We see that y is very small compared with 5.0 and 10.0 atm, so our approximations are valid. The equilibrium pressures are:

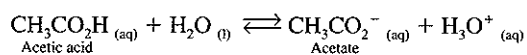$$(p_{NO})_{eq} = y = 2.2 \times 10^{-6} \text{ atm}$$

$$(p_{O_2})_{eq} = 5.0 \text{ atm} + 0.5y = 5.0 \text{ atm} \qquad (p_{NO_2})_{eq} = 10.0 \text{ atm} - y = 10.0 \text{ atm}$$

The sample problems illustrate the general approach to equilibrium problems. In Chapter 16 we apply these ideas to the important types of equilibria that occur in aqueous solutions. Box 15-2 discusses the carbon cycle and chemical equilibria.

SECTION EXERCISES

15.4.1 Barium sulfate is a salt that is opaque to x rays. It is used as an imaging agent for medical radiographs of the gastrointestinal tract. (See Figure 4-11.) The concentration of Ba^{2+} ions in a saturated aqueous solution is 1.05×10^{-5} M. Determine K_{sp} for barium sulfate.

15.4.2 A solution of acetic acid in water is described by the following equilibrium:

$$\underset{\text{Acetic acid}}{CH_3CO_2H_{(aq)}} + H_2O_{(l)} \rightleftharpoons \underset{\text{Acetate}}{CH_3CO_2^-}{}_{(aq)} + H_3O^+{}_{(aq)}$$

The equilibrium constant for this acid-base reaction is $K_a = 1.8 \times 10^{-5}$ M. Calculate the equilibrium concentrations of acetic acid, acetate ion, and hydronium ion in a 2.5 M solution of acetic acid.

15.4.3 The key step in the synthesis of sulfuric acid is the combustion of SO_2 to give sulfur trioxide:

$$2 SO_{2\,(g)} + O_{2\,(g)} \overset{\text{Catalyst}}{\rightleftharpoons} 2 SO_{3\,(g)} \qquad K_{eq} = 5.60 \times 10^4 \text{ atm}^{-1} \text{ at } 350 \text{ °C}$$

Sulfur dioxide and oxygen are mixed initially at 0.350 atm and 0.762 atm, respectively, at 350 °C. What are the partial pressures of the three gases when the mixture reaches equilibrium?

15.5 THERMODYNAMICS AND EQUILIBRIUM

Equilibrium constants have values covering a very large range. Why do some reactions reach equilibrium when hardly any of the starting materials have been consumed, whereas others go virtually to completion? At the molecular level, bond energies and molecular organization are the determining factors. Macroscopically, these translate into the thermodynamic properties of enthalpy and entropy. As discussed in Chapter 13, free energy (G) is a state function that combines these properties. Free energy provides information about the spontaneous direction of a reaction. In this section we establish the connection between free energy and the equilibrium constant.

THE CONCENTRATION QUOTIENT

When the reaction is *at equilibrium,* the ratio of product concentrations to reactant concentrations is equal to the equilibrium constant, K_{eq}:

$$aA + bB \rightleftharpoons cC + dD \qquad K_{eq} = \frac{[C]^c_{eq}\,[D]^d_{eq}}{[A]^a_{eq}\,[B]^b_{eq}}$$
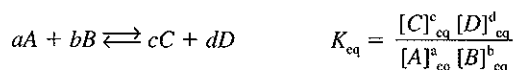
When a chemical system is *not at equilibrium,* the ratio of concentrations is called the **concentration quotient, (Q).** The concentration quotient has the same form as the equilibrium concentration ratio, but the concentrations *are not equilibrium values:* Consequently, Q can have *any* value.

$$K_{eq} = \frac{[C]^c_{eq}\,[D]^d_{eq}}{[A]^a_{eq}\,[B]^b_{eq}} \qquad Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The subscript "eq" indicates that these are equilibrium concentrations.

These are not equilibrium concentrations.

The NO_2/N_2O_4 system can be used to show how Q is related to K_{eq}. We have seen that NO_2 gas reacts to produce N_2O_4 until an equilibrium is established between the two gases. If a sample contained only NO_2, the partial pressure of N_2O_4 would be zero and $Q = 0$. This system would react to form N_2O_4 and consume NO_2, and the value of Q would increase until $Q = K_{eq}$. At these concentrations, the system would be at equilibrium. If, on the other hand, a sample contained only N_2O_4 but no NO_2, the partial pressure of NO_2 would be zero and $Q = \infty$. Under these conditions, the system would react to form NO_2 and consume N_2O_4, and the value of Q would decrease, again until $Q = K_{eq}$. Thus we see that the direction in which a reaction proceeds depends on the relationship between Q and K_{eq}:

Q < K$_{eq}$ reaction goes to the right to make products.

Q > K$_{eq}$ reaction goes to the left to make reactants.

Notice that if the concentration of any *product* is zero, $Q = 0$, and the reaction must go to the *right,* toward products. If any *reactant* concentration is zero, $Q = \infty$, and the reaction must go to the *left,* toward reactants.

The relationship between Q and K_{eq} signals the direction of a chemical reaction. The free energy change, ΔG (introduced in Chapter 13), also signals the direction of a chemical reaction. These two criteria can be compared:

Reaction goes right when	Equilibrium when	Reaction goes left when
$Q < K_{eq}$	$Q = K_{eq}$	$Q > K_{eq}$
$\Delta G_{rxn} < 0$	$\Delta G_{rxn} = 0$	$\Delta G_{rxn} > 0$

The similarities suggest a link among Q, K_{eq}, and ΔG. This link can be found from the equations of thermodynamics. The concentration quotient appears in Equation 13-12 as a link between the standard free energy change for a reaction and its free energy change under nonstandard conditions:

$$\Delta G = \Delta G° + RT \ln Q \tag{13-12}$$

At equilibrium, $\Delta G = 0$ and $Q = K_{eq}$. Substituting these equalities into Equation 13-12, we obtain:

$$0 = \Delta G° + RT \ln K_{eq}$$

This rearranges to:

$$\Delta G° = -RT \ln K_{eq} \tag{15-5}$$

Equation 15-5 is an extremely important relationship, because it links thermody-
namic data with equilibrium constants. Because many values of ΔG_f° appear in tables,
K can be calculated from Equation 15-5 for many reactions. This equation is
applied to the Haber process in Sample Problem 15-9.

SAMPLE PROBLEM 15-9   THERMODYNAMICS AND K_{eq}

Using standard thermodynamic data, find the value of K_{eq} at 298 K for the Haber reaction:

$$N_{2\,(g)} + 3\,H_{2\,(g)} \rightleftharpoons 2\,NH_{3\,(g)}$$
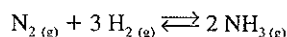
METHOD: Equation 15-5 provides the link between thermodynamic data and K_{eq}. We must
first calculate ΔG_{rxn}° from tabulated standard free energies of formation.

$$\Delta G_{rxn}^\circ = \Sigma \text{ (coeff) } \Delta G_f^\circ \text{ (products)} - \Sigma \text{ (coeff) } \Delta G_f^\circ \text{ (reactants)}$$

Appendix E contains the appropriate values:

$$\Delta G_f^\circ \text{ (kJ/mol): } N_{2\,(g)}, 0; H_{2\,(g)}, 0; NH_{3\,(g)}, -16.4 \text{ kJ/mol}$$

$$\Delta G^\circ = (2 \text{ mol } NH_3)(-16.4 \text{ kJ/mol } NH_3) - 3(0) - 1(0) = -32.8 \text{ kJ}$$

To determine the equilibrium constant, Equation 15-5 must be rearranged to isolate $\ln K_{eq}$.

$$\ln K_{eq} = -\frac{\Delta G^\circ}{RT} = \frac{-(-32.8 \text{ kJ})(10^3 \text{ J/kJ})}{(8.314 \text{ J/K})(298 \text{ K})} = 13.24$$

$$K_{eq} = e^{13.4} = 5.6 \times 10^5 \text{ atm}^{-2}$$

The exponential gives a dimensionless number, since e^x is always a pure number. However,
we assign units to K_{eq} as required by the concentration quotient. Remember that the super-
script "o" in ΔG° refers to standard conditions that include concentrations of 1 M for solutes
and 1 atm partial pressure for gases.

Remember that ΔG_f° for any element
in its standard state is zero.

EQUILIBRIUM CONSTANTS AND TEMPERATURE

Studies of the effect of temperature on equilibria reveal a consistent pattern. The
equilibrium constant of an *exothermic* reaction *decreases* with increasing tempera-
ture, whereas the equilibrium constant of an *endothermic* reaction *increases* with
increasing temperature. Equation 15-5 provides a thermodynamic explanation for
this behavior. Recall that free energy is related to enthalpy and entropy through
Equation 13-9:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad \qquad \textbf{(13-9)}$$

This equality can be substituted into Equation 15-5 to show how $\ln K_{eq}$ depends on
ΔH°, ΔS°, and T:

$$\Delta H^\circ - T\Delta S^\circ = -RT \ln K_{eq}$$

which rearranges to give:

$$\ln K_{eq} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad \qquad \textbf{(15-6)}$$

An exothermic reaction has a negative ΔH°, making the first term on the right of
Equation 15-6 positive. As T increases, this term *decreases,* causing K_{eq} to decrease.
An endothermic reaction, in contrast, has a positive ΔH°, making the first term on the
right of Equation 15-6 negative. As T increases, this term becomes less negative,

causing K_{eq} to increase. These variations in K_{eq} with temperature, which can be substantial, can be estimated using Equation 15-6 and standard thermodynamic functions. Sample Problem 15-10 applies Equation 15-6 to the Haber synthesis.

SAMPLE PROBLEM 15-10 K_{eq} AND TEMPERATURE

Use tabulated thermodynamic data to estimate K_{eq} for the Haber reaction at 500 °C.

METHOD: Values for $\Delta H°$ and $\Delta S°$ can be calculated using tabulated thermodynamic values. Then Equation 15-6 can be applied to determine the value of the equilibrium constant at 500 °C. First, we need $\Delta H°_{rxn}$ and $\Delta S°_{rxn}$:

$$\Delta H°_{rxn} = \Sigma \text{ (coeff) } \Delta H°_f \text{ (products)} - \Sigma \text{ (coeff) } \Delta H°_f \text{ (reactants)}$$

$$\Delta S°_{rxn} = \Sigma \text{ (coeff) } S° \text{ (products)} - \Sigma \text{ (coeff) } S° \text{ (reactants)}$$

Appendix E contains the appropriate values:

$\Delta H°_f$ (kJ/mol)	$N_{2\,(g)}$: 0	$H_{2\,(g)}$: 0	$NH_{3\,(g)}$: −46
$S°$ (J/mol K)	$N_{2\,(g)}$: 191.6	$H_{2\,(g)}$: 130.7	$NH_{3\,(g)}$: 192.45

$$\Delta H°_{rxn} = (2)(-46 \text{ kJ/mol}) - 3(0) - 0 = -92 \text{ kJ/mol}$$

$$\Delta S°_{rxn} = (2)(192.45 \text{ J/mol K}) - (3)(130.7 \text{ J/mol K}) - 191.6 \text{ J/mol K}$$

$$\Delta S°_{rxn} = -198.8 \text{ J/mol K}$$

Now calculate K_{eq} at 500 °C using Equation 15-6:

$$\ln K_{eq} = \frac{\Delta H°}{RT} + \frac{\Delta S°}{R}$$

$$\ln K_{eq} = -\frac{(-92 \text{ kJ/mol})(10^3 \text{ J/kJ})}{(8.314 \text{ J/mol K})(500 + 273 \text{ K})} + \frac{(-198.8 \text{ J/mol K})}{(8.314 \text{ J/mol K})}$$

$$\ln K_{eq} = 14.3 - 23.9 = -9.6$$

Taking the anti*ln*, or e^x, of −9.6 gives the estimated equilibrium constant at 500 °C:

$$K_{eq} = 6.7 \times 10^{-5} \text{ atm}^{-2}$$

Sample Problems 15-9 and 15-10 underscore the dilemma faced by industrial chemists and engineers. At 298 K, the equilibrium position of the Haber reaction strongly favors the formation of ammonia. Why, then, is the Haber synthesis not carried out at 298 K, where equilibrium strongly favors the desired product? The reason is that even with a catalyst, the reaction is much too slow to be useful at this temperature. At low temperature, thermodynamics favors ammonia, but kinetics prohibits the reaction from occurring at a discernible rate. To make the reaction proceed at a practical rate, the temperature must be increased. Unfortunately, the equilibrium constant falls dramatically as temperature increases. At 773 K, a realistic temperature for the Haber reaction, the equilibrium position does not favor NH_3:

$$N_2 + 3 H_2 \rightleftharpoons 2 NH_3$$
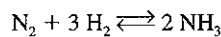
$$K_{eq,\,298\,K} = 5.6 \times 10^5 \text{ atm}^{-2} \qquad\qquad K_{eq,\,773\,K} = 6.7 \times 10^{-5} \text{ atm}^{-2}$$

Nature has solved this problem with the enzyme nitrogenase. This enzyme is found in bacteria that live in nodules among the roots of leguminous plants such as soybeans and clover (Figure 15-12). Nitrogenase catalyzes the formation of ammonia from atmospheric nitrogen. Chemists are studying the mechanism of nitro-

FIGURE 15-12
Rhizobium bacteria, which form colonies in nodules on the roots of leguminous plants, have an enzyme that allows them to manufacture ammonia from molecular nitrogen at ambient temperature.

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genase, but its chemistry is so complicated that we still have incomplete knowledge of how the enzyme converts nitrogen to ammonia. Perhaps further research will uncover its secret and make it possible to design new commercial catalysts for nitrogen fixation that operate at 298 K.

The Haber reaction is a practical example of the effect of temperature on an exothermic reaction. A practical example of an endothermic reaction is the use of methane and steam to produce the molecular hydrogen needed for the Haber reaction. This reaction is highly endothermic, so it is carried out at temperatures much greater than 1000 K to force the equilibrium toward the products:

$$CH_{4\,(g)} + H_2O_{\,(g)} \rightleftharpoons CO_{\,(g)} + 3\,H_{2\,(g)} \qquad \Delta H^\circ = +206 \text{ kJ}$$
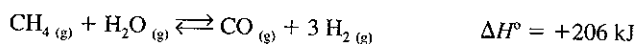
$$K_{eq,\,298\,K} = 1.2 \times 10^{-25} \text{ atm}^{-2} \qquad K_{eq,\,1500\,K} = 1.1 \times 10^4 \text{ atm}^{-2}$$

SECTION EXERCISES

15.5.1 Use thermodynamic data to determine K_{eq} for the oxidation of NO at 298 K:

$$2\,NO_{\,(g)} + O_{2\,(g)} \rightleftharpoons 2\,NO_{2\,(g)}$$
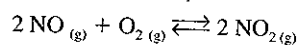
15.5.2 Does K_{eq} for the reaction described in 15.5.1 increase or decrease when the temperature is raised above room temperature? Give your reasoning.

15.5.3 Use thermodynamic data to estimate K_{eq} at 1000 °C for the reaction in 15.5.1.

15.6 SHIFTS IN EQUILIBRIUM

We call K_{eq} the equilibrium *constant* because it has the *same value* regardless of the amounts of reactants and products that we put into the system. In other words, K_{eq} is independent of initial concentrations. No matter what value Q has before the reaction occurs, equilibrium will be reached when concentrations have changed so that $Q = K_{eq}$.

LE CHÂTELIER'S PRINCIPLE

What happens if we change the conditions on a system that is already at equilibrium? Suppose we vary the amounts or concentrations of one or more substances, or change the temperature of the system. How does a system that is at equilibrium respond to these changes? Although the equations that describe equilibrium provide quantitative answers to these questions, a simple principle can be applied to obtain a quick qualitative indication. This principle, which was first formulated by Henri-Louis Le Châtelier, a French industrial chemist of the early twentieth century, states:

> *When a change is imposed on a system at equilibrium,*
> *the system will react, if possible, in the direction*
> *that reduces the amount of change.*

According to **Le Châtelier's principle,** if we introduce more of one reactant, the reaction will proceed in the direction that consumes this reactant. If we reduce the temperature, thereby removing heat from the system, the reaction will proceed in the exothermic direction, producing some heat.