# 10.6: Mean Ionic Activity Coefficients from Osmotic Coefficients

Recall that $\gamma_\pm$ is the mean ionic activity coefficient of a strong electrolyte, or the stoichiometric activity coefficient of an electrolyte that does not dissociate completely.

The general procedure described in this section for evaluating $\gamma_\pm$ requires knowledge of the osmotic coefficient $\phi_m$ as a function of molality. $\phi_m$ is commonly evaluated by the isopiestic method (Sec. 9.6.4) or from measurements of freezing-point depression (Sec. 12.2).

The osmotic coefficient of a binary solution of an electrolyte is defined by

$$\phi_m \overset{\text{def}}{=} \frac{\mu_A^* - \mu_A}{RT M_A \nu m_B} \qquad\qquad \text{(10.6.1)}$$
$$\text{(binary electrolyte solution)}$$

That is, for an electrolyte the sum $\sum_{i \neq A} m_i$ appearing in the definition of $\phi_m$ for a nonelectrolyte solution (Eq. 9.6.11) is replaced by $\nu m_B$, the sum of the ion molalities assuming complete dissociation. It will now be shown that $\phi_m$ defined this way can be used to evaluate $\gamma_\pm$.

The derivation is like that described in Sec. 9.6.3 for a binary solution of a nonelectrolyte. Solving Eq. 10.6.1 for $\mu_A$ and taking the differential of $\mu_A$ at constant $T$ and $p$, we obtain

$$d\mu_A = -RT M_A \nu (\phi_m \, dm_B + m_B \, d\phi_m) \qquad\qquad \text{(10.6.2)}$$

From Eq. 10.3.9, we obtain

$$d\mu_B = RT\nu \left( d\ln\gamma_\pm + \frac{dm_B}{m_B} \right) \qquad\qquad \text{(10.6.3)}$$

Substitution of these expressions in the Gibbs–Duhem equation $n_A \, d\mu_A + n_B \, d\mu_B = 0$, together with the substitution $n_A M_A = n_B / m_B$, yields

$$d\ln\gamma_\pm = d\phi_m + \frac{\phi_m - 1}{m_B} \, dm_B \qquad\qquad \text{(10.6.4)}$$

Then integration from $m_B = 0$ to any desired molality $m_B'$ gives the result

$$\ln\gamma_\pm(m_B') = \phi_m(m_B') - 1 + \int_0^{m_B'} \frac{\phi_m - 1}{m_B} \, dm_B \qquad\qquad \text{(10.6.5)}$$

The right side of this equation is the same expression as derived for $\ln\gamma_{m,B}$ for a nonelectrolyte (Eq. 9.6.20).

The integrand of the integral on the right side of Eq. 10.6.5 approaches $-\infty$ as $m_B$ approaches zero, making it difficult to evaluate the integral by numerical integration starting at $m_B = 0$. (This difficulty does not exist when the solute is a nonelectrolyte.) Instead, we can split the integral into two parts

$$\int_0^{m_B'} \frac{\phi_m - 1}{m_B} \, dm_B = \int_0^{m_B''} \frac{\phi_m - 1}{m_B} \, dm_B + \int_{m_B''}^{m_B'} \frac{\phi_m - 1}{m_B} \, dm_B \qquad\qquad \text{(10.6.6)}$$

where the integration limit $m_B''$ is a low molality at which the value of $\phi_m$ is available and at which $\gamma_\pm$ can either be measured or estimated from the Debye–Hückel equation.

We next rewrite Eq. 10.6.5 with $m_B'$ replaced with $m_B''$:

$$\ln\gamma_\pm(m_B'') = \phi_m(m_B'') - 1 + \int_0^{m_B''} \frac{\phi_m - 1}{m_B} \, dm_B \qquad\qquad \text{(10.6.7)}$$

By eliminating the integral with an upper limit of $m_B''$ from Eqs. 10.6.6 and 10.6.7, we obtain

$$\int_0^{m_B'} \frac{\phi_m - 1}{m_B} \, dm_B = \ln\gamma_\pm(m_B'') - \phi_m(m_B'') + 1 + \int_{m_B''}^{m_B'} \frac{\phi_m - 1}{m_B} \, dm_B \qquad\qquad \text{(10.6.8)}$$

Equation 10.6.5 becomes

$$\ln\gamma_{\pm}(m'_{\mathrm{B}}) = \phi_m(m'_{\mathrm{B}}) - \phi_m(m''_{\mathrm{B}}) + \ln\gamma_{\pm}(m''_{\mathrm{B}}) + \int_{m''_{\mathrm{B}}}^{m'_{\mathrm{B}}} \frac{\phi_m - 1}{m_{\mathrm{B}}}\,\mathrm{d}m_{\mathrm{B}} \qquad (10.6.9)$$

The integral on the right side of this equation can easily be evaluated by numerical integration.

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