure of B? Explain.
- 15.12** Consider the reaction $A + B \rightleftharpoons C + D$. Assume that both the forward reaction and the reverse reaction are elementary processes and that the value of the equilibrium constant is very large. (a) Which species predominate at equilibrium, reactants or products? (b) Which reaction has the larger rate constant, the forward or the reverse? Explain.
- 15.13** Write the expression for K_c for the following reactions. In each case indicate whether the reaction is homogeneous or heterogeneous.
- (a) $3 \text{ NO}(g) \rightleftharpoons \text{N}_2\text{O}(g) + \text{NO}_2(g)$
 (b) $\text{CH}_4(g) + 2 \text{ H}_2\text{S}(g) \rightleftharpoons \text{CS}_2(g) + 4 \text{ H}_2(g)$
 (c) $\text{Ni}(\text{CO})_4(g) \rightleftharpoons \text{Ni}(s) + 4 \text{ CO}(g)$
 (d) $\text{HF}(aq) \rightleftharpoons \text{H}^+(aq) + \text{F}^-(aq)$
 (e) $2 \text{ Ag}(s) + \text{Zn}^{2+}(aq) \rightleftharpoons 2 \text{ Ag}^+(aq) + \text{Zn}(s)$
- 15.14** Write the expressions for K_c for the following reactions. In each case indicate whether the reaction is homogeneous or heterogeneous.
- (a) $2 \text{ O}_3(g) \rightleftharpoons 3 \text{ O}_2(g)$
 (b) $\text{Ti}(s) + 2 \text{ Cl}_2(g) \rightleftharpoons \text{TiCl}_4(l)$
 (c) $2 \text{ C}_2\text{H}_4(g) + 2 \text{ H}_2\text{O}(g) \rightleftharpoons 2 \text{ C}_2\text{H}_6(g) + \text{O}_2(g)$
 (d) $\text{C}(s) + 2 \text{ H}_2(g) \rightleftharpoons \text{CH}_4(g)$
 (e) $4 \text{ HCl}(aq) + \text{O}_2(g) \rightleftharpoons 2 \text{ H}_2\text{O}(l) + 2 \text{ Cl}_2(g)$
- 15.15** When the following reactions come to equilibrium, does the equilibrium mixture contain mostly reactants or mostly products?
 (a) $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{ NO}(g)$; $K_c = 1.5 \times 10^{-10}$
 (b) $2 \text{ SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{ SO}_3(g)$; $K_p = 2.5 \times 10^9$
- 15.16** Which of the following reactions lies to the right, favoring the formation of products, and which lies to the left, favoring formation of reactants?
 (a) $2 \text{ NO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{ NO}_2(g)$; $K_p = 5.0 \times 10^{12}$
 (b) $2 \text{ HBr}(g) \rightleftharpoons \text{H}_2(g) + \text{Br}_2(g)$; $K_c = 5.8 \times 10^{-18}$
- 15.17** If $K_c = 0.042$ for $\text{PCl}_3(g) + \text{Cl}_2(g) \rightleftharpoons \text{PCl}_5(g)$ at 500 K, what is the value of K_p for this reaction at this temperature?
- 15.18** Calculate K_c at 303 K for $\text{SO}_2(g) + \text{Cl}_2(g) \rightleftharpoons \text{SO}_2\text{Cl}_2(g)$ if $K_p = 34.5$ at this temperature.
- 15.19** The equilibrium constant for the reaction

$$2 \text{ NO}(g) + \text{Br}_2(g) \rightleftharpoons 2 \text{ NOBr}(g)$$
 is $K_c = 1.3 \times 10^{-2}$ at 1000 K. (a) Calculate K_c for $2 \text{ NOBr}(g) \rightleftharpoons 2 \text{ NO}(g) + \text{Br}_2(g)$. (b) At this temperature does the equilibrium favor NO and Br_2 , or does it favor NOBr?
- 15.20** Consider the following equilibrium:

$$2 \text{ H}_2(g) + \text{S}_2(g) \rightleftharpoons 2 \text{ H}_2\text{S}(g) \quad K_c = 1.08 \times 10^7 \text{ at } 700^\circ\text{C}$$
 (a) Calculate K_p . (b) Does the equilibrium mixture contain mostly H_2 and S_2 or mostly H_2S ?
- 15.21** At 1000 K, $K_p = 1.85$ for the reaction

$$\text{SO}_2(g) + \frac{1}{2} \text{ O}_2(g) \rightleftharpoons \text{SO}_3(g)$$
 (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)?
- 15.22** Consider the following equilibrium, for which $K_p = 0.0752$ at 480°C :

$$2 \text{ Cl}_2(g) + 2 \text{ H}_2\text{O}(g) \rightleftharpoons 4 \text{ HCl}(g) + \text{O}_2(g)$$
 (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 $\text{Cl}_2(g) + \text{H}_2\text{O}(g) \rightleftharpoons 2 \text{ HCl}(g) + \frac{1}{2} \text{ O}_2(g)$? (c) What is the value of K_c for the reaction in part (b)?
- 15.23** The following equilibria were attained at 823 K:

$$\text{CoO}(s) + \text{H}_2(g) \rightleftharpoons \text{Co}(s) + \text{H}_2\text{O}(g) \quad K_c = 67$$

$$\text{CoO}(s) + \text{CO}(g) \rightleftharpoons \text{Co}(s) + \text{CO}_2(g) \quad K_c = 490$$
 Based on these equilibria, calculate the equilibrium constant for $\text{H}_2(g) + \text{CO}_2(g) \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O}(g)$ at 823 K.
- 15.24** Consider the equilibrium

$$\text{N}_2(g) + \text{O}_2(g) + \text{Br}_2(g) \rightleftharpoons 2 \text{ NOBr}(g)$$
 Calculate the equilibrium constant K_p for this reaction, given the following information (at 298 K):

$$2 \text{ NO}(g) + \text{Br}_2(g) \rightleftharpoons 2 \text{ NOBr}(g) \quad K_c = 2.0$$

$$2 \text{ NO}(g) \rightleftharpoons \text{N}_2(g) + \text{O}_2(g) \quad K_c = 2.1 \times 10^{30}$$
- 15.25** 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-constant expression for this reaction in terms of partial pressures. (b) Explain why we normally exclude pure solids and liquids from equilibrium-constant expressions.
- 15.26** 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-constant expression for this reaction in terms of partial pressures. (b) Why doesn't the concentration of Na_2O appear in the equilibrium-constant expression?

Calculating Equilibrium Constants

- 15.27** Gaseous hydrogen iodide is placed in a closed container at 425°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 $[\text{HI}] = 3.53 \times 10^{-3} \text{ M}$, $[\text{H}_2] = 4.79 \times 10^{-4} \text{ M}$, and $[\text{I}_2] = 4.79 \times 10^{-4} \text{ M}$. What is the value of K_c at this temperature?

- 15.28** Methanol (CH_3OH) is produced commercially by the catalyzed reaction of carbon monoxide and hydrogen: $\text{CO}(\text{g}) + 2 \text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$. An equilibrium mixture in a 2.00-L vessel is found to contain 0.0406 mol CH_3OH , 0.170 mol CO , and 0.302 mol H_2 at 500 K. Calculate K_c at this temperature.
- 15.29** The equilibrium $2 \text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{NOCl}(\text{g})$ is established at 500 K. An equilibrium mixture of the three gases has partial pressures of 0.095 atm, 0.171 atm, and 0.28 atm for NO , Cl_2 , and NOCl , respectively. Calculate K_p for this reaction at 500 K.
- 15.30** Phosphorus trichloride gas and chlorine gas react to form phosphorus pentachloride gas: $\text{PCl}_3 + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g})$. A gas vessel is charged with a mixture of $\text{PCl}_3(\text{g})$ and $\text{Cl}_2(\text{g})$, which is allowed to equilibrate at 450 K. At equilibrium the partial pressures of the three gases are $P_{\text{PCl}_3} = 0.124$ atm, $P_{\text{Cl}_2} = 0.157$ atm, and $P_{\text{PCl}_5} = 1.30$ atm. (a) What is the value of K_p at this temperature? (b) Does the equilibrium favor reactants or products?
- 15.31** A mixture of 0.10 mol of NO , 0.050 mol of H_2 , and 0.10 mol of H_2O is placed in a 1.0-L vessel at 300 K. The following equilibrium is established:

$$2 \text{NO}(\text{g}) + 2 \text{H}_2(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$$
At equilibrium $[\text{NO}] = 0.062 \text{ M}$. (a) Calculate the equilibrium concentrations of H_2 , N_2 , and H_2O . (b) Calculate K_c .

Applications of Equilibrium Constants

- 15.35** (a) How does a reaction quotient differ from an equilibrium constant? (b) If $Q_c < K_c$, in which direction will a reaction proceed in order to reach equilibrium? (c) What condition must be satisfied so that $Q_c = K_c$?
- 15.36** (a) How is a reaction quotient used to determine whether a system is at equilibrium? (b) If $Q_c > K_c$, how must the reaction proceed to reach equilibrium? (c) At the start of a certain reaction, only reactants are present; no products have been formed. What is the value of Q_c at this point in the reaction?
- 15.37** At 100 °C the equilibrium constant for the reaction $\text{COCl}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{Cl}_2(\text{g})$ has the value $K_c = 2.19 \times 10^{-10}$. Are the following mixtures of COCl_2 , CO , and Cl_2 at 100 °C at equilibrium? If not, indicate the direction that the reaction must proceed to achieve equilibrium. (a) $[\text{COCl}_2] = 2.00 \times 10^{-3} \text{ M}$, $[\text{CO}] = 3.3 \times 10^{-6} \text{ M}$, $[\text{Cl}_2] = 6.62 \times 10^{-6} \text{ M}$; (b) $[\text{COCl}_2] = 4.50 \times 10^{-2} \text{ M}$, $[\text{CO}] = 1.1 \times 10^{-7} \text{ M}$, $[\text{Cl}_2] = 2.25 \times 10^{-6} \text{ M}$; (c) $[\text{COCl}_2] = 0.0100 \text{ M}$, $[\text{CO}] = [\text{Cl}_2] = 1.48 \times 10^{-6} \text{ M}$
- 15.38** As shown in Table 15.2, K_p for the equilibrium

$$\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$$
is 4.51×10^{-5} at 450 °C. For each of the mixtures listed here, indicate whether the mixture is at equilibrium at 450 °C. If it is not at equilibrium, indicate the direction (toward product or toward reactants) in which the mixture must shift to achieve equilibrium.
(a) 98 atm NH_3 , 45 atm N_2 , 55 atm H_2
(b) 57 atm NH_3 , 143 atm N_2 , no H_2
(c) 13 atm NH_3 , 27 atm N_2 , 82 atm H_2
- 15.32** A mixture of 1.374 g of H_2 and 70.31 g of Br_2 is heated in a 2.00-L vessel at 700 K. These substances react as follows:

$$\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2 \text{HBr}(\text{g})$$
At equilibrium the vessel is found to contain 0.566 g of H_2 . (a) Calculate the equilibrium concentrations of H_2 , Br_2 , and HBr . (b) Calculate K_c .
- 15.33** A mixture of 0.2000 mol of CO_2 , 0.1000 mol of H_2 , and 0.1600 mol of H_2O is placed in a 2.000-L vessel. The following equilibrium is established at 500 K:

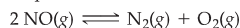
$$\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$$
(a) Calculate the initial partial pressures of CO_2 , H_2 , and H_2O . (b) At equilibrium $P_{\text{H}_2\text{O}} = 3.51$ atm. Calculate the equilibrium partial pressures of CO_2 , H_2 , and CO . (c) Calculate K_p for the reaction.
- 15.34** A flask is charged with 1.500 atm of $\text{N}_2\text{O}_4(\text{g})$ and 1.00 atm $\text{NO}_2(\text{g})$ at 25 °C, and the following equilibrium is achieved:

$$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$$
After equilibrium is reached, the partial pressure of NO_2 is 0.512 atm. (a) What is the equilibrium partial pressure of N_2O_4 ? (b) Calculate the value of K_p for the reaction.
- 15.39** At 100 °C, $K_c = 0.078$ for the reaction

$$\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$$
In an equilibrium mixture of the three gases, the concentrations of SO_2Cl_2 and SO_2 are 0.108 M and 0.052 M, respectively. What is the partial pressure of Cl_2 in the equilibrium mixture?
- 15.40** At 900 K the following reaction has $K_p = 0.345$:

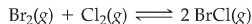
$$2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$$
In an equilibrium mixture the partial pressures of SO_2 and O_2 are 0.135 atm and 0.455 atm, respectively. What is the equilibrium partial pressure of SO_3 in the mixture?
- 15.41** (a) At 1285 °C the equilibrium constant for the reaction $\text{Br}_2(\text{g}) \rightleftharpoons 2 \text{Br}(\text{g})$ is $K_c = 1.04 \times 10^{-3}$. A 0.200-L vessel containing an equilibrium mixture of the gases has 0.245 g $\text{Br}_2(\text{g})$ in it. What is the mass of $\text{Br}(\text{g})$ in the vessel? (b) For the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$, $K_c = 55.3$ at 700 K. In a 2.00-L flask containing an equilibrium mixture of the three gases, there are 0.056 g H_2 and 4.36 g I_2 . What is the mass of HI in the flask?
- 15.42** (a) At 800 K the equilibrium constant for $\text{I}_2(\text{g}) \rightleftharpoons 2 \text{I}(\text{g})$ is $K_c = 3.1 \times 10^{-5}$. If an equilibrium mixture in a 10.0-L vessel contains 2.67×10^{-2} g of $\text{I}(\text{g})$, how many grams of I_2 are in the mixture? (b) For $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$, $K_p = 3.0 \times 10^4$ at 700 K. In a 2.00-L vessel the equilibrium mixture contains 1.17 g of SO_3 and 0.105 g of O_2 . How many grams of SO_2 are in the vessel?

- 15.43** At 2000 °C the equilibrium constant for the reaction



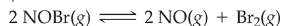
is $K_c = 2.4 \times 10^3$. If the initial concentration of NO is 0.200 M, what are the equilibrium concentrations of NO, N_2 , and O_2 ?

- 15.44** For the equilibrium



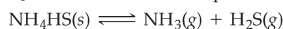
at 400 K, $K_c = 7.0$. If 0.25 mol of Br_2 and 0.25 mol of Cl_2 are introduced into a 1.0-L container at 400 K, what will be the equilibrium concentrations of Br_2 , Cl_2 , and BrCl ?

- 15.45** At 373 K, $K_p = 0.416$ for the equilibrium



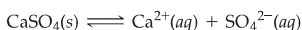
If the pressures of $\text{NOBr}(g)$ and $\text{NO}(g)$ are equal, what is the equilibrium pressure of $\text{Br}_2(g)$?

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



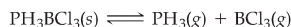
Calculate the equilibrium concentrations of NH_3 and H_2S if a sample of solid NH_4HS is placed in a closed vessel and decomposes until equilibrium is reached.

- 15.47** Consider the reaction



At 25 °C the equilibrium constant is $K_c = 2.4 \times 10^{-5}$ for this reaction. **(a)** If excess $\text{CaSO}_4(s)$ is mixed with water at 25 °C to produce a saturated solution of CaSO_4 , what are the equilibrium concentrations of Ca^{2+} and SO_4^{2-} ? **(b)** If the resulting solution has a volume of 3.0 L, what is the minimum mass of $\text{CaSO}_4(s)$ needed to achieve equilibrium?

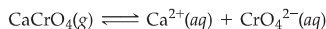
- 15.48** At 80 °C, $K_c = 1.87 \times 10^{-3}$ for the reaction



(a) Calculate the equilibrium concentrations of PH_3 and BCl_3 if a solid sample of PH_3BCl_3 is placed in a closed vessel and decomposes until equilibrium is reached. **(b)** If the flask has a volume of 0.500 L, what is the minimum mass of $\text{PH}_3\text{BCl}_3(s)$ that must be added to the flask to achieve equilibrium?

- 15.49** For the reaction $\text{I}_2 + \text{Br}_2(g) \rightleftharpoons 2 \text{IBr}(g)$, $K_c = 280$ at 150 °C. Suppose that 0.500 mol IBr in a 1.00-L flask is allowed to reach equilibrium at 150 °C. What are the equilibrium concentrations of IBr, I_2 , and Br_2 ?

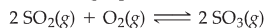
- 15.50** At 25 °C the reaction



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

Le Châtelier's Principle

- 15.51** Consider the following equilibrium, for which $\Delta H < 0$



How will each of the following changes affect an equilibrium mixture of the three gases? **(a)** $\text{O}_2(g)$ is added to the system; **(b)** the reaction mixture is heated; **(c)** the volume of the reaction vessel is doubled; **(d)** a catalyst is added to the mixture; **(e)** the total pressure of the system is increased by adding a noble gas; **(f)** $\text{SO}_3(g)$ is removed from the system.

- 15.52** Consider $4 \text{NH}_3(g) + 5 \text{O}_2(g) \rightleftharpoons 4 \text{NO}(g) + 6 \text{H}_2\text{O}(g)$, $\Delta H = -904.4 \text{ kJ}$. How does each of the following changes affect the yield of NO at equilibrium? Answer increase, decrease, or no change: **(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.

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

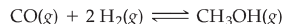
- 15.54** For a certain gas-phase reaction, the fraction of products in an equilibrium mixture is increased by increasing the temperature and increasing the volume of the reaction vessel. **(a)** What can you conclude about the reaction from the influence of temperature on the equilibrium? **(b)** What can you conclude from the influence of increasing the volume?

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



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

- 15.56** Methanol (CH_3OH) can be made by the reaction of CO with H_2 :



(a) Use thermochemical data in Appendix C to calculate ΔH° 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?

ADDITIONAL EXERCISES

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



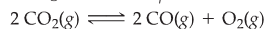
At 25 °C the rate constants for the forward and reverse reactions are $1.4 \times 10^{-28} \text{ M}^{-1} \text{ s}^{-1}$ and $9.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, respectively. **(a)** What is the value for the equilibrium constant at 25 °C? **(b)** Are reactants or products more plentiful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

- 15.58 If $K_c = 1$ for the equilibrium $2 A(g) \rightleftharpoons B(g)$, what is the relationship between $[A]$ and $[B]$ at equilibrium?
- 15.59 A mixture of CH_4 and H_2O is passed over a nickel catalyst at 1000 K. The emerging gas is collected in a 5.00-L flask and is found to contain 8.62 g of CO , 2.60 g of H_2 , 43.0 g of CH_4 , and 48.4 g of H_2O . Assuming that equilibrium has been reached, calculate K_c and K_p for the reaction.
- 15.60 When 2.00 mol of SO_2Cl_2 is placed in a 2.00-L flask at 303 K, 56% of the SO_2Cl_2 decomposes to SO_2 and Cl_2 :
- $$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$
- Calculate K_c for this reaction at this temperature.
- 15.61 A mixture of H_2 , S , and H_2S is held in a 1.0-L vessel at 90 °C until the following equilibrium is achieved:
- $$H_2(g) + S(s) \rightleftharpoons H_2S(g)$$
- At equilibrium the mixture contains 0.46 g of H_2S and 0.40 g H_2 . (a) Write the equilibrium-constant expression for this reaction. (b) What is the value of K_c for the reaction at this temperature? (c) Why can we ignore the amount of S when doing the calculation in part (b)?
- 15.62 A sample of nitrosyl bromide (NOBr) decomposes according to the equation
- $$2 NOBr(g) \rightleftharpoons 2 NO(g) + Br_2(g)$$
- An equilibrium mixture in a 5.00-L vessel at 100 °C contains 3.22 g of NOBr, 3.08 g of NO, and 4.19 g of Br_2 . (a) Calculate K_c . (b) What is the total pressure exerted by the mixture of gases?
- 15.63 Consider the hypothetical reaction $A(g) \rightleftharpoons 2 B(g)$. A flask is charged with 0.75 atm of pure A, after which it is allowed to reach equilibrium at 0 °C. At equilibrium the partial pressure of A is 0.36 atm. (a) What is the total pressure in the flask at equilibrium? (b) What is the value of K_p ?
- 15.64 As shown in Table 15.2, the equilibrium constant for the reaction $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$ is $K_p = 4.34 \times 10^{-3}$ at 300 °C. Pure NH_3 is placed in a 1.00-L flask and allowed to reach equilibrium at this temperature. There are 1.05 g NH_3 in the equilibrium mixture. (a) What are the masses of N_2 and H_2 in the equilibrium mixture? (b) What was the initial mass of ammonia placed in the vessel? (c) What is the total pressure in the vessel?
- 15.65 For the equilibrium
- $$2 IBr(g) \rightleftharpoons I_2(g) + Br_2(g)$$
- $K_p = 8.5 \times 10^{-3}$ at 150 °C. If 0.025 atm of IBr is placed in a 2.0-L container, what is the partial pressure of this substance after equilibrium is reached?
- 15.66 For the equilibrium
- $$PH_3BCl_3(s) \rightleftharpoons PH_3(g) + BCl_3(g)$$
- $K_p = 0.052$ at 60 °C. (a) Calculate K_c . (b) Some solid PH_3BCl_3 is added to a closed 0.500-L vessel at 60 °C; the vessel is then charged with 0.0128 mol of $BCl_3(g)$. What is the equilibrium concentration of PH_3 ?
- [15.67] Solid NH_4HS is introduced into an evacuated flask at 24 °C. The following reaction takes place:
- $$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$
- At equilibrium the total pressure (for NH_3 and H_2S taken together) is 0.614 atm. What is K_p for this equilibrium at 24 °C?
- [15.68] A 0.831-g sample of SO_3 is placed in a 1.00-L container and heated to 1100 K. The SO_3 decomposes to SO_2 and O_2 .
- $$2 SO_3(g) \rightleftharpoons 2 SO_2(g) + O_2(g)$$
- At equilibrium the total pressure in the container is 1.300 atm. Find the values of K_p and K_c for this reaction at 1100 K.
- 15.69 Nitric oxide (NO) reacts readily with chlorine gas as follows:
- $$2 NO(g) + Cl_2(g) \rightleftharpoons 2 NOCl(g)$$
- At 700 K the equilibrium constant K_p for this reaction is 0.26. Predict the behavior of each of the following mixtures at this temperature: (a) $P_{NO} = 0.15$ atm, $P_{Cl_2} = 0.31$ atm, and $P_{NOCl} = 0.11$ atm; (b) $P_{NO} = 0.12$ atm, $P_{Cl_2} = 0.10$ atm, and $P_{NOCl} = 0.050$ atm; (c) $P_{NO} = 0.15$ atm, $P_{Cl_2} = 0.20$ atm, and $P_{NOCl} = 5.10 \times 10^{-3}$ atm.
- 15.70 At 900 °C, $K_c = 0.0108$ for the reaction
- $$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$
- A mixture of $CaCO_3$, CaO , and CO_2 is placed in a 10.0-L vessel at 900 °C. For the following mixtures, will the amount of $CaCO_3$ increase, decrease, or remain the same as the system approaches equilibrium?
- (a) 15.0 g $CaCO_3$, 15.0 g CaO , and 4.25 g CO_2
 (b) 2.50 g $CaCO_3$, 25.0 g CaO , and 5.66 g CO_2
 (c) 30.5 g $CaCO_3$, 25.5 g CaO , and 6.48 g CO_2 .
- 15.71 When 1.50 mol CO_2 and 1.50 mol H_2 are placed in a 0.750-L container at 395 °C, the following equilibrium is achieved: $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$. If $K_c = 0.802$, what are the concentrations of each substance in the equilibrium mixture?
- 15.72 The equilibrium constant K_c for $C(s) + CO_2(g) \rightleftharpoons 2 CO(g)$ is 1.9 at 1000 K and 0.133 at 298 K. (a) If excess C is allowed to react with 25.0 g of CO_2 in a 3.00-L vessel at 1000 K, how many grams of CO_2 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) If the reaction is endothermic, how does increasing the temperature affect the equilibrium constant?
- 15.73 NiO is to be reduced to nickel metal in an industrial process by use of the reaction
- $$NiO(s) + CO(g) \rightleftharpoons Ni(s) + CO_2(g)$$
- At 1600 K the equilibrium constant for the reaction is $K_p = 6.0 \times 10^2$. If a CO pressure of 150 torr is to be employed in the furnace and total pressure never exceeds 760 torr, will reduction occur?
- [15.74] At 700 K the equilibrium constant for the reaction
- $$CCl_4(g) \rightleftharpoons C(s) + 2 Cl_2(g)$$
- is $K_p = 0.76$. A flask is charged with 2.00 atm of CCl_4 , which then reaches equilibrium at 700 K. (a) What fraction of the CCl_4 is converted into C and Cl_2 ? (b) What are the partial pressures of CCl_4 and Cl_2 at equilibrium?
- [15.75] The reaction $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ has $K_p = 0.0870$ at 300 °C. A flask is charged with 0.50 atm PCl_3 , 0.50 atm Cl_2 , and 0.20 atm PCl_5 at this temperature. (a) Use the reaction quotient to determine the direction the reaction must proceed to reach equilibrium. (b) Calculate the equilibrium partial pressures of the gases. (c) What effect will increasing the volume of the system have on the mole fraction of Cl_2 in the equilibrium mixture? (d) The reaction is exothermic. What effect will increasing the temperature of the system have on the mole fraction of Cl_2 in the equilibrium mixture?

- [15.76] An equilibrium mixture of H_2 , I_2 , and HI at 458°C contains 0.112 mol H_2 , 0.112 mol I_2 , and 0.775 mol HI in a 5.00-L vessel. What are the equilibrium partial pressures when equilibrium is reestablished following the addition of 0.100 mol of HI ?
- [15.77] Consider the hypothetical reaction $\text{A}(\text{g}) + 2\text{B}(\text{g}) \rightleftharpoons 2\text{C}(\text{g})$, for which $K_c = 0.25$ at some 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.)

- 15.78 At 1200 K , the approximate temperature of automobile exhaust gases (Figure 15.16), K_p for the reaction



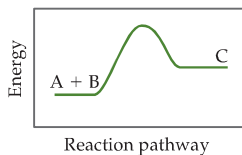
is about 1×10^{-13} . Assuming that the exhaust gas (total pressure 1 atm) contains 0.2% CO , 12% CO_2 , and 3% O_2 by volume, is the system at equilibrium with respect to the above reaction? Based on your conclusion, would the CO concentration in the exhaust be decreased or increased by a catalyst that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

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

INTEGRATIVE EXERCISES

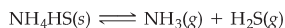
- 15.80 Consider the equilibrium $\text{IO}_4^-(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_4\text{IO}_6^-(\text{aq})$, $K_c = 3.5 \times 10^{-2}$. If you start with 20.0 mL of a 0.905 M solution of NaIO_4 , and then dilute it with water to 250.0 mL , what is the concentration of H_4IO_6^- at equilibrium?
- 15.81 Consider the following equilibria in aqueous solution:
- $\text{Na}(\text{s}) + \text{Ag}^+(\text{aq}) \rightleftharpoons \text{Na}^+(\text{aq}) + \text{Ag}(\text{s})$
 - $3\text{Hg}(\text{l}) + 2\text{Al}^{3+}(\text{aq}) \rightleftharpoons 3\text{Hg}^{2+}(\text{aq}) + 2\text{Al}(\text{s})$
 - $\text{Zn}(\text{s}) + 2\text{H}^+(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$
- (a) For each reaction, write the equilibrium-constant expression for K_c . (b) Using information provided in Table 4.5, predict whether K_c is large ($K_c \gg 1$) or small ($K_c \ll 1$). Explain your reasoning. (c) At 25°C the reaction $\text{Cd}(\text{s}) + \text{Fe}^{2+}(\text{aq}) \rightleftharpoons \text{Cd}^{2+}(\text{aq}) + \text{Fe}(\text{s})$ has $K_c = 6 \times 10^{-2}$. If Cd were added to Table 4.5, would you expect it to be above or below iron? Explain.
- 15.82 Silver chloride, $\text{AgCl}(\text{s})$, is an insoluble strong electrolyte. (a) Write the equation for the dissolution of $\text{AgCl}(\text{s})$ in $\text{H}_2\text{O}(\text{l})$. (b) Write the expression for K_c for the reaction in part (a). (c) Based on the thermochemical data in Appendix C and Le Châtelier's principle, predict whether the solubility of AgCl in H_2O increases or decreases with increasing temperature.
- 15.83 The hypothetical reaction $\text{A} + \text{B} \rightleftharpoons \text{C}$ occurs in the forward direction in a single step. The energy profile of the reaction is shown in the drawing. (a) Is the forward or reverse reaction faster at equilibrium? (b) Would you expect the equilibrium to favor reactants or products? (c) In general, how would a catalyst affect the energy profile

shown? (d) How would a catalyst affect the ratio of the rate constants for the forward and reverse reactions? (e) How would you expect the equilibrium constant of the reaction to change with increasing temperature?



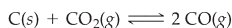
- [15.84] Consider the equilibrium $\text{A} \rightleftharpoons \text{B}$ in which both the forward and reverse reactions are elementary (single-step) reactions. Assume that the only effect of a catalyst on the reaction is to lower the activation energies of the forward and reverse reactions, as shown in Figure 15.15. Using the Arrhenius equation (Section 14.5), prove that the equilibrium constant is the same for the catalyzed reaction as for the uncatalyzed one.

- [15.85] At 25°C the reaction



has $K_p = 0.120$. A 5.00-L flask is charged with 0.300 g of pure $\text{H}_2\text{S}(\text{g})$ at 25°C . Solid NH_4HS is then added until there is excess unreacted solid remaining. (a) What is the initial pressure of $\text{H}_2\text{S}(\text{g})$ in the flask? (b) Why does no reaction occur until NH_4HS is added? (c) What are the partial pressures of NH_3 and H_2S at equilibrium? (d) What is the mole fraction of H_2S in the gas mixture at equilibrium? (e) What is the minimum mass, in grams, of NH_4HS that must be added to the flask to achieve equilibrium?

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

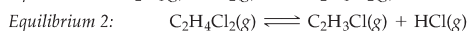
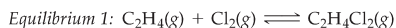


The table included below shows the relative mole percentages of $\text{CO}_2(g)$ and $\text{CO}(g)$ at a total pressure of 1 atm for several temperatures. Calculate the value of K_p at each temperature. Is the reaction exothermic or endothermic? Explain.

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

- 15.87 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?

- [15.88] Polyvinyl chloride (PVC) is one of the most commercially important polymers (Table 12.5). PVC is made by addition polymerization of vinyl chloride ($\text{C}_2\text{H}_3\text{Cl}$). Vinyl chloride is synthesized from ethylene (C_2H_4) in a two-step process involving the following equilibria:



The product of Equilibrium 1 is 1,2-dichloroethane, a compound in which one Cl atom is bonded to each C atom. (a) Draw Lewis structures for $\text{C}_2\text{H}_4\text{Cl}_2$ and $\text{C}_2\text{H}_3\text{Cl}$. What are the C—C bond orders in these two compounds? (b) Use average bond enthalpies (Table 8.4) to estimate the enthalpy changes in the two equilibria. (c) How would the yield of $\text{C}_2\text{H}_4\text{Cl}_2$ in Equilibrium 1 vary with temperature and volume? (d) How would the yield of $\text{C}_2\text{H}_3\text{Cl}$ in Equilibrium 2 vary with temperature and volume? (e) Look up the normal boiling points of 1,2-dichloroethane and vinyl chloride in a sourcebook, such as the *CRC Handbook of Chemistry and Physics*. Based on these data, propose a reactor design (analogous to Figure 15.12) that could be used to maximize the amount of $\text{C}_2\text{H}_3\text{Cl}$ produced by using the two equilibria.