Quiz 5.4 – Ion Activities

Name: Key

Activities and ξ

A mixture is made by dissolving 0.025 *moles* of substance B into 1.5 *moles* of substance A. These two substances have endothermic mixing, with $\xi = 0.63$. Use the Margules equations to find γ_A and γ_B

$\chi_A = \frac{1.5 \text{ moles}}{1.525 \text{ moles}} = 0.984$ $\chi_B = \frac{0.025 \text{ moles}}{1.525 \text{ moles}} = 0.016$

$\ln \gamma_A = \xi \chi_B^2 = 0.63 \cdot 0.016^2 = 1.6 \cdot 10^{-4} \rightarrow \gamma_A = 1.0002$

$\ln \gamma_B = \xi \chi_A^2 = 0.63 \cdot 0.984^2 = 0.6100 \rightarrow \gamma_B = 1.84$

Extended Debye-Hückel Law

Consider a solution made by adding 0.75 *moles* of NaCl and 1.50 *moles* of $Fe(NO_3)_3$ to 1.00 *kg* of water solvent

↳ 0.75 m → $I = 0.75$ ↳ 1.50 m → $I = 6 \cdot 1.5 = 9$

Find the activity coefficients $\gamma_\pm$ for NaCl and $Fe(NO_3)_3$ in this solution. Use the extended Debye-Hückel law, with $A = 0.5085$ and $B = 0.9843$ (values for water at 25°C and typical ion sizes).

$I = 9.75$ $\log \gamma_\pm = - \frac{A |z_+ z_-| \sqrt{I}}{1 + B\sqrt{I}}$

NaCl: $\log \gamma_\pm = - \frac{0.5085 |1 \cdot 1| \sqrt{9.75}}{1 + 0.9843\sqrt{9.75}} = -0.390 \rightarrow \gamma_\pm (NaCl) = 0.408$

$Fe(NO_3)_3$: $\log \gamma_\pm = - \frac{0.5085 |3 \cdot 1| \sqrt{9.75}}{1 + 0.9843\sqrt{9.75}} = -1.17 \rightarrow \gamma_\pm (Fe(NO_3)_3) = 0.0677$

Debye-Hückel Limiting Law

CaF_2 is a sparingly soluble salt whose solubility product is $K_{SP} = 1.6 \times 10^{-10}$. Give the molar concentration of CaF_2 in (1) pure water, and (2) an aqueous solution buffered with 0.50 *molal* $NaNO_3$. Use the Debye-Hückel limiting law, with $A = 0.5085$

$$K_{sp} = \gamma_\pm^3 [Ca^{2+}][F^-]^2 = \gamma_\pm^3 (m)(2m)^2 = \gamma_\pm^3 \cdot 4m^3 \rightarrow m = \sqrt[3]{\frac{K_{sp}}{4\gamma_\pm^3}}$$

(1) first iteration: $m = \sqrt[3]{\frac{1.6 \cdot 10^{-10}}{4 \cdot 1^3}} = 3.42 \cdot 10^{-4} m$

Second iteration: $I = 3 \cdot m = 1.03 \cdot 10^{-3}$

$$\log \gamma_\pm = -0.5085 |2 \cdot -1| \sqrt{1.03 \cdot 10^{-3}} = -0.0326 \rightarrow \gamma_\pm = 0.928$$

$$m = \sqrt[3]{\frac{1.6 \cdot 10^{-10}}{4 \cdot 0.928^3}} = 3.69 \cdot 10^{-4} m$$

(2) $I = 0.50$

$$\log \gamma_\pm = -0.5085 |2 \cdot -1| \sqrt{0.50} = -0.719 \rightarrow \gamma_\pm = 0.191$$

$$m = \sqrt[3]{\frac{1.6 \cdot 10^{-10}}{4 \cdot 0.191^3}} = 1.79 \cdot 10^{-3} m$$