

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 Electrochemistry

- 3/11: • Example from last time: Calculate the mean ionic activity of ZnCl_2 at 0.02 molal.

- The mean molality is $m_{\pm} = \sqrt{(0.02)^1(0.04)^2} = 3.17 \times 10^{-2}$.
- The ionic strength is

$$I = \frac{1}{2}[(0.02)(+2)^2 + (0.04)(-1)^2] \\ = 0.06$$

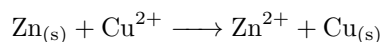
- Calculate the Debye-Hückel mean ionic activity coefficient:

$$\ln \gamma_{\pm} = -1.173 |z_+ z_-| \sqrt{I_c} \\ = -1.173 (2 \cdot 1) \sqrt{0.06} \\ = -0.574$$

- Thus, by plotting $\ln \gamma_{\pm}$ vs. c for small concentrations, we can find that $\sqrt{c} \approx 0.14$.

- Electrochemistry: Exchanging chemical free energy with electrical energy.

- Zinc and copper electrodes in a solution of CuSO_4 .
 - The zinc silvery metal turns red (it's getting coated in copper) and the copper electrode doesn't change.
- Now picture zinc in a solution of ZnSO_4 and copper in a solution of CuSO_4 , the two containers being connected by a salt bridge and an ammeter.
 - The zinc electrode corrodes (gets smaller and smaller).
 - The copper electrode grows (copper gets deposited).
 - What we have is $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2\text{e}^-$ and $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$, so electrons flow through the wire from the zinc anode to the copper cathode.
 - The overall redox reaction is



- The relevant molar Gibbs energies of formation ($\Delta \bar{G}_f^\circ$) are zero for the metals, -147 kJ mol^{-1} for $\text{Zn}_{(\text{aq})}^{2+}$, and 65 kJ mol^{-1} for $\text{Cu}_{(\text{aq})}^{2+}$.
 - Thus, this reaction is spontaneous with $\Delta \bar{G}^\circ = -147 - 65 = -212 \text{ kJ mol}^{-1}$.
- We know that $\Delta \bar{G}^\circ = w_{\text{non PV}} = \Delta \bar{Q} \cdot E$ at constant T, P , where E is the electrochemical potential.
- We also know that $\Delta \bar{Q} = -2eN_A = -2F$ (negative since we're losing electrons) where

$$F = 96\,485 \text{ C}$$

is the **Faraday constant**.

- Thus,

$$E = \frac{\Delta \bar{G}^\circ}{2F} = \frac{-212}{-2F} = \frac{-212000}{-2 \cdot 96485} = 1.1 \text{ V}$$

- Using the Gibbs free energy with the electrostatic potential energy.

- Hydrogen electrode: You have a reference, and then you bubble H_2 through the solution with $P_{\text{H}_2} = 1 \text{ atm}$, using a solution of $\text{pH} = 1$.
 - Recall that this does not imply that $[\text{H}_3\text{O}^+] = 1 \text{ M}$; it means that $\log a_{\text{H}_3\text{O}^+} = 1$.

■ Know that $2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$.

- Nernst equation.

$$E = E_0 - \frac{RT}{nF} \ln \frac{a_{\text{reductant}}}{a_{\text{oxidant}}}$$

- In the case of the standard hydrogen electrode,

$$\begin{aligned} E_{\text{H}_2} &= E_0 - \frac{RT}{2F} \ln \frac{P_{\text{H}_2}}{a_{\text{H}}^2} \\ &= E_0 - \frac{0.0592}{2} \log \frac{P_{\text{H}_2}}{a_{\text{H}}^2} \\ &= E_0 - \frac{0.0592}{2} \log P_{\text{H}_2} + 0.0592 \text{ pH} \end{aligned}$$

- Membrane potential.

- In a cell, ion pumps establish an electric potential across a membrane of up to 20 times.
- Assuming that the chemical potentials inside and outside the membrane are equal, we have

$$\mu_{\text{in}} = \mu_+^* + RT \ln c_{\text{in}} + q\phi \qquad \mu_{\text{out}} = \mu_+^* + RT \ln c_{\text{out}} + q \cdot 0$$

where ϕ is the electrical potential difference between the inside and outside of the cell.

- Setting the two equations equal to each other and noting that $q = eN_A = F$ yields

$$\begin{aligned} RT \ln c_{\text{in}} + R\phi &= RT \ln c_{\text{out}} \\ \phi &= \frac{RT}{F} \ln \frac{c_{\text{out}}}{c_{\text{in}}} \\ &= -75 \text{ mV} \end{aligned}$$

for $T = 300 \text{ K}$ and the concentration on the inside being 20 times that on the outside.

- Corrosion and concentration gradients.

- Metal corrosion occurs when $[\text{M}^+]$ is smallest. Here, $\text{M}^+ + \text{e}^- \longrightarrow \text{M}$.

■ Electrons flow from negative to positive.

- Corrosion occurs where O_2 concentration is the lowest.

■ $\text{O}_2 + 4\text{e}^- + 4\text{H}^+ \longrightarrow 2\text{H}_2\text{O}$.

■ Low $[\text{O}_2]$ implies that

$$E = E_0 - \frac{RT}{4F} - \ln \frac{1}{[\text{H}^+]^4 P_{\text{O}_2}}$$

so E becomes more negative.

■ It is the low potential at places that lack oxygen that causes corrosion.

- Few lines summary of CHEM 26200.

1. We first thought of $\langle E \rangle = \sum p_i E_i$, i.e., the energy as dependent on the states of a system.
2. We then defined the entropy $S = -k_B \sum p_i \ln p_i$ that maximizes when everything is most equally distributed. Tells us where nature goes, i.e., toward the most probable outcome.
3. We can combine energy with the tendency of nature to go to the highest entropy to define the **Lagrange multipliers** $F = U - TS$ and $G = H - TS$; minima of F, G are where the system goes spontaneously.
4. The partition function $q = \sum e^{-E_i/k_B T}$ allows us to calculate every property of the system it describes. We can also extend this from molecules to systems of distinguishable and indistinguishable particles.
5. The probabilities of each state depend on their energy via $p_i = e^{E_i/k_B T}/q$.

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