Chapter 3

(3-2) Calculate the standard enthalpy of formation ΔH_f° for $CO_2(g)$, given:

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H^\circ = -94.0 \text{ Kcal}$$

$$CO_{2(g)} + \tfrac{1}{2} O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H^\circ = -67.6 \text{ Kcal}$$

rewriting

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H = -94.0$$

$$CO_{2(g)} \rightarrow \tfrac{1}{2} O_2 + CO_{(g)} \qquad \Delta H = +67.6$$

$$C_{(s)} + \tfrac{1}{2} O_2 \rightarrow CO_{(g)} \qquad \Delta H^\circ = -26.4 \text{ Kcal/mol}$$

(3-5) Find ΔG° given:

$$CH_3COO^- + 2O_{2(aq)} \rightarrow HCO_3^- + CO_{2(aq)} + H_2O_{(\ell)}$$

$$\Delta G^\circ = \left(\sum Y_i G_{fi}^\circ\right)_{\text{products}} - \left(\sum Y_i G_{fi}^\circ\right)_{\text{reactants}}$$

	ΔG_f°
CH_3COO^-	-89.0 Kcal/mol
$O_{2(aq)}$	~~+3.39~~ + 3.93
HCO_3^-	-140.31
$CO_{2(aq)}$	-92.31
$H_2O_{(\ell)}$	-56.69

$$\Delta G^\circ = \left[(-140.3) + (-92.31) + (-56.69)\right] - \left[2(3.93) + (-89.0)\right]$$

$$\Delta G^\circ = -208.16 \text{ Kcal}$$

(3-6) Given:

$$NH_{3(aq)} + H_2O \rightleftharpoons NH_4^+ + OH^-$$

find:

(a) K at 25°C

(b) If pH = 9, $[NH_3] = 10^{-5}$ M $[NH_4^+] = 10^{-6}$ M,

Is reaction at equilibrium?

We know, at equilibrium

$$\Delta G^\circ = -RT \ln K$$

OR

$$K = \exp\left(\frac{-\Delta G}{RT}\right)$$

$$\Delta G^\circ = \left[(-19) + (-37.6)\right] - \left[(-6.37) + (-56.7)\right]$$

$$\Delta G^\circ = 6.47 \text{ Kcal/mol}$$

$$K = \exp\left(\frac{-6.47 \text{ Kcal/mol}\left(\frac{1000 \text{ cal}}{\text{Kcal}}\right)}{\left(1.987 \frac{\text{cal}}{\text{mol K}}\right)(298 \text{ K})}\right)$$

$$\underline{K = 1.8 \times 10^{-5}}$$

(b) $\Delta G = \Delta G^\circ + RT \ln Q$

$$\Delta G = 6.47 \times 10^3 \text{ cal} + \left(1.98 \frac{\text{cal}}{\text{K}}\right)(298 \text{ K}) \ln \frac{[NH_4^+][OH^-]}{[H_2O][NH_3]}$$

$[NH_4^+] = 10^{-6}$

$[NH_3] = 10^{-5}$

$[OH^-] = 10^{(14-pH)} = 10^{(14-9)} = 10^{-5}$

$$\Delta G = 6.5 \times 10^3 + 590 \ln \frac{(10^{-6})(10^{-5})}{(1)(10^{-5})}$$

$\Delta G = -1651$ Kcal $< 0 \Rightarrow$ reaction proceeds as written

reaction is <u>not</u> at equilibrium

(3-7) Given:

$H^+ + NO_3^- \rightleftharpoons HNO_3\,(aq)$ at equilibrium

what % C_{T,NO_3} is present as HNO_3 at pH = 1 ?

First, find K

$$K = \exp\left(\frac{-\Delta G^\circ}{RT}\right)$$

$$\Delta G^\circ = (-26.41) - [(-26.43) + (0)]$$

$$\Delta G^\circ = 0.02 \text{ Kcal}$$

$$K = \exp\left(-\frac{0.02 \times 10^3 \text{ cal}}{(1.98)(298)}\right) = 0.97$$

$$K = \frac{[HNO_3]}{[H^+][NO_3^-]} \quad \underline{OR} \quad \frac{[HNO_3]}{[NO_3^-]} = K[H^+]$$

$$= (0.97)(10^{-1})$$

$$= 0.097$$

$$[HNO_3] = 0.097[NO_3^-]$$

$$[NO_3^-] = \frac{[HNO_3]}{0.097}$$

$$\% \text{ as } HNO_3 = \frac{[HNO_3]}{[HNO_3] + [NO_3^-]} * (100)$$

$$= \frac{[HNO_3]}{[HNO_3] + \frac{[HNO_3]}{0.097}} * 100 = \frac{1}{1 + \frac{1}{0.097}} * 100$$

% as HNO_3 = 8.8 %