

## 18.10: Free Energy and Equilibrium Relating $\Delta G_{\text{rxn}}^{\circ}$ to the Equilibrium Constant ( $K$ )

We have seen that  $\Delta G_{\text{rxn}}^{\circ}$  determines the spontaneity of a reaction when the reactants and products are in their standard states. In [Chapter 15](#), we learned that the equilibrium constant ( $K$ ) determines how far a reaction goes toward products, a measure of spontaneity. Therefore, as you might expect, the standard free energy change of a reaction and the equilibrium constant are related—the equilibrium constant becomes larger as the standard free energy change becomes more negative. In other words, if, on one hand, the reactants in a particular reaction undergo a large *negative* free energy change as they become products, then the reaction has a large equilibrium constant, with products strongly favored at equilibrium. If, on the other hand, the reactants in a particular reaction undergo a large *positive* free energy change as they become products, then the reaction has a small equilibrium constant, with reactants strongly favored at equilibrium.

We can derive a relationship between  $\Delta G_{\text{rxn}}^{\circ}$  and  $K$  from [Equation 18.13](#). We know that at equilibrium  $Q = K$  and  $\Delta G_{\text{rxn}} = 0$ . Making these substitutions:

$$\begin{aligned}\Delta G_{\text{rxn}} &= \Delta G_{\text{rxn}}^{\circ} + RT \ln Q \\ 0 &= \Delta G_{\text{rxn}}^{\circ} + RT \ln K\end{aligned}$$

[18.14]

$$\Delta G_{\text{rxn}}^{\circ} = -RT \ln K$$

In [Equation 18.14](#) as in all thermodynamic equations, we use  $K_p$  for reactions involving gases, and we use  $K_c$  for reactions involving substances dissolved in solution.

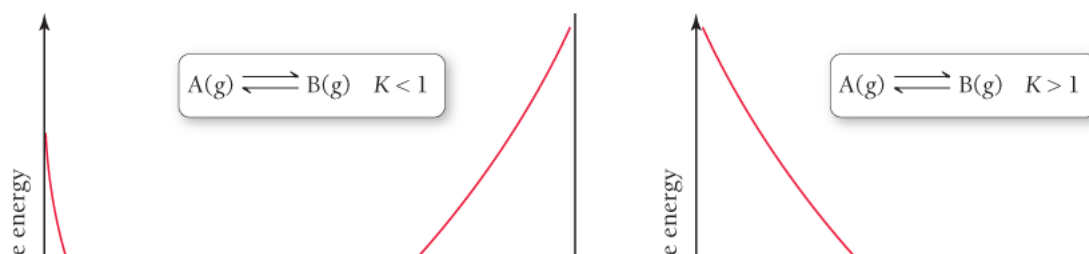
We can better understand the relationship between  $\Delta G_{\text{rxn}}^{\circ}$  and  $K$  by considering the following ranges of values for  $K$ , as summarized in [Figure 18.11](#):

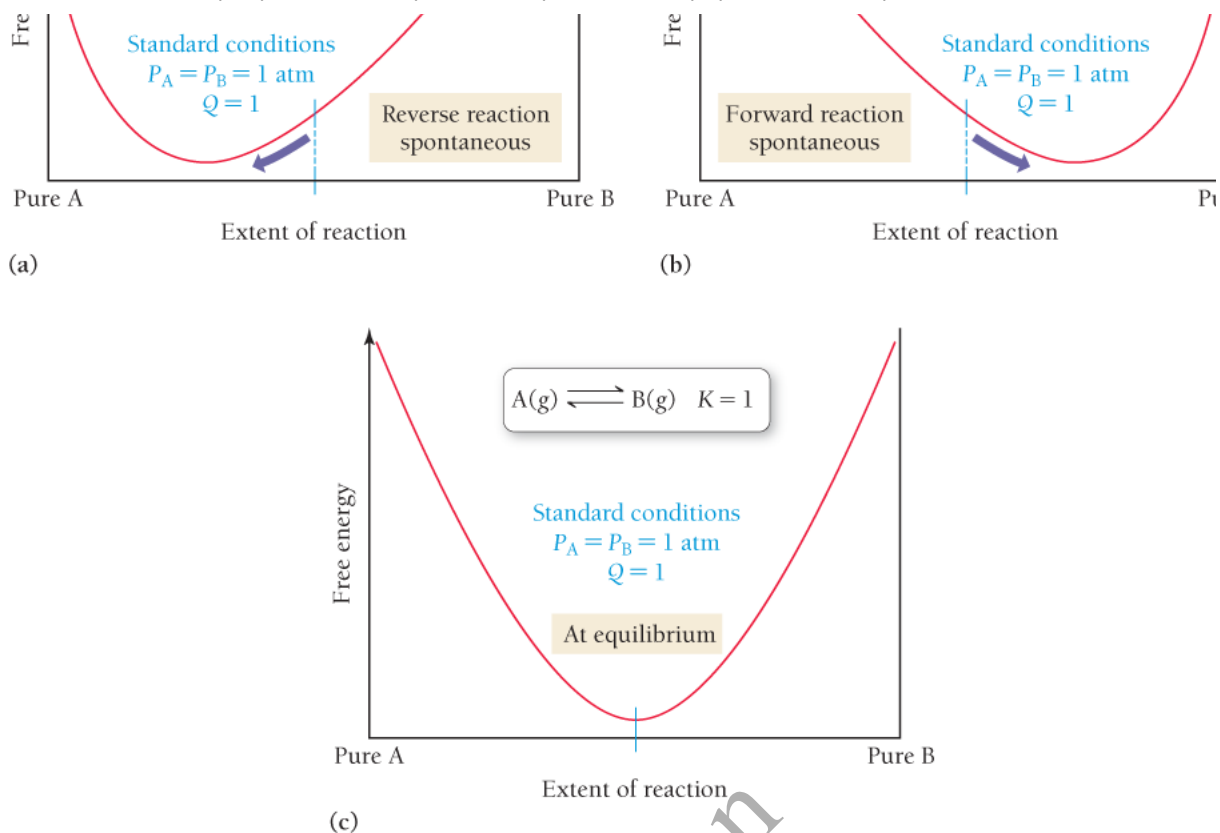
- When  $K < 1$ ,  $\ln K$  is negative and  $\Delta G_{\text{rxn}}^{\circ}$  is positive. Under standard conditions (when  $Q = 1$ ), the reaction is spontaneous in the reverse direction.
- When  $K > 1$ ,  $\ln K$  is positive and  $\Delta G_{\text{rxn}}^{\circ}$  is negative. Under standard conditions (when  $Q = 1$ ), the reaction is spontaneous in the forward direction.
- When  $K = 1$ ,  $\ln K$  is zero and  $\Delta G_{\text{rxn}}^{\circ}$  is zero. The reaction happens to be at equilibrium under standard conditions.

**Figure 18.11 Free Energy and the Equilibrium Constant**

(a) Free energy curve for a reaction with a small equilibrium constant. (b) Free energy curve for a reaction with a large equilibrium constant. (c) Free energy curve for a reaction in which  $K = 1$ .

### Free Energy and the Equilibrium Constant

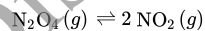




The relationship between  $\Delta G_{\text{rxn}}^\circ$  and  $K$  is logarithmic—small changes in  $\Delta G_{\text{rxn}}^\circ$  have a large effect on  $K$ .

### Example 18.11 The Equilibrium Constant and $\Delta G_{\text{rxn}}^\circ$

Use tabulated free energies of formation to calculate the equilibrium constant for the reaction at 298 K.



**SOLUTION** Look up (in [Appendix IIB](#)) the standard free energies of formation for each reactant and product.

Calculate  $\Delta G_{\text{rxn}}^\circ$  by substituting into [Equation 18.13](#).

Reactant or product	$\Delta G_f^\circ$ (in kJ/mol)
$\text{N}_2\text{O}_4(g)$	99.8
$\text{NO}_2(g)$	51.3

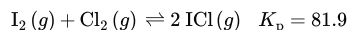
$$\begin{aligned}
 \Delta G_{\text{rxn}}^\circ &= \sum n_p \Delta G_f^\circ (\text{products}) - \sum n_r \Delta G_f^\circ (\text{reactants}) \\
 &= 2[\Delta G_f^\circ, \text{NO}_2(g)] - \Delta G_f^\circ, \text{N}_2\text{O}_4(g) \\
 &= 2(51.3 \text{ kJ}) - 99.8 \text{ kJ} \\
 &= 2.8 \text{ kJ}
 \end{aligned}$$

Calculate  $K$  from  $\Delta G_{\text{rxn}}^\circ$  by solving [Equation 18.14](#) for  $K$  and substituting the values of  $\Delta G_{\text{rxn}}^\circ$  and temperature.

$$\Delta G_{\text{rxn}}^\circ = -RT \ln K$$

$$\begin{aligned}
 \ln K &= \frac{\Delta G_{\text{rxn}}^{\circ}}{RT} \\
 &= \frac{-2.8 \times 10^3 \text{ J/mol}}{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} (298 \text{ K})} \\
 &= -1.13 \\
 K &= e^{-1.13} \\
 &= 0.32
 \end{aligned}$$

**FOR PRACTICE 18.11** Calculate  $\Delta G_{\text{rxn}}^{\circ}$  at 298 K for the reaction:



**Interactive Worked Example 18.11 The Equilibrium Constant and  $\Delta G_{\text{rxn}}^{\circ}$**

**Conceptual Connection 18.6  $K$  and  $\Delta G_{\text{rxn}}^{\circ}$**

**Conceptual Connection 18.7 The Conditions of Spontaneity**

## The Temperature Dependence of the Equilibrium Constant

We now have an equation that relates the standard free energy change for a reaction ( $\Delta G_{\text{rxn}}^{\circ}$ ) to the equilibrium constant for a reaction ( $K$ ):

[18.15]

$$\Delta G_{\text{rxn}}^{\circ} = -RT \ln K$$

We also have an equation for how the free energy change for a reaction ( $\Delta G_{\text{rxn}}^{\circ}$ ) depends on temperature ( $T$ ):

[18.16]

$$\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ}$$

We can combine these two equations to obtain an equation that indicates how the equilibrium constant depends on temperature. Combining [Equations 18.15](#) and [18.16](#), we get:

[18.17]

$$-RT \ln K = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ}$$

We can then divide both sides of [Equation 18.17](#) by the quantity  $RT$ :

$$-\ln K = \frac{\Delta H_{\text{rxn}}^{\circ}}{RT} - \frac{\cancel{T} \Delta S_{\text{rxn}}^{\circ}}{R \cancel{T}}$$

Canceling and rearranging, we get this important result:

[18.18]

$$\ln K = \frac{\Delta H_{\text{rxn}}^{\circ}}{R} \left( \frac{1}{T} \right) + \frac{\Delta S_{\text{rxn}}^{\circ}}{R}$$

$$y = mx + b$$

Equation 18.18 is in the form of a straight line. A plot of the natural log of the equilibrium constant ( $\ln K$ ) versus the inverse of the temperature in kelvins ( $1/T$ ) yields a straight line with a slope of  $-\Delta H_{\text{rxn}}^{\circ}/R$  and a  $y$ -intercept of  $-\Delta S_{\text{rxn}}^{\circ}/R$ . Such a plot is useful for obtaining thermodynamic data (namely,  $(\Delta H_{\text{rxn}}^{\circ})$  and  $\Delta S_{\text{rxn}}^{\circ}$ ) from measurements of  $K$  as a function of temperature. However, since  $\Delta H_{\text{rxn}}^{\circ}$  and  $\Delta S_{\text{rxn}}^{\circ}$  can themselves be slightly temperature dependent, this analysis works only over a relatively limited temperature range. We can also express the equation in a two-point form:

[18.19]

$$\ln \frac{K_2}{K_1} = \frac{\Delta H_{\text{rxn}}^{\circ}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

We can use this equation to find  $\Delta H_{\text{rxn}}^{\circ}$  from a measurement of the equilibrium constant at two different temperatures or to find the equilibrium constant at some other temperature if we know the equilibrium constant at a given temperature and  $\Delta H_{\text{rxn}}^{\circ}$ .

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