

16.17: Activities of Electrolytes - The Mean Activity Coefficient

We can find the activity of a salt in its aqueous salt solutions. For example, we can measure the freezing point depression for aqueous solutions of sodium chloride, find the activity of water in these solutions as a function of the sodium chloride concentration, and use the [Gibbs-Duhem equation](#) to find the activity of the dissolved sodium chloride as a function of its concentration. When we do so, we find some marked differences from our observations on molecular solutes.

For molecular solutes, the activity approaches the solute concentration as the concentration approaches zero; that is, the activity coefficient for a molecular solute approaches unity as the concentration approaches zero. For sodium chloride, and other 1:1 electrolytes, we find that the activity we measure in this way approaches the square of the solute concentration as the concentration approaches zero. For other salts, the measured activity approaches other powers of the solute concentration as the concentration approaches zero.

The dissociation of the solid salt into solvated ions explains these observations. Let us consider a solution made by dissolving n moles of a salt, A_pB_q , in n_{solvent} moles of solvent. (Let A be the cation and B the anion.) For present purposes, the cation and anion charges are not important. We use p and q to designate the composition of the salt. Typically, we are interested in dilute solutions, and it is convenient to use the hypothetical one-molal solution as the standard state for the activity of a solute species. We can represent the Gibbs free energy of this solution as

$$G = n_{\text{solvent}}\mu_{\text{solvent}} + n\mu_{A_pB_q}$$

where μ_{solvent} and $\mu_{A_pB_q}$ are the partial molar Gibbs free energies of the solvent and the solute in the solution. We can also write

$$\mu_{A_pB_q} = \tilde{\mu}_{A_pB_q}^{\circ} + RT\ln \tilde{a}_{A_pB_q}$$

where $\tilde{\mu}_{A_pB_q}^{\circ}$ is the partial molar Gibbs free energy when $\tilde{a}_{A_pB_q} = \underline{m}_{A_pB_q} \gamma_{A_pB_q} = 1$ in the activity standard state of the salt.

We assume that A_pB_q is a strong electrolyte; its solution contains np moles of the cation, A , and nq moles of the anion, B . In principle, we can also represent the Gibbs free energy of the solution as

$$G = n_{\text{solvent}}\mu_{\text{solvent}} + np\mu_A + nq\mu_B$$

and the individual-ion chemical potentials as $\mu_A = \tilde{\mu}_A^{\circ} + RT\ln \tilde{a}_A$ and $\mu_B = \tilde{\mu}_B^{\circ} + RT\ln \tilde{a}_B$, where $\tilde{\mu}_A^{\circ}$ and $\tilde{\mu}_B^{\circ}$ are the partial molar Gibbs free energies of the ions A and B in their hypothetical one-molal activity standard states. Equating the two equations for the Gibbs free energy of the solution, we have

$$\mu_{A_pB_q} = p\mu_A + q\mu_B$$

and

$$\tilde{\mu}_{A_pB_q}^{\circ} + RT\ln \tilde{a}_{A_pB_q} = p\tilde{\mu}_A^{\circ} + RT\ln \tilde{a}_A^p + q\tilde{\mu}_B^{\circ} + RT\ln \tilde{a}_B^q$$

While it is often experimentally challenging to do so, we can measure $\tilde{\mu}_{A_pB_q}^{\circ}$ and $\tilde{a}_{A_pB_q}$. In principle, the meanings of the individual-ion activities, \tilde{a}_A and \tilde{a}_B , and their standard-state chemical potentials, $\tilde{\mu}_A^{\circ}$ and $\tilde{\mu}_B^{\circ}$, are unambiguous; however, since we cannot prepare a solution that contains cation A and no anion, we cannot make measurements of \tilde{a}_A or $\tilde{\mu}_A^{\circ}$ that are independent of the properties of B , or some other anion. Consequently, we must adopt some conventions to relate these properties of the ions, which we cannot measure, to those of the salt solution, which we can.

The universally adopted convention for the standard chemical potentials is to equate the sum of the standard chemical potentials of the constituent ions to that of the salt. We can think of this as assigning an equal share of the standard-state chemical potential of the salt to each of its ions; that is, we let

$$\tilde{\mu}_A^{\circ} = \tilde{\mu}_B^{\circ} = \frac{\tilde{\mu}_{A_pB_q}^{\circ}}{p+q}$$

Then,

$$\tilde{\mu}_{A_pB_q}^{\circ} = p\tilde{\mu}_A^{\circ} + q\tilde{\mu}_B^{\circ}$$

and the activities of the individual ions are related to that of the salt by

$$\tilde{a}_{A_p B_q} = \tilde{a}_A^p \tilde{a}_B^q$$

We can develop the convention for the activities of the individual ions by representing each activity as the product of a concentration and an activity coefficient. That is, we represent the activity of each individual ion in the same way that we represent the activity of a molecular solute. In effect, this turns the problem of developing a convention for the activities of the individual ions into the problem of developing a convention for their activity coefficients. Using the hypothetical one-molal standard state for each ion, we write $\tilde{a}_A = \underline{m}_A \gamma_A$ and $\tilde{a}_B = \underline{m}_B \gamma_B$, where \underline{m}_A , γ_A , \underline{m}_B , and γ_B are the molalities and activity coefficients for ions A and B, respectively. Let the molality of the salt, $A_p B_q$, be \underline{m} . Then $\underline{m}_A = p\underline{m}$ and $\underline{m}_B = q\underline{m}$, and

$$\tilde{a}_{A_p B_q} = \tilde{a}_A^p \tilde{a}_B^q = (p\underline{m}\gamma_A)^p (q\underline{m}\gamma_B)^q = (p^p q^q) \underline{m}^{p+q} \gamma_A^p \gamma_B^q$$

Now we introduce the geometric mean of the activity coefficients γ_A and γ_B ; that is, we define the geometric **mean activity coefficient**, γ_{\pm} , by

$$\gamma_{\pm} = (\gamma_A^p \gamma_B^q)^{1/(p+q)}$$

The activity of the dissolved salt is then given by

$$\tilde{a}_{A_p B_q} = (p^p q^q) \underline{m}^{p+q} \gamma_{\pm}^{p+q}$$

The mean activity coefficient, γ_{\pm} , can be determined experimentally as a function of $\underline{m}_{A_p B_q}$, but the individual activity coefficients, γ_A and γ_B , cannot. It is common to present the results of activity measurements on electrolytic solutions as a table or a graph that shows the mean activity coefficient as a function of the salt molality.

While we cannot determine the activity or activity coefficient for an individual ion experimentally, no principle prohibits a theoretical model that estimates individual ion activities. Debye and Hückel developed such a theory. The [Debye-Hückel theory](#) gives reasonably accurate predictions for the activity coefficients of ions for solutions in which the total ion concentration is about 0.01 molal or less. We summarize the results of the Debye-Hückel theory in [Section 16.18](#).

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