

Homework Set #7

5.60

The ionic strength of the solution is

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

(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^- ,

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

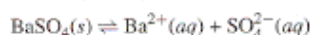
$$\gamma_- = 0.913 = 0.91$$

(b) The mean ionic activity coefficient is

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

5.74 Calculate the solubility of BaSO_4 (in g L^{-1}) in (a) water and (b) a $6.5 \times 10^{-5} \text{ M}$ 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



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

$$K_{\text{sp}} = 1.1 \times 10^{-10} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = x \cdot x$$

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

Therefore,

$$\text{the solubility of BaSO}_4 = (1.05 \times 10^{-5} \text{ mol L}^{-1}) \left(\frac{233.4 \text{ g}}{1 \text{ mol}} \right) = 2.5 \times 10^{-3} \text{ g L}^{-1}$$

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

$$K_{\text{sp}} = 1.1 \times 10^{-10} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = x (x + 6.5 \times 10^{-5})$$

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

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

Therefore,

$$\text{the solubility of BaSO}_4 = (1.65 \times 10^{-6} \text{ mol L}^{-1}) \left(\frac{233.4 \text{ g}}{1 \text{ mol}} \right) = 3.9 \times 10^{-4} \text{ g L}^{-1}$$

- 5.75 The thermodynamic solubility product of AgCl is 1.6×10^{-10} . What is $[\text{Ag}^+]$ 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, $z_+ = 1$, $z_- = -1$, $m_+ = m_- = 0.020 \text{ m}$.

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

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

$$\gamma_{\pm} = 0.847$$

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

$$K_{\text{sp}}^{\circ} = 1.6 \times 10^{-10} = a_+ a_- = \gamma_+ m_+ \gamma_- m_-$$

$$= \gamma_{\pm}^2 m_+^2$$

$$= (0.847)^2 m_+^2$$

$$m_+ = 1.5 \times 10^{-5}$$

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

(b) The ionic strength of the 0.020 M KCl ($\approx 0.020 \text{ m}$) 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, $m_- = m_+ + 0.020 \text{ m}$.

$$K_{\text{sp}}^{\circ} = 1.6 \times 10^{-10} = a_+ a_- = \gamma_+ m_+ \gamma_- m_-$$

$$= \gamma_{\pm}^2 m_+ m_-$$

$$= (0.847)^2 m_+ (m_+ + 0.020)$$

$$m_+ (m_+ + 0.020) = 2.23 \times 10^{-10}$$

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

$$m_+ (0.020) = 2.23 \times 10^{-10}$$

$$m_+ = 1.1 \times 10^{-8}$$

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, $[\text{Ag}^+] = 1.1 \times 10^{-8} \text{ M}$.

- 5.78 A 0.010 m aqueous solution of the ionic compound $\text{Co}(\text{NH}_3)_5\text{Cl}_3$ 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 $[\text{Co}(\text{NH}_3)_5\text{Cl}]_2\text{Cl}_2$, which on dissolution, dissociates into $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ and 2Cl^- .

5.69 The concentrations of K^+ and Na^+ ions in the intracellular fluid of a nerve cell are approximately 400 mM and 50 mM , respectively, but in the extracellular fluid the K^+ and Na^+ concentrations are 20 mM and 440 mM , 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^+ :

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

For Na^+ :

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