Chem 531: Problem Set #8 **SOLUTIONS**

Due in class: Thursday, November 30th

(1) Calculate the value of the mean ionic molality $m_\pm$ in 5.0 x 10^{-4} molal solutions of (a) KCl, (b) $Ca(NO_3)_2$, and (c) $ZnSO_4$. Assume complete dissociation.

a) KCl $m_\pm = \left(\nu_+^{\nu_+}\nu_-^{\nu_-}\right)^{1/\nu} m$

$m_\pm = \left(1^1 1^1\right)^{1/2} m = m = 5.0 \times 10^{-4}$ mol/kg

b) $Ca(NO_3)_2$ $m_\pm = \left(1^1 2^2\right)^{1/3} m = 4^{1/3} m$

$= 7.9 \times 10^{-4}$ mol/kg

c) $ZnSO_4$ $m_\pm = m = 5.0 \times 10^{-4}$ mol/kg

(2) Express the mean ionic activity $a_\pm$ in terms of m_+ and m_- for (a) NaCl, (b) $MgBr_2$, (c) Li_3PO_4, and (d) $Ca(NO_3)_2$. Assume complete dissociation.

a) NaCl

$$a_\pm = \gamma_\pm m_\pm = \gamma_\pm \left(m_+^{\nu_+} m_-^{\nu_-}\right)^{1/\nu} = \gamma_\pm (m_+ m_-)^{1/2}$$

b) $MgBr_2$

$$a_\pm = \gamma_\pm \left(m_+ m_-^2\right)^{1/3}$$

c) Li_3PO_4

$$a_\pm = \gamma_\pm \left(m_+^3 m_-\right)^{1/4}$$

d) $Ca(NO_3)_2$

$$a_\pm = \gamma_\pm \left(m_+ m_-^2\right)^{1/3}$$

(3) Calculate the mean ionic molality and mean ionic activity of a 0.150 *m* $Ca(NO_3)_2$ solution for which the mean ionic activity coefficient is 0.165.

$$m_\pm = \left(m_+^1 m_-^2\right)^{1/3} = \left(1^1 2^2\right)^{1/3} m$$

$$= \left(4^{1/3}\right)(0.150)$$

$$= 0.238 \text{ mol/kg}$$

$$a_\pm = \gamma_\pm m_\pm = (0.165)(0.238) = 0.0393 \text{ mol/kg}$$

(4) Calculate the ionic strength *I*, the mean ionic activity coefficient $\gamma_\pm$, and the mean ionic activity $a_\pm$ for a 0.0325 *m* solution of $K_4Fe(CN)_6$ at 298 K. For the latter two quantities, utilize the Debye-Hückel limiting law.

$$I = \frac{1}{2} \sum_i z_i^2 m_i \qquad K_4Fe(CN)_6 \rightarrow 4K^+ + Fe(CN)_6^{4-}$$

$$I = \frac{1}{2}\left((1^2)(4)(0.0325) + (-4)^2(0.0325)\right)$$

$$= 0.325 \text{ mol/kg}$$

Using Debye-Hückel: $\ln \gamma_\pm = 1.173\, z_+ z_- \sqrt{I}$

$$\ln \gamma_\pm = (1.173)(1)(-4)\sqrt{0.325}$$

$$\gamma_\pm = 0.0689$$

$$a_\pm = \gamma_\pm m_\pm = \gamma_\pm \left(m_+^4 m_-\right)^{1/5} = \gamma_\pm \left[(4m)^4 (m)\right]^{1/5}$$

$$= (0.0689)(0.09852) = 6.79 \times 10^{-3}$$