SOLUTION: We first calculate the reaction quotient under these conditions. According to Equation 26.25,

$$Q_P = \frac{P^2_{SO_3}}{P^2_{SO_2}P_{O_2}} = \frac{(1.0 \times 10^{-4})^2}{(1.0 \times 10^{-3})^2(0.20)} = 5.0 \times 10^{-2}$$

Note that these quantities are unitless because the pressures are taken relative to one bar. Using Equation 26.26, we have

$$\begin{aligned}\Delta_r G &= RT \ln \frac{Q_P}{K_P} \\ &= (8.314\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}})(960\ \mathrm{K}) \ln \frac{5.0 \times 10^{-2}}{10} \\ &\doteq -42.3\ \mathrm{kJ \cdot mol^{-1}}\end{aligned}$$

The fact that $\Delta_r G < 0$ implies that the reaction will proceed from left to right as written. This may also be seen from the fact that $Q_P < K_P$.

26–6. The Sign of $\Delta_r G$ And Not That of $\Delta_r G^\circ$ Determines the Direction of Reaction Spontaneity

It is important to appreciate the difference between $\Delta_r G$ and $\Delta_r G^\circ$. The superscript $^\circ$ on $\Delta_r G^\circ$ emphasizes that this is the value of $\Delta_r G$ when all the reactants and products are unmixed at partial pressures equal to one bar; $\Delta_r G^\circ$ is the *standard* Gibbs energy change. If $\Delta_r G^\circ < 0$, then $K_P > 1$, meaning that the reaction will proceed from reactants to products if all the species are mixed at one bar partial pressures. If $\Delta_r G^\circ > 0$, then $K_P < 1$, meaning that the reaction will proceed from products to reactants if all the species are mixed at one bar partial pressures. The fact that $\Delta_r G^\circ > 0$ does *not* mean that the reaction will not proceed from reactants to products if the species are mixed under all conditions. For example, consider the reaction described by

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

for which $\Delta_r G^\circ = 4.729\ \mathrm{kJ \cdot mol^{-1}}$ at 298.15 K. The corresponding value of $K_P(T)$ is 0.148. The fact that $\Delta_r G^\circ = +4.729\ \mathrm{kJ \cdot mol^{-1}}$ does *not* mean that no $N_2O_4(g)$ will dissociate when we place some of it in a reaction vessel at 298.15 K. The value of $\Delta_r G$ for the dissociation of $N_2O_4(g)$ is given by

$$\begin{aligned}\Delta_r G &= \Delta_r G^\circ + RT \ln Q_P \\ &= 4.729\ \mathrm{kJ \cdot mol^{-1}} + (2.479\ \mathrm{kJ \cdot mol^{-1}}) \ln \frac{P^2_{NO_2}}{P_{N_2O_4}}\end{aligned} \tag{26.27}$$

Let's say that we fill a container with $N_2O_4(g)$ and no $NO_2(g)$. Initially then, the logarithm term and $\Delta_r G$ in Equation 26.27 will be essentially negative infinity. Therefore, the dissociation of $N_2O_4(g)$ takes place spontaneously. The partial pressure of $N_2O_4(g)$ decreases and that of $NO_2(g)$ increases until equilibrium is reached. The equilibrium state is determined by the condition $\Delta_r G = 0$, at which point $Q_P = K_P$. Thus, initially $\Delta_r G$ has a large negative value and increases to zero as the reaction goes to equilibrium.

We should point out here that even though $\Delta_r G < 0$, the reaction may not occur at a detectable rate. For example, consider the reaction given by

$$2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(l)$$

The value of $\Delta_r G^\circ$ at 25°C for this reaction is −237 kJ per mole of $H_2O(l)$ formed. Consequently, $H_2O(l)$ at one bar and 25°C is much more stable than a mixture of $H_2(g)$ and $O_2(g)$ under those conditions. Yet, a mixture of $H_2(g)$ and $O_2(g)$ can be kept indefinitely. If a spark or a catalyst is introduced into this mixture, however, then the reaction occurs explosively. This observation serves to illustrate an important point: The "no" of thermodynamics is emphatic. If thermodynamics says that a certain process will not occur spontaneously, then it will not occur. The "yes" of thermodynamics, on the other hand, is actually a "maybe". The fact that a process will occur spontaneously does not imply that it will necessarily occur at a detectable rate. We shall study the rates of chemical reactions in Chapters 28 through 31.

26–7. The Variation of an Equilibrium Constant with Temperature Is Given by the Van't Hoff Equation

We can use the Gibbs-Helmoltz equation (Equation 22.61)

$$\left(\frac{\partial \Delta G^\circ/T}{\partial T}\right)_P = -\frac{\Delta H^\circ}{T^2} \tag{26.28}$$

to derive an equation for the temperature dependence of $K_P(T)$. Substitute $\Delta G^\circ(T) = -RT \ln K_P(T)$ into Equation 26.28 to obtain

$$\left(\frac{\partial \ln K_P(T)}{\partial T}\right)_P = \frac{d \ln K_P(T)}{dT} = \frac{\Delta_r H^\circ}{RT^2} \tag{26.29}$$

Note that if $\Delta_r H^\circ > 0$ (endothermic reaction), then $K_P(T)$ increases with temperature, and if $\Delta_r H^\circ < 0$ (exothermic reaction), then $K_P(T)$ decreases with increasing temperature. This is another example of Le Châtelier's principle.

Equation 26.29 can be integrated to give

$$\ln \frac{K_P(T_2)}{K_P(T_1)} = \int_{T_1}^{T_2} \frac{\Delta_r H^\circ(T)dT}{RT^2} \tag{26.30}$$

If the temperature range is small enough that we can consider $\Delta_r H^\circ$ to be a constant, then we can write

$$\ln \frac{K_P(T_2)}{K_P(T_1)} = -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{26.31}$$

Equation 26.31 suggests that a plot of $\ln K_P(T)$ versus $1/T$ should be a straight line with a slope of $-\Delta_r H^\circ/R$ over a sufficiently small temperature range. Figure 26.3 shows such a plot for the reaction $H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)$ over the temperature range 600°C to 900°C.

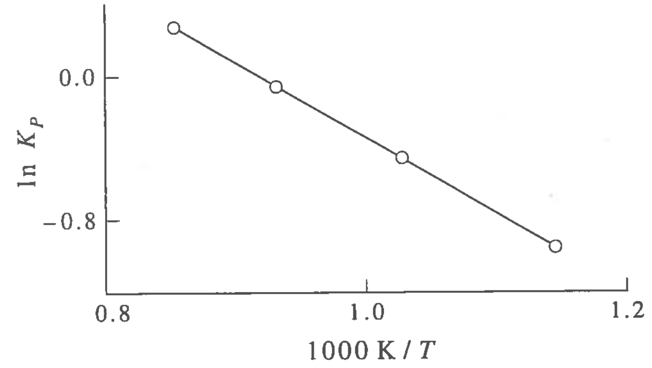

FIGURE 26.3
A plot of $\ln K_P(T)$ versus $1/T$ for the reaction $H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)$ over the temperature range 600°C to 900°C. The circles represent experimental data

EXAMPLE 26–6

Given that $\Delta_r H^\circ$ has an average value of $-69.8\ \mathrm{kJ\cdot mol^{-1}}$ over the temperature range 500 K to 700 K for the reaction described by

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

estimate K_P at 700 K given that $K_P = 0.0408$ at 500 K.

SOLUTION: We use Equation 26.31 with the above values

$$\ln \frac{K_P}{0.0408} = -\frac{-69.8 \times 10^3\ \mathrm{J\cdot mol^{-1}}}{8.3145\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}}\left(\frac{1}{700\ \mathrm{K}} - \frac{1}{500\ \mathrm{K}}\right)$$
$$= -4.80$$

or

$$K_P(T) = (0.0408)e^{-4.80} = 3.36 \times 10^{-4}$$

Note that the reaction is exothermic and so $K_P(T = 700\ \mathrm{K})$ is less than $K_P(T = 500\ \mathrm{K})$.

In Section 19–12 we discussed the temperature variation of $\Delta_r H^\circ$. In particular, we derived the equation

$$\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \int_{T_1}^{T_2} \Delta C_P^\circ(T) dT \tag{26.32}$$

where ΔC_P° is the difference between the heat capacities of the products and reactants. Experimental heat capacity data over temperature ranges are often presented as polynomials in the temperature, and if this is the case, then $\Delta_r H^\circ(T)$ can be expressed in the form (see Example 19–13)

$$\Delta_r H^\circ(T) = \alpha + \beta T + \gamma T^2 + \delta T^3 + \cdots \tag{26.33}$$

If this form for $\Delta_r H^\circ(T)$ is substituted into Equation 26.29, and both sides integrated indefinitely, then we find that

$$\ln K_P(T) = -\frac{\alpha}{RT} + \frac{\beta}{R}\ln T + \frac{\gamma}{R}T + \frac{\delta T^2}{2R} + A \tag{26.34}$$

The constants α through δ are known from Equation 26.33 and A is an integration constant that can be evaluated from a knowledge of $K_P(T)$ at some particular temperature. We could also have integrated Equation 26.29 from some temperature T_1 at which the value of $K_P(T)$ is known to an arbitrary temperature T to obtain

$$\ln K_P(T) = \ln K_P(T_1) + \int_{T_1}^{T} \frac{\Delta_r H^\circ(T')dT'}{RT'^2} \tag{26.35}$$

Equations 26.34 and 26.35 are generalizations of Equation 26.31 to the case where the temperature dependence of $\Delta_r H^\circ$ is not ignored. Equation 26.34 shows that if $\ln K_P(T)$ is plotted against $1/T$, then the slope is not constant, but has a slight curvature. Figure 26.4 shows $\ln K_P(T)$ plotted versus $1/T$ for the ammonia synthesis reaction. Note that $\ln K_P(T)$ does not vary linearly with $1/T$, showing that $\Delta_r H^\circ$ is temperature dependent.

EXAMPLE 26–7

Consider the reaction described by

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

The molar heat capacities of $N_2(g)$, $H_2(g)$, and $NH_3(g)$ can be expressed in the form

$$C_P^\circ[N_2(g)]/J\cdot K^{-1}\cdot mol^{-1} = 24.98 + 5.912 \times 10^{-3}T - 0.3376 \times 10^{-6}T^2$$

$$C_P^\circ[H_2(g)]/J\cdot K^{-1}\cdot mol^{-1} = 29.07 - 0.8368 \times 10^{-3}T + 2.012 \times 10^{-6}T^2$$

$$C_P^\circ[NH_3(g)]/J\cdot K^{-1}\cdot mol^{-1} = 25.93 + 32.58 \times 10^{-3}T - 3.046 \times 10^{-6}T^2$$

over the temperature range 300 K to 1500 K. Given that $\Delta_f H^\circ[\mathrm{NH_3(g)}] = -46.11\ \mathrm{kJ\cdot mol^{-1}}$ at 300 K and that $K_P = 6.55 \times 10^{-3}$ at 725 K, derive a general expression for the variation of $K_P(T)$ with temperature in the form of Equation 26.34.

SOLUTION: We first use Equation 26.32

$$\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \int_{T_1}^{T_2} \Delta C_P^\circ(T)dT$$

with $T_1 = 300$ K and $\Delta_r H^\circ(T_1 = 300\ \mathrm{K}) = -46.11\ \mathrm{kJ\cdot mol^{-1}}$ and

$$\Delta C_P^\circ = C_P^\circ[\mathrm{NH_3(g)}] - \frac{1}{2}C_P^\circ[\mathrm{N_2(g)}] - \frac{3}{2}C_P^\circ[\mathrm{H_2(g)}]$$

Integration gives

$$\begin{aligned}\Delta_r H^\circ(T)/\mathrm{J\cdot mol^{-1}} &= -46.11 \times 10^3 + \int_{300\ \mathrm{K}}^{T} \Delta C_P^\circ(T)dT \\ &= -46.11 \times 10^3 - 31.17(T - 300) \\ &\quad + \frac{30.88 \times 10^{-3}}{2}(T^2 - (300)^2) - \frac{5.895 \times 10^{-6}}{3}(T^3 - (300)^3)\end{aligned}$$

or

$$\Delta_r H^\circ(T)/\mathrm{J\cdot mol^{-1}} = -38.10 \times 10^3 - 31.17T + 15.44 \times 10^{-3}T^2 - 1.965 \times 10^{-6}T^3$$

Now we use Equation 26.35 with $T_1 = 725$ K and $K_P(T = 725\ \mathrm{K}) = 6.55 \times 10^{-3}$.

$$\begin{aligned}\ln K_P(T) &= \ln K_P(T = 725\ \mathrm{K}) + \int_{725}^{T} \frac{\Delta_r H^\circ(T')}{RT'^2}dT' \\ &= -5.028 + \frac{1}{R}\left[+38.10\left(\frac{1}{T} - \frac{1}{725}\right) - 31.17(\ln T - \ln 725)\right. \\ &\quad \left. + 15.44 \times 10^{-3}(T - 725) - \frac{1.965 \times 10^{-6}}{2}(T^2 - (725)^2)\right] \\ &= 12.06 + \frac{4583}{T} - 3.749 \ln T + 1.857 \times 10^{-3}T - 0.118 \times 10^{-6}T^2\end{aligned}$$

This equation was used to generate Figure 26.4. At 600 K, $\ln K_P = -3.21$, or $K_P = 0.040$, in excellent agreement with the experimental value of 0.041.

It is interesting to compare the results of this section to those of Section 23–4, where we derived the Clausius-Clapeyron equation, Equation 23.13. Note that Equations 26.31 and 23.13 are essentially the same because the vaporization of a liquid can be represented by the "chemical equation"

$$\mathrm{X(l)} \rightleftharpoons \mathrm{X(g)}$$

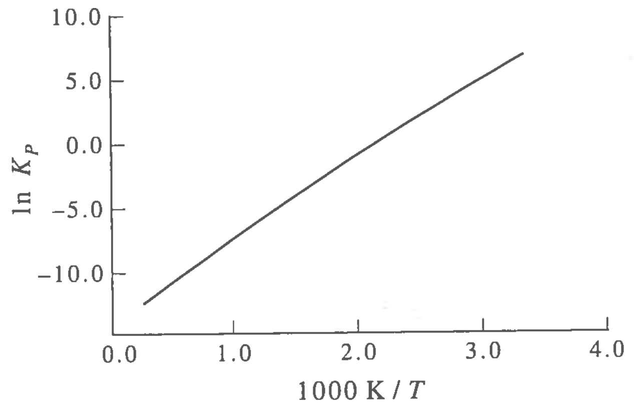

FIGURE 26.4
A plot of ln $K_p(T)$ versus $1/T$ for the ammonia synthesis reaction, $\frac{3}{2}H_2(g) + \frac{1}{2}N_2(g) \rightleftharpoons NH_3(g)$.

26–8. We Can Calculate Equilibrium Constants in Terms of Partition Functions

An important chemical application of statistical thermodynamics is the calculation of equilibrium constants in terms of molecular parameters. Consider the general homogeneous gas-phase chemical reaction

$$\nu_A A(g) + \nu_B B(g) \rightleftharpoons \nu_Y Y(g) + \nu_Z Z(g)$$

in a reaction vessel at fixed volume and temperature. In this case we have (cf. Equation 23.26)

$$dA = \mu_A dn_A + \mu_B dn_B + \mu_Y dn_Y + \mu_Z dn_Z \qquad \text{(constant } T \text{ and } V)$$

instead of Equation 26.3. Introducing the extent of reaction through Equations 26.2, however, leads to the same condition for chemical equilbrium as in Section 26–1,

$$\nu_Y \mu_Y + \nu_Z \mu_Z - \nu_A \mu_A - \nu_B \mu_B = 0 \qquad (26.36)$$

We now introduce statistical thermodynamics through the relation between the chemical potential and a partition function. In a mixture of ideal gases, the species are independent, and so the partition function of the mixture is a product of the partition functions of the individual components. Thus

$$\begin{aligned} Q(N_A, N_B, N_Y, N_Z, V, T) &= Q(N_A, V, T)Q(N_B, V, T)Q(N_Y, V, T)Q(N_Z, V, T) \\ &= \frac{q_A(V, T)^{N_A}}{N_A!}\frac{q_B(V, T)^{N_B}}{N_B!}\frac{q_Y(V, T)^{N_Y}}{N_Y!}\frac{q_Z(V, T)^{N_Z}}{N_Z!} \end{aligned}$$

The chemical potential of each species is given by an equation such as (Problem 26–33)

$$\mu_A = -RT\left(\frac{\partial \ln Q}{\partial N_A}\right)_{N_j,V,T} = -RT\ln\frac{q_A(V,T)}{N_A} \tag{26.37}$$

where Stirling's approximation has been used for $N_A!$. The N_j subscript on the partial derivative indicates that the numbers of particles of the other species are held fixed. Equation 26.37 simply says that the chemical potential of one species of an ideal gas mixture is calculated as if the other species were not present. This, of course, is the case for an ideal gas mixture.

If we substitute Equation 26.37 into Equation 26.36, then we get

$$\frac{N_Y^{\nu_Y}N_Z^{\nu_Z}}{N_A^{\nu_A}N_B^{\nu_B}} = \frac{q_Y^{\nu_Y}q_Z^{\nu_Z}}{q_A^{\nu_A}q_B^{\nu_B}} \tag{26.38}$$

For an ideal gas, the molecular partition function is of the form $f(T)V$ (Section 18–6) so that q/V is a function of temperature only. If we divide each factor on both sides of Equation 26.38 by V^{ν_j} and denote the number density N_j/V by ρ_j, then we have

$$K_c(T) = \frac{\rho_Y^{\nu_Y}\rho_Z^{\nu_Z}}{\rho_A^{\nu_A}\rho_B^{\nu_B}} = \frac{(q_Y/V)^{\nu_Y}(q_Z/V)^{\nu_Z}}{(q_A/V)^{\nu_A}(q_B/V)^{\nu_B}} \tag{26.39}$$

Note that K_c is a function of temperature only. Recall that $K_P(T)$ and $K_c(T)$ are related by (Equation 26.17)

$$K_P(T) = \frac{P_Y^{\nu_Y}P_Z^{\nu_Z}}{P_A^{\nu_A}P_B^{\nu_B}} = K_c(T)\left(\frac{c^\circ RT}{P^\circ}\right)^{\nu_Y+\nu_Z-\nu_A-\nu_B}$$

By means of Equation 26.17 and Equation 26.39, along with the results of Chapter 18, we can calculate equilibrium constants in terms of molecular parameters. This is best illustrated by means of examples.

A. A Chemical Reaction Involving Diatomic Molecules

We shall calculate the equilibrium constant for the reaction

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

from 500 K to 1000 K. The equilibrium constant is given by

$$K(T) = \frac{(q_{HI}/V)^2}{(q_{H_2}/V)(q_{I_2}/V)} = \frac{q_{HI}^2}{q_{H_2}q_{I_2}} \tag{26.40}$$

Using Equation 18.39 for the molecular partition functions gives

$$K(T) = \left(\frac{m_{\mathrm{HI}}^2}{m_{\mathrm{H}_2} m_{\mathrm{I}_2}}\right)^{3/2} \left(\frac{4\Theta_{\mathrm{rot}}^{\mathrm{H}_2}\Theta_{\mathrm{rot}}^{\mathrm{I}_2}}{(\Theta_{\mathrm{rot}}^{\mathrm{HI}})^2}\right) \frac{(1-e^{-\Theta_{\mathrm{vib}}^{\mathrm{H}_2}/T})(1-e^{-\Theta_{\mathrm{vib}}^{\mathrm{I}_2}/T})}{(1-e^{-\Theta_{\mathrm{vib}}^{\mathrm{HI}}/T})^2} \times \exp\frac{2D_0^{\mathrm{HI}} - D_0^{\mathrm{H}_2} - D_0^{\mathrm{I}_2}}{RT} \qquad (26.41)$$

where we have replaced D_e in Equation 18.39 by $D_0 + h\nu/2$ (Figure 18.2). All the necessary parameters are given in Table 18.2. Table 26.2 gives the numerical values of $K_p(T)$ and Figure 26.5 shows $\ln K$ plotted versus $1/T$. From the slope of the line in Figure 26.5 we get $\Delta_r \overline{H} = -12.9\ \mathrm{kJ\cdot mol^{-1}}$ compared to the experimental value of $-13.4\ \mathrm{kJ\cdot mol^{-1}}$. The discrepancy is due to the inadequacy of the rigid rotator-harmonic oscillator approximation at these temperatures.

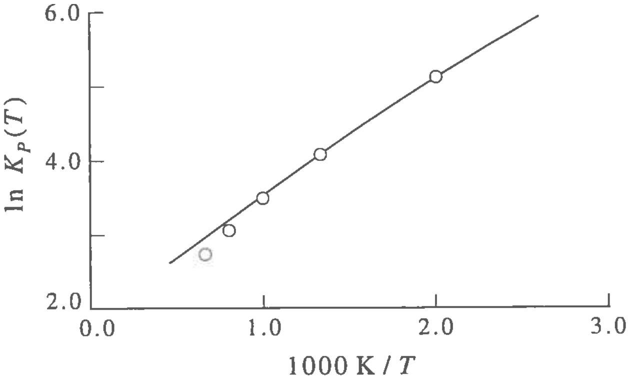

FIGURE 26.5
The logarithm of the equilibrium constant versus $1/T$ for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$. The line is calculated from Equation 26.41 and the circles are the experimental values.

TABLE 26.2
The values of $K_p(T)$ for the reaction described by $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$ calculated according to Equation 26.41.

T/K	$K_p(T)$	$\ln K_p(T)$
500	138	4.92
750	51.1	3.93
1000	28.5	3.35
1250	19.1	2.95
1500	14.2	2.65