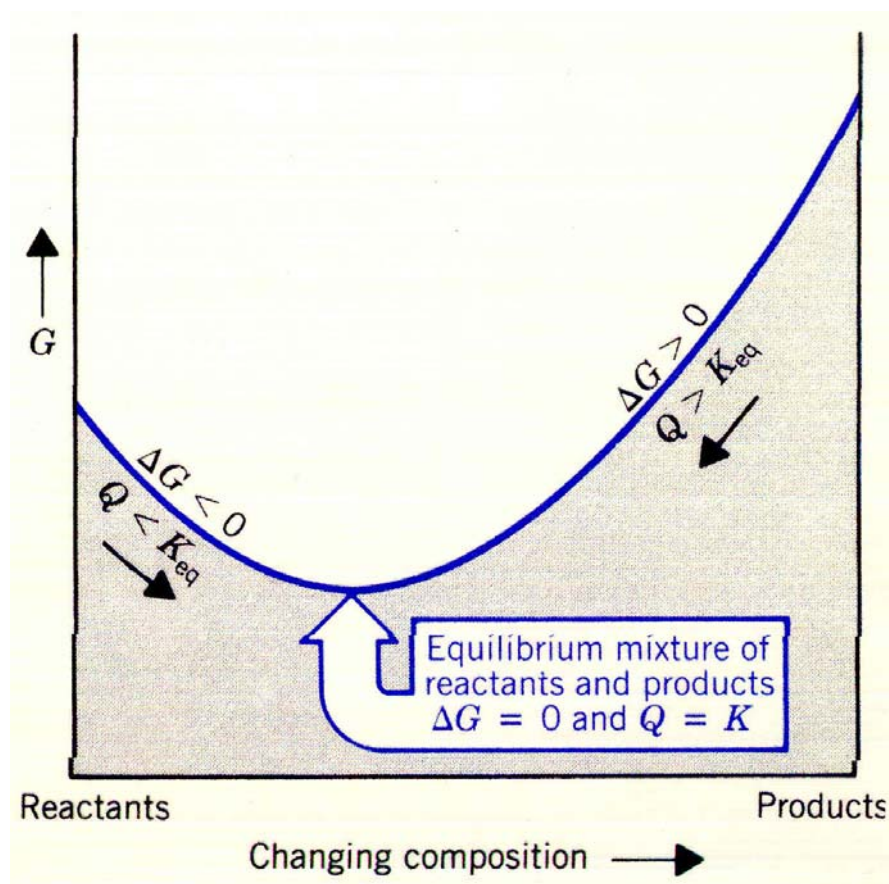


Topic 5I - Equilibrium Calculations



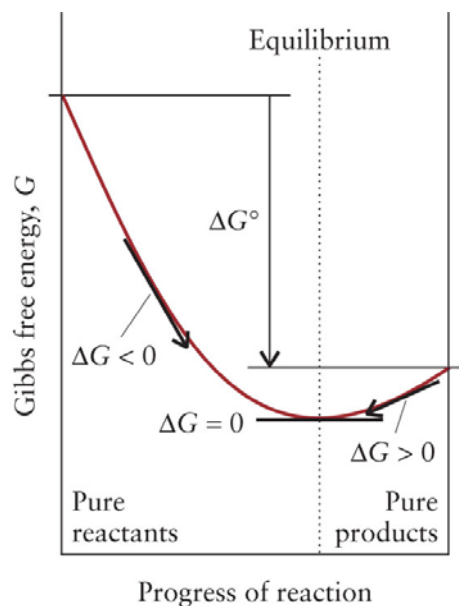


FIGURE 11.4 The variation of Gibbs free energy of a reaction mixture with composition. A reaction mixture has a spontaneous tendency to change in the direction of decreasing Gibbs free energy. Note that ΔG is the slope of the line at each composition, whereas ΔG° is the difference between the standard Gibbs free energies of the pure reactants and those of the pure products.

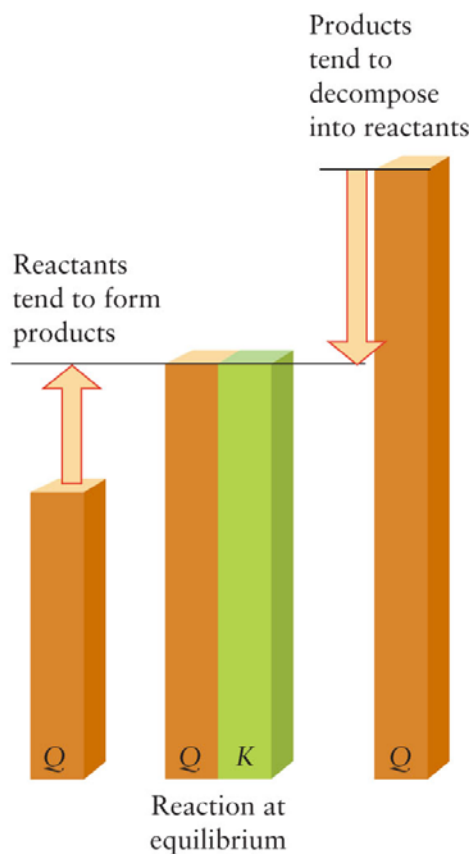


FIGURE 11.6 The relative sizes of the reaction quotient Q and the equilibrium constant K indicate the direction in which a reaction mixture tends to change. The arrows show that when $Q < K$, reactants form products (left), and when $Q > K$, products form reactants (right). There is no tendency to change once the reaction quotient has become equal to the equilibrium constant.

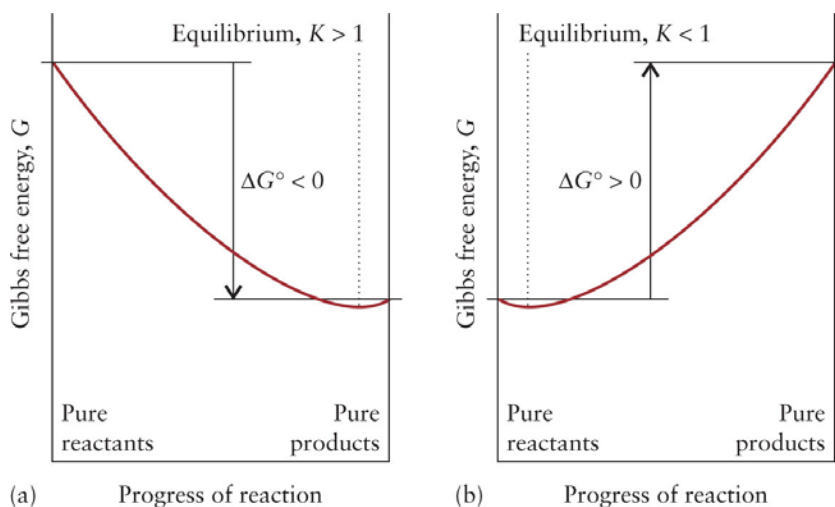
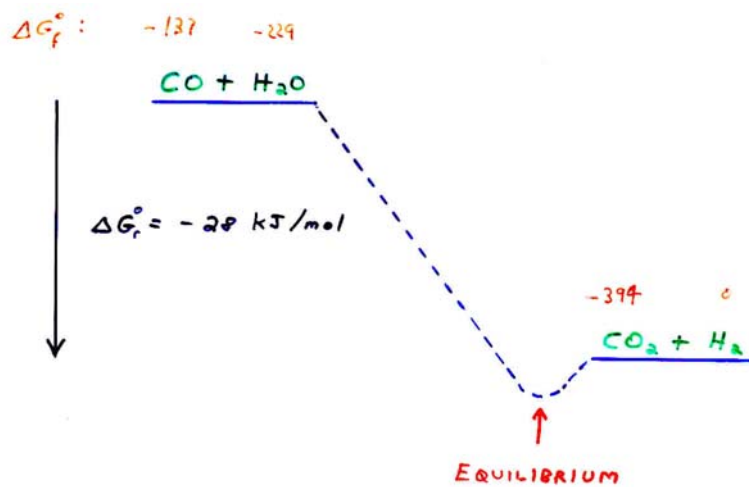


FIGURE 11.7 (a) A reaction that has the potential to go to completion ($K > 1$) is one in which the minimum of the free-energy curve (the position of equilibrium) lies close to pure products. (b) A reaction that has little tendency to form products ($K < 1$) is one in which the minimum of the free-energy curve lies close to pure reactants.



$$K_{eq} = \frac{P_{\text{CO}_2}^{eq} \times P_{\text{H}_2}^{eq}}{P_{\text{CO}}^{eq} \times P_{\text{H}_2\text{O}}^{eq}}$$

$$\Delta G^\circ = -RT \ln(K_{eq})$$

$$\begin{aligned}
 K_{eq} &= e^{-\Delta G^\circ/RT} \\
 &= e^{-(-28,000)/(8.315 \times 298)} \\
 &= 2.1 \times 10^4
 \end{aligned}$$

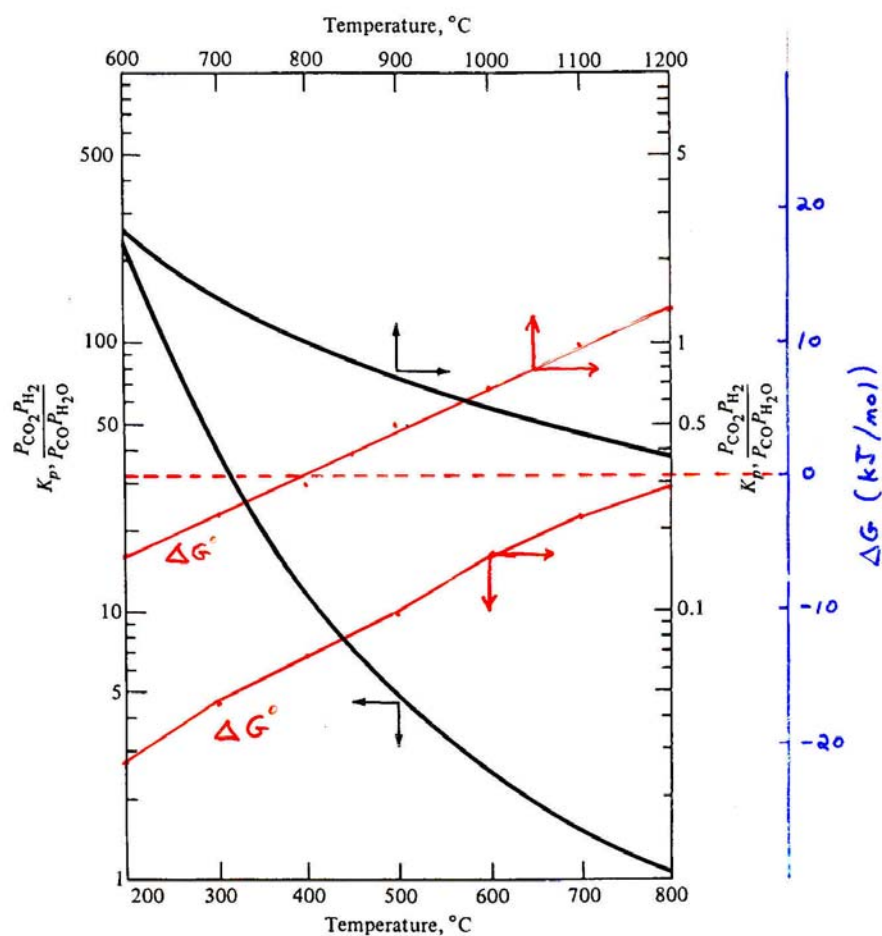


Figure 10.3 Water-gas shift equilibrium. K_p as a function of temperature.

Example of Equilibrium Table Use

For the reaction:



for which

$$K_p = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2} = 6.96 \text{ atm}^{-1} \quad (\text{at } 298\text{K})$$

For $P_{\text{initial}} (\text{NO}_2) = 3 \text{ atm}$,

	$\text{NO}_2 \text{ (atm)}$	$\text{N}_2\text{O}_4 \text{ (atm)}$
Initial	3	0
Change	-x	+0.5 x
Equilibrium	3 - x	0.5 x

$$K_p = \frac{0.5 x}{(3 - x)^2} = 6.96 \text{ atm}^{-1}$$

$$6.96 x^2 - 42.26 x + 62.64 = 0$$

Solving for x, using the quadratic formula, gives

$$x = 3.50, \underline{2.57}$$

Because the $x = 3.50$ root is physically impossible, we choose $x = 2.57$.

Thus,

$$P^{\text{eq}} (\text{NO}_2) = 3 - 2.57 = \underline{0.43 \text{ atm}}$$

$$P^{\text{eq}} (\text{N}_2\text{O}_4) = 0.5 \times 2.57 = \underline{1.285 \text{ atm}}$$



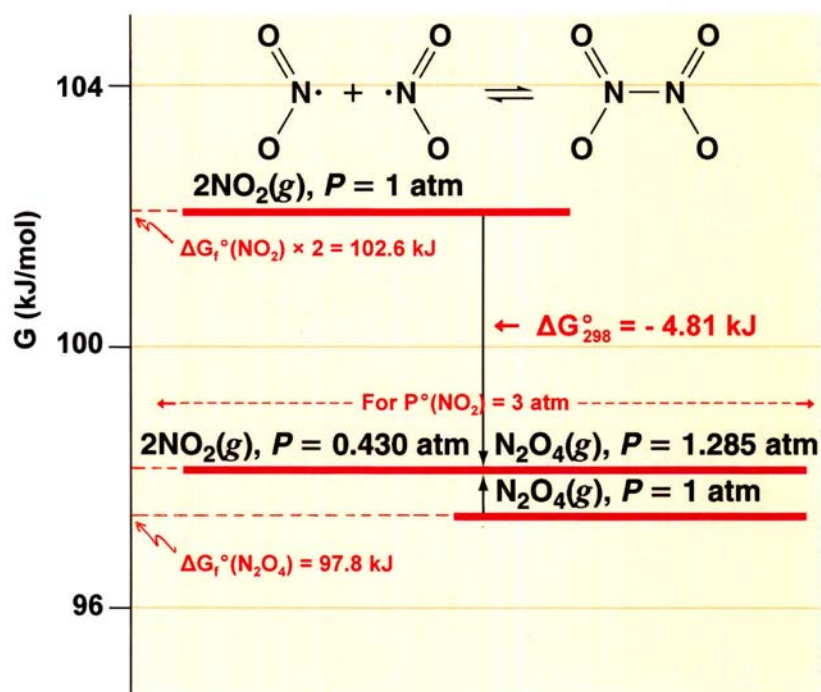
$$\Delta H_{298}^{\circ} = -57.2 \text{ kJ}$$

$$\Delta S_{298}^{\circ} = -175.8 \text{ J/K}$$

$$\Delta G_{298}^{\circ} = -RT \ln K_{298} = -4.81 \text{ kJ}$$

$$K_{298} = \frac{(P_{\text{N}_2\text{O}_4})}{(P_{\text{NO}_2})^2} = \exp\left(-\frac{\Delta G_{298}^{\circ}}{RT}\right)$$

$$= \exp\left(-\frac{-4,810 \text{ J}}{8.314 \text{ J/K} \times 298.15 \text{ K}}\right) = 6.96$$



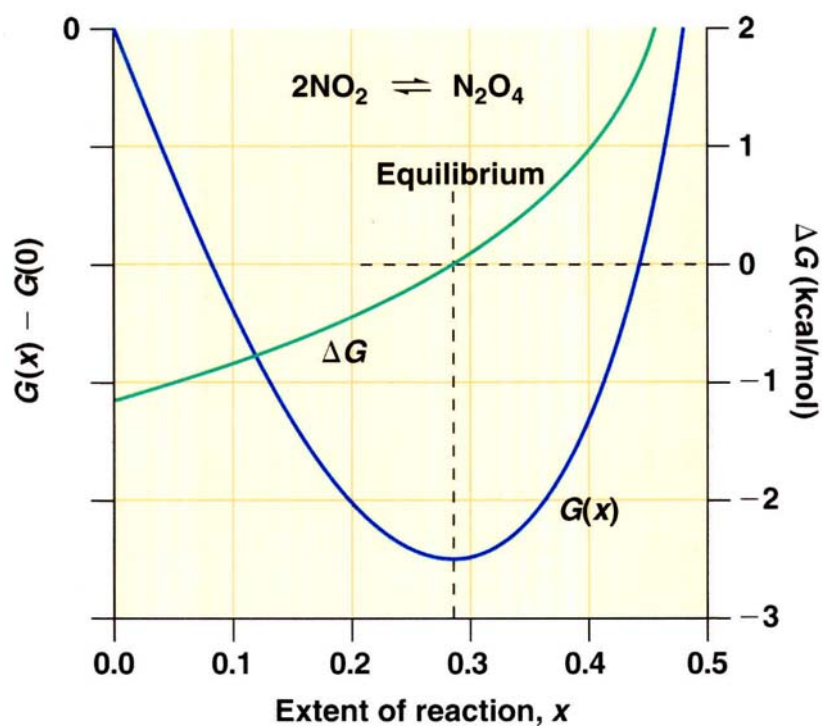


Figure 12.3

Dependence of G and ΔG on the extent of reaction variable x , starting on the left from standard conditions, and holding the temperature constant at 298 K. Where ΔG passes through zero, G passes through its minimum value; G thus acts as a chemical potential that determines the position of equilibrium and prevents the system from departing from it. The ΔG curve becomes singular (approaching $+\infty$) as $x \rightarrow 0.5$.