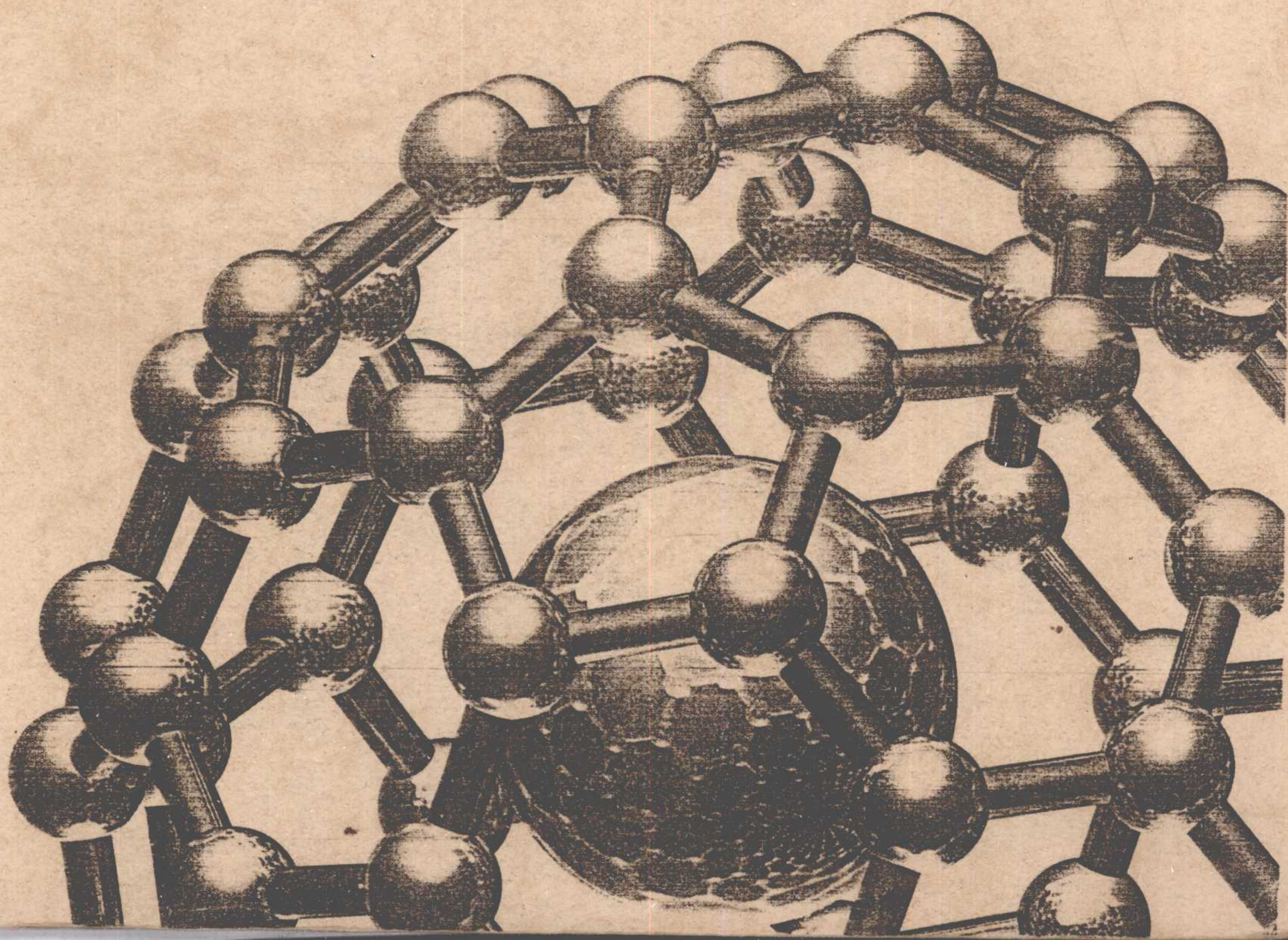


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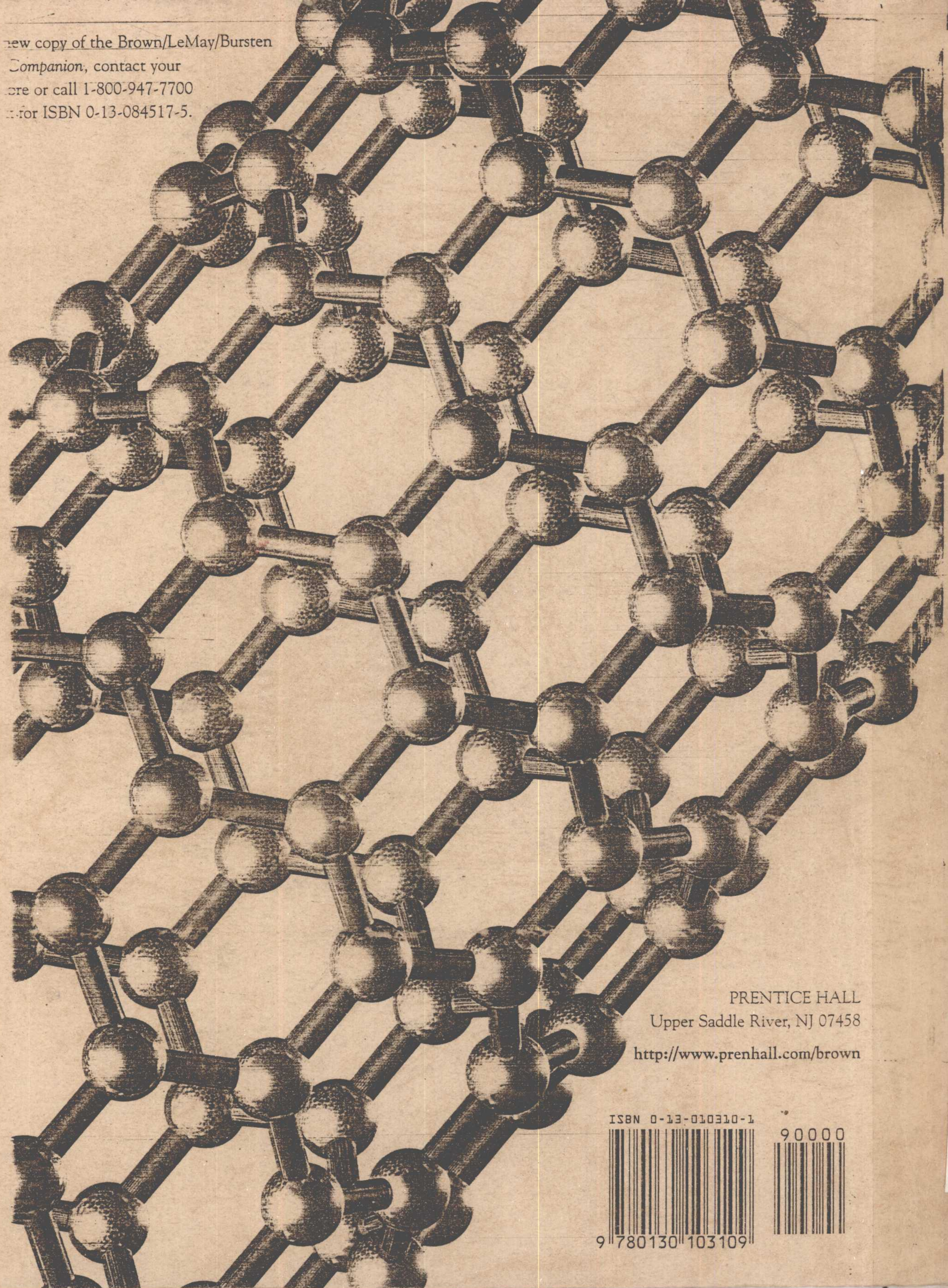
# CHEMISTRY

THE CENTRAL SCIENCE

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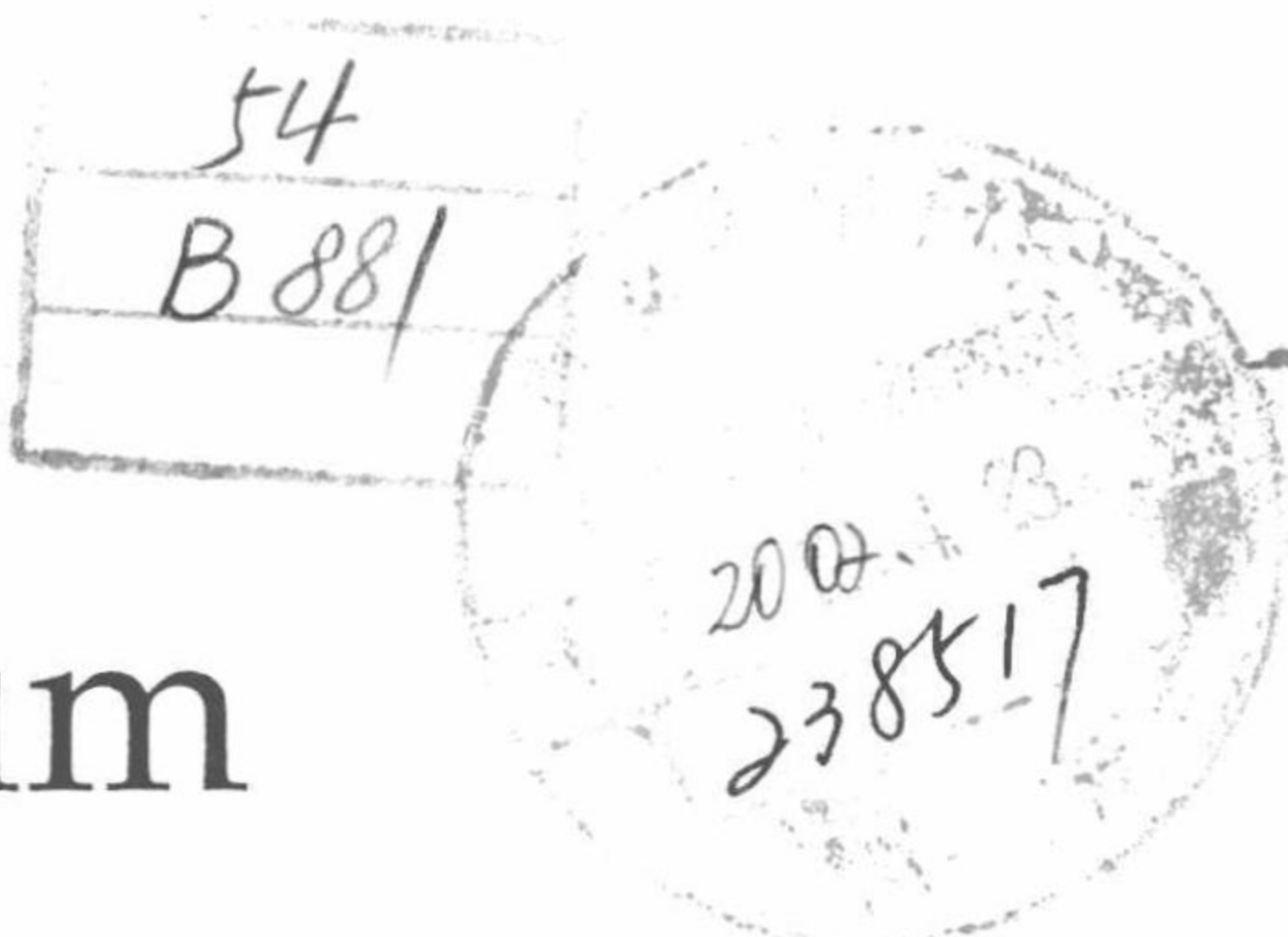


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# Chemical Equilibrium



# 15

- 15.1 The Concept of Equilibrium
- 15.2 The Equilibrium Constant
- 15.3 Heterogeneous Equilibria
- 15.4 Calculating Equilibrium Constants
- 15.5 Applications of Equilibrium Constants
- 15.6 Le Châtelier's Principle

In the laboratory portion of your chemistry course you have had the opportunity to observe a number of chemical reactions. After a certain amount of time many of these reactions appear to “stop”—colors stop changing, gases stop evolving, and so forth. In several of these instances the process apparently stops before the reaction is complete, leading to a mixture of reactants and products.

For example, we can consider the interconversion of the gaseous nitrogen oxides shown in Figure 15.1 ►. When pure frozen  $\text{N}_2\text{O}_4$  is warmed above its boiling point ( $21.2^\circ\text{C}$ ), the gas in the sealed tube turns progressively darker as colorless  $\text{N}_2\text{O}_4$  gas dissociates into brown  $\text{NO}_2$  gas (Figure 15.2 ►):



Eventually the color change stops even though there is still  $\text{N}_2\text{O}_4$  in the tube. We are left with a mixture of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  in which the concentrations of the gases no longer change.

The condition in which the concentrations of all reactants and products in a closed system cease to change with time is called **chemical equilibrium**. *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. For equilibrium to occur, neither reactants nor products can escape from the system.

We have already seen several instances of equilibria. For example, the vapor above a liquid is in equilibrium with the liquid phase.  $\infty$  (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. As another example, in a saturated solution of sodium chloride, the solid sodium chloride is in equilibrium with the ions dispersed in water.  $\infty$  (Section 13.3) 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.

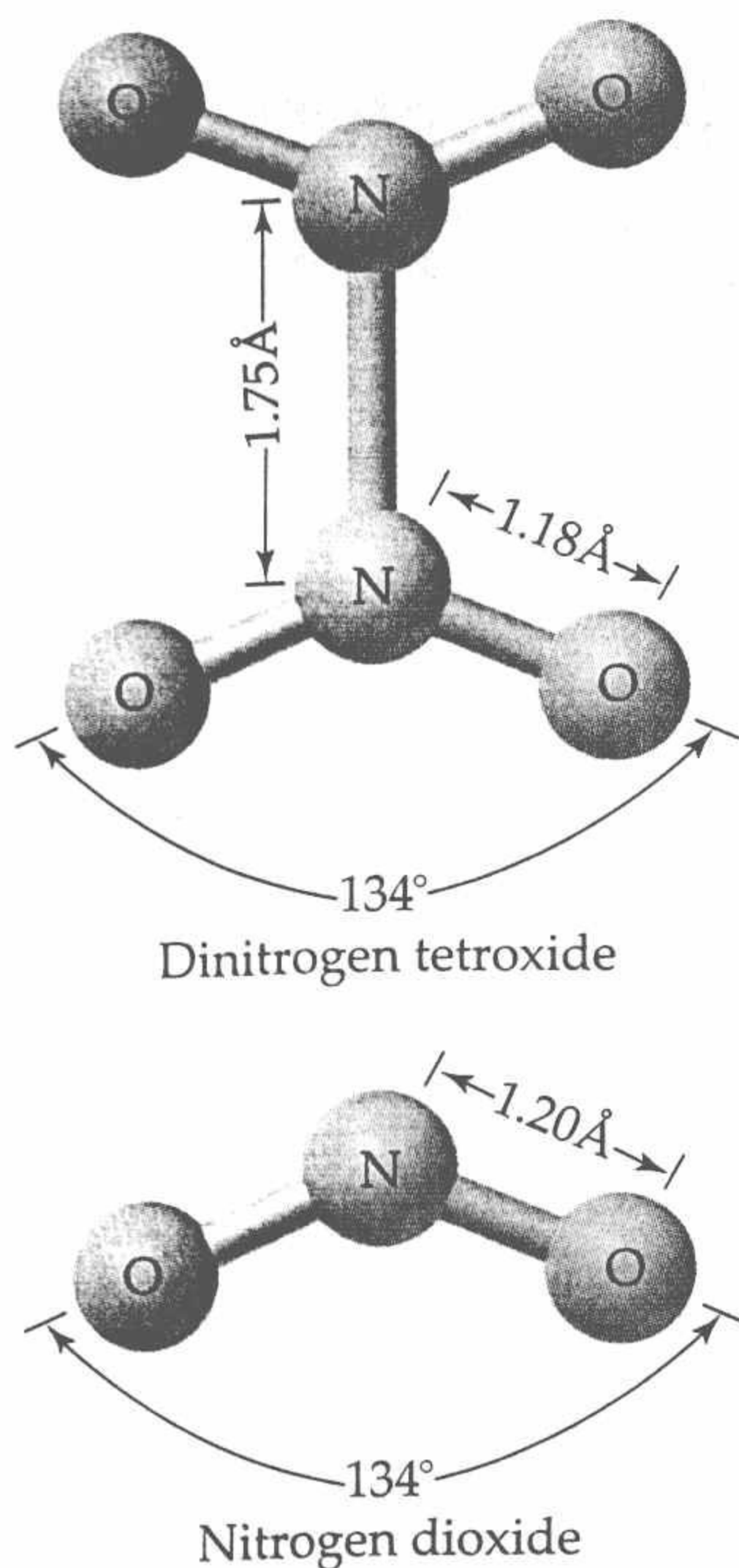
Chemical equilibria are of importance in explaining a great many natural phenomena, and they play important roles in many industrial processes. In this and the next two chapters we will explore chemical equilibria in some detail. Here we will learn how to express the equilibrium position of a reaction in quantitative terms, and we will study the factors that deter-

In this decorative fountain, water is continually circulating, but the amount of water in the basin is constant: Water is pumped out of the bottom of the basin at the same rate that new water is supplied by the jets at the top. Like the fountain, chemical equilibrium is characterized by two opposing processes that occur at the same rate.

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▲ **Figure 15.1** Structures of the  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  molecules. Both substances are gases at room temperature and atmospheric pressure. Dinitrogen tetroxide,  $\text{N}_2\text{O}_4$ , is colorless, whereas nitrogen dioxide,  $\text{NO}_2$ , is brown. The molecules readily interconvert:  $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$ .

mine the relative concentrations of reactants and products at equilibrium. We begin by exploring the relationship between the rates of opposing reactions and how this relationship leads to chemical equilibrium.

## 15.1 The Concept of Equilibrium

At equilibrium the rate at which products are produced from reactants equals the rate at which reactants are produced from products. We can use some of the concepts developed in Chapter 14 to illustrate how equilibrium is reached. Let's imagine that we have a simple reaction  $\text{A} \longrightarrow \text{B}$  and that both this reaction and its reverse ( $\text{B} \longrightarrow \text{A}$ ) are elementary processes. As we learned in Section 14.5, the rates of these unimolecular reactions are



where  $k_f$  and  $k_r$  are the rate constants for the forward and reverse reactions, respectively.

Now, let's suppose that we start with pure compound A in a closed container. As A reacts to form compound B, the concentration of A decreases while the concentration of B increases [Figure 15.3(a) ►]. As [A] decreases, the rate of the forward reaction decreases, as shown in Figure 15.3(b). Likewise, as [B] increases, the rate of the reverse reaction increases. Eventually the reaction reaches a point at which the forward and reverse rates are the same [Figure 15.3(b)]; compounds A and B are in equilibrium. At equilibrium, therefore,

$$\begin{array}{ccc} k_f[\text{A}] & = & k_r[\text{B}] \\ \text{Forward} & & \text{Reverse} \\ \text{rate} & & \text{rate} \end{array}$$

Rearranging this equation gives

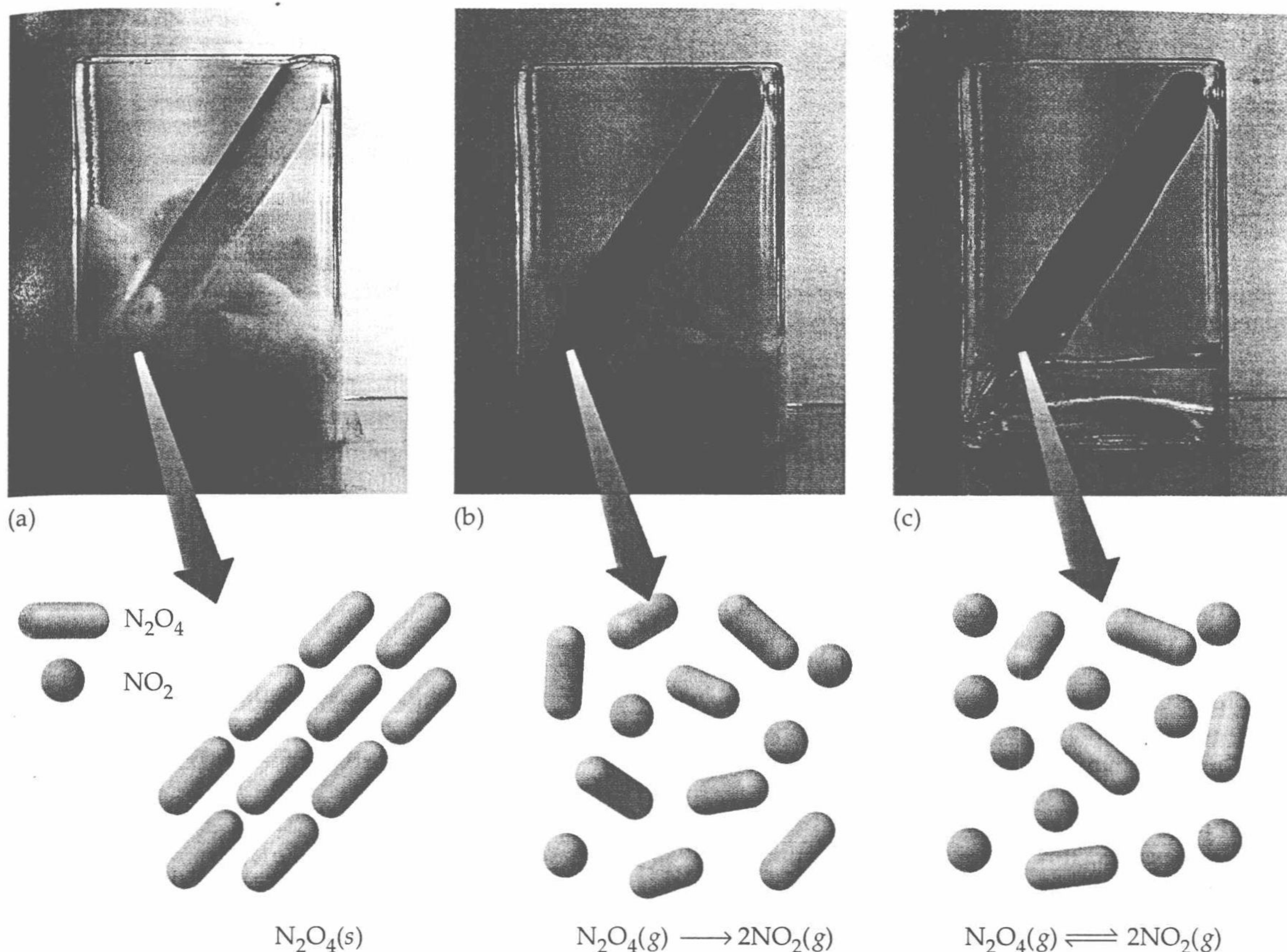
$$\frac{[\text{B}]}{[\text{A}]} = \frac{k_f}{k_r} = \text{a constant} \quad [15.3]$$

The quotient of two constants such as  $k_f$  and  $k_r$  is itself a constant. Thus, at equilibrium the ratio of the concentrations of A and B equals a constant as shown in Equation 15.3. (We will consider this constant in Section 15.2.) It makes no difference whether we start with A or B, or even with some mixture of the two. At equilibrium the ratio equals a definite value.

Once equilibrium is established, the concentrations of A and B do not change [Figure 15.3(a)]. The result is a mixture of A and B that we call an *equilibrium mixture*. The fact that the composition of the equilibrium mixture remains constant with time does not mean that A and B stop reacting, however. On the contrary, the equilibrium is dynamic  $\rightleftharpoons$  (Section 11.5) Compound A is still converted to compound B, and B to A, but both processes occur at the same rate. To indicate that the reaction proceeds in both the forward and reverse directions, we use a double arrow:

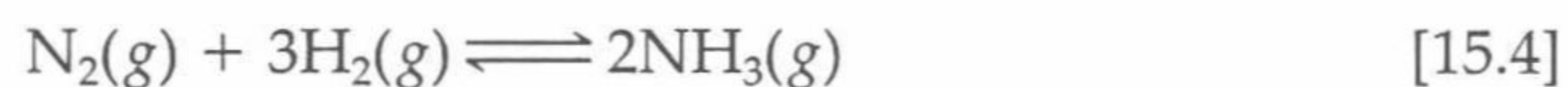


This example illustrates that opposing reactions naturally lead to an equilibrium situation. In order to examine equilibrium for a real chemical system,

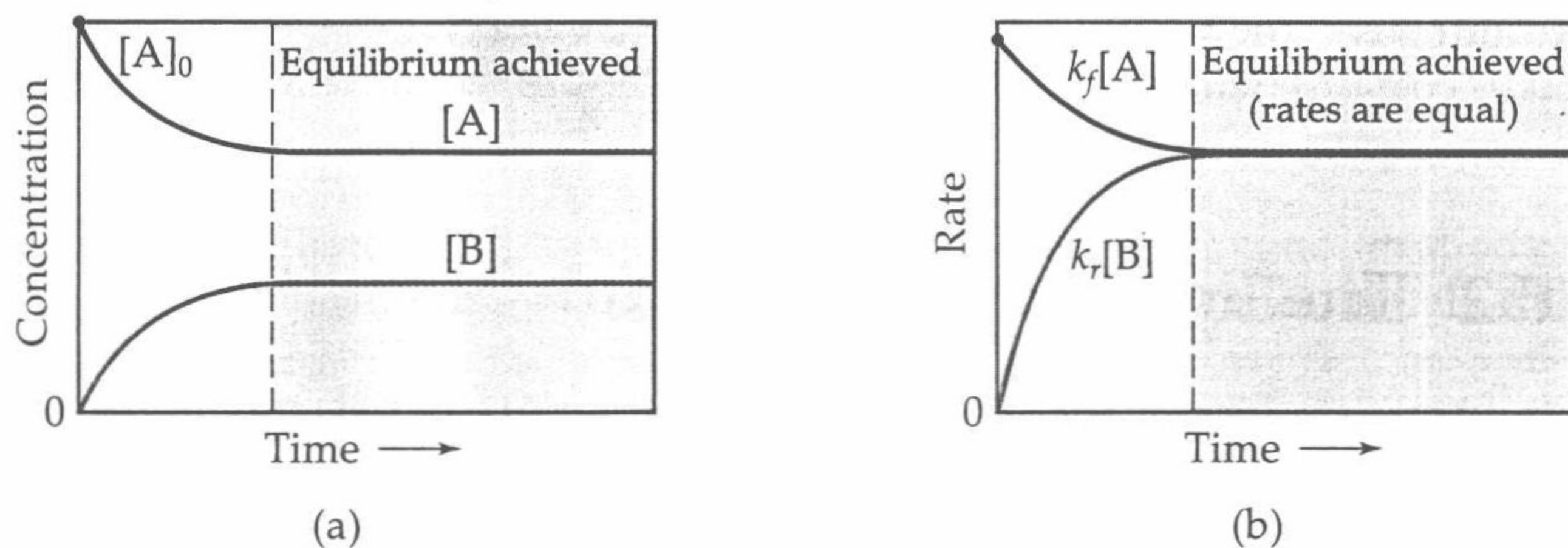


▲ **Figure 15.2** Establishing an equilibrium between  $N_2O_4$  (represented by blue ellipsoids) and  $NO_2$  (represented by red spheres). (a) Frozen  $N_2O_4$  is nearly colorless. (b) As  $N_2O_4$  is warmed above its boiling point, it starts to dissociate into brown  $NO_2$  gas. (c) Eventually the color stops changing as  $N_2O_4(g)$  and  $NO_2(g)$  reach concentrations at which they are interconverting at the same rate. The two gases are in equilibrium.

we will focus on an extremely important chemical reaction, namely, the synthesis of ammonia from nitrogen and hydrogen:

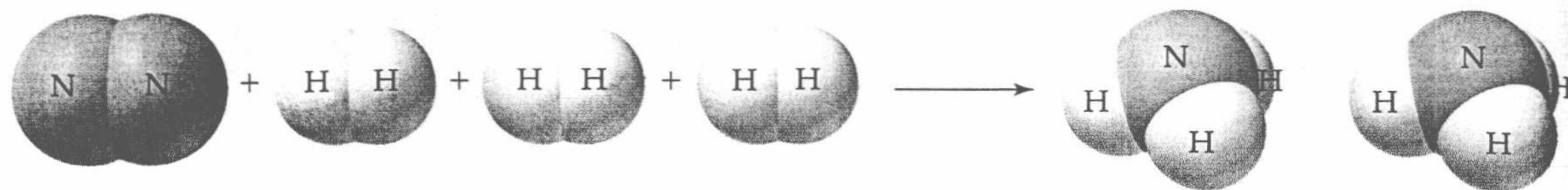


This reaction is the basis for the **Haber process** for synthesizing ammonia.



◀ **Figure 15.3** Achieving chemical equilibrium for the reaction  $A \rightleftharpoons B$ . (a) The reaction of pure compound A, with initial concentration  $[A]_0$ . After a time the concentrations of A and B do not change. The reason is that (b) the rates of the forward reaction ( $k_f[A]$ ) and the reverse reaction ( $k_r[B]$ ) become equal.

### Chemistry at Work The Haber Process



▲ **Figure 15.4** The Haber process is used to convert  $\text{N}_2(g)$  and  $\text{H}_2(g)$  to  $\text{NH}_3(g)$ , a process that, although exothermic, requires breaking the very strong triple bond in  $\text{N}_2$ .

We presented a “Chemistry and Life” box in Section 14.6 that discussed *nitrogen fixation*, the processes that convert  $\text{N}_2$  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; human agriculture requires substantial amounts of ammonia-based fertilizers that can be applied directly to croplands. Therefore, 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  $500^\circ\text{C}$  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 was dependent on nitrate deposits in Chile for the nitrogen-containing compounds needed to manufacture explosives. During the war the Allied naval blockade of South America cut off this supply. However, by fixing nitrogen from air, Germany was able to continue production of explosives. Experts have estimated that World War I would have ended several years 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 scientists

to manufacture 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,  $(\text{NH}_4)_2\text{SO}_4$ , or ammonium hydrogen phosphate,  $(\text{NH}_4)_2\text{HPO}_4$ —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.

▼ **Figure 15.5** Liquid 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  $\text{NH}_3$ .



## 15.2 The Equilibrium Constant

The Haber process consists of putting together  $\text{N}_2$  and  $\text{H}_2$  in a high-pressure tank at a total pressure of several hundred atmospheres, in the presence of a catalyst, and at a temperature of several hundred degrees Celsius. Under these con-

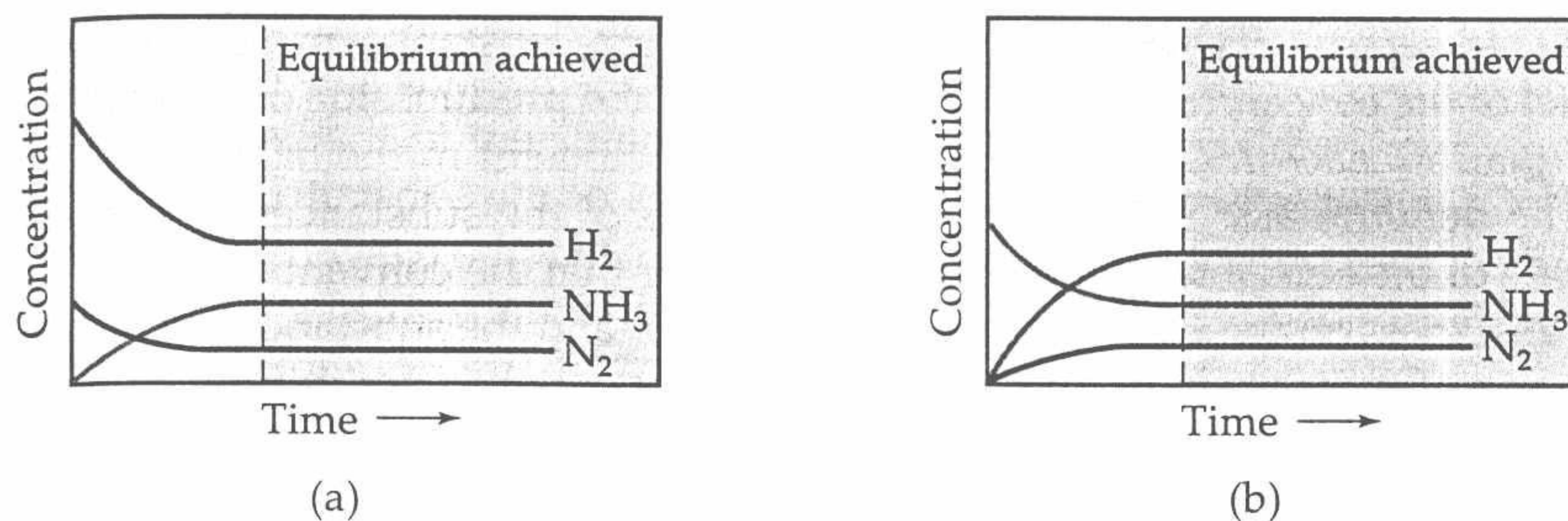
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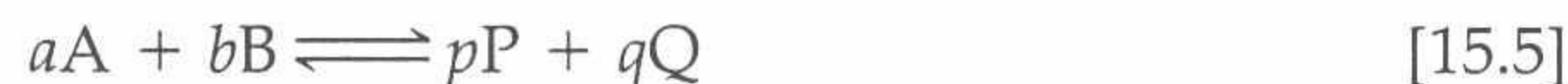


◀ **Figure 15.6** Variation in concentrations in the approach to equilibrium for  $\text{N}_2 + \text{H}_2 \rightleftharpoons 2\text{NH}_3$ . (a) The equilibrium is approached beginning with  $\text{H}_2$  and  $\text{N}_2$  in the ratio 3:1. (b) The equilibrium is approached beginning with  $\text{NH}_3$ .

ditions the two gases react to form ammonia. But the reaction does not lead to complete consumption of the  $\text{N}_2$  and  $\text{H}_2$ . Rather, at some point the reaction appears to stop, with all three components of the reaction mixture present at the same time.

The manner in which the concentrations of  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{NH}_3$  vary with time is shown in Figure 15.6(a) ▲. The situation is analogous to the one shown in Figure 15.3(a). The relative amounts of  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$  present at equilibrium do not depend on the amount of catalyst present. However, they do depend on the relative amounts of  $\text{H}_2$  and  $\text{N}_2$  at the beginning of the reaction. Furthermore, if only ammonia is placed in the tank under the same reaction conditions, there is again a mixture of  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$  at equilibrium. The variations in concentrations as a function of time for this situation are shown in Figure 15.6(b). At equilibrium the relative concentrations of  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{NH}_3$  are the same, regardless of whether the starting mixture was a 3:1 molar ratio of  $\text{H}_2$  and  $\text{N}_2$  or pure  $\text{NH}_3$ . *The equilibrium condition can be reached from either direction.*

Earlier we saw that when the reaction  $\text{A} \rightleftharpoons \text{B}$  reaches equilibrium, the ratio of the concentrations A and B has a constant value (Equation 15.3). A similar relationship governs the concentrations of  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$  at equilibrium. If we were to systematically change the relative amounts of the three gases in the starting mixture and then analyze the gas mixtures at equilibrium, we could determine the relationship among the equilibrium concentrations. Chemists carried out studies of this kind on other chemical systems in the nineteenth century, before Haber's work. In 1864 Cato Maximilian Guldberg (1836–1902) and Peter Waage (1833–1900) postulated their **law of mass action**, which expresses the relationship between the concentrations of the reactants and products at equilibrium in any reaction. Suppose we have the general equilibrium equation



where A, B, P, and Q are the chemical species involved, and  $a$ ,  $b$ ,  $p$ , and  $q$  are their coefficients in the balanced chemical equation. According to the law of mass action, the equilibrium condition is expressed by the equation

$$K_c = \frac{[\text{P}]^p[\text{Q}]^q}{[\text{A}]^a[\text{B}]^b} \quad [15.6]$$

(As before, the square brackets in this equation signify molar concentrations.) 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 actual equilibrium concentrations into the equilibrium-constant expression. The subscript  $c$  indicates that concentrations (expressed in molarity) are used.

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 the power of its coefficient in the balanced equation. The denominator is similarly given in terms of the substances on the reactant side of the equilibrium equation. (Remember that the convention is to write the substances on the *product* side in the *numerator* and the substances on the *reactant* side in the *denominator*.) For the reaction  $A \rightleftharpoons B$ , the equilibrium expression is  $K_c = [B]/[A]$ , in accord with Equation 15.3. For the Haber process (Equation 15.4), the equilibrium-constant expression is

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

Note that once we know the balanced chemical equation for an equilibrium, we can write the equilibrium-constant expression even if we don't 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 concentrations 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 product. The value of the equilibrium constant does vary with temperature, however.

We can illustrate how the law of mass action was discovered empirically, by considering the gas-phase equilibrium between dinitrogen tetroxide and nitrogen dioxide:



Figure 15.2 shows this equilibrium being reached after starting with pure  $\text{N}_2\text{O}_4$ . Because  $\text{NO}_2$  is a dark brown gas and  $\text{N}_2\text{O}_4$  is colorless, the amount of  $\text{NO}_2$  in the mixture can be determined by measuring the intensity of the brown color of the gas mixture.

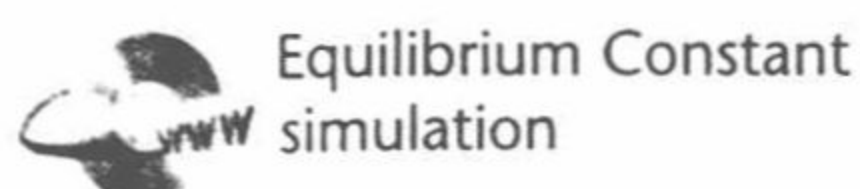
The equilibrium expression for Equation 15.7 is

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \quad [15.8]$$

How can we determine the numerical value for  $K_c$  and verify that it is constant regardless of the starting concentrations of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ ? We could perform experiments in which we start with several sealed tubes containing different concentrations of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ , as summarized in Table 15.1 ▼. The tubes are kept at  $100^\circ\text{C}$  until no further change in the color of the gas is noted. We then analyze the mixtures and determine the equilibrium concentrations of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  as shown in Table 15.1.

TABLE 15.1 Initial and Equilibrium Concentrations ( $M$ ) of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  in the Gas Phase at  $100^\circ\text{C}$

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



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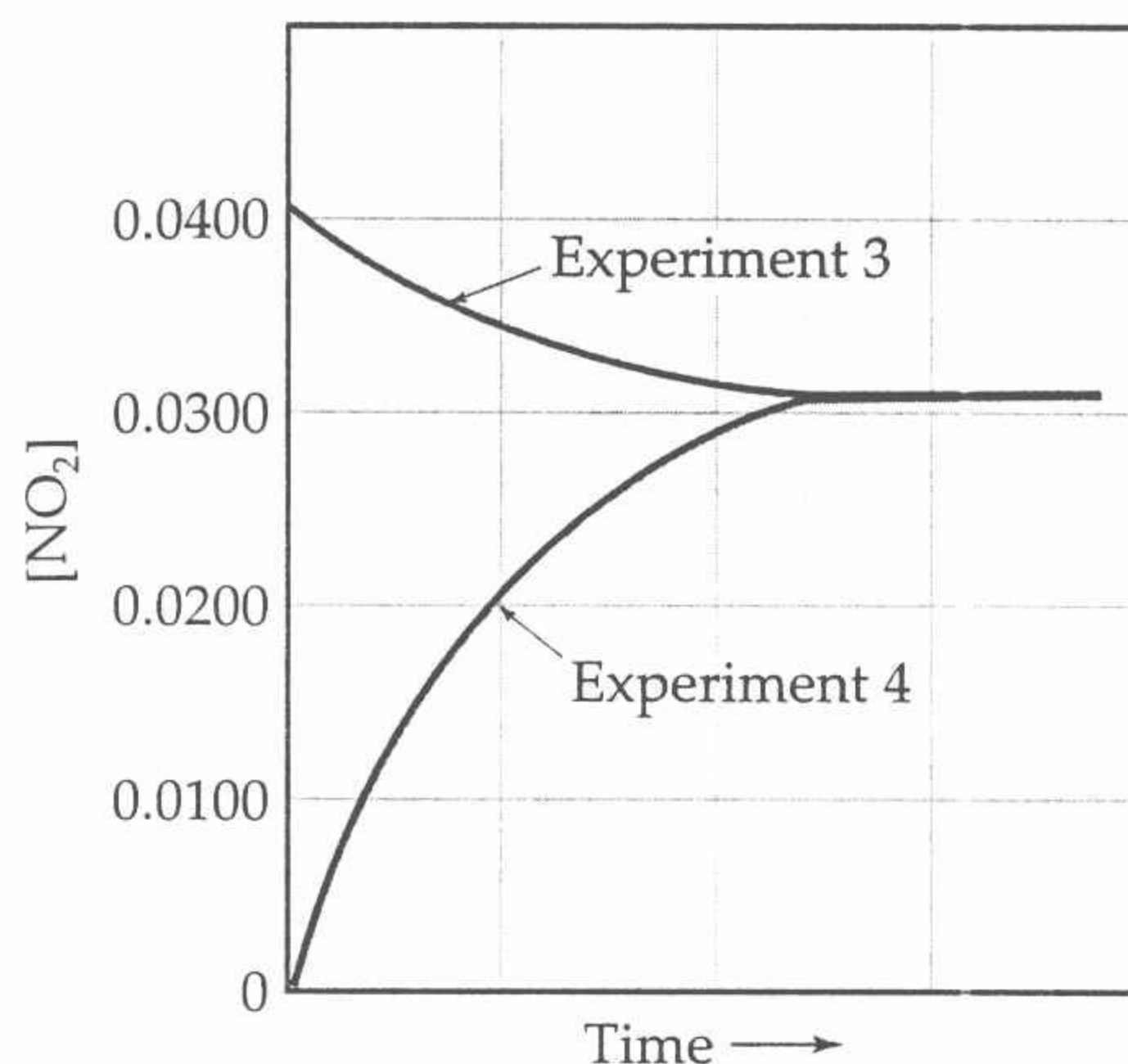
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◀ **Figure 15.7** As seen in Table 15.1, the same equilibrium mixture is produced starting with either 0.0400 M NO<sub>2</sub> (experiment 3) or 0.0200 M N<sub>2</sub>O<sub>4</sub> (experiment 4).

To evaluate the equilibrium constant,  $K_c$ , the equilibrium concentrations are inserted into the equilibrium-constant expression, Equation 15.8. For example, using the first set of data,  $[\text{NO}_2] = 0.0172 \text{ M}$  and  $[\text{N}_2\text{O}_4] = 0.00140 \text{ M}$ :

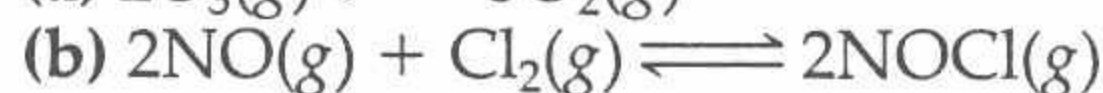
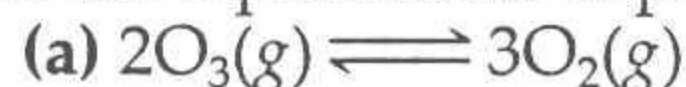
$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(0.0172)^2}{0.00140} = 0.211$$

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 attained beginning with N<sub>2</sub>O<sub>4</sub> as well as with NO<sub>2</sub>. That is, equilibrium can be approached from either direction. Figure 15.7 ▲ shows how both experiments 3 and 4 result in the same equilibrium mixture even though one begins with 0.0400 M NO<sub>2</sub> and the other with 0.0200 M N<sub>2</sub>O<sub>4</sub>.

Notice that no units are given for the values of  $K_c$  in Table 15.1 or in the preceding calculation. The common practice is to write equilibrium constants as dimensionless quantities.

#### SAMPLE EXERCISE 15.1

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



**Solution** (a) As indicated by Equation 15.6, the equilibrium-constant expression has the form of a quotient. The numerator contains the concentrations of the 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 obtained using the substances on the reactant side of the equation:

$$K_c = \frac{[\text{O}_2]^3}{[\text{O}_3]^2}$$

(b) In this case we have

$$K_c = \frac{[\text{NOCl}]^2}{[\text{NO}]^2[\text{Cl}_2]}$$

#### PRACTICE EXERCISE

Write the equilibrium-constant expression for  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ .

**Answer:**  $K_c = [\text{HI}]^2/[\text{H}_2][\text{I}_2]$

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### Equilibrium Constants in Terms of Pressure

When the reactants and products in a chemical equation 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 denote the equilibrium constant as  $K_p$  (where the subscript  $p$  stands for pressure). For the general reaction in Equation 15.5 the expression for  $K_p$  is

$$K_p = \frac{(P_P)^p(P_Q)^q}{(P_A)^a(P_B)^b} \quad [15.9]$$

where  $P_A$  is the partial pressure of A in atmospheres, and so forth.

The numerical values of  $K_c$  and  $K_p$  are generally different. We must therefore take care to indicate which of these we are using by means of the subscripts. It is possible, however, to calculate one from the other.

For gaseous substances we can use the ideal-gas equation (Section 10.4) to convert between concentration (in molarity,  $M$ ) and pressure (in atm):

$$PV = nRT; \text{ therefore, } P = (n/V)RT = MRT$$

Using the usual units,  $n/V$  has the units of mol/L, or  $M$ . For substance A we therefore see that

$$P_A = [A](RT) \quad [15.10]$$

When we substitute Equation 15.10 and like expressions for the other gaseous components of the reaction into the expression for  $K_p$  (Equation 15.9), we obtain a general expression relating  $K_p$  and  $K_c$ :

$$K_p = K_c(RT)^{\Delta n} \quad [15.11]$$

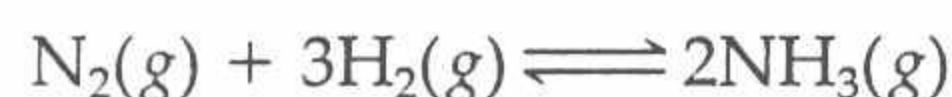
The quantity  $\Delta n$  is the change in the number of moles of gas in the chemical equation for the reaction. It equals the sum of the coefficients of the gaseous products minus the sum of the coefficients of the gaseous reactants. For example, in the reaction



there are 2 mol of the product  $\text{NO}_2$  (the coefficient in the balanced equation) and 1 mol of the reactant  $\text{N}_2\text{O}_4$ . Therefore,  $\Delta n = 2 - 1 = 1$ , and  $K_p = K_c(RT)$  for this reaction. From Equation 15.11, we see that  $K_p = K_c$  only when the same number of moles of gas appear on both sides of the balanced chemical equation.

#### SAMPLE EXERCISE 15.2

In the synthesis of ammonia from nitrogen and hydrogen,  $K_c = 9.60$  at  $300^\circ\text{C}$ :



Calculate  $K_p$  for this reaction at this temperature.

**Solution** The relationship between  $K_c$  and  $K_p$  is given by Equation 15.11. There are 2 mol of gaseous products ( $2\text{NH}_3$ ) and 4 mol of gaseous reactants ( $1\text{N}_2 + 3\text{H}_2$ ). Therefore,  $\Delta n = 2 - 4 = -2$ . (Remember that  $\Delta$  functions are always based on products minus reactants.) The temperature,  $T$ , is  $273 + 300 = 573$  K. The value for the ideal-gas constant,  $R$ , is  $0.0821$  L-atm/mol-K. Using  $K_c = 9.60$ , we therefore have

$$K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2}P_{\text{H}_2}^3} = K_c(RT)^{\Delta n} = (9.60)(0.0821 \times 573)^{-2} = 4.34 \times 10^{-3}$$

#### PRACTICE EXERCISE

For the equilibrium  $2\text{SO}_3(g) \rightleftharpoons 2\text{SO}_2(g) + \text{O}_2(g)$  at a temperature of  $1000$  K,  $K_c$  has the value  $4.08 \times 10^{-3}$ . Calculate the value for  $K_p$ . **Answer:**  $0.335$

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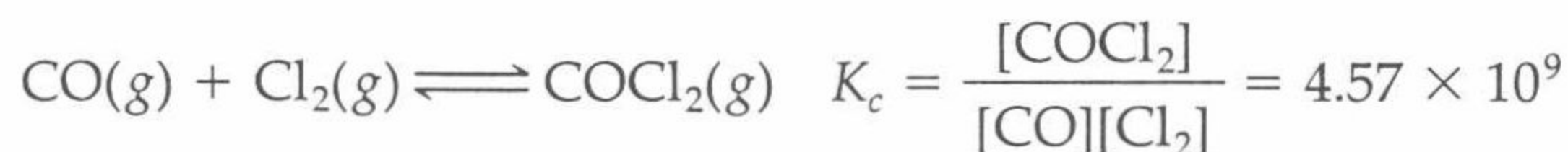
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### The Magnitude of Equilibrium Constants

Equilibrium constants can be very large or very small. The magnitude of the constant provides us with important information about the equilibrium mixture. For example, consider the reaction of carbon monoxide and chlorine gases at 100°C to form phosgene,  $\text{COCl}_2$ , a toxic gas that is used in the manufacture of certain polymers and insecticides.



In order 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  $\text{COCl}_2$  must be much greater than that of  $\text{CO}$  or  $\text{Cl}_2$ ; an equilibrium mixture of the three gases is essentially pure  $\text{COCl}_2$ . We say that the equilibrium *lies to the right*, that is, toward the product side. Likewise, an equilibrium constant much less than 1 indicates that the equilibrium mixture contains mostly reactants. We then say that the equilibrium *lies to the left*. In general,

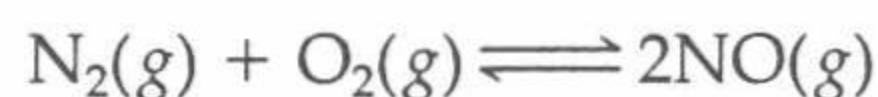
$K \gg 1$ : Equilibrium lies to the right; products favored.

$K \ll 1$ : Equilibrium lies to the left; reactants favored.

These situations are summarized in Figure 15.8 ►.

#### SAMPLE EXERCISE 15.3

The reaction of  $\text{N}_2$  with  $\text{O}_2$  to form  $\text{NO}$  might be considered a means of “fixing” nitrogen:



The value for the equilibrium constant for this reaction at 25°C is  $K_c = 1 \times 10^{-30}$ . Describe the feasibility of this reaction for nitrogen fixation.

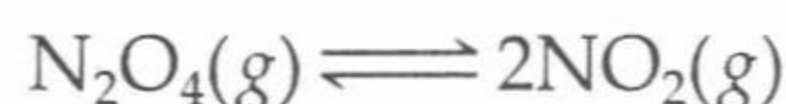
**Solution** Because  $K_c$  is so small, very little  $\text{NO}$  will form at 25°C. The equilibrium lies to the left, favoring the reactants. Consequently, this reaction is an extremely poor choice for nitrogen fixation, at least at 25°C.

#### PRACTICE EXERCISE

The equilibrium constant for the reaction  $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$  varies with temperature in the following way:  $K_c = 794$  at 298 K;  $K_c = 54$  at 700 K. Is the formation of  $\text{HI}$  favored more at the higher or lower temperature? **Answer:** at the lower temperature because of the larger  $K_c$  value

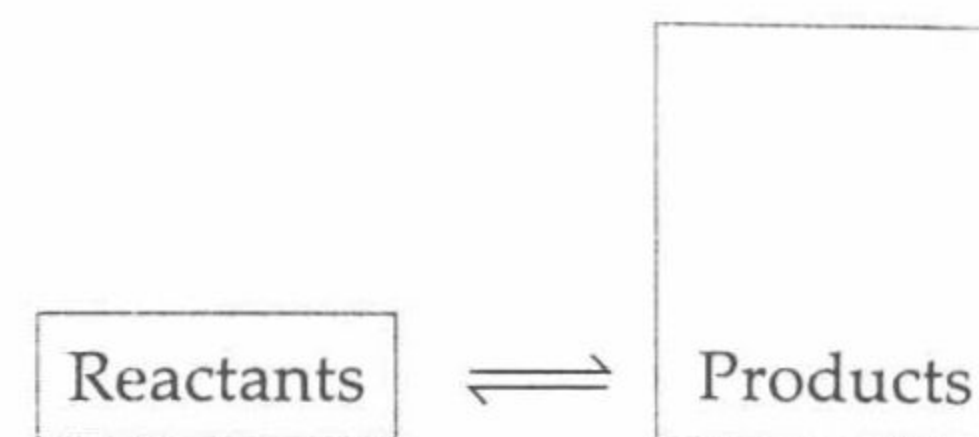
### The Direction of the Chemical Equation and $K$

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

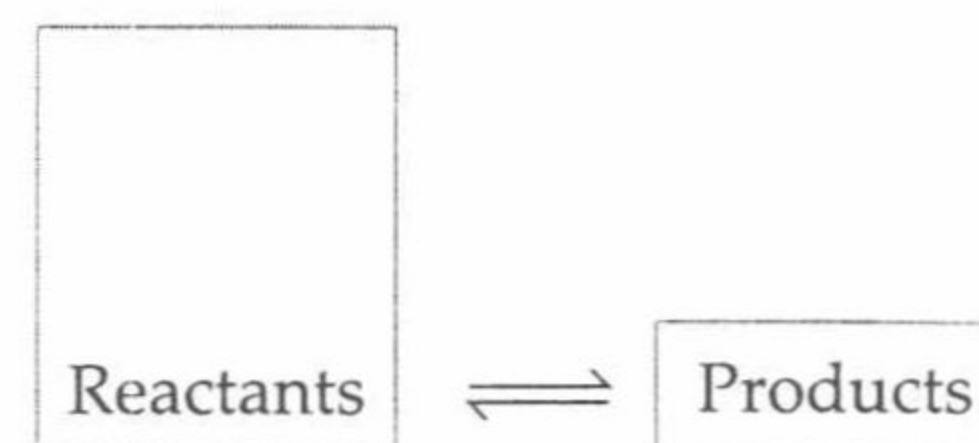


For this equation we can write

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 0.212 \quad (\text{at } 100^\circ\text{C}) \quad [15.12]$$



(a)  $K \gg 1$



(b)  $K \ll 1$

▲ **Figure 15.8** 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 could equally well consider this same equilibrium in terms of the reverse reaction:



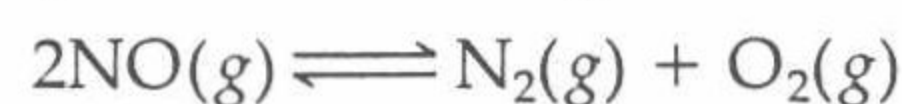
The equilibrium expression is then given by

$$K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{1}{0.212} = 4.72 \quad (\text{at } 100^\circ\text{C}) \quad [15.13]$$

Notice that Equation 15.13 is just the reciprocal of Equation 15.12. *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  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  is 0.212 or 4.72 unless we indicate how the equilibrium reaction is written and also specify the temperature.

#### SAMPLE EXERCISE 15.4

(a) Write the expression for  $K_c$  for the following reaction:



(b) Using information in Sample Exercise 15.3, determine the value of this equilibrium constant at  $25^\circ\text{C}$ :

**Solution** (a) Writing products over reactants, we have

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

(b) The reaction is just the reverse of the one given in Sample Exercise 15.3. Thus, both the equilibrium-constant expression and the value of the equilibrium constant are the reciprocals of those for the reverse reaction:

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

Either way we express the equilibrium among  $\text{NO}$ ,  $\text{N}_2$ , and  $\text{O}_2$ , we see that the equilibrium at  $25^\circ\text{C}$  lies on the side that favors  $\text{N}_2$  and  $\text{O}_2$ .

#### PRACTICE EXERCISE

For the formation of  $\text{NH}_3$  from  $\text{N}_2$  and  $\text{H}_2$ ,  $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$ ,  $K_p = 4.34 \times 10^{-3}$  at  $300^\circ\text{C}$ . What is the value of  $K_p$  for the reverse reaction? *Answer:*  $2.30 \times 10^2$

## 15.3 Heterogeneous Equilibria

Many equilibria of importance, 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 decomposition of calcium carbonate:



This system involves a gas in equilibrium with two solids. If we write the equilibrium-constant expression for this process in the usual way, we obtain

$$K_c = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]} \quad [15.15]$$

This example presents a problem we have not encountered previously: How do we express the concentration of a solid substance? The concentration of a pure substance, liquid or solid, equals its density divided by its molar mass,  $\mathcal{M}$ :

$$\frac{\text{Density}}{\mathcal{M}} = \frac{\text{g/cm}^3}{\text{g/mol}} = \frac{\text{mol}}{\text{cm}^3}$$

The density of a pure liquid or solid is a constant at any given temperature and changes very little with temperature. Thus, the effective concentration of a pure solid or liquid is a constant, regardless of how much pure solid or liquid is present. We can use this fact to simplify the equilibrium expression. For example, Equation 15.15 simplifies to

$$K_c = \frac{(\text{constant 1})[\text{CO}_2]}{\text{constant 2}}$$

where constant 1 is the concentration of CaO and constant 2 is the concentration of CaCO<sub>3</sub>. Moving the constants to the left side of the equation, we have

$$K'_c = K_c \frac{\text{constant 2}}{\text{constant 1}} = [\text{CO}_2] \quad [15.16]$$

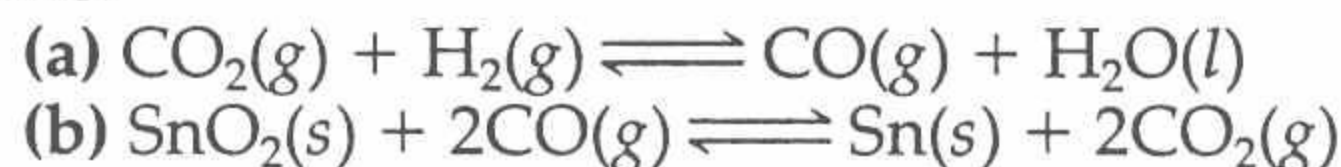
We have in effect excluded the concentrations of the solids from the equilibrium-constant expression.

We can generalize this result to other situations involving not only pure solids but pure liquids as well: *If 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.* The concentrations of gases and substances in solution, however, are included in equilibrium-constant expressions because these concentrations can vary.

Equation 15.16 tells us that, at a given temperature, an equilibrium among CaO, CaCO<sub>3</sub>, and CO<sub>2</sub> will always lead to the same concentration of CO<sub>2</sub> as long as all three components are present. As shown in Figure 15.9, we would have the same pressure of CO<sub>2</sub> regardless of the relative amounts of CaO and CaCO<sub>3</sub>. Of course, if one of the three components is missing, we cannot have an equilibrium. *Even though they do not appear in the equilibrium-constant expression, the pure solids and liquids participating in the reaction must be present for an equilibrium to be established.*

### SAMPLE EXERCISE 15.5

Write the equilibrium-constant expressions for  $K_c$  and  $K_p$  for each of the following reactions:



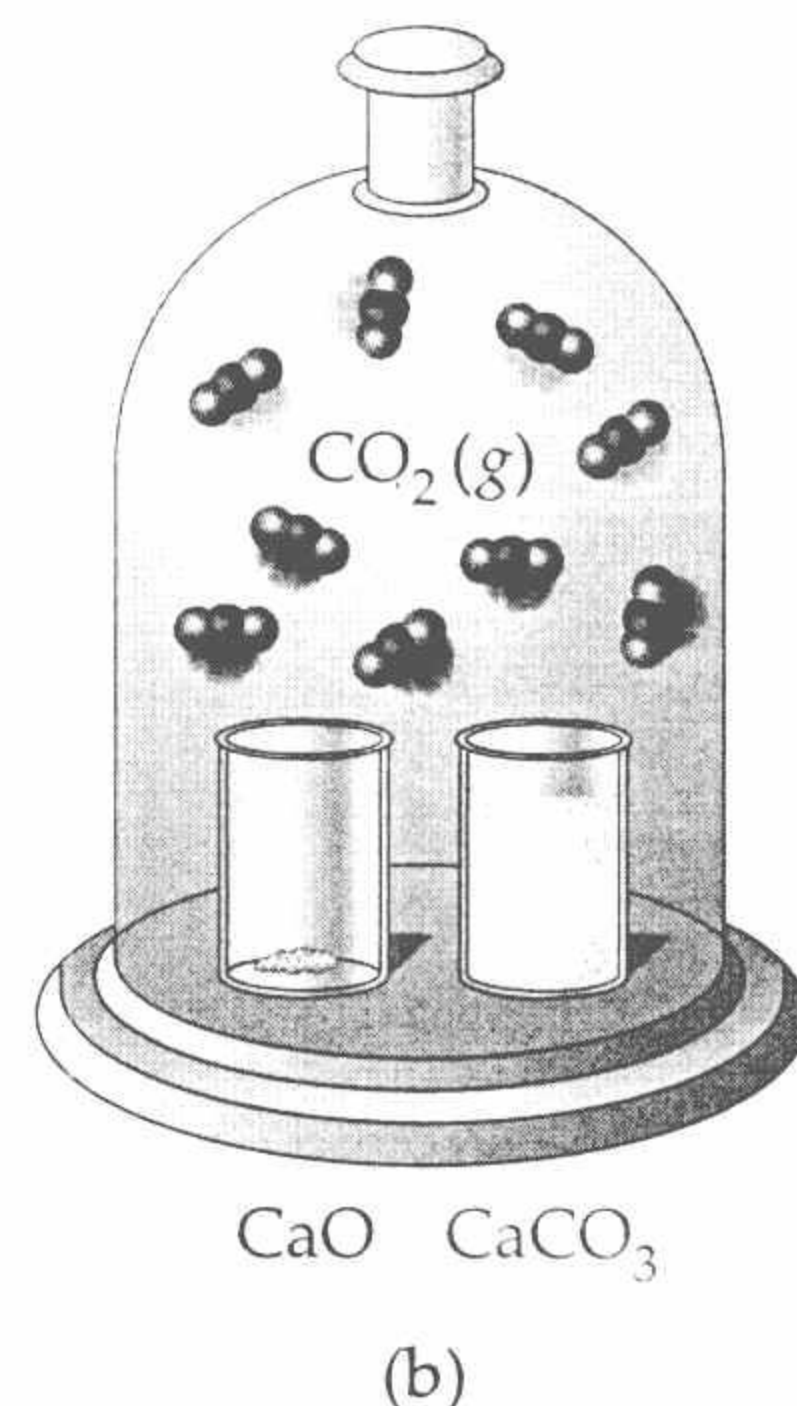
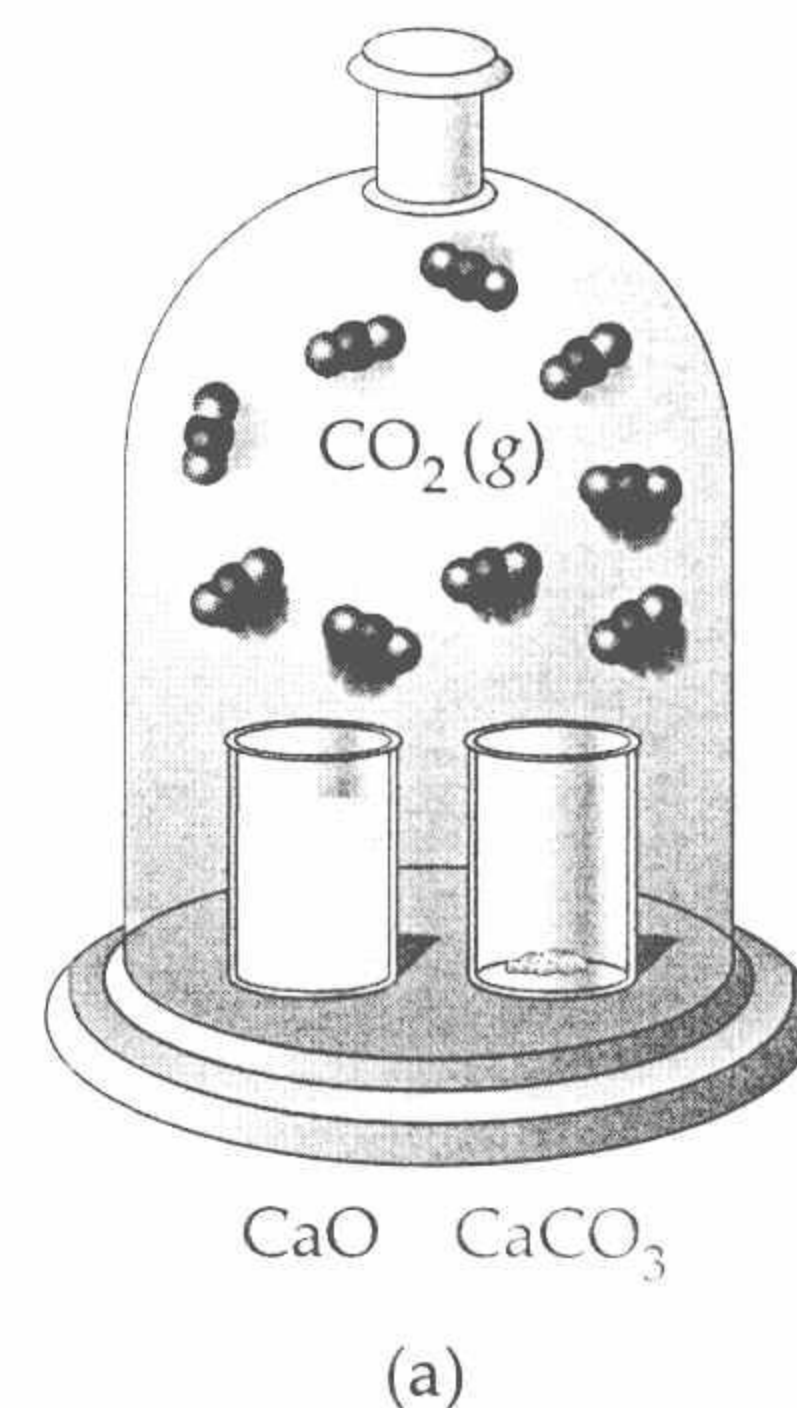
**Solution** (a) The equilibrium-constant expressions are

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

Because H<sub>2</sub>O appears in the reaction as a pure liquid, its concentration does not appear in either equilibrium-constant expression.

(b) The equilibrium-constant expressions are

$$K_c = \frac{[\text{CO}_2]^2}{[\text{CO}]^2} \quad \text{and} \quad K_p = \frac{P_{\text{CO}_2}^2}{P_{\text{CO}}^2}$$



▲ **Figure 15.9** The decomposition of CaCO<sub>3</sub> is an example of a heterogeneous equilibrium. At the same temperature the equilibrium pressure of CO<sub>2</sub> is the same in the two bell jars even though the relative amounts of pure CaCO<sub>3</sub> and CaO differ greatly.

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

#### PRACTICE EXERCISE

Write the equilibrium expressions for  $K_c$  and  $K_p$  for 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:*  $K_c = [\text{H}_2]^4/[\text{H}_2\text{O}]^4$ ;  $K_p = P_{\text{H}_2}^4/P_{\text{H}_2\text{O}}^4$

#### SAMPLE EXERCISE 15.6

Each of the following mixtures was placed in a closed container and allowed to stand. Which of these mixtures is capable of attaining the equilibrium expressed by Equation 15.14: (a) pure  $\text{CaCO}_3$ ; (b)  $\text{CaO}$  and a pressure of  $\text{CO}_2$  greater than the value of  $K_p$ ; (c) some  $\text{CaCO}_3$  and a pressure of  $\text{CO}_2$  greater than the value of  $K_p$ ; (d)  $\text{CaCO}_3$  and  $\text{CaO}$ ?

**Solution** Equilibrium can be reached in all cases except (c) as long as sufficient quantities of solids are present. In (a)  $\text{CaCO}_3$  simply decomposes, forming  $\text{CaO}(s)$  and  $\text{CO}_2(g)$  until the equilibrium pressure of  $\text{CO}_2$  is attained. There must be enough  $\text{CaCO}_3$ , however, to allow the  $\text{CO}_2$  pressure to reach equilibrium. In (b)  $\text{CO}_2$  combines with the  $\text{CaO}$  present until its pressure decreases to the equilibrium value. In (c), because there is no  $\text{CaO}$  present, equilibrium can't be attained since there is no way in which the  $\text{CO}_2$  pressure can decrease to its equilibrium value. In (d) the situation is essentially the same as in (a):  $\text{CaCO}_3$  decomposes until equilibrium is attained. The presence of  $\text{CaO}$  initially makes no difference.

#### PRACTICE EXERCISE

Which one of the following substances— $\text{H}_2(g)$ ,  $\text{H}_2\text{O}(g)$ ,  $\text{O}_2(g)$ —when added to  $\text{Fe}_3\text{O}_4(s)$  in a closed container at high temperature, permits attainment of equilibrium 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  $\text{H}_2(g)$

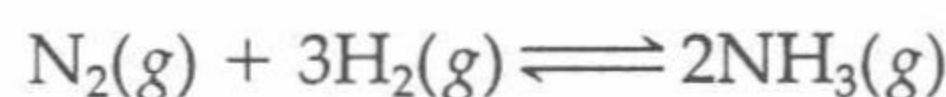
## 15.4 Calculating Equilibrium Constants

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  $\text{NH}_3$  at various temperatures. If the value of  $K$  for Equation 15.4 were very small, then the amount of  $\text{NH}_3$  in an equilibrium mixture would be small relative to the amounts of  $\text{N}_2$  and  $\text{H}_2$ . Clearly, if the equilibrium lies too far to the left, it would not be possible to develop a satisfactory synthesis of 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  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$ , 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 15.7

A mixture of hydrogen and nitrogen in a reaction vessel is allowed to attain equilibrium at  $472^\circ\text{C}$ . The equilibrium mixture of gases was analyzed and found to contain  $0.1207\text{ M H}_2$ ,  $0.0402\text{ M N}_2$ , and  $0.00272\text{ M NH}_3$ . From these data calculate the equilibrium constant,  $K_c$ , for



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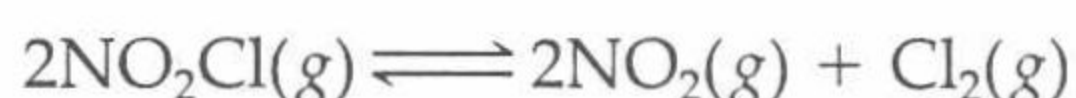
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**Solution**

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.00272)^2}{(0.0402)(0.1207)^3} = 0.105$$

**PRACTICE EXERCISE**

Nitryl chloride,  $\text{NO}_2\text{Cl}$ , is in equilibrium with  $\text{NO}_2$  and  $\text{Cl}_2$ :



At equilibrium the concentrations of the substances are  $[\text{NO}_2\text{Cl}] = 0.00106 \text{ M}$ ,  $[\text{NO}_2] = 0.0108 \text{ M}$ , and  $[\text{Cl}_2] = 0.00538 \text{ M}$ . From these data calculate the equilibrium constant,  $K_c$ . *Answer:* 0.558

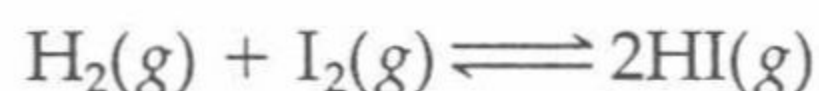
We often don't know the equilibrium concentrations of all chemical species in an equilibrium. However, if we know the equilibrium concentration of at least one species, we can generally use the stoichiometry of the reaction to deduce the equilibrium concentrations of the other species in the chemical equation. We will use the following procedure to do this:

1. Tabulate the known initial and equilibrium concentrations of all species involved in the equilibrium.
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 used to evaluate the equilibrium constant.

We illustrate the procedure in Sample Exercise 15.8.

**SAMPLE EXERCISE 15.8**

A mixture of  $5.000 \times 10^{-3} \text{ mol}$  of  $\text{H}_2$  and  $1.000 \times 10^{-2} \text{ mol}$  of  $\text{I}_2$  is placed in a 5.000-L container at  $448^\circ\text{C}$  and allowed to come to equilibrium. Analysis of the equilibrium mixture shows that the concentration of  $\text{HI}$  is  $1.87 \times 10^{-3} \text{ M}$ . Calculate  $K_c$  at  $448^\circ\text{C}$  for the reaction



**Solution** First, we tabulate the initial and equilibrium concentrations of all the species in the equilibrium. 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.

In this exercise the initial concentrations of  $\text{H}_2$  and  $\text{I}_2$  must be calculated:

$$[\text{H}_2]_{\text{initial}} = \frac{5.000 \times 10^{-3} \text{ mol}}{5.000 \text{ L}} = 1.000 \times 10^{-3} \text{ M}$$

$$[\text{I}_2]_{\text{initial}} = \frac{1.000 \times 10^{-2} \text{ mol}}{5.000 \text{ L}} = 2.000 \times 10^{-3} \text{ M}$$

Thus, the first entries in the table are:

$$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$$

Initial	$1.000 \times 10^{-3} \text{ M}$	$2.000 \times 10^{-3} \text{ M}$	$0 \text{ M}$
Change			
Equilibrium			$1.87 \times 10^{-3} \text{ M}$

Second, we calculate the change in concentration of HI, using the initial and equilibrium values. The change is the difference between the equilibrium and initial values,  $1.87 \times 10^{-3} \text{ M}$ .

Third, we use the stoichiometry of the reaction to calculate the changes in the other species. The balanced chemical equation indicates that for each 2 mol of HI formed, 1 mol of  $\text{H}_2$  must be consumed. Thus, the amount of  $\text{H}_2$  consumed is

$$\left(1.87 \times 10^{-3} \frac{\text{mol HI}}{\text{L}}\right) \left(\frac{1 \text{ mol H}_2}{2 \text{ mol HI}}\right) = 0.935 \times 10^{-3} \text{ mol H}_2/\text{L}$$

The same line of reasoning gives us the amount of  $\text{I}_2$  consumed, which is also  $0.935 \times 10^{-3} \text{ M}$ .

Fourth, we calculate the equilibrium concentrations, using the initial concentrations and the changes. The equilibrium concentration of  $\text{H}_2$  is the initial concentration minus that consumed:

$$[\text{H}_2] = 1.000 \times 10^{-3} \text{ M} - 0.935 \times 10^{-3} \text{ M} = 0.065 \times 10^{-3} \text{ M}$$

Likewise, the equilibrium concentration of  $\text{I}_2$  is

$$[\text{I}_2] = 2.000 \times 10^{-3} \text{ M} - 0.935 \times 10^{-3} \text{ M} = 1.065 \times 10^{-3} \text{ M}$$

The completed table now looks like this:

$$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$$

Initial	$1.000 \times 10^{-3} \text{ M}$	$2.000 \times 10^{-3} \text{ M}$	$0 \text{ M}$
Change	$-0.935 \times 10^{-3} \text{ M}$	$-0.935 \times 10^{-3} \text{ M}$	$+1.87 \times 10^{-3} \text{ M}$
Equilibrium	$0.065 \times 10^{-3} \text{ M}$	$1.065 \times 10^{-3} \text{ M}$	$1.87 \times 10^{-3} \text{ M}$

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:

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(1.87 \times 10^{-3})^2}{(0.065 \times 10^{-3})(1.065 \times 10^{-3})} = 51$$

#### PRACTICE EXERCISE

Sulfur trioxide decomposes at high temperature in a sealed container:  $2\text{SO}_3(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$ . Initially the vessel is charged at 1000 K with  $\text{SO}_3(\text{g})$  at a concentration of  $6.09 \times 10^{-3} \text{ M}$ . At equilibrium the  $\text{SO}_3$  concentration is  $2.44 \times 10^{-3} \text{ M}$ . Calculate the value of  $K_c$  at 1000 K. *Answer:*  $4.08 \times 10^{-3}$

## 15.5 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 reaction will tend to proceed far to the right; if  $K$  is much less than 1, the equilibrium mixture will contain mainly reactants. The equilibrium constant also allows us (1) to predict the direction in which a reac-

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tion mixture will proceed to achieve equilibrium, and (2) to calculate the concentrations of reactants and products once equilibrium has been reached.

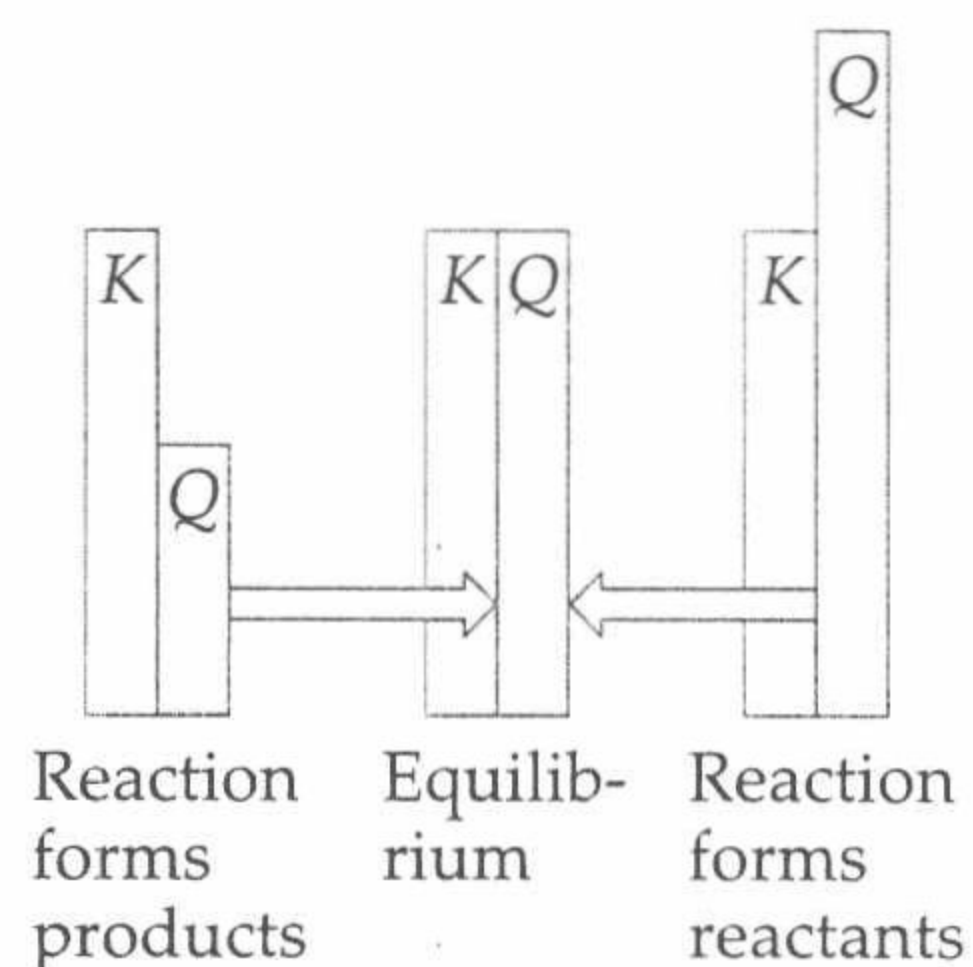
### Predicting the Direction of Reaction

Suppose we place a mixture of 2.00 mol of  $\text{H}_2$ , 1.00 mol of  $\text{N}_2$ , and 2.00 mol of  $\text{NH}_3$  in a 1.00-L container at  $472^\circ\text{C}$ . Will  $\text{N}_2$  and  $\text{H}_2$  react to form more  $\text{NH}_3$ ? If we insert the starting molar concentrations of  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$  into the equilibrium-constant expression, we have

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

According to Sample Exercise 15.7, at this temperature  $K_c = 0.105$ . Therefore, the quotient  $[\text{NH}_3]^2/[\text{N}_2][\text{H}_2]^3$  will need to change from 0.500 to 0.105 for the system to achieve equilibrium. This change can happen only if  $[\text{NH}_3]$  decreases and  $[\text{N}_2]$  and  $[\text{H}_2]$  increase. Thus, the reaction proceeds toward equilibrium with the formation of  $\text{N}_2$  and  $\text{H}_2$  from  $\text{NH}_3$ ; that is, the reaction proceeds from right to left.

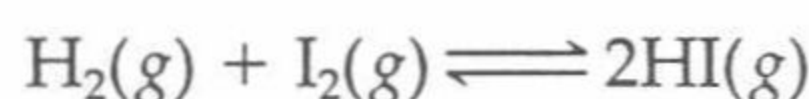
When we substitute reactant and product concentrations into the equilibrium-constant expression, the result is known as the **reaction quotient** and is represented by the letter  $Q$ . *The reaction quotient will equal the equilibrium constant,  $K$ , only if the system is at equilibrium:  $Q = K$  only at equilibrium.* We have seen that when  $Q > K$ , 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. Conversely, if  $Q < K$ , the reaction will achieve equilibrium by forming more products; it moves from left to right. These relationships are summarized in Figure 15.10 ►.



▲ **Figure 15.10** 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  $Q = K$ .

#### SAMPLE EXERCISE 15.9

At  $448^\circ\text{C}$  the equilibrium constant,  $K_c$ , for the reaction



is 51. Predict how the reaction will proceed to reach equilibrium at  $448^\circ\text{C}$  if we start with  $2.0 \times 10^{-2}$  mol of  $\text{HI}$ ,  $1.0 \times 10^{-2}$  mol of  $\text{H}_2$ , and  $3.0 \times 10^{-2}$  mol of  $\text{I}_2$  in a 2.0-L container.

**Solution** The initial concentrations are

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

$$[\text{H}_2] = 1.0 \times 10^{-2} \text{ mol} / 2.0 \text{ L} = 5.0 \times 10^{-3} \text{ M}$$

$$[\text{I}_2] = 3.0 \times 10^{-2} \text{ mol} / 2.0 \text{ L} = 1.5 \times 10^{-2} \text{ M}$$

The reaction quotient is

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

Because  $Q < K_c$ ,  $[\text{HI}]$  will need to increase and  $[\text{H}_2]$  and  $[\text{I}_2]$  decrease to reach equilibrium; the reaction will proceed from left to right.

#### PRACTICE EXERCISE

At 1000 K the value of  $K_c$  for the reaction  $2\text{SO}_3(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$  is  $4.08 \times 10^{-3}$ . Calculate the value for  $Q$ , and predict the direction in which the reaction will proceed toward equilibrium if the initial concentrations of reactants are  $[\text{SO}_3] = 2 \times 10^{-3} \text{ M}$ ;  $[\text{SO}_2] = 5 \times 10^{-3} \text{ M}$ ;  $[\text{O}_2] = 3 \times 10^{-2} \text{ M}$ . **Answer:**  $Q = 0.2$ ; the reaction will proceed from right to left, forming more  $\text{SO}_3$ .