

7.8: Non-ideality in Solutions - Activity

The bulk of the discussion in this chapter dealt with ideal solutions. However, real solutions will deviate from this kind of behavior. So much as in the case of gases, where fugacity was introduced to allow us to use the ideal models, **activity** is used to allow for the deviation of real solutes from limiting ideal behavior. The activity of a solute is related to its concentration by

$$a_B = \gamma \frac{m_B}{m^o}$$

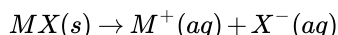
where γ is the **activity coefficient**, m_B is the molality of the solute, and m^o is unit molality. The activity coefficient is unitless in this definition, and so the activity itself is also unitless. Furthermore, the activity coefficient approaches unity as the molality of the solute approaches zero, insuring that dilute solutions behave ideally. The use of activity to describe the solute allows us to use the simple model for chemical potential by inserting the activity of a solute in place of its mole fraction:

$$\mu_B = \mu_B^o + RT \ln a_B$$

The problem that then remains is the measurement of the activity coefficients themselves, which may depend on temperature, pressure, and even concentration.

Activity Coefficients for Ionic Solutes

For an ionic substance that dissociates upon dissolving



the chemical potential of the cation can be denoted μ_+ and that of the anion as μ_- . For a solution, the total molar Gibbs function of the solutes is given by

$$G = \mu_+ + \mu_-$$

where

$$\mu = \mu^* + RT \ln a$$

where μ^* denotes the chemical potential of an ideal solution, and a is the activity of the solute. Substituting this into the above relationship yields

$$G = \mu_+^* + RT \ln a_+ + \mu_-^* + RT \ln a_-$$

Using a molal definition for the activity coefficient

$$a_i = \gamma_i m_i$$

The expression for the total molar Gibbs function of the solutes becomes

$$G = \mu_+^* + RT \ln \gamma_+ m_+ + \mu_-^* + RT \ln \gamma_- m_-$$

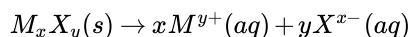
This expression can be rearranged to yield

$$G = \mu_+^* + \mu_-^* + RT \ln m_+ m_- + RT \ln \gamma_+ \gamma_-$$

where all of the deviation from ideal behavior comes from the last term. Unfortunately, it is impossible to experimentally deconvolute the term into the specific contributions of the two ions. So instead, we use a geometric average to define the **mean activity coefficient**, γ_{\pm} .

$$\gamma_{\pm} = \sqrt{\gamma_+ \gamma_-}$$

For a substance that dissociates according to the general process



the expression for the mean activity coefficient is given by

$$\gamma_{\pm} = (\gamma_+^x \gamma_-^y)^{1/(x+y)}$$

Debye-Hückel Law

In 1923, Debye and Hückel (Debye & Hückel, 1923) suggested a means of calculating the mean activity coefficients from experimental data. Briefly, they suggest that

$$\log_{10} \gamma_{\pm} = \frac{1.824 \times 10^6}{(\epsilon T)^{3/2}} |z_+ + z_-| \sqrt{I}$$

where ϵ is the dielectric constant of the solvent, T is the temperature in K, z_+ and z_- are the charges on the ions, and I is the **ionic strength** of the solution. I is given by

$$I = \frac{1}{2} \frac{m_+ z_+^2 + m_- z_-^2}{m^o}$$

For a solution in water at 25 °C,

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