Fundamental Equilibrium Concepts

Section 87 – Gibbs Energy and Equilibrium

1. Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.

   (a) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$ $\quad T = 2000\,°C \quad K_P = 4.1 \times 10^{-4}$

   (b) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$ $\quad T = 400\,°C \quad K_P = 50.0$

   (c) $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$ $\quad T = 980\,°C \quad K_P = 1.67$

   (d) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$ $\quad T = 900\,°C \quad K_P = 1.04$

   (e) $HF(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + F^-(aq)$ $\quad T = 25\,°C \quad K_P = 7.2 \times 10^{-4}$

   (f) $AgBr(s) \longrightarrow Ag^+(aq) + Br^-(aq)$ $\quad T = 25\,°C \quad K_P = 3.3 \times 10^{-13}$

   Solution

   (a) $\Delta G° = -RT \ln K_P = -(8.314\ J\ K^{-1})(2273.15\ K)(\ln 4.1 \times 10^{-4}) = 147\ kJ = 1.5 \times 10^2\ kJ$

   (b) $\Delta G° = -(8.314\ J\ K^{-1})(673.15\ K)(\ln 50.0) = -21{,}893\ J = -21.9\ kJ$

   (c) $\Delta G° = -(8.314\ J\ K^{-1})(1253.15\ K)(\ln 1.67) = -5.34\ kJ$

   (d) $\Delta G° = -(8.314\ J\ K^{-1})(1173.15\ K)(\ln 1.04) = -0.383\ kJ$

   (e) $\Delta G° = -(8.314\ J\ K^{-1})(298.15\ K)(\ln 7.2 \times 10^{-4}) = 17{,}937\ J = 18\ kJ$

   (f) $\Delta G° = -(8.314\ J\ K^{-1})(298.15\ K)(\ln 3.3 \times 10^{-13}) = 71{,}240\ J = 71\ kJ$

2. Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.

(a) $Cl_2(g) + Br_2(g) \longrightarrow 2BrCl(g)$ $T = 25\ °C$ $K_P = 4.7 \times 10^{-2}$

(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $T = 500\ °C$ $K_P = 48.2$

(c) $H_2O(l) \rightleftharpoons H_2O(g)$ $T = 60\ °C$ $K_P = 0.196$

(d) $CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g)$ $T = 550\ °C$ $K_P = 4.90 \times 10^2$

(e)$CH_3NH_2(aq) + H_2O(l) \longrightarrow CH_3NH_3{}^+(aq) + OH^-(aq)$ $T = 25\ °C K_P = 4.4 \times 10^{-4}$

(f) $PbI_2(s) \longrightarrow Pb^{2+}(aq) + 2I^-(aq)$ $T = 25\ °C$ $K_P = 8.7 \times 10^{-9}$

Solution

(a) $\Delta G° = -RT\ln K_p = (8.314\ J\ K^{-1})(298.15\ K)(\ln 4.7 \times 10^{-2}) = 7579\ J = 7.6\ kJ$;

(b) $\Delta G° = -(8.314\ J\ K^{-1})(773.15\ K)(\ln 48.2) = 24{,}911\ J = 24.9\ kJ$;

(c) $\Delta G° = -(8.314\ J\ K^{-1})(333.15\ K)(\ln 0.196) = 4513.8\ J = 4.51\ kJ$;

(d) $\Delta G° = -(8.314\ J\ K^{-1})(823.15\ K)(\ln 4.90 \times 10^2) = -42{,}392\ J = -42.4\ kJ$;

(e) $\Delta G° = -(8.314\ J\ K^{-1})(298.15\ K)(\ln 4.4 \times 10^{-4}) = 19{,}158\ J = 19\ kJ$;

(f) $\Delta G° = -(8.314\ J\ K^{-1})(298.15\ K)(\ln 8.7 \times 10^{-19}) = 103{,}084\ J = 1.0 \times 10^2\ kJ$

3. Calculate the equilibrium constant at 25°C for each of the following reactions from the value of $\Delta G°$ given.

(a) $O_2(g) + 2F_2(g) \longrightarrow 2OF_2(g)$ $\Delta G° = -9.2\ kJ$

(b) $I_2(s) + Br_2(l) \longrightarrow 2IBr(g)$ $\Delta G° = 7.3\ kJ$

(c) $2LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g)$ $\Delta G° = -79\ kJ$

(d) $N_2O_3(g) \longrightarrow NO(g) + NO_2(g)$ $\Delta G° = -1.6\ kJ$

Solution

Equilibrium constants are calculated from the equation *ΔG°* = *-RT lnK*, which can be rearranged to $ln\,K = \frac{-\Delta\ °}{RT}$. Note that *K* is a function of *T* and thus changes as *T* changes.

(a) $ln\,K = -\left[\frac{-9.2\times10^{3}\ \text{J}}{(8.314\ \text{J mol}^{-1}\ \text{K}^{-1}\times 298.15\ \text{K})}\right] = 3.71$, *K* = 41;

(b) $ln\,K = \frac{-7300\ \text{J}}{(8.314\ \text{J mol}^{-1}\ \text{K}^{-1}\times 298.15\ \text{K})} = -2.945$, *K* = 0.053;

(c) $ln\,K = -\left[\frac{-79\times10^{3}\ \text{J}}{(8.314\ \text{J mol}^{-1}\ \text{K}^{-1}\times 298.15\ \text{K})}\right] = 31.870$, *K* = 6.9 × 10^{13};

(d) $ln\,K = -\left[\frac{-1.6\times10^{3}\ \text{J}}{(8.314\ \text{J mol}^{-1}\ \text{K}^{-1}\times 298.15\ \text{K})}\right] = 0.645$, *K* = 1.9;

4. What happens to ΔG_r (becomes more negative or more positive) for the following chemical reactions when the partial pressure of oxygen is increased?

(a) $S(s) + O_2(g) \longrightarrow SO_2(g)$

(b) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$

(c) $2\ HgO(s) \longrightarrow 2\ Hg(l) + O_2(g)$

Solution

(a) Increasing P_{O_2} will shift the equilibrium toward the products, which increases the value of *Q*. ΔG_r therefore becomes more negative.

(b) Increasing P_{O_2} will shift the equilibrium toward the products, which increases the value of *Q*. ΔG_r therefore becomes more negative.

(c) Increasing P_{O_2} will shift the equilibrium toward the reactants, which decreases the value of *Q*. ΔG_r therefore becomes more positive.

5. One of the important reactions in the biochemical pathway glycolysis is the reaction of glucose-6-phosphate (G6P) to form fructose-6-phosphate (F6P):

$$\text{G6P} \rightleftharpoons \text{F6P} \qquad \Delta G^{\circ} = 1.7\ \text{kJ}$$

(a) Is the reaction spontaneous or nonspontaneous under standard thermodynamic conditions?

(b) Standard thermodynamic conditions imply the concentrations of G6P and F6P to be 1 *M*, however, in a typical cell, they are not even close to these values. Calculate Δ*G* when the concentrations of G6P and F6P are 120 μ*M* and 28 μ*M* respectively, and discuss the spontaneity of the forward reaction under these conditions. Assume the temperature is 37 °C.

Solution

(a) Nonspontaneous as $\Delta G^{\circ} > 0$; (b) ΔG = ΔG° + RT ln*Q*, $\Delta G = 1.7 \times 10^3 + \left(8.314 \times 310 \times ln\ \frac{28}{120}\right) = -2.1$ kJ. The forward reaction to produce F6P is spontaneous under these conditions.