

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

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

- 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**, 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

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

– Thus,

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

– We can do something similar for 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.

9.2 Debye-Hückel Model

3/9:

- For ionic solutions, ϕ is fitted to a function of the form $\phi = \sum a_i m^{i/2}$.
- For neutral solutes, ϕ is fitted to a function of the form $\phi = \sum a_i m^i$.
- Debye-Hückel model for small concentrations: $\ln \gamma_{\pm} \propto m^{1/2}$.
- We define $\text{pH} = -\log a_1$, not $\text{pH} = -\log[\text{H}_3\text{O}^+]$.
 - Thus, $\text{pH} = -\log \gamma_{\pm} - \log[\text{H}_3\text{O}^+]$.
 - This also gives a method of determining γ_{\pm} .
- Activity coefficients and interaction between solutes.
 - If there are *unfavorable* interactions between solutes (as in sucrose), $\gamma > 1$.
 - If there are *favorable* interactions between solutes (as in NaCl), $\gamma < 1$.
 - In terms of energy:

$$\begin{aligned} \mu &= \bar{\mu} + P\bar{V} - T\bar{S} \\ &= \mu^*(x) + RT \ln x \\ &= \mu_{\text{ideal}}^* + (\mu^*(x) - \mu_{\text{ideal}}^*) + RT \ln x \\ &= \mu_{\text{ideal}}^* + RT \ln a \\ &= \mu_{\text{ideal}}^* + RT \ln \gamma + RT \ln x \end{aligned}$$

- It follows that

$$RT \ln \gamma = \mu^*(x) - \mu_{\text{ideal}}$$

$$\gamma = \exp \left(\frac{\mu^*(x) - \mu_{\text{ideal}}}{RT} \right)$$

using only $\bar{\mu} \rightarrow \gamma = \exp \left(\frac{\mu^*(x) - \mu_{\text{ideal}}}{RT} \right)$.

- This mathematically shows that if we stabilize the ion energetically, then $\gamma < 1$.
- Interactions between ions. The Debye length arises due to the screening of the charges. Calculated from the Boltzmann factor.
 - Imagine a charge of magnitude q at the center of our coordinate system.
 - We have a charge density $\rho(r)$ at a distance r from the nucleus.
 - We have

$$\rho(r) = \sum_i q_i \left(\frac{N_i}{V} \right) \cdot e^{-q_i \phi(r)/k_B T}$$

where the latter term is the Boltzmann factor and $\phi(r)$ is the electrostatic potential.

- We also have the Poisson equation,

$$\nabla \phi(r) = -\frac{\rho(r)}{\epsilon \epsilon_0}$$

- Since everything is depending on each other, it seems we are in a pickle.
- But if

$$\frac{q_i \phi(r)}{k_B T} < 1$$

then

$$e^{q_i \phi(r)/k_B T} = 1 - \frac{q_i \phi(r)}{k_B T}$$

- Therefore,

$$\rho(r) = \sum_i q_i \left(\frac{N_i}{V} \right) \cdot \left(1 - \frac{q_i \phi(r)}{k_B T} \right) = \sum_i q_i \left(\frac{N_i}{V} \right) - \phi(r) \sum \frac{q_i^2 \left(\frac{N_i}{V} \right)}{k_B T}$$

where the left term in the right expression above evaluates to zero.

- We can only have an excess of 1000 ions of one type of charge per liter of solution.
- It follows that

$$\nabla \phi(r) = \left(\frac{\sum q_i^2 \left(\frac{N_i}{V} \right)}{\epsilon \epsilon_0 k_B T} \right) \cdot \phi(r)$$

$$\frac{\partial^2 \phi}{\partial r^2} + \dots = \kappa^2 \cdot \phi$$

- **Debye length:** κ^{-1} .
- In the one-dimensional case,

$$\frac{\partial^2 \phi}{\partial x^2} = \kappa^2 \phi$$

$$\phi(x) = A e^{\kappa x} + B e^{-\kappa x}$$

- In other words, all interactions take place within the Debye length.

- The distance over which ion concentration differs from perfectly mixed ion potential around a charge.
- In electrochemistry, this is where everything happens.
- Ions **screen** other ions.
- We have

$$\kappa^2 = \frac{\sum q_i^2 \left(\frac{N_i}{V} \right)}{\varepsilon \varepsilon_0 k_B T}$$

- **Ionic strength:** The following quantity. Denoted by I_c . Given by

$$I_c = \frac{1}{2} \sum z_i^2 c_i$$

- Thus, we have

$$\kappa^{-1} = \frac{1}{\sqrt{I_c}} \cdot \sqrt{\frac{10^{-3}}{e^2 N_A} \cdot \frac{\varepsilon \varepsilon_0 k_B T}{2}}$$

- Calculating the Debye length of NaCl.

- For water, $\varepsilon \approx 80$.
- For 1 M NaCl,

$$I_c = \frac{1}{2}(1 \cdot 1 + 1 \cdot 1) = 1 \text{ M}$$

- Thus, $\kappa^{-1} = 3 \text{ \AA}$.

- Calculating the Debye length of CaCl_2 .

- $I_c = 3 \text{ M}$.

- Interactions lead to the Debye-Hückel model for the mean ionic activity.

- We have

$$\mu = -\frac{\kappa q^2}{8\pi\varepsilon\varepsilon_0}$$

which implies that

$$\ln \gamma = -\frac{\kappa q^2}{8\pi\varepsilon\varepsilon_0 k_B T}$$

- Hence, by Problem 25.58,

$$\ln \gamma_{\pm} = \frac{|z_+ z_-| e^2 \kappa}{8\pi\varepsilon\varepsilon_0 k_B T}$$

where $e^2 \kappa / 8\pi\varepsilon\varepsilon_0$ comes from the Coulombic attraction.

- Thus, by the Debye-Hückel model,

$$\ln \gamma_{\pm} = -1.333 |z_+ z_-| \sqrt{I_c}$$

- One empirical extension of the Debye-Hückel model is

$$\ln \gamma_{\pm} = \frac{-1.173 |z_+ z_-| \sqrt{I_c}}{1 + \sqrt{I_c}} + c_m$$

9.3 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., CaCl_2 vs. NaCl) are produced, the deviation from ideality is exacerbated.

- **a-b electrolyte:** An electrolyte for which $\nu_+ = a$ and $\nu_- = b$.

– For example, 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

$$\mu_2^\circ + RT \ln a_2 = \nu_+ (\mu_+^\circ + RT \ln a_+) + \nu_- (\mu_-^\circ + RT \ln a_-)$$

$$RT \ln a_2 = \nu_+ RT \ln a_+ + \nu_- RT \ln a_-$$

$$\ln a_2 = \nu_+ \ln a_+ + \nu_- \ln a_-$$

$$a_2 = a_+^{\nu_+} a_-^{\nu_-}$$

- 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 ν^{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

$$m_+ = \nu_+ m$$

$$m_- = \nu_- m$$

- We define single-ion activity coefficients by

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

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

- **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 γ_\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 ν , 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^{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 $q_- = z_- e$, ϵ_r is the (unitless) relative permittivity of the solvent, and κ 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

$$\kappa^2 = N_A (1000 \text{ L m}^{-3}) \sum_{j=1}^s \frac{q_j^2 c_j}{\epsilon_0 \epsilon_r k_B T}$$

- 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^{th} ionic species.

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

$$\kappa^2 = \frac{2e^2 N_A (1000 \text{ L m}^{-3})}{\epsilon_0 \epsilon_r k_B T} (I_c / \text{mol L}^{-1})$$

- In the Debye-Hückel limiting law, $\ln \gamma_{\pm} \propto \kappa \propto \sqrt{I_c} \propto \sqrt{c}$.

- This is why we curve fit ϕ 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 κ .

- 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 κ^{-1} , so we say that κ 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 ϵ_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 ρ 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 $y = \pi\rho d^3/6$.