

## 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  $\phi$ . 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  $\nu_+$   $C^{z_+}$  ions and  $\nu_-$   $A^{z_-}$  ions where

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

for charge neutrality.

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

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

- 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**,  $\gamma_\pm$  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  $\text{CaCl}_2$  with molality  $m$ .

– It has

$$m_+ = m \qquad m_- = 2m$$

– Thus,

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

– We can do something similar for  $\gamma_{\pm}$  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  $\nu$  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.

## 9.2 Chapter 25: Solutions II — Solid-Liquid Solutions

*From McQuarrie and Simon (1997).*

3/8:

- Oppositely charged ions in solution interact with each other via a Coulombic potential, which varies proportionally to  $1/r$ .
  - Note the difference between the strength of this potential and the LDF potential of  $1/r^6$  attracting ordinary neutral molecules.
  - It follows that solutions of electrolytes deviate from ideality much more quickly (i.e., at much lower concentrations).
- When ions with higher charges (e.g.,  $\text{CaCl}_2$  vs.  $\text{NaCl}$ ) are produced, the deviation from ideality is exacerbated.
- ***a-b* electrolyte:** An electrolyte for which  $\nu_+ = a$  and  $\nu_- = b$ .
  - For example,  $\text{CaCl}_2$  is a 1-2 electrolyte and  $\text{Gd}_2(\text{SO}_4)_3$  is a 2-3 electrolyte.
- The chemical potential of a salt depends on the potentials of its constituent ions as per

$$\mu_2 = \nu_+ \mu_+ + \nu_- \mu_-$$

where  $\mu_j = \mu_j^\circ + RT \ln a_j$  for  $j = 2, +, -$ .

- It follows from the above and the fact that  $\mu_2^\circ = \nu_+ \mu_+^\circ + \nu_- \mu_-^\circ$ , too, that

$$\begin{aligned}\mu_2^\circ + RT \ln a_2 &= \nu_+ (\mu_+^\circ + RT \ln a_+) + \nu_- (\mu_-^\circ + RT \ln a_-) \\ RT \ln a_2 &= \nu_+ RT \ln a_+ + \nu_- RT \ln a_- \\ \ln a_2 &= \nu_+ \ln a_+ + \nu_- \ln a_- \\ a_2 &= a_+^{\nu_+} a_-^{\nu_-}\end{aligned}$$

- We define  $\nu = \nu_+ + \nu_-$ .
- **Mean ionic activity:** The following quantity. Denoted by  $a_\pm$ . Given by

$$a_\pm^\nu = a_+^{\nu_+} a_-^{\nu_-}$$

- We take the activity  $a_2$  of an electrolyte to be its mean ionic activity to the  $\nu^{\text{th}}$  power, i.e.,  $a_2 = a_\pm^\nu$ .
- We cannot determine the activities of single ions.
- We define the molalities of individual ions by

$$m_+ = \nu_+ m \qquad m_- = \nu_- m$$

- We define single-ion activity coefficients by

$$\gamma_+ = \frac{a_+}{m_+} \qquad \gamma_- = \frac{a_-}{m_-}$$

- **Mean ionic molarity:** The following quantity. Denoted by  $m_\pm$ . Given by

$$m_\pm^\nu = m_+^{\nu_+} m_-^{\nu_-}$$

- **Mean ionic activity coefficient:** The following quantity. Denoted by  $\gamma_\pm$ . Given by

$$\gamma_\pm^\nu = \gamma_+^{\nu_+} \gamma_-^{\nu_-}$$

- It follows that

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

- McQuarrie and Simon (1997) derives

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

- For colligative properties, since  $x_2$  is scaled up by a factor of  $\nu$ , we get

$$\Delta T_{\text{fus}} = \nu K_f m \qquad \Delta T_{\text{vap}} = \nu K_b m \qquad \Pi = \nu c R T$$

for solutions of electrolytes.

- Debye and Hückel showed theoretically in 1925 that at low concentrations, the natural logarithms of the  $j^{\text{th}}$  ion's activity coefficient and the mean ionic activity coefficient are given by

$$\ln \gamma_j = -\frac{\kappa q_j^2}{8\pi\epsilon_0\epsilon_r k_B T} \qquad \ln \gamma_\pm = -|q_+ q_-| \frac{\kappa}{8\pi\epsilon_0\epsilon_r k_B T}$$

where  $q_+ = z_+ e$  and  $q_- = z_- e$ ,  $\epsilon_r$  is the (unitless) relative permittivity of the solvent, and  $\kappa$  is given by

$$\kappa^2 = \sum_{j=1}^s \frac{q_j^2}{\epsilon_0 \epsilon_r k_B T} \left( \frac{N_j}{V} \right)$$

$s$  being the number of ionic species and  $N_j/V$  being the number density of species  $j$ .

- Converting  $N_j/V$  to molarity allows us to rewrite the above as

$$\kappa^2 = N_A(1000 \text{ L m}^{-3}) \sum_{j=1}^s \frac{q_j^2 c_j}{\varepsilon_0 \varepsilon_r k_B T}$$

- This result is derived in Problems 25-50 through 25-58.

- **Debye-Hückel limiting law:** The above expression for  $\ln \gamma_{\pm}$ .
- **Ionic strength:** The following quantity. Denoted by  $I_c$ . Given by

$$I_c = \frac{1}{2} \sum_{j=1}^s z_j^2 c_j$$

- $c_j$  is the molarity of the  $j^{\text{th}}$  ionic species.

- Having defined the ionic strength, we can write express  $\kappa$  in a third form as

$$\kappa^2 = \frac{2e^2 N_A(1000 \text{ L m}^{-3})}{\varepsilon_0 \varepsilon_r k_B T} (I_c / \text{mol L}^{-1})$$

- In the Debye-Hückel limiting law,  $\ln \gamma_{\pm} \propto \kappa \propto \sqrt{I_c} \propto \sqrt{c}$ .
  - This is why we curve fit  $\phi$  vs.  $m$  data to a polynomial in  $m^{1/2}$ .
- As  $m \rightarrow 0$ , all curves  $\ln \gamma_{\pm}$  vs.  $m$  converge to the same straight line (hence this being a *limiting* law).
- Physically interpreting  $\kappa$ .
  - The net charge in a spherical shell of radius  $r$  and thickness  $dr$  surrounding an ion of charge  $q_i$  is given by

$$p_i(r) dr = -q_i \kappa^2 r e^{-\kappa r} dr$$

- Integrating this equation over all space yields  $-q_i$ .
- Thus, “the total charge surrounding an ion of charge  $q_i$  is equal and of the opposite sign to  $q_i$ . In other words, it expresses the electroneutrality of the solution” (McQuarrie & Simon, 1997, pp. 1033–34).
- The above equation describes the **ionic atmosphere** about the central ion.
- Additionally, its maximum occurs at  $\kappa^{-1}$ , so we say that  $\kappa$  is a measure of the thickness of the ionic atmosphere.
- For a 1-1 electrolyte in aqueous solution at 25 °C,

$$\kappa = \frac{304 \text{ pm}}{\sqrt{c / \text{mol L}^{-1}}}$$

- Assumptions of the Debye-Hückel theory:
  - Ions are point particles.
  - They interact with a purely Coulombic potential.
  - The solvent is a continuous medium with a uniform relative permittivity  $\varepsilon_r$ .
- Clearly, these will start to break down as their concentration increases.
- The Debye-Hückel model has been of important utility mainly in that all models that attempt to treat higher concentrations must reduce to it at lower temperatures.

- Real progress toward a more general theory wasn't made until the 1970s, though.
- **Primitive model:** Ions are considered hard spheres with charges at their centers and the solvent is considered a continuous medium with a uniform relative permittivity.
  - Although, well, primitive, long-range Coulombic interactions and short-range repulsions, which this model encapsulates well, turn out to be major considerations, so the model is pretty good.
- The mean spherical approximation (MSA) provides analytical solutions.
  - A central result is that

$$\ln \gamma_{\pm} = \ln \gamma_{\pm}^{\text{el}} + \ln \gamma^{\text{HS}}$$

where  $\ln \gamma_{\pm}^{\text{el}}$  is an electrostatic (Coulombic) contribution to  $\ln \gamma_{\pm}$  and  $\ln \gamma^{\text{HS}}$  is a hard-sphere contribution.

- For a 1-1 electrolyte,

$$\ln \gamma_{\pm}^{\text{el}} = \frac{x\sqrt{1+2x} - x - x^2}{4\pi\rho d^3}$$

where  $\rho$  is the number density of charged particles,  $d$  is the sum of the radius of a cation and anion, and  $x = \kappa d$ . Also,

$$\ln \gamma^{\text{HS}} = \frac{4y - \frac{9}{4}y^2 + \frac{3}{8}y^3}{\left(1 - \frac{y}{2}\right)^3}$$

where  $y = \pi\rho d^3/6$ .