
Problems with Electrolytes

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Ion Activities

Intro

For non-electrolytes the interactions between solute particles are so weak that the replacement of activity with molality is justified. For electrolytes the interactions between ions is so strong that we must find an expression for an activity coefficient (γ) such that

$$a = \gamma m/m^\circ$$

Mean activity and the activity coefficient

Charge neutrality dictates that for every + ion in solution there is a negative counter ion. This means that the activity of a + ion will depend on the activity of the negative ion and makes it impossible for us to determine the activity of an isolated ion.

For an ideal solution

$$G = \mu^+ + \mu^-$$

There is no way experimentally to disentangle $\gamma^+\gamma^-$ so we define quantities γ^\pm , m^\pm , and a^\pm

Suppose we have a salt M_pX_q dissolved in water

Example – Calculate the mean activity of 8.25×10^{-4} m $\text{Al}_2(\text{SO}_4)_3$ at 25°C given that the mean activity coefficient at this temp is 0.9913 and the compound dissociates completely.

Debye-Huckel Limiting Law

The interactions of the ions are coulombic in nature. The solution is electrically neutral, but near any given ion there is an excess of counter ions of opposite charge. This lowers the chemical potential and is quantified by $RT \ln \gamma_{\pm}$.

At very low concentration (less than 0.001 m) the Debye-Huckel limiting law is

$$\log_{10} g_{\pm} = -\zeta z_+ z_- \zeta A I^{1/2}$$

z = charge on ion

A is a constant that involves Avogadro's #, charge on the electron, the thickness of ionic atmosphere, the dielectric constant of solvent and the temp

$A = .509$ at 25°

I is the Ionic Strength

$$I = \frac{1}{2} \sum z_i^2 m_i / m^\circ$$

Example – What is I for a 0.100 m solution of CaCl_2 ?

Question for thought – What is the relationship between M (Molarity) and m (molality) at very low concentrations in aqueous solution?

To use this equation we assume

1. all ions have the same diameter
2. the dielectric constant is the same everywhere in the solution
3. the counter-ions form a spherical cloud
4. only long range electrostatic forces occur

At slightly higher concentrations (0.0100 m) the extended Debye-Huckel Law is

$$\log_{10} \gamma_{\pm} = \frac{-|z_+z_-| A I^{1/2}}{1 + B I^{1/2}}$$

The constant B includes a parameter for the closest approach of the ions to each other.

Example – (long and tedious)

Calculate the voltage of the cell below at 25°C. For the purpose of this example calculate the E° value for the cell from ΔG_f° values and use the Debye-Huckel limiting law to obtain activities for the reaction quotient.

