Homework Set #6

5.60

The ionic strength of the solution is

$$I = \frac{1}{2}\sum_i m_i z_i^2 = \frac{1}{2}\left[(0.0020\ m)\,(2)^2 + (0.0040\ m)\,(-1)^2\right] = 0.0060\ m$$

(a) The activity coefficients of Mg^{2+} and Cl^- can be evaluated using

$$\log \gamma_i = -0.509 z_i^2 \sqrt{I}$$

For Mg^{2+},

$$\log \gamma_+ = -0.509\,(2)^2\,\sqrt{0.0060} = -0.158$$

$$\gamma_+ = 0.695 = 0.70$$

For Cl^-,

$$\log \gamma_- = -0.509\,(-1)^2\,\sqrt{0.0060} = -3.94 \times 10^{-2}$$

$$\gamma_- = 0.913 = 0.91$$

(b) The mean ionic activity coefficient is

$$\gamma_\pm = \left(\gamma_+^{\nu_+}\gamma_-^{\nu_-}\right)^{1/\nu} = \left[(0.695)\,(0.913)^2\right]^{1/3} = 0.83$$

5.74 Calculate the solubility of $BaSO_4$ (in g L^{-1}) in **(a)** water and **(b)** a 6.5×10^{-5} *M* $MgSO_4$ solution. The solubility product of $BaSO_4$ is 1.1×10^{-10}. Assume ideal behavior.

The equation for the dissolution of $BaSO_4$ is

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

(a) If the solubility of $BaSO_4$ is x *M*, then there are x *M* of Ba^{2+} and x *M* SO_4^{2-} in the solution.

$$K_{sp} = 1.1 \times 10^{-10} = [Ba^{2+}][SO_4^{2-}] = x \cdot x$$

$$x = 1.05 \times 10^{-5}$$

Therefore,

$$\text{the solubility of } BaSO_4 = \left(1.05 \times 10^{-5}\ \text{mol L}^{-1}\right)\left(\frac{233.4\ \text{g}}{1\ \text{mol}}\right) = 2.5 \times 10^{-3}\ \text{g L}^{-1}$$

(b) The $MgSO_4$ solution contains 6.5×10^{-5} *M* of SO_4^{2-}. If the solubility of $BaSO_4$ is x *M*, then there are x *M* of Ba^{2+} and $x + 6.5 \times 10^{-5}$ *M* SO_4^{2-} in the solution.

$$K_{sp} = 1.1 \times 10^{-10} = [Ba^{2+}][SO_4^{2-}] = x\left(x + 6.5 \times 10^{-5}\right)$$

$$x^2 + 6.5 \times 10^{-5}x - 1.1 \times 10^{-10} = 0$$

$$x = 1.65 \times 10^{-6} \qquad \text{or} \qquad x = -6.67 \times 10^{-5}\ \text{(nonphysical)}$$

Therefore,

$$\text{the solubility of } BaSO_4 = \left(1.65 \times 10^{-6}\ \text{mol L}^{-1}\right)\left(\frac{233.4\ \text{g}}{1\ \text{mol}}\right) = 3.9 \times 10^{-4}\ \text{g L}^{-1}$$

5.75 The thermodynamic solubility product of AgCl is 1.6×10^{-10}. What is $[Ag^+]$ in **(a)** a 0.020 M KNO_3 solution and **(b)** a 0.020 M KCl solution?

(a) First calculate the ionic strength and the mean ionic activity coefficient of the KNO_3 solution. Since this solution is dilute, its molality has the same numerical value as its molarity. For this solution, $z_+ = 1$, $z_- = -1$, $m_+ = m_- = 0.020\ m$.

$$I = \frac{1}{2}\left[(0.020\ m)\ (1)^2 + (0.020\ m)\ (-1)^2\right] = 0.020\ m$$

$$\log \gamma_\pm = -0.509\ |(1)\ (-1)|\ \sqrt{0.020} = -7.20 \times 10^{-2}$$

$$\gamma_\pm = 0.847$$

The molalities of Ag^+ (m_+) and Cl^- (m_-) are the same. m_+ is calculated from K°_{sp} and $\gamma_\pm$:

$$\begin{aligned} K^\circ_{sp} = 1.6 \times 10^{-10} &= a_+a_- = \gamma_+m_+\gamma_-m_- \\ &= \gamma_\pm^2 m_+^2 \\ &= (0.847)^2\ m_+^2 \\ m_+ &= 1.5 \times 10^{-5} \end{aligned}$$

Since the concentration of Ag is very small, its molarity has the same numerical value as its molality. Thus, $[Ag^+] = 1.5 \times 10^{-5}\ M$.

(b) The ionic strength of the 0.020 M KCl ($\approx 0.020\ m$) solution is the same as the 0.020 M KNO_3 solution in **(a)**. However, when AgCl dissolves in this solution, the molalities of Ag^+ (m_+) and Cl^- (m_-) are no longer the same, as KCl contributes extra Cl^-. In fact, $m_- = m_+ + 0.020\ m$.

$$\begin{aligned} K^\circ_{sp} = 1.6 \times 10^{-10} &= a_+a_- = \gamma_+m_+\gamma_-m_- \\ &= \gamma_\pm^2 m_+m_- \\ &= (0.847)^2\ m_+\ (m_+ + 0.020) \\ m_+\ (m_+ + 0.020)\ &= 2.23 \times 10^{-10} \end{aligned}$$

Since m_+ is expected to be much smaller than 0.020, $m_+ + 0.020 \approx 0.020$. Therefore,

$$\begin{aligned} m_+\ (0.020)\ &= 2.23 \times 10^{-10} \\ m_+ &= 1.1 \times 10^{-8} \end{aligned}$$

Indeed, m_+ is insignificant compared with 0.020.

Since the concentration of Ag^+ is very small, its molarity has the same numerical value as its molality. Thus, $[Ag^+] = 1.1 \times 10^{-8}\ M$.

5.78 A 0.010 m aqueous solution of the ionic compound $Co(NH_3)_5Cl_3$ has a freezing-point depression of 0.0558 K. What can you conclude about its structure? Assume the compound is a strong electrolyte.

The van't Hoff factor is

$$i = \frac{\Delta T}{K_f m_2} = \frac{0.0558\ \text{K}}{(1.86\ \text{K mol}^{-1}\ \text{kg})\ (0.010\ \text{mol kg}^{-1})} = 3.0$$

There are 3 particles in the solution per 1 particle before dissociation. Thus, the compound is probably $[Co(NH_3)_5Cl]Cl_2$, which on dissolution, dissociates into $[Co(NH_3)_5Cl]^{2+}$ and $2Cl^-$.

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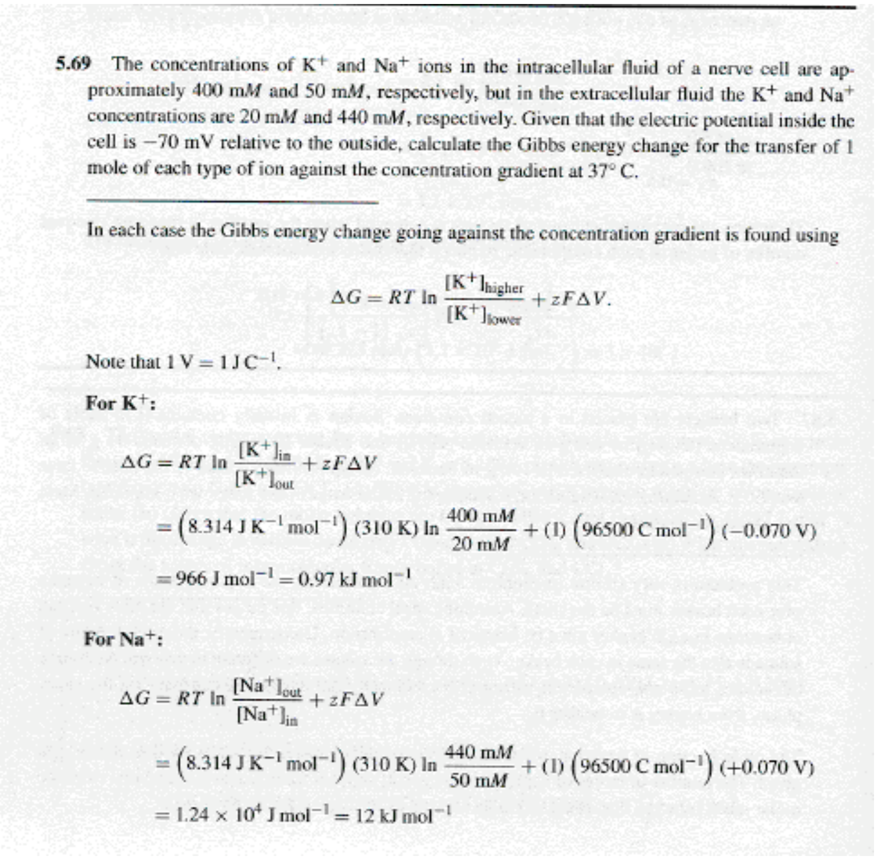

5.69 The concentrations of K^+ and Na^+ ions in the intracellular fluid of a nerve cell are approximately 400 m*M* and 50 m*M*, respectively, but in the extracellular fluid the K^+ and Na^+ concentrations are 20 m*M* and 440 m*M*, respectively. Given that the electric potential inside the cell is −70 mV relative to the outside, calculate the Gibbs energy change for the transfer of 1 mole of each type of ion against the concentration gradient at 37° C.

In each case the Gibbs energy change going against the concentration gradient is found using

$$\Delta G = RT \ln \frac{[K^+]_{\text{higher}}}{[K^+]_{\text{lower}}} + zF\Delta V.$$

Note that $1\ \text{V} = 1\ \text{J C}^{-1}$.

For K^+:

$$\begin{aligned}\Delta G &= RT \ln \frac{[K^+]_{\text{in}}}{[K^+]_{\text{out}}} + zF\Delta V \\ &= \left(8.314\ \text{J K}^{-1}\ \text{mol}^{-1}\right)(310\ \text{K}) \ln \frac{400\ \text{m}M}{20\ \text{m}M} + (1)\left(96500\ \text{C mol}^{-1}\right)(-0.070\ \text{V}) \\ &= 966\ \text{J mol}^{-1} = 0.97\ \text{kJ mol}^{-1}\end{aligned}$$

For Na^+:

$$\begin{aligned}\Delta G &= RT \ln \frac{[Na^+]_{\text{out}}}{[Na^+]_{\text{in}}} + zF\Delta V \\ &= \left(8.314\ \text{J K}^{-1}\ \text{mol}^{-1}\right)(310\ \text{K}) \ln \frac{440\ \text{m}M}{50\ \text{m}M} + (1)\left(96500\ \text{C mol}^{-1}\right)(+0.070\ \text{V}) \\ &= 1.24 \times 10^4\ \text{J mol}^{-1} = 12\ \text{kJ mol}^{-1}\end{aligned}$$