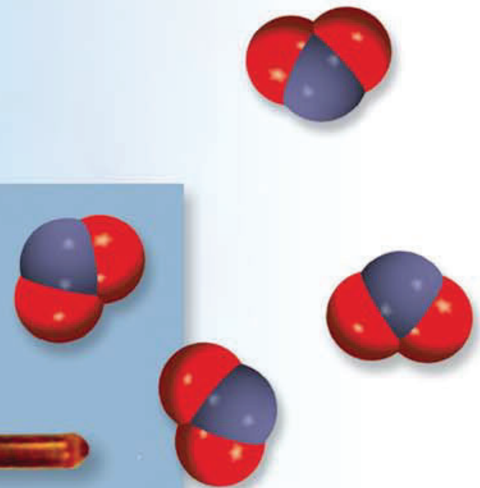
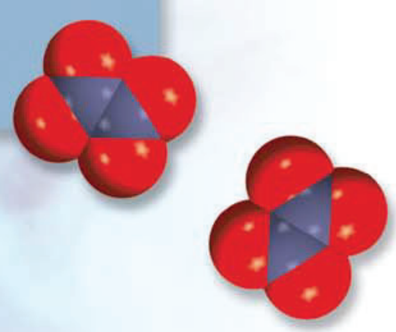
Chemical Equilibrium

14





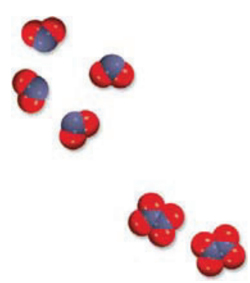
The equilibrium between dinitrogen tetroxide (colorless) and nitrogen dioxide (brown color) gases favor the formation of the latter as temperature increases (from bottom to top). The models show dinitrogen tetroxide and nitrogen dioxide molecules.

Chapter Outline

A Look Ahead

- We begin by discussing the nature of equilibrium and the difference between chemical and physical equilibrium. We define the equilibrium constant in terms of the law of mass action. (14.1)
- We then learn to write the equilibrium constant expression for homogeneous and heterogeneous equilibria. We see how to express equilibrium constants for multiple equilibria. (14.2)
- Next, we examine the relationship between the rate constants and equilibrium constant of a reaction. This exercise shows why the equilibrium constant is a constant and why it varies with temperature. (14.3)
- We see that knowing the equilibrium constant enables us to predict the direction of a net reaction towards equilibrium and to calculate equilibrium concentrations. (14.4)
- The chapter concludes with a discussion of the four factors that can possibly affect the position of an equilibrium: concentration, volume or pressure, temperature, and catalyst. We learn to use Le Châtelier's principle to predict the changes. (14.5)

Equilibrium is a state in which there are no observable changes as time goes by. When a chemical reaction has reached the equilibrium state, the concentrations of reactants and products remain constant over time, and there are no visible changes in the system. However, there is much activity at the molecular level because reactant molecules continue to form product molecules while product molecules react to yield reactant molecules. This dynamic equilibrium situation is the subject of this chapter. Here we will discuss different types of equilibrium reactions, the meaning of the equilibrium constant and its relationship to the rate constant, and factors that can disrupt a system at equilibrium.



14.1 The Concept of Equilibrium and the Equilibrium Constant

Few chemical reactions proceed in only one direction. Most are reversible, at least to some extent. At the start of a reversible process, the reaction proceeds toward the formation of products. As soon as some product molecules are formed, the reverse process begins to take place and reactant molecules are formed from product molecules. ***Chemical equilibrium*** is achieved when *the rates of the forward and reverse reactions are equal and the concentrations of the reactants and products remain constant*.

Chemical equilibrium is a dynamic process. As such, it can be likened to the movement of skiers at a busy ski resort, where the number of skiers carried up the mountain on the chair lift is equal to the number coming down the slopes. Although there is a constant transfer of skiers, the number of people at the top and the number at the bottom of the slope do not change.

Liquid water in equilibrium with its vapor in a closed system at room temperature.

Note that chemical equilibrium involves different substances as reactants and products. Equilibrium between two phases of the same substance is called ***physical equilibrium*** because *the changes that occur are physical processes*. The vaporization of water in a closed container at a given temperature is an example of physical equilibrium. In this instance, the number of H_2O molecules leaving and the number returning to the liquid phase are equal:

$$H_2O(l) \rightleftharpoons H_2O(g)$$

(Recall from Chapter 4 that the double arrow means that the reaction is reversible.)

The study of physical equilibrium yields useful information, such as the equilibrium vapor pressure (see Section 11.8). However, chemists are particularly interested in chemical equilibrium processes, such as the reversible reaction involving nitrogen dioxide (NO_2) and dinitrogen tetroxide (N_2O_4) (Figure 14.1). The progress of the reaction

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

NO_2 and N_2O_4 gases at equilibrium.

can be monitored easily because N_2O_4 is a colorless gas, whereas NO_2 has a dark-brown color that makes it sometimes visible in polluted air. Suppose that N_2O_4 is injected into an evacuated flask. Some brown color appears immediately, indicating the formation of NO_2 molecules. The color intensifies as the dissociation of N_2O_4 continues until eventually equilibrium is reached. Beyond that point, no further change in color is evident because the concentrations of both N_2O_4 and NO_2 remain constant. We can also bring about an equilibrium state by starting with pure NO_2. As some of the NO_2 molecules combine to form N_2O_4, the color fades. Yet another way to create an equilibrium state is to start with a mixture of NO_2 and N_2O_4 and monitor the system until the color stops changing. These studies demonstrate that the preceding

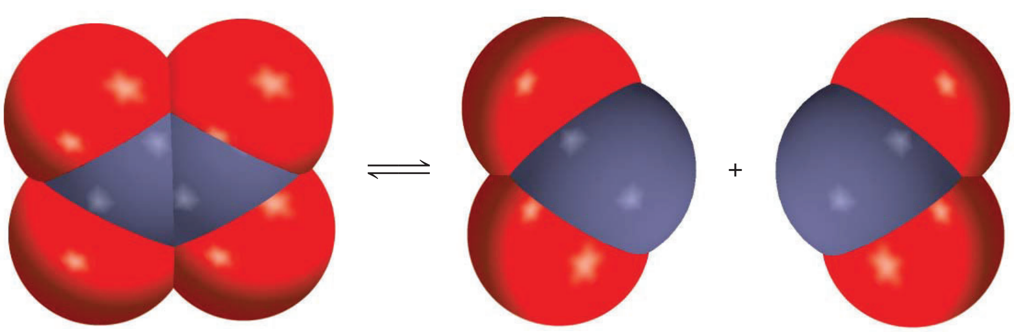


Figure 14.1 *A reversible reaction between N_2O_4 and NO_2 molecules.*

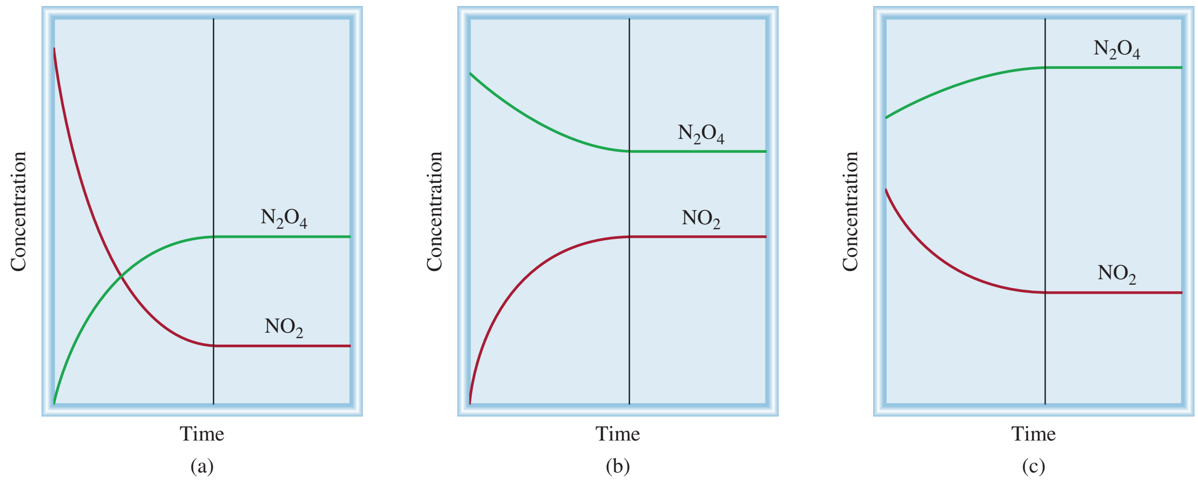


Figure 14.2 *Change in the concentrations of NO_2 and N_2O_4 with time, in three situations. (a) Initially only NO_2 is present. (b) Initially only N_2O_4 is present. (c) Initially a mixture of NO_2 and N_2O_4 is present. In each case, equilibrium is established to the right of the vertical line.*

reaction is indeed reversible, because a pure component (N_2O_4 or NO_2) reacts to give the other gas. The important thing to keep in mind is that at equilibrium, the conversions of N_2O_4 to NO_2 and of NO_2 to N_2O_4 are still going on. We do not see a color change because the two rates are equal—the removal of NO_2 molecules takes place as fast as the production of NO_2 molecules, and N_2O_4 molecules are formed as quickly as they dissociate. Figure 14.2 summarizes these three situations.

The Equilibrium Constant

Table 14.1 shows some experimental data for the reaction just described at 25°C. The gas concentrations are expressed in molarity, which can be calculated from the number of moles of gases present initially and at equilibrium and the volume of the flask in liters. Note that the equilibrium concentrations of NO_2 and N_2O_4 vary, depending on the starting concentrations. We can look for relationships between $[NO_2]$ and $[N_2O_4]$ present at equilibrium by comparing the ratio of their concentrations. The simplest ratio, that is, $[NO_2]/[N_2O_4]$, gives scattered values. But if we examine other possible mathematical relationships, we find that the ratio $[NO_2]^2/[N_2O_4]$ at equilibrium

TABLE 14.1 The NO_2–N_2O_4 System at 25°C

Initial Concentrations (M)		Equilibrium Concentrations (M)		Ratio of Concentrations at Equilibrium	
$[NO_2]$	$[N_2O_4]$	$[NO_2]$	$[N_2O_4]$	$\frac{[NO_2]}{[N_2O_4]}$	$\frac{[NO_2]^2}{[N_2O_4]}$
0.000	0.670	0.0547	0.643	0.0851	4.65×10^{-3}
0.0500	0.446	0.0457	0.448	0.102	4.66×10^{-3}
0.0300	0.500	0.0475	0.491	0.0967	4.60×10^{-3}
0.0400	0.600	0.0523	0.594	0.0880	4.60×10^{-3}
0.200	0.000	0.0204	0.0898	0.227	4.63×10^{-3}

gives a nearly constant value that averages 4.63×10^{-3}, regardless of the initial concentrations present:

$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3} \qquad (14.1)$$

where K is a constant. Note that the exponent 2 for $[NO_2]$ in this expression is the same as the stoichiometric coefficient for NO_2 in the reversible reaction.

We can generalize this phenomenon with the following reaction at equilibrium:

$$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$$

where a, b, c, and d are the stoichiometric coefficients for the reacting species A, B, C, and D. For the reaction at a particular temperature

$$K = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b} \qquad (14.2)$$

where K is the ***equilibrium constant.*** Equation (14.2) was formulated by two Norwegian chemists, Cato Guldberg† and Peter Waage,‡ in 1864. It is the mathematical expression of their ***law of mass action,*** which holds that *for a reversible reaction at equilibrium and a constant temperature, a certain ratio of reactant and product concentrations has a constant value, K (the equilibrium constant).* Note that although the concentrations may vary, as long as a given reaction is at equilibrium and the temperature does not change, according to the law of mass action, the value of K remains constant. The validity of Equation (14.2) and the law of mass action has been established by studying many reversible reactions.

The signs $\gg$ and $\ll$ mean "much greater than" and "much smaller than," respectively.

The equilibrium constant, then, is defined by a *quotient,* the numerator of which is obtained by multiplying together the equilibrium concentrations of the *products,* each raised to a power equal to its stoichiometric coefficient in the balanced equation. Applying the same procedure to the equilibrium concentrations of *reactants* gives the denominator. The magnitude of the equilibrium constant tells us whether an equilibrium reaction favors the products or reactants. If K is much greater than 1 (that is, $K \gg 1$), the equilibrium will lie to the right and favors the products. Conversely, if the equilibrium constant is much smaller than 1 (that is, $K \ll 1$), the equilibrium will lie to the left and favor the reactants (Figure 14.3). In this context, any number greater than 10 is considered to be much greater than 1, and any number less than 0.1 is much less than 1.

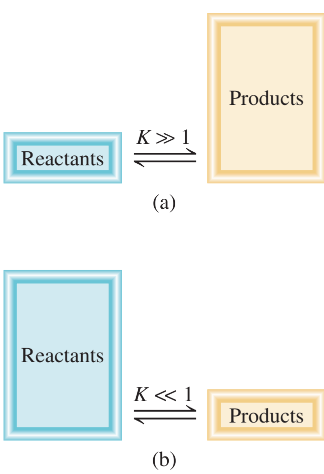


Figure 14.3 *(a) At equilibrium, there are more products than reactants, and the equilibrium is said to lie to the right. (b) In the opposite situation, when there are more reactants than products, the equilibrium is said to lie to the left.*

Although the use of the words "reactants" and "products" may seem confusing because any substance serving as a reactant in the forward reaction also is a product of the reverse reaction, it is in keeping with the convention of referring to substances on the left of the equilibrium arrows as "reactants" and those on the right as "products."

14.2 Writing Equilibrium Constant Expressions

The concept of equilibrium constants is extremely important in chemistry. As you will soon see, equilibrium constants are the key to solving a wide variety of stoichiometry problems involving equilibrium systems. For example, an industrial chemist who

†Cato Maximilian Guldberg (1836–1902). Norwegian chemist and mathematician. Guldberg's research was mainly in thermodynamics.

‡Peter Waage (1833–1900). Norwegian chemist. Like that of his coworker, Guldberg, Waage's research was primarily in thermodynamics.

wants to maximize the yield of sulfuric acid, say, must have a clear understanding of the equilibrium constants for all the steps in the process, starting from the oxidation of sulfur and ending with the formation of the final product. A physician specializing in clinical cases of acid-base imbalance needs to know the equilibrium constants of weak acids and bases. And a knowledge of equilibrium constants of pertinent gas-phase reactions will help an atmospheric chemist better understand the process of ozone destruction in the stratosphere.

To use equilibrium constants, we must express them in terms of the reactant and product concentrations. Our only guide is the law of mass action [Equation (14.2)], which is the general formula for finding equilibrium concentrations. However, because the concentrations of the reactants and products can be expressed in different units and because the reacting species are not always in the same phase, there may be more than one way to express the equilibrium constant for the *same* reaction. To begin with, we will consider reactions in which the reactants and products are in the same phase.

Homogeneous Equilibria

The term ***homogeneous equilibrium*** applies to reactions in which *all reacting species are in the same phase*. An example of homogeneous gas-phase equilibrium is the dissociation of N_2O_4. The equilibrium constant, as given in Equation (14.1), is

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

Note that the subscript in K_c indicates that the concentrations of the reacting species are expressed in molarity or moles per liter. The concentrations of reactants and products in gaseous reactions can also be expressed in terms of their partial pressures. From Equation (5.8) we see that at constant temperature the pressure P of a gas is directly related to the concentration in mol/L of the gas; that is, $P = (n/V)RT$. Thus, for the equilibrium process

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

we can write

$$K_P = \frac{P^2_{NO_2}}{P_{N_2O_4}} \tag{14.3}$$

where P_{NO_2} and $P_{N_2O_4}$ are the equilibrium partial pressures (in atm) of NO_2 and N_2O_4, respectively. The subscript in K_P tells us that equilibrium concentrations are expressed in terms of pressure.

In general, K_c is not equal to K_P, because the partial pressures of reactants and products are not equal to their concentrations expressed in moles per liter. A simple relationship between K_P and K_c can be derived as follows. Let us consider the following equilibrium in the gas phase:

$$a\text{A}(g) \rightleftharpoons b\text{B}(g)$$

where a and b are stoichiometric coefficients. The equilibrium constant K_c is given by

$$K_c = \frac{[\text{B}]^b}{[\text{A}]^a}$$

and the expression for K_P is

$$K_P = \frac{P^b_\text{B}}{P^a_\text{A}}$$

Equilibrium Constant and Units

Note that it is general practice not to include units for the equilibrium constant. In thermodynamics, the equilibrium constant is defined in terms of *activities* rather than concentrations. For an ideal system, the activity of a substance is the ratio of its concentration (or partial pressure) to a standard value, which is 1 *M* (or 1 atm). This procedure eliminates all units but does not alter the numerical parts of the concentration or pressure. Consequently, *K* has no units. We will extend this practice to acid-base equilibria and solubility equilibria in Chapters 15 and 16.

For nonideal systems, the activities are not exactly numerically equal to concentrations. In some cases, the differences can be appreciable. Unless otherwise noted, we will treat all systems as ideal.

Examples 14.1 through 14.3 illustrate the procedure for writing equilibrium constant expressions and calculating equilibrium constants and equilibrium concentrations.

EXAMPLE 14.1

Write expressions for K_c, and K_P if applicable, for the following reversible reactions at equilibrium:

(a) $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$

(b) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

(c) $CH_3COOH(aq) + C_2H_5OH(aq) \rightleftharpoons CH_3COOC_2H_5(aq) + H_2O(l)$

Strategy Keep in mind the following facts: (1) the K_P expression applies only to gaseous reactions and (2) the concentration of solvent (usually water) does not appear in the equilibrium constant expression.

Solution (a) Because there are no gases present, K_P does not apply and we have only K_c.

$$K'_c = \frac{[H_3O^+][F^-]}{[HF][H_2O]}$$

HF is a weak acid, so that the amount of water consumed in acid ionizations is negligible compared with the total amount of water present as solvent. Thus, we can rewrite the equilibrium constant as

$$K_c = \frac{[H_3O^+][F^-]}{[HF]}$$

(b) $$K_c = \frac{[NO_2]^2}{[NO]^2[O_2]} \qquad K_P = \frac{P^2_{NO_2}}{P^2_{NO}P_{O_2}}$$

(Continued)

(c) The equilibrium constant K'_c is given by

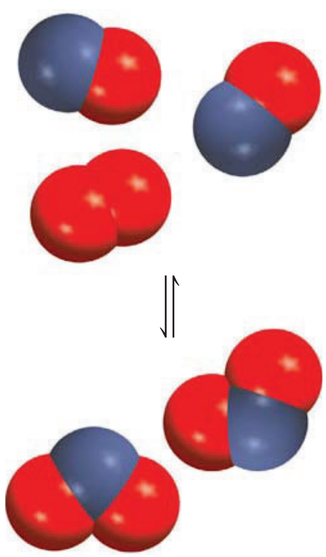
$$K'_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

Because the water produced in the reaction is negligible compared with the water solvent, the concentration of water does not change. Thus, we can write the new equilibrium constant as

$$K_c = \frac{[CH_3COOC_2H_5]}{[CH_3COOH][C_2H_5OH]}$$

Practice Exercise Write K_c and K_P for the decomposition of nitrogen pentoxide:

$$2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$$



$2NO + O_2 \rightleftharpoons 2NO_2$

EXAMPLE 14.2

The following equilibrium process has been studied at 230°C:

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

In one experiment, the concentrations of the reacting species at equilibrium are found to be [NO] = 0.0542 *M*, $[O_2]$ = 0.127 *M*, and $[NO_2]$ = 15.5 *M*. Calculate the equilibrium constant (K_c) of the reaction at this temperature.

Strategy The concentrations given are equilibrium concentrations. They have units of mol/L, so we can calculate the equilibrium constant (K_c) using the law of mass action [Equation (14.2)].

Solution The equilibrium constant is given by

$$K_c = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

Substituting the concentrations, we find that

$$K_c = \frac{(15.5)^2}{(0.0542)^2(0.127)} = 6.44 \times 10^5$$

Check Note that K_c is given without units. Also, the large magnitude of K_c is consistent with the high product (NO_2) concentration relative to the concentrations of the reactants (NO and O_2).

Practice Exercise Carbonyl chloride ($COCl_2$), also called phosgene, was used in World War I as a poisonous gas. The equilibrium concentrations for the reaction between carbon monoxide and molecular chlorine to form carbonyl chloride

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

at 74°C are [CO] = 1.2×10^{-2} *M*, $[Cl_2]$ = 0.054 *M*, and $[COCl_2]$ = 0.14 *M*. Calculate the equilibrium constant (K_c).

EXAMPLE 14.3

The equilibrium constant K_P for the decomposition of phosphorus pentachloride to phosphorus trichloride and molecular chlorine

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

is found to be 1.05 at 250°C. If the equilibrium partial pressures of PCl_5 and PCl_3 are 0.875 atm and 0.463 atm, respectively, what is the equilibrium partial pressure of Cl_2 at 250°C?

Strategy The concentrations of the reacting gases are given in atm, so we can express the equilibrium constant in K_P. From the known K_P value and the equilibrium pressures of PCl_3 and PCl_5, we can solve for P_{Cl_2}.

Solution First, we write K_P in terms of the partial pressures of the reacting species

$$K_P = \frac{P_{PCl_3}P_{Cl_2}}{P_{PCl_5}}$$

Knowing the partial pressures, we write

$$1.05 = \frac{(0.463)(P_{Cl_2})}{(0.875)}$$

or

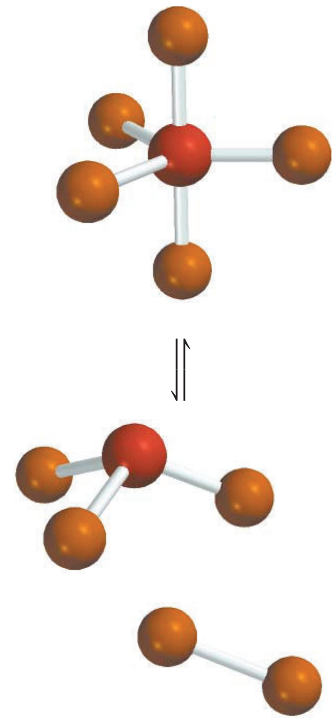
$$P_{Cl_2} = \frac{(1.05)(0.875)}{(0.463)} = 1.98 \text{ atm}$$

Check Note that we have added atm as the unit for P_{Cl_2}.

Practice Exercise The equilibrium constant K_P for the reaction

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

is 158 at 1000 K. Calculate P_{O_2} if $P_{NO_2} = 0.400$ atm and $P_{NO} = 0.270$ atm.



$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Similar problem: 14.19.

Heterogeneous Equilibria

The mineral calcite is made of calcium carbonate, as are chalk and marble.

As you might expect, a ***heterogeneous equilibrium*** results from *a reversible reaction involving reactants and products that are in different phases*. For example, when calcium carbonate is heated in a closed vessel, the following equilibrium is attained:

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

The two solids and one gas constitute three separate phases. At equilibrium, we might write the equilibrium constant as

$$K_c' = \frac{[CaO][CO_2]}{[CaCO_3]} \tag{14.6}$$

(Again, the prime for K_c here is to distinguish it from the final form of equilibrium constant to be derived shortly.) However, the "concentration" of a solid, like its density, is an intensive property and does not depend on how much of the substance is present. For example, the "molar concentration" of copper (density: 8.96 g/cm^3) at 20°C is the same, whether we have 1 gram or 1 ton of the metal:

$$[Cu] = \frac{8.96 \text{ g}}{1 \text{ cm}^3} \times \frac{1 \text{ mol}}{63.55 \text{ g}} = 0.141 \text{ mol/cm}^3 = 141 \text{ mol/L}$$

For this reason, the terms $[CaCO_3]$ and $[CaO]$ are themselves constants and can be combined with the equilibrium constant. We can simplify Equation (14.6) by writing

$$\frac{[CaCO_3]}{[CaO]} K_c' = K_c = [CO_2] \tag{14.7}$$

where K_c, the "new" equilibrium constant, is conveniently expressed in terms of a single concentration, that of CO_2. Note that the value of K_c does not depend on how much $CaCO_3$ and CaO are present, as long as some of each is present at equilibrium (Figure 14.4).

The situation becomes simpler if we replace concentrations with activities. In thermodynamics, the activity of a pure solid is 1. Thus, the concentration terms for $CaCO_3$ and CaO are both unity, and from the preceding equilibrium equation, we can immediately write $K_c = [CO_2]$. Similarly, the activity of a pure liquid is also 1. Thus, if a reactant or a product is a liquid, we can omit it in the equilibrium constant expression.

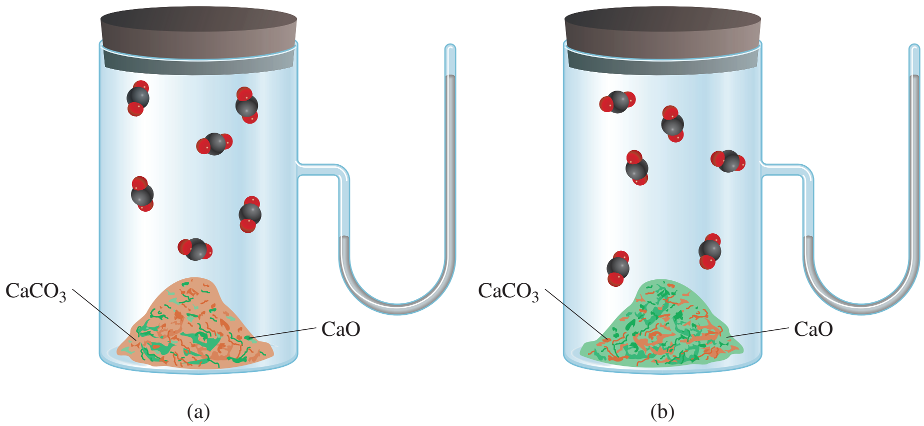


Figure 14.4 *In (a) and (b) the equilibrium pressure of CO_2 is the same at the same temperature, despite the presence of different amounts of $CaCO_3$ and CaO.*

Alternatively, we can express the equilibrium constant as

$$K_P = P_{CO_2} \tag{14.8}$$

The equilibrium constant in this case is numerically equal to the pressure of CO_2 gas, an easily measurable quantity.

EXAMPLE 14.5

Write the equilibrium constant expression K_c, and K_P if applicable, for each of the following heterogeneous systems:

(a) $(NH_4)_2Se(s) \rightleftharpoons 2NH_3(g) + H_2Se(g)$
(b) $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
(c) $P_4(s) + 6Cl_2(g) \rightleftharpoons 4PCl_3(l)$

Strategy We omit any pure solids or pure liquids in the equilibrium constant expression because their activities are unity.

Solution (a) Because $(NH_4)_2Se$ is a solid, the equilibrium constant K_c is given by

$$K_c = [NH_3]^2[H_2Se]$$

Alternatively, we can express the equilibrium constant K_P in terms of the partial pressures of NH_3 and H_2Se:

$$K_P = P^2_{NH_3}P_{H_2Se}$$

(b) Here AgCl is a solid so the equilibrium constant is given by

$$K_c = [Ag^+][Cl^-]$$

Because no gases are present, there is no K_P expression.

(c) We note that P_4 is a solid and PCl_3 is a liquid, so they do not appear in the equilibrium constant expression. Thus, K_c is given by

$$K_c = \frac{1}{[Cl_2]^6}$$

(Continued)

Alternatively, we can express the equilibrium constant in terms of the pressure of Cl_2:

$$K_P = \frac{1}{P_{Cl_2}^6}$$

Practice Exercise Write equilibrium constant expressions for K_c and K_P for the formation of nickel tetracarbonyl, which is used to separate nickel from other impurities:

$$Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g)$$

EXAMPLE 14.6

Consider the following heterogeneous equilibrium:

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

At 800°C, the pressure of CO_2 is 0.236 atm. Calculate (a) K_P and (b) K_c for the reaction at this temperature.

Strategy Remember that pure solids do not appear in the equilibrium constant expression. The relationship between K_P and K_c is given by Equation (14.5).

Solution (a) Using Equation (14.8) we write

$$K_P = P_{CO_2} = 0.236$$

(b) From Equation (14.5), we know

$$K_P = K_c(0.0821T)^{\Delta n}$$

In this case, $T = 800 + 273 = 1073$ K and $\Delta n = 1$, so we substitute these values in the equation and obtain

$$0.236 = K_c(0.0821 \times 1073)$$
$$K_c = 2.68 \times 10^{-3}$$

Practice Exercise Consider the following equilibrium at 395 K:

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

The partial pressure of each gas is 0.265 atm. Calculate K_P and K_c for the reaction.

Multiple Equilibria

The reactions we have considered so far are all relatively simple. A more complicated situation is one in which the product molecules in one equilibrium system are involved in a second equilibrium process:

$$\mathrm{A + B \rightleftharpoons C + D}$$
$$\mathrm{C + D \rightleftharpoons E + F}$$

The products formed in the first reaction, C and D, react further to form products E and F. At equilibrium we can write two separate equilibrium constants:

$$K'_c = \frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]}$$

and

$$K''_c = \frac{[\mathrm{E}][\mathrm{F}]}{[\mathrm{C}][\mathrm{D}]}$$

The overall reaction is given by the sum of the two reactions

$$\begin{array}{lll} & \mathrm{A + B \rightleftharpoons C + D} & K'_c \\ & \mathrm{C + D \rightleftharpoons E + F} & K''_c \\ \hline \text{Overall reaction:} & \mathrm{A + B \rightleftharpoons E + F} & K_c \end{array}$$

and the equilibrium constant K_c for the overall reaction is

$$K_c = \frac{[\mathrm{E}][\mathrm{F}]}{[\mathrm{A}][\mathrm{B}]}$$

We obtain the same expression if we take the product of the expressions for K'_c and K''_c:

$$K'_c K''_c = \frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]} \times \frac{[\mathrm{E}][\mathrm{F}]}{[\mathrm{C}][\mathrm{D}]} = \frac{[\mathrm{E}][\mathrm{F}]}{[\mathrm{A}][\mathrm{B}]}$$

Therefore,

$$K_c = K'_c K''_c \qquad (14.9)$$

We can now make an important statement about multiple equilibria: *If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.*

Among the many known examples of multiple equilibria is the ionization of diprotic acids in aqueous solution. The following equilibrium constants have been determined for carbonic acid (H_2CO_3) at 25°C:

$$\mathrm{H_2CO_3}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{HCO_3^-}(aq) \qquad K'_c = \frac{[\mathrm{H^+}][\mathrm{HCO_3^-}]}{[\mathrm{H_2CO_3}]} = 4.2 \times 10^{-7}$$

$$\mathrm{HCO_3^-}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{CO_3^{2-}}(aq) \qquad K''_c = \frac{[\mathrm{H^+}][\mathrm{CO_3^{2-}}]}{[\mathrm{HCO_3^-}]} = 4.8 \times 10^{-11}$$

The overall reaction is the sum of these two reactions

$$H_2CO_3(aq) \rightleftharpoons 2H^+(aq) + CO_3^{2-}(aq)$$

and the corresponding equilibrium constant is given by

$$K_c = \frac{[H^+]^2[CO_3^{2-}]}{[H_2CO_3]}$$

Using Equation (14.9) we arrive at

$$\begin{aligned} K_c &= K'_c K''_c \\ &= (4.2 \times 10^{-7})(4.8 \times 10^{-11}) \\ &= 2.0 \times 10^{-17} \end{aligned}$$

*R*e.

The Form of *K* and the Equilibrium Equation

Before concluding this section, let us look at two important rules for writing equilibrium constants:

The reciprocal of *x* is 1/*x*.

1. When the equation for a reversible reaction is written in the opposite direction, the equilibrium constant becomes the reciprocal of the original equilibrium constant. Thus, if we write the NO_2–N_2O_4 equilibrium as

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

then at 25°C,

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$

However, we can represent the equilibrium equally well as

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

and the equilibrium constant is now given by

$$K'_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{K_c} = \frac{1}{4.63 \times 10^{-3}} = 216$$

You can see that $K_c = 1/K'_c$ or $K_cK'_c = 1.00$. Either K_c or K'_c is a valid equilibrium constant, but it is meaningless to say that the equilibrium constant for the NO_2–N_2O_4 system is 4.63×10^{-3}, or 216, unless we also specify how the equilibrium equation is written.

2. The value of K also depends on how the equilibrium equation is balanced. Consider the following ways of describing the same equilibrium:

$$\tfrac{1}{2}N_2O_4(g) \rightleftharpoons NO_2(g) \qquad K'_c = \frac{[NO_2]}{[N_2O_4]^{\frac{1}{2}}}$$

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

Looking at the exponents we see that $K'_c = \sqrt{K_c}$. In Table 14.1 we find $K_c = 4.63 \times 10^{-3}$; therefore $K'_c = 0.0680$.

According to the law of mass action, each concentration term in the equilibrium constant expression is raised to a power equal to its stoichiometric coefficient. Thus, if you double a chemical equation throughout, the corresponding equilibrium constant will be the square of the original value; if you triple the equation, the equilibrium constant will be the cube of the original value, and so on. The NO_2–N_2O_4 example illustrates once again the need to write the chemical equation when quoting the numerical value of an equilibrium constant.

Example 14.7 deals with the relationship between the equilibrium constants for differently balanced equations describing the same reaction.

EXAMPLE 14.7

The reaction for the production of ammonia can be written in a number of ways:

(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
(b) $\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$
(c) $\tfrac{1}{3}N_2(g) + H_2(g) \rightleftharpoons \tfrac{2}{3}NH_3(g)$

Write the equilibrium constant expression for each formulation. (Express the concentrations of the reacting species in mol/L.)

(d) How are the equilibrium constants related to one another?

Strategy We are given three different expressions for the same reacting system. Remember that the equilibrium constant expression depends on how the equation is balanced, that is, on the stoichiometric coefficients used in the equation.

Solution

(a) $$K_a = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

(b) $$K_b = \frac{[NH_3]}{[N_2]^{\frac{1}{2}}[H_2]^{\frac{3}{2}}}$$

(c) $$K_c = \frac{[NH_3]^{\frac{2}{3}}}{[N_2]^{\frac{1}{3}}[H_2]}$$

(d) $$K_a = K_b^2$$
$$K_a = K_c^3$$
$$K_b^2 = K_c^3 \quad \text{or} \quad K_b = K_c^{\frac{3}{2}}$$

Similar problem: 14.20.

Practice Exercise Write the equilibrium expression (K_c) for each of the following reactions and show how they are related to each other: (a) $3O_2(g) \rightleftharpoons 2O_3(g)$, (b) $O_2(g) \rightleftharpoons \tfrac{2}{3}O_3(g)$.

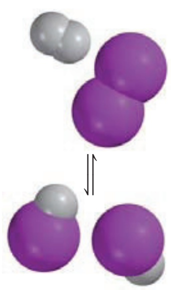
Summary of Guidelines for Writing Equilibrium Constant Expressions

1. The concentrations of the reacting species in the condensed phase are expressed in mol/L; in the gaseous phase, the concentrations can be expressed in mol/L or in atm.
2. The concentrations of pure solids, pure liquids (in heterogeneous equilibria), and solvents (in homogeneous equilibria) do not appear in the equilibrium constant expressions.
3. The equilibrium constant (K_c or K_P) is a dimensionless quantity.
4. In quoting a value for the equilibrium constant, we must specify the balanced equation and the temperature.
5. If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

14.4 What Does the Equilibrium Constant Tell Us?

We have seen that the equilibrium constant for a given reaction can be calculated from known equilibrium concentrations. Once we know the value of the equilibrium constant, we can use Equation (14.2) to calculate unknown equilibrium concentrations—remembering, of course, that the equilibrium constant has a constant value only if the temperature does not change. In general, the equilibrium constant helps us to predict the direction in which a reaction mixture will proceed to achieve equilibrium and to calculate the concentrations of reactants and products once equilibrium has been reached. These uses of the equilibrium constant will be explored in this section.

Predicting the Direction of a Reaction



$H_2 + I_2 \rightleftharpoons 2HI$

The equilibrium constant K_c for the formation of hydrogen iodide from molecular hydrogen and molecular iodine in the gas phase

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

is 54.3 at 430°C. Suppose that in a certain experiment we place 0.243 mole of H_2, 0.146 mole of I_2, and 1.98 moles of HI all in a 1.00-L container at 430°C. Will there be a net reaction to form more H_2 and I_2 or more HI? Inserting the starting concentrations in the equilibrium constant expression, we write

$$\frac{[HI]_0^2}{[H_2]_0[I_2]_0} = \frac{(1.98)^2}{(0.243)(0.146)} = 111$$

where the subscript 0 indicates initial concentrations (before equilibrium is reached). Because the quotient $[HI]_0^2/[H_2]_0[I_2]_0$ is greater than K_c, this system is not at equilibrium.

Keep in mind that the method for calculating *Q* is the same as that for *K*, except that nonequilibrium concentrations are used.

For reactions that have not reached equilibrium, such as the formation of HI considered above, we obtain the ***reaction quotient*** (Q_c), instead of the equilibrium constant *by substituting the initial concentrations into the equilibrium constant expression.* To determine the direction in which the net reaction will proceed to achieve equilibrium, we compare the values of Q_c and K_c. The three possible cases are as follows:

- $Q_c < K_c$ The ratio of initial concentrations of products to reactants is too small. To reach equilibrium, reactants must be converted to products. The system proceeds from left to right (consuming reactants, forming products) to reach equilibrium.
- $Q_c = K_c$ The initial concentrations are equilibrium concentrations. The system is at equilibrium.
- $Q_c > K_c$ The ratio of initial concentrations of products to reactants is too large. To reach equilibrium, products must be converted to reactants. The system proceeds from right to left (consuming products, forming reactants) to reach equilibrium.

Figure 14.5 shows a comparison of K_c with Q_c.

Example 14.8 shows how the value of Q_c can help us determine the direction of net reaction toward equilibrium.

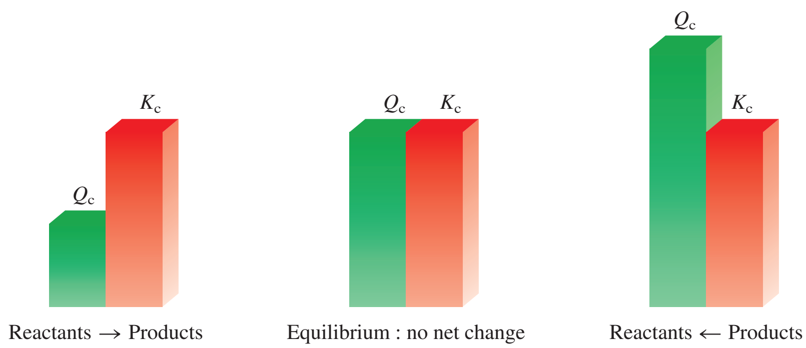


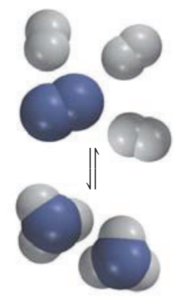
Figure 14.5 *The direction of a reversible reaction to reach equilibrium depends on the relative magnitudes of Q_c and K_c. Note that K_c is a constant at a given temperature, but Q_c varies according to the relative amounts of reactants and products present.*

EXAMPLE 14.8

At the start of a reaction, there are 0.249 mol N_2, 3.21×10^{-2} mol H_2, and 6.42×10^{-4} mol NH_3 in a 3.50-L reaction vessel at 375°C. If the equilibrium constant (K_c) for the reaction

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

is 1.2 at this temperature, decide whether the system is at equilibrium. If it is not, predict which way the net reaction will proceed.



Strategy We are given the initial amounts of the gases (in moles) in a vessel of known volume (in liters), so we can calculate their molar concentrations and hence the reaction quotient (Q_c). How does a comparison of Q_c with K_c enable us to determine if the system is at equilibrium or, if not, in which direction will the net reaction proceed to reach equilibrium?

Solution The initial concentrations of the reacting species are

$$[N_2]_0 = \frac{0.249 \text{ mol}}{3.50 \text{ L}} = 0.0711\ M$$

$$[H_2]_0 = \frac{3.21 \times 10^{-2} \text{ mol}}{3.50 \text{ L}} = 9.17 \times 10^{-3}\ M$$

$$[NH_3]_0 = \frac{6.42 \times 10^{-4} \text{ mol}}{3.50 \text{ L}} = 1.83 \times 10^{-4}\ M$$

Next we write

$$Q_c = \frac{[NH_3]_0^2}{[N_2]_0[H_2]_0^3} = \frac{(1.83 \times 10^{-4})^2}{(0.0711)(9.17 \times 10^{-3})^3} = 0.611$$

Because Q_c is smaller than K_c (1.2), the system is not at equilibrium. The net result will be an increase in the concentration of NH_3 and a decrease in the concentrations of N_2 and H_2. That is, the net reaction will proceed from left to right until equilibrium is reached.

Practice Exercise The equilibrium constant (K_c) for the formation of nitrosyl chloride, an orange-yellow compound, from nitric oxide and molecular chlorine

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

is 6.5×10^4 at 35°C. In a certain experiment, 2.0×10^{-2} mole of NO, 8.3×10^{-3} mole of Cl_2, and 6.8 moles of NOCl are mixed in a 2.0-L flask. In which direction will the system proceed to reach equilibrium?

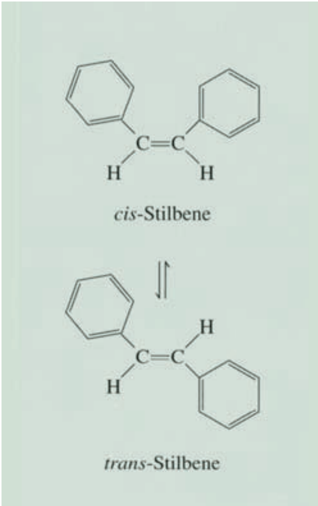
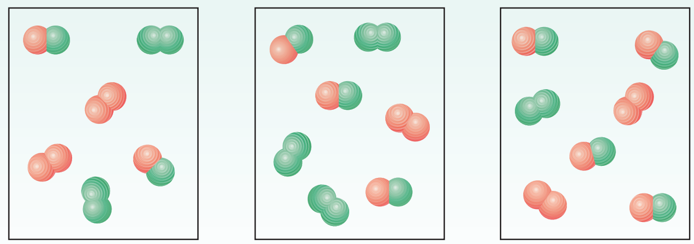


Figure 14.6 *The equilibrium between cis-stilbene and trans-stilbene. Note that both molecules have the same molecular formula ($C_{14}H_{12}$) and also the same type of bonds. However, in cis-stilbene, the benzene rings are on one side of the C═C bond and the H atoms are on the other side, whereas in trans-stilbene, the benzene rings (and the H atoms) are across from the C═C bond. These compounds have different melting points and dipole moments.*

Review of Concepts

The equilibrium constant (K_c) for the $A_2 + B_2 \rightleftharpoons 2AB$ reaction is 3 at a certain temperature. Which of the diagrams shown here corresponds to the reaction at equilibrium? For those mixtures that are not at equilibrium, will the net reaction move in the forward or reverse direction to reach equilibrium?



(a) (b) (c)

Calculating Equilibrium Concentrations

If we know the equilibrium constant for a particular reaction, we can calculate the concentrations in the equilibrium mixture from the initial concentrations. Commonly, only the initial reactant concentrations are given. Let us consider the following system involving two organic compounds, *cis*-stilbene and *trans*-stilbene, in a nonpolar hydrocarbon solvent (Figure 14.6):

$$cis\text{-stilbene} \rightleftharpoons trans\text{-stilbene}$$

The equilibrium constant (K_c) for this system is 24.0 at 200°C. Suppose that initially only *cis*-stilbene is present at a concentration of 0.850 mol/L. How do we calculate the concentrations of *cis*- and *trans*-stilbene at equilibrium? From the stoichiometry of the reaction we see that for every mole of *cis*-stilbene converted, 1 mole of *trans*-stilbene is formed. Let x be the equilibrium concentration of *trans*-stilbene in mol/L; therefore, the equilibrium concentration of *cis*-stilbene must be $(0.850 - x)$ mol/L. It is useful to summarize the changes in concentration as follows:

This procedure of solving equilibrium concentrations is sometimes referred to as the ICE method, where the acronym stands for Initial, Change, and Equilibrium.

	cis-stilbene	$\rightleftharpoons$	*trans*-stilbene
Initial (M):	0.850		0
Change (M):	$-x$		$+x$
Equilibrium (M):	$(0.850 - x)$		x

A positive (+) change represents an increase and a negative (−) change a decrease in concentration at equilibrium. Next, we set up the equilibrium constant expression

$$K_c = \frac{[trans\text{-stilbene}]}{[cis\text{-stilbene}]}$$

$$24.0 = \frac{x}{0.850 - x}$$

$$x = 0.816\ M$$

Having solved for x, we calculate the equilibrium concentrations of *cis*-stilbene and *trans*-stilbene as follows:

$$[cis\text{-stilbene}] = (0.850 - 0.816)\ M = 0.034\ M$$
$$[trans\text{-stilbene}] = 0.816\ M$$

To check the results we could use the equilibrium concentrations to calculate K_c.

We summarize our approach to solving equilibrium constant problems as follows:

1. Express the equilibrium concentrations of all species in terms of the initial concentrations and a single unknown x, which represents the change in concentration.
2. Write the equilibrium constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant, solve for x.
3. Having solved for x, calculate the equilibrium concentrations of all species.

Examples 14.9 and 14.10 illustrate the application of this three-step procedure.

EXAMPLE 14.9

A mixture of 0.500 mol H_2 and 0.500 mol I_2 was placed in a 1.00-L stainless-steel flask at 430°C. The equilibrium constant K_c for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 54.3 at this temperature. Calculate the concentrations of H_2, I_2, and HI at equilibrium.

Strategy We are given the initial amounts of the gases (in moles) in a vessel of known volume (in liters), so we can calculate their molar concentrations. Because initially no HI was present, the system could not be at equilibrium. Therefore, some H_2 would react with the same amount of I_2 (why?) to form HI until equilibrium was established.

Solution We follow the preceding procedure to calculate the equilibrium concentrations.

Step 1: The stoichiometry of the reaction is 1 mol H_2 reacting with 1 mol I_2 to yield 2 mol HI. Let x be the depletion in concentration (mol/L) of H_2 and I_2 at equilibrium. It follows that the equilibrium concentration of HI must be $2x$. We summarize the changes in concentrations as follows:

	H_2	+	I_2	$\rightleftharpoons$	2HI
Initial (M):	0.500		0.500		0.000
Change (M):	$-x$		$-x$		$+2x$
Equilibrium (M):	$(0.500 - x)$		$(0.500 - x)$		$2x$

Step 2: The equilibrium constant is given by

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

Substituting, we get

$$54.3 = \frac{(2x)^2}{(0.500 - x)(0.500 - x)}$$

Taking the square root of both sides, we get

$$7.37 = \frac{2x}{0.500 - x}$$
$$x = 0.393\ M$$

(Continued)

Step 3: At equilibrium, the concentrations are

$$[H_2] = (0.500 - 0.393)\ M = 0.107\ M$$
$$[I_2] = (0.500 - 0.393)\ M = 0.107\ M$$
$$[HI] = 2 \times 0.393\ M = 0.786\ M$$

Check You can check your answers by calculating K_c using the equilibrium concentrations. Remember that K_c is a constant for a particular reaction at a given temperature.

Practice Exercise Consider the reaction in Example 14.9. Starting with a concentration of 0.040 *M* for HI, calculate the concentrations of HI, H_2, and I_2 at equilibrium.

14.5 Factors That Affect Chemical Equilibrium

Chemical equilibrium represents a balance between forward and reverse reactions. In most cases, this balance is quite delicate. Changes in experimental conditions may disturb the balance and shift the equilibrium position so that more or less of the desired product is formed. When we say that an equilibrium position shifts to the right, for example, we mean that the net reaction is now from left to right. Variables that can be controlled experimentally are concentration, pressure, volume, and temperature. Here we will examine how each of these variables affects a reacting system at equilibrium. In addition, we will examine the effect of a catalyst on equilibrium.

Le Châtelier's Principle

There is a general rule that helps us to predict the direction in which an equilibrium reaction will move when a change in concentration, pressure, volume, or temperature occurs. The rule, known as ***Le Châtelier's*† *principle,*** states that *if an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset as the system reaches a new equilibrium position.* The word "stress" here means a change in concentration, pressure, volume, or temperature that removes the system from the equilibrium state. We will use Le Châtelier's principle to assess the effects of such changes.

Changes in Concentration

Iron(III) thiocyanate [$Fe(SCN)_3$] dissolves readily in water to give a red solution. The red color is due to the presence of hydrated $FeSCN^{2+}$ ion. The equilibrium between undissociated $FeSCN^{2+}$ and the Fe^{3+} and SCN^- ions is given by

$$\underset{\text{red}}{FeSCN^{2+}(aq)} \rightleftharpoons \underset{\text{pale yellow}}{Fe^{3+}(aq)} + \underset{\text{colorless}}{SCN^-(aq)}$$

What happens if we add some sodium thiocyanate (NaSCN) to this solution? In this case, the stress applied to the equilibrium system is an increase in the concentration of SCN^- (from the dissociation of NaSCN). To offset this stress, some Fe^{3+} ions react with the added SCN^- ions, and the equilibrium shifts from right to left:

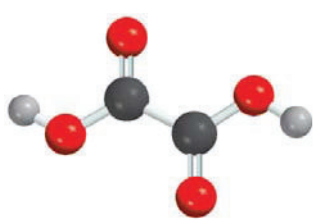
$$FeSCN^{2+}(aq) \longleftarrow Fe^{3+}(aq) + SCN^-(aq)$$

Both Na^+ and NO_3^- are colorless spectator ions.

Consequently, the red color of the solution deepens (Figure 14.7). Similarly, if we added iron(III) nitrate [$Fe(NO_3)_3$] to the original solution, the red color would also deepen because the additional Fe^{3+} ions [from $Fe(NO_3)_3$] would shift the equilibrium from right to left.

Now suppose we add some oxalic acid ($H_2C_2O_4$) to the original solution. Oxalic acid ionizes in water to form the oxalate ion, $C_2O_4^{2-}$, which binds strongly to the Fe^{3+} ions. The formation of the stable yellow ion $Fe(C_2O_4)_3^{3-}$ removes free Fe^{3+} ions in solution. Consequently, more $FeSCN^{2+}$ units dissociate and the equilibrium shifts from left to right:

$$FeSCN^{2+}(aq) \longrightarrow Fe^{3+}(aq) + SCN^-(aq)$$



Oxalic acid is sometimes used to remove bathtub rings that consist of rust, or Fe_2O_3.

The red solution will turn yellow due to the formation of $Fe(C_2O_4)_3^{3-}$ ions.

†Henri Louis Le Châtelier (1850–1936). French chemist. Le Châtelier did work on metallurgy, cements, glasses, fuels, and explosives. He was also noted for his skills in industrial management.

Figure 14.7 *Effect of concentration change on the position of equilibrium. (a) An aqueous $Fe(SCN)_3$ solution. The color of the solution is due to both the red $FeSCN^{2+}$ and the yellow Fe^{3+} ions. (b) After the addition of some NaSCN to the solution in (a), the equilibrium shifts to the left. (c) After the addition of some $Fe(NO_3)_3$ to the solution in (a), the equilibrium shifts to the left. (d) After the addition of some $H_2C_2O_4$ to the solution in (a), the equilibrium shifts to the right. The yellow color is due to the $Fe(C_2O_4)_3^{3-}$ ions.*

This experiment demonstrates that all reactants and products are present in the reacting system at equilibrium. Second, increasing the concentrations of the products (Fe^{3+} or SCN^-) shifts the equilibrium to the left, and decreasing the concentration of the product Fe^{3+} shifts the equilibrium to the right. These results are just as predicted by Le Châtelier's principle.

The effect of a change in concentration on the equilibrium position is shown in Example 14.11.

Le Châtelier's principle simply summarizes the observed behavior of equilibrium systems; therefore, it is incorrect to say that a given equilibrium shift occurs "because of" Le Châtelier's principle.

EXAMPLE 14.11

At 720°C, the equilibrium constant K_c for the reaction

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

is 2.37×10^{-3}. In a certain experiment, the equilibrium concentrations are $[N_2] = 0.683\ M$, $[H_2] = 8.80\ M$, and $[NH_3] = 1.05\ M$. Suppose some NH_3 is added to the mixture so that its concentration is increased to 3.65 M. (a) Use Le Châtelier's principle to predict the shift in direction of the net reaction to reach a new equilibrium. (b) Confirm your prediction by calculating the reaction quotient Q_c and comparing its value with K_c.

Strategy (a) What is the stress applied to the system? How does the system adjust to offset the stress? (b) At the instant when some NH_3 is added, the system is no longer at equilibrium. How do we calculate the Q_c for the reaction at this point? How does a comparison of Q_c with K_c tell us the direction of the net reaction to reach equilibrium.

Solution (a) The stress applied to the system is the addition of NH_3. To offset this stress, some NH_3 reacts to produce N_2 and H_2 until a new equilibrium is established. The net reaction therefore shifts from right to left; that is,

$$N_2(g) + 3H_2(g) \longleftarrow 2NH_3(g)$$

(b) At the instant when some of the NH_3 is added, the system is no longer at equilibrium. The reaction quotient is given by

$$\begin{aligned} Q_c &= \frac{[NH_3]_0^2}{[N_2]_0[H_2]_0^3} \\ &= \frac{(3.65)^2}{(0.683)(8.80)^3} \\ &= 2.86 \times 10^{-2} \end{aligned}$$

Because this value is greater than 2.37×10^{-3}, the net reaction shifts from right to left until Q_c equals K_c.

(Continued)

Similar problem: 14.46.

Figure 14.8 shows qualitatively the changes in concentrations of the reacting species.

Practice Exercise At 430°C, the equilibrium constant (K_P) for the reaction

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

is 1.5×10^5. In one experiment, the initial pressures of NO, O_2, and NO_2 are 2.1×10^{-3} atm, 1.1×10^{-2} atm, and 0.14 atm, respectively. Calculate Q_P and predict the direction that the net reaction will shift to reach equilibrium.

Changes in Volume and Pressure

Changes in pressure ordinarily do not affect the concentrations of reacting species in condensed phases (say, in an aqueous solution) because liquids and solids are virtually incompressible. On the other hand, concentrations of gases are greatly affected by changes in pressure. Let us look again at Equation (5.8):

$$PV = nRT$$
$$P = \left(\frac{n}{V}\right)RT$$

Note that P and V are related to each other inversely: The greater the pressure, the smaller the volume, and vice versa. Note, too, that the term (n/V) is the concentration of the gas in mol/L, and it varies directly with pressure.

Suppose that the equilibrium system

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

is in a cylinder fitted with a movable piston. What happens if we increase the pressure on the gases by pushing down on the piston at constant temperature? Because the volume decreases, the concentration (n/V) of both NO_2 and N_2O_4 increases. Note that the concentration of NO_2 is squared in the equilibrium constant expression, so the increase in pressure increases the numerator more than the denominator. The system is no longer at equilibrium and we write

$$Q_c = \frac{[NO_2]_0^2}{[N_2O_4]_0}$$

Thus, $Q_c > K_c$ and the net reaction will shift to the left until $Q_c = K_c$ (Figure 14.9). Conversely, a decrease in pressure (increase in volume) would result in $Q_c < K_c$, and the net reaction would shift to the right until $Q_c = K_c$. (This conclusion is also predicted by Le Châtelier's principle.)

In general, an increase in pressure (decrease in volume) favors the net reaction that decreases the total number of moles of gases (the reverse reaction, in this case), and a decrease in pressure (increase in volume) favors the net reaction that increases the total number of moles of gases (here, the forward reaction). For reactions in which there is no change in the number of moles of gases, a pressure (or volume) change has no effect on the position of equilibrium.

It is possible to change the pressure of a system without changing its volume. Suppose the NO_2–N_2O_4 system is contained in a stainless-steel vessel whose volume is constant. We can increase the total pressure in the vessel by adding an inert gas (helium, for example) to the equilibrium system. Adding helium to the equilibrium

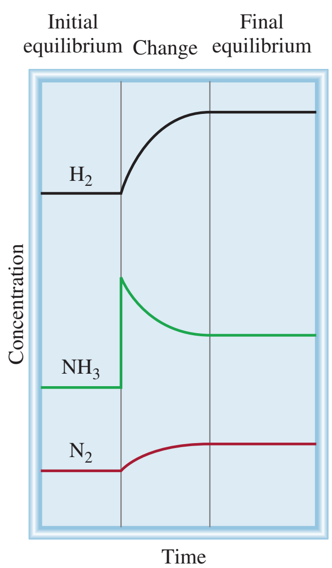


Figure 14.8 *Changes in concentration of H_2, N_2, and NH_3 after the addition of NH_3 to the equilibrium mixture. When the new equilibrium is established, all the concentrations are changed but K_c remains the same because temperature remains constant.*

mixture at constant volume increases the total gas pressure and decreases the mole fractions of both NO_2 and N_2O_4; but the partial pressure of each gas, given by the product of its mole fraction and total pressure (see Section 5.6), does not change. Thus, the presence of an inert gas in such a case does not affect the equilibrium.

Example 14.12 illustrates the effect of a pressure change on the equilibrium position.

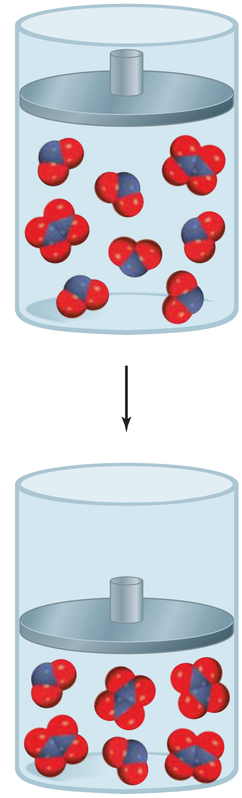


Figure 14.9 *The effect of an increase in pressure on the* $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ *equilibrium.*

EXAMPLE 14.12

Consider the following equilibrium systems:

(a) $2PbS(s) + 3O_2(g) \rightleftharpoons 2PbO(s) + 2SO_2(g)$

(b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

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

Predict the direction of the net reaction in each case as a result of increasing the pressure (decreasing the volume) on the system at constant temperature.

Strategy A change in pressure can affect only the volume of a gas, but not that of a solid because solids (and liquids) are much less compressible. The stress applied is an increase in pressure. According to Le Châtelier's principle, the system will adjust to partially offset this stress. In other words, the system will adjust to decrease the pressure. This can be achieved by shifting to the side of the equation that has fewer moles of gas. Recall that pressure is directly proportional to moles of gas: $PV = nRT$ so $P \propto n$.

Solution (a) Consider only the gaseous molecules. In the balanced equation, there are 3 moles of gaseous reactants and 2 moles of gaseous products. Therefore, the net reaction will shift toward the products (to the right) when the pressure is increased.

(b) The number of moles of products is 2 and that of reactants is 1; therefore, the net reaction will shift to the left, toward the reactant.

(c) The number of moles of products is equal to the number of moles of reactants, so a change in pressure has no effect on the equilibrium.

Check In each case, the prediction is consistent with Le Châtelier's principle.

Similar problem: 14.56.

Practice Exercise Consider the equilibrium reaction involving nitrosyl chloride, nitric oxide, and molecular chlorine

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

Predict the direction of the net reaction as a result of decreasing the pressure (increasing the volume) on the system at constant temperature.

Changes in Temperature

A change in concentration, pressure, or volume may alter the equilibrium position, that is, the relative amounts of reactants and products, but it does not change the value of the equilibrium constant. Only a change in temperature can alter the equilibrium constant. To see why, let us consider the reaction

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

The forward reaction is endothermic (absorbs heat, $\Delta H° > 0$):

$$\text{heat} + N_2O_4(g) \longrightarrow 2NO_2(g) \qquad \Delta H° = 58.0 \text{ kJ/mol}$$

so the reverse reaction is exothermic (releases heat, $\Delta H° < 0$):

$$2NO_2(g) \longrightarrow N_2O_4(g) + \text{heat} \qquad \Delta H° = -58.0 \text{ kJ/mol}$$

At equilibrium at a certain temperature, the heat effect is zero because there is no net reaction. If we treat heat as though it were a chemical reagent, then a rise in temperature "adds" heat to the system and a drop in temperature "removes" heat from the system. As with a change in any other parameter (concentration, pressure, or volume), the system shifts to reduce the effect of the change. Therefore, a temperature increase favors the endothermic direction of the reaction (from left to right of the equilibrium equation), which decreases $[N_2O_4]$ and increases $[NO_2]$. A temperature decrease favors the exothermic direction of the reaction (from right to left of the equilibrium equation), which decreases $[NO_2]$ and increases $[N_2O_4]$. Consequently, the equilibrium constant, given by

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

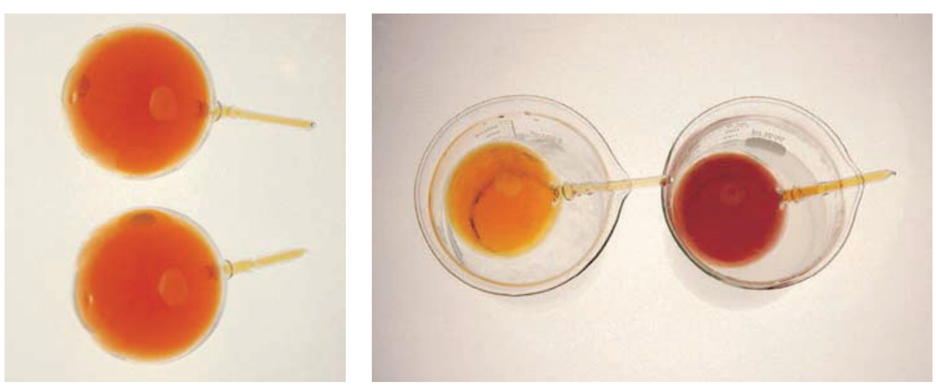
increases when the system is heated and decreases when the system is cooled (Figure 14.10).

As another example, consider the equilibrium between the following ions:

$$\underset{\text{blue}}{CoCl_4^{2-}} + 6H_2O \rightleftharpoons \underset{\text{pink}}{Co(H_2O)_6^{2+}} + 4Cl^-$$

The formation of $CoCl_4^{2-}$ is endothermic. On heating, the equilibrium shifts to the left and the solution turns blue. Cooling favors the exothermic reaction [the formation of $Co(H_2O)_6^{2+}$] and the solution turns pink (Figure 14.11).

In summary, *a temperature increase favors an endothermic reaction, and a temperature decrease favors an exothermic reaction.*



(a) (b)

Figure 14.10 *(a) Two bulbs containing a mixture of NO_2 and N_2O_4 gases at equilibrium. (b) When one bulb is immersed in ice water (left), its color becomes lighter, indicating the formation of colorless N_2O_4 gas. When the other bulb is immersed in hot water, its color darkens, indicating an increase in NO_2.*

Figure 14.11 *(Left) Heating favors the formation of the blue $CoCl_4^{2-}$ ion. (Right) Cooling favors the formation of the pink $Co(H_2O)_6^{2+}$ ion.*

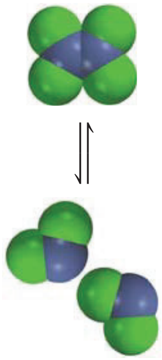
The Effect of a Catalyst

We know that a catalyst enhances the rate of a reaction by lowering the reaction's activation energy (Section 13.6). However, as Figure 13.23 shows, a catalyst lowers the activation energy of the forward reaction and the reverse reaction to the same extent. We can therefore conclude that the presence of a catalyst does not alter the equilibrium constant, nor does it shift the position of an equilibrium system. Adding a catalyst to a reaction mixture that is not at equilibrium will simply cause the mixture to reach equilibrium sooner. The same equilibrium mixture could be obtained without the catalyst, but we might have to wait much longer for it to happen.

Summary of Factors That May Affect the Equilibrium Position

We have considered four ways to affect a reacting system at equilibrium. It is important to remember that, of the four, *only a change in temperature changes the value of the equilibrium constant.* Changes in concentration, pressure, and volume can alter the equilibrium concentrations of the reacting mixture, but they cannot change the equilibrium constant as long as the temperature does not change. A catalyst can speed up the process, but it has no effect on the equilibrium constant or on the equilibrium concentrations of the reacting species. Two processes that illustrate the effects of changed conditions on equilibrium processes are discussed in Chemistry in Action essays on pp. 645 and 646.

The effects of temperature, concentration, and pressure change, as well as the addition of an inert gas, on an equilibrium system are treated in Example 14.13.



$N_2F_4 \rightleftharpoons 2NF_2$

EXAMPLE 14.13

Consider the following equilibrium process between dinitrogen tetrafluoride (N_2F_4) and nitrogen difluoride (NF_2):

$$N_2F_4(g) \rightleftharpoons 2NF_2(g) \qquad \Delta H° = 38.5 \text{ kJ/mol}$$

Predict the changes in the equilibrium if (a) the reacting mixture is heated at constant volume; (b) some N_2F_4 gas is removed from the reacting mixture at constant temperature and volume; (c) the pressure on the reacting mixture is decreased at constant temperature; and (d) a catalyst is added to the reacting mixture.

Strategy (a) What does the sign of $\Delta H°$ indicate about the heat change (endothermic or exothermic) for the forward reaction? (b) Would the removal of some N_2F_4 increase or decrease the Q_c of the reaction? (c) How would the decrease in pressure change the volume of the system? (d) What is the function of a catalyst? How does it affect a reacting system not at equilibrium? at equilibrium?

Solution (a) The stress applied is the heat added to the system. Note that the $N_2F_4 \longrightarrow 2NF_2$ reaction is an endothermic process ($\Delta H° > 0$), which absorbs heat from the surroundings. Therefore, we can think of heat as a reactant

$$\text{heat} + N_2F_4(g) \rightleftharpoons 2NF_2(g)$$

The system will adjust to remove some of the added heat by undergoing a decomposition reaction (from left to right). The equilibrium constant

$$K_c = \frac{[NF_2]^2}{[N_2F_4]}$$

will therefore increase with increasing temperature because the concentration of NF_2 has increased and that of N_2F_4 has decreased. Recall that the equilibrium constant is a constant only at a particular temperature. If the temperature is changed, then the equilibrium constant will also change.

(b) The stress here is the removal of N_2F_4 gas. The system will shift to replace some of the N_2F_4 removed. Therefore, the system shifts from right to left until equilibrium is reestablished. As a result, some NF_2 combines to form N_2F_4.

Comment The equilibrium constant remains unchanged in this case because temperature is held constant. It might seem that K_c should change because NF_2 combines to produce N_2F_4. Remember, however, that initially some N_2F_4 was removed. The system adjusts to replace only some of the N_2F_4 that was removed, so that overall the amount of N_2F_4 has decreased. In fact, by the time the equilibrium is reestablished, the amounts of both NF_2 and N_2F_4 have decreased. Looking at the equilibrium constant expression, we see that dividing a smaller numerator by a smaller denominator gives the same value of K_c.

(c) The stress applied is a decrease in pressure (which is accompanied by an increase in gas volume). The system will adjust to remove the stress by increasing the pressure. Recall that pressure is directly proportional to the number of moles of a gas. In the balanced equation we see that the formation of NF_2 from N_2F_4 will increase the total number of moles of gases and hence the pressure. Therefore, the system will shift from left to right to reestablish equilibrium. The equilibrium constant will remain unchanged because temperature is held constant.

(d) The function of a catalyst is to increase the rate of a reaction. If a catalyst is added to a reacting system not at equilibrium, the system will reach equilibrium faster than

(Continued)

CHEMISTRY

in Action

Life at High Altitudes and Hemoglobin Production

In the human body, countless chemical equilibria must be maintained to ensure physiological well-being. If environmental conditions change, the body must adapt to keep functioning. The consequences of a sudden change in altitude dramatize this fact. Flying from San Francisco, which is at sea level, to Mexico City, where the elevation is 2.3 km (1.4 mi), or scaling a 3-km mountain in two days can cause headache, nausea, extreme fatigue, and other discomforts. These conditions are all symptoms of hypoxia, a deficiency in the amount of oxygen reaching body tissues. In serious cases, the victim may slip into a coma and die if not treated quickly. And yet a person living at a high altitude for weeks or months gradually recovers from altitude sickness and adjusts to the low oxygen content in the atmosphere, so that he or she can function normally.

The combination of oxygen with the hemoglobin (Hb) molecule, which carries oxygen through the blood, is a complex reaction, but for our purposes it can be represented by a simplified equation:

$$\mathrm{Hb}(aq) + \mathrm{O_2}(aq) \rightleftharpoons \mathrm{HbO_2}(aq)$$

where HbO_2 is oxyhemoglobin, the hemoglobin-oxygen complex that actually transports oxygen to tissues. The equilibrium constant is

$$K_c = \frac{[\mathrm{HbO_2}]}{[\mathrm{Hb}][\mathrm{O_2}]}$$

At an altitude of 3 km the partial pressure of oxygen is only about 0.14 atm, compared with 0.2 atm at sea level. According to Le Châtelier's principle, a decrease in oxygen concentration will shift the equilibrium shown in the equation above from right to left. This change depletes the supply of oxyhemoglobin, causing hypoxia. Given enough time, the body copes with this problem by producing more hemoglobin molecules. The equilibrium will then gradually shift back toward the formation of oxyhemoglobin. It takes two to three weeks for the increase in hemoglobin production to meet the body's basic needs adequately. A return to full capacity may require several years to occur. Studies show that long-time residents of high-altitude areas have high hemoglobin levels in their blood—sometimes as much as 50 percent more than individuals living at sea level!

Mountaineers need weeks or even months to become acclimatized before scaling summits such as Mount Everest.

if left undisturbed. If a system is already at equilibrium, as in this case, the addition of a catalyst will not affect either the concentrations of NF_2 and N_2F_4 or the equilibrium constant.

Practice Exercise Consider the equilibrium between molecular oxygen and ozone

$$3\mathrm{O_2}(g) \rightleftharpoons 2\mathrm{O_3}(g) \qquad \Delta H^\circ = 284\ \mathrm{kJ/mol}$$

What would be the effect of (a) increasing the pressure on the system by decreasing the volume, (b) adding O_2 to the system at constant volume, (c) decreasing the temperature, and (d) adding a catalyst?

CHEMISTRY *in Action*

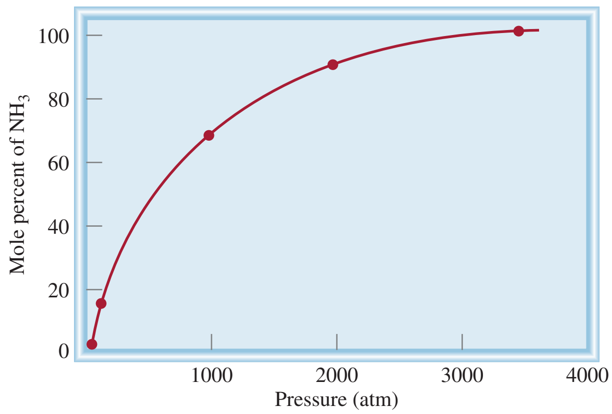
The Haber Process

Knowing the factors that affect chemical equilibrium has great practical value for industrial applications, such as the synthesis of ammonia. The Haber process for synthesizing ammonia from molecular hydrogen and nitrogen uses a heterogeneous catalyst to speed up the reaction (see p. 596). Let us look at the equilibrium reaction for ammonia synthesis to determine whether there are factors that could be manipulated to enhance the yield.

Suppose, as a prominent industrial chemist at the turn of the twentieth century, you are asked to design an efficient procedure for synthesizing ammonia from hydrogen and nitrogen. Your main objective is to obtain a high yield of the product while keeping the production costs down. Your first step is to take a careful look at the balanced equation for the production of ammonia:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H° = -92.6 \text{ kJ/mol}$$

Two ideas strike you: *First,* because 1 mole of N_2 reacts with 3 moles of H_2 to produce 2 moles of NH_3, a higher yield of NH_3 can be obtained at equilibrium if the reaction is carried out under high pressures. This is indeed the case, as shown by the plot of mole percent of NH_3 versus the total pressure of the reacting system. *Second,* the exothermic nature of the forward reaction tells you that the equilibrium constant for the reaction will decrease with increasing temperature. Thus, for maximum yield of NH_3, the reaction should be run at the lowest possible temperature.



Mole percent of NH_3 as a function of the total pressures of the gases at 425°C.

The graph on p. 647 shows that the yield of ammonia increases with decreasing temperature. A low-temperature operation (say, 220 K or −53°C) is desirable in other respects too. The boiling point of NH_3 is −33.5°C, so as it formed it would quickly condense to a liquid, which could be conveniently removed from the reacting system. (Both H_2 and N_2 are still gases at this temperature.) Consequently, the net reaction would shift from left to right, just as desired.

Key Equations

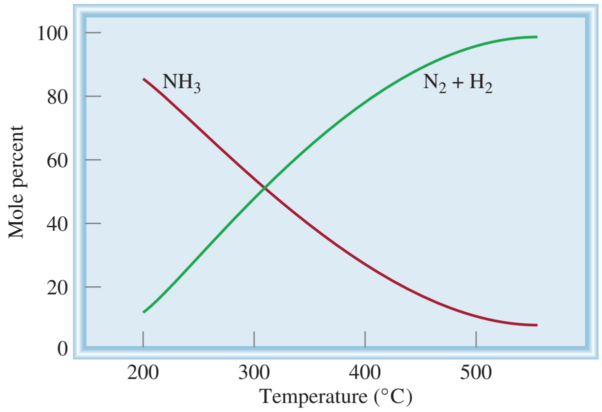
$K = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$ (14.2)		Law of mass action. General expression of equilibrium constant.
$K_c = K'_c K''_c$ (14.9)		The equilibrium constant for the overall reaction is given by the product of the equilibrium constants for the individual reactions.

Summary of Facts and Concepts

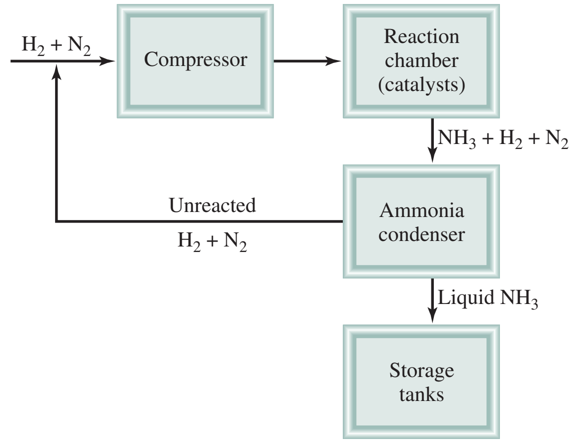
1. Dynamic equilibria between phases are called physical equilibria. Chemical equilibrium is a reversible process in which the rates of the forward and reverse reactions are equal and the concentrations of reactants and products do not change with time.
2. For the general chemical reaction

$$aA + bB \rightleftharpoons cC + dD$$

the concentrations of reactants and products at equilibrium (in moles per liter) are related by the equilibrium constant expression [Equation (14.2)].
3. The equilibrium constant for gases, K_P, expresses the relationship of the equilibrium partial pressures (in atm) of reactants and products.
4. A chemical equilibrium process in which all reactants and products are in the same phase is homogeneous. If



The composition (mole percent) of $H_2 + N_2$ and NH_3 at equilibrium (for a certain starting mixture) as a function of temperature.



Schematic diagram of the Haber process for ammonia synthesis. The heat generated from the reaction is used to heat the incoming gases.

On paper, then, these are your conclusions. Let us compare your recommendations with the actual conditions in an industrial plant. Typically, the operating pressures are between 500 atm and 1000 atm, so you are right to advocate high pressure. Furthermore, in the industrial process the NH_3 never reaches its equilibrium value but is constantly removed from the reaction mixture in a continuous process operation. This design makes sense, too, as you had anticipated. The only discrepancy is that the operation is usually carried out at about 500°C. This high-temperature operation is costly and the yield of NH_3 is low. The justification for this choice is that the *rate* of NH_3 production increases with increasing temperature. Commercially, faster production of NH_3 is preferable even if it means a lower yield and higher operating cost. For this reason, the combination of high-pressure, high-temperature conditions and the proper catalyst is the most efficient way to produce ammonia on a large scale.

the reactants and products are not all in the same phase, the equilibrium is heterogeneous. The concentrations of pure solids, pure liquids, and solvents are constant and do not appear in the equilibrium constant expression of a reaction.

5. If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.
6. The value of K depends on how the chemical equation is balanced, and the equilibrium constant for the reverse of a particular reaction is the reciprocal of the equilibrium constant of that reaction.
7. The equilibrium constant is the ratio of the rate constant for the forward reaction to that for the reverse reaction.
8. The reaction quotient Q has the same form as the equilibrium constant, but it applies to a reaction that may not be at equilibrium. If $Q > K$, the reaction will proceed from right to left to achieve equilibrium. If $Q < K$, the reaction will proceed from left to right to achieve equilibrium.
9. Le Châtelier's principle states that if an external stress is applied to a system at chemical equilibrium, the system will adjust to partially offset the stress.
10. Only a change in temperature changes the value of the equilibrium constant for a particular reaction. Changes in concentration, pressure, or volume may change the equilibrium concentrations of reactants and products. The addition of a catalyst hastens the attainment of equilibrium but does not affect the equilibrium concentrations of reactants and products.

Key Words

Answers to Practice Exercises

14.1 $K_c = \frac{[NO_2]^4[O_2]}{[N_2O_5]^2}$; $K_P = \frac{P^4_{NO_2}P_{O_2}}{P^2_{N_2O_5}}$ **14.2** 2.2×10^2
14.3 347 atm **14.4** 1.2
14.5 $K_c = \frac{[Ni(CO)_4]}{[CO]^4}$; $K_P = \frac{P_{Ni(CO)_4}}{P^4_{CO}}$
14.6 $K_P = 0.0702$; $K_c = 6.68 \times 10^{-5}$
14.7 (a) $K_a = \frac{[O_3]^2}{[O_2]^3}$ (b) $K_b = \frac{[O_3]^{\frac{2}{3}}}{[O_2]}$; $K_a = K_b^3$

14.8 From right to left. **14.9** [HI] = 0.031 *M*, $[H_2] = 4.3 \times 10^{-3}$ *M*, $[I_2] = 4.3 \times 10^{-3}$ *M* **14.10** $[Br_2] = 0.065$ *M*, $[Br] = 8.4 \times 10^{-3}$ *M* **14.11** $Q_P = 4.0 \times 10^5$; the net reaction will shift from right to left. **14.12** Left to right.
14.13 The equilibrium will shift from (a) left to right, (b) left to right, and (c) right to left. (d) A catalyst has no effect on the equilibrium.