

Week 9

Solid-Liquid Solutions and Electrochemistry

9.1 Solute Activity

3/7:

- At low concentration, solute activity is unity, with the chosen measure of concentration.
- Activity of ions in electrolytes initially decreases rapidly with concentration below 1 M. The effect is much stronger than for neutral solutes.
- The Debye-Hückel model reasonably explains why ion activity drops so quickly.
- Practical solution concentration measures are the **molarity** and **molality**, in addition to the mole fraction x .
- **Molality**: The number of moles of solute per kilogram solvent. *Denoted by m . Given by*

$$m = \frac{n_2}{1 \text{ kg solvent}}$$

- **Concentration**: The number of moles of solute per liter solution. *Also known as **molarity**. Denoted by c . Given by*

$$c = \frac{n_2}{1 \text{ L solution}}$$

- As the solvent gets purer, its vapor pressure approaches the Raoult's law limit.
 - $a_1 = P_1/P_1^* \rightarrow x_1$ as $x_1 \rightarrow 1$.
- As the solute's concentration diminishes, the solute activity approaches the Henry's law limit.
 - $a_2 = P_2/k_H \rightarrow x_2$ as $x_2 \rightarrow 0$.
- Using the vapor pressure of the solvent to determine the activity of the non-volatile solute.
 - Use the Gibbs-Duhem relation,

$$\begin{aligned} 0 &= n_1 d \ln a_1 + n_2 d \ln a_2 \\ &= (55.506 \text{ mol kg}^{-1}) d \ln a_1 + m d \ln a_2 \\ \ln a_2 &= \int_0^m -\frac{55.506}{m'} d(\ln a_1) dm' \end{aligned}$$

- But $d(\ln a_1)$ may not be very precise; thus, we define the **osmotic coefficient**.

- With this quantity, we have

$$d \ln a_1 = -d(m\phi) \cdot \frac{1}{55.506}$$

- Thus, we have that

$$\begin{aligned} 0 &= -d(m\phi) + m d \ln a_2 \\ \phi dm + m d\phi &= m d \ln \gamma_2 + dm \\ \frac{dm}{m} \phi + d\phi &= d \ln \gamma_2 + \frac{dm}{m} \\ d \ln \gamma_2 &= d\phi + \left(\frac{\phi - 1}{m} \right) dm \\ \ln \gamma_2 &= (\phi - 1) + \int_0^m \frac{\phi - 1}{m'} dm' \end{aligned}$$

- **Osmotic coefficient:** The following quantity. Denoted by ϕ . Given by

$$\phi = -\frac{\ln a_1}{x_2} = -\ln a_1 \cdot \frac{55.506 \text{ mol kg}^{-1}}{m}$$

- It is called the osmotic coefficient since $\Pi \bar{V} = -RT \ln a_1$ implies that as $x_2 \rightarrow 0$, $\ln a_1 \rightarrow -x_2$, so $\phi \rightarrow 1$.
- Even in the case of an ideal solution, $\phi \neq 1$ exactly, though, since we must mathematically approximate $\ln a_1 \approx -x_2$.
- Ionic solutions deviate strongly from ideal solution, even at small molality.
- Mean ionic activity, molality, and activity coefficient.

- The salt $C_{\nu_+} A_{\nu_-}$ dissociates into ν_+ C^{z+} ions and ν_- A^{z-} ions where

$$\nu_+ z_+ + \nu_- z_- = 0$$

for charge neutrality.

- Let $\nu = \nu_+ + \nu_-$.
- The chemical potential of the salt is

$$\begin{aligned} \mu_{\text{salt}} &= \nu_+ \mu_+ + \nu_- \mu_- \\ &= \nu_+ \mu_+^\circ + \nu_- \mu_-^\circ + RT(\nu_+ \ln a_+ + \nu_- \ln a_-) + RT \ln \left(\underbrace{a_+^{\nu_+} a_-^{\nu_-}}_{a_2} \right) \end{aligned}$$

- Hence,

$$\begin{aligned} a_2 &= a_+^{\nu_+} a_-^{\nu_-} \\ &= (\gamma_+^{\nu_+} \gamma_-^{\nu_-}) (m_+^{\nu_+} m_-^{\nu_-}) \\ &= a_{\pm}^{\nu} \\ &= \gamma_{\pm}^{\nu} m_{\pm}^{\nu} \end{aligned}$$

where a_{\pm} is the **mean activity**, γ_{\pm} is the **mean activity coefficient**, and m_{\pm} is the **mean molality**.

- It follows that

$$\begin{aligned} \mu_2 &= \mu_2^\circ + RT \ln a_{\pm}^{\nu} \\ &= \mu_2^\circ + \nu RT \ln a_{\pm} \end{aligned}$$

- Consider a solution of CaCl_2 with molality m .

- It has

$$m_+ = m$$

$$m_- = 2m$$

- Thus,

$$\begin{aligned} m_{\pm} &= \sqrt{m_+^1 m_-^2} \\ &= \sqrt{4m^3} \\ &= 4^{1/3}m \end{aligned}$$

- We can do something similar for γ_{\pm} and a_{\pm} .

- Determining the activity of electrolytes.

- The derivation is pretty similar to before (for nonvolatile solvents), except that now $\ln a_1 = -\nu m\phi/55.506$.

- It follows that

$$\begin{aligned} 0 &= n_1 \, d \ln a_1 + n_2 \, d \ln a_2 \\ &= -\nu \, d(m\phi) + m\nu \, d \ln a_{\pm} \end{aligned}$$

so ν cancels.

- This yields the same overall equation as before:

$$\ln \gamma_{\pm} = (\phi - 1) + \int_0^m \frac{\phi - 1}{m'} \, dm'$$

- We can do the above, but ion activity can also be measured by electrochemistry.