10.2: Solution of a Symmetrical Electrolyte

Let us consider properties of an electrolyte solute as a whole. The simplest case is that of a binary solution in which the solute is a symmetrical strong electrolyte—a substance whose formula unit has one cation and one anion that dissociate completely. This condition will be indicated by $\nu = 2$, where ν is the number of ions per formula unit. In an aqueous solution, the solute with ν equal to 2 might be a 1:1 salt such as NaCl, a 2:2 salt such as $MgSO_4$, or a strong monoprotic acid such as HCl.

In this binary solution, the chemical potential of the solute as a whole is defined in the usual way as the partial molar Gibbs energy

$$\mu_B \overset{\text{def}}{=} \left(\frac{\partial G}{\partial n_B} \right)_{T,p,n_A} \tag{10.2.1}$$

and is a function of T, p, and the solute molality m_B. Although μ_B under given conditions must in principle have a definite value, we are not able to actually evaluate it because we have no way to measure precisely the energy brought into the system by the solute. This energy contributes to the internal energy and thus to G. We can, however, evaluate the differences $\mu_B - \mu_{m,B}^{\text{ref}}$ and $\mu_B - \mu_{m,B}^{\circ}$.

We can write the additivity rule (Eq. 9.2.25) for G as either

$$G = n_A \mu_A + n_B \mu_B \tag{10.2.2}$$

or

$$G = n_A \mu_A + n_+ \mu_+ + n_- \mu_- \tag{10.2.3}$$

A comparison of these equations for a symmetrical electrolyte ($n_B = n_+ = n_-$) gives us the relation

$$\mu_B = \mu_+ + \mu_- \tag{10.2.4}$$
$$(\nu=2)$$

We see that the solute chemical potential in this case is the *sum* of the single-ion chemical potentials.

The solution is a phase of electric potential ϕ. From Eqs. 10.1.4 and 10.1.5, the sum $\mu_+ + \mu_-$ appearing in Eq. 10.2.4 is

$$\mu_+(\phi) + \mu_-(\phi) = \mu_+(0) + \mu_-(0) + (z_+ + z_-)F\phi \tag{10.2.5}$$

For the symmetrical electrolyte, the sum $(z_+ + z_-)$ is zero, so that μ_B is equal to $\mu_+(0) + \mu_-(0)$. We substitute the expressions of Eq. 10.1.10, use the relation $\mu_{m,B}^{\text{ref}} = \mu_+^{\text{ref}} + \mu_-^{\text{ref}}$ with reference states at $\phi=0$, set the ion molalities m_+ and m_- equal to m_B, and obtain

$$\mu_B = \mu_{m,B}^{\text{ref}} + RT \ln \left[\gamma_+ \gamma_- \left(\frac{m_B}{m^{\circ}} \right)^2 \right] \tag{10.2.6}$$
$$(\nu=2)$$

The important feature of this relation is the appearance of the *second* power of m_B/m°, instead of the first power as in the case of a nonelectrolyte. Also note that μ_B does not depend on ϕ, unlike μ_+ and μ_-.

Although we cannot evaluate γ_+ or γ_- individually, we can evaluate the product $\gamma_+ \gamma_-$. This product is the square of the **mean ionic activity coefficient** $\gamma_{\pm}$, defined for a symmetrical electrolyte by

$$\gamma_{\pm} \overset{\text{def}}{=} \sqrt{\gamma_+ \gamma_-} \tag{10.2.7}$$
$$(\nu=2)$$

With this definition, Eq. 10.2.6 becomes

$$\mu_B = \mu_{m,B}^{\text{ref}} + RT \ln \left[(\gamma_{\pm})^2 \left(\frac{m_B}{m^{\circ}} \right)^2 \right] \tag{10.2.8}$$
$$(\nu=2)$$

Since it is possible to determine the value of $\mu_B - \mu_{m,B}^{\text{ref}}$ for a solution of known molality, $\gamma_{\pm}$ is a measurable quantity.

> If the electrolyte (e.g., HCl) is sufficiently volatile, its mean ionic activity coefficient in a solution can be evaluated from partial pressure measurements of an equilibrated gas phase. Section 10.6 will describe a general method by

which $\gamma_\pm$ can be found from osmotic coefficients. Section 14.5 describes how, in favorable cases, it is possible to evaluate $\gamma_\pm$ from the equilibrium cell potential of a galvanic cell.

The activity $a_{m,\mathrm{B}}$ of a solute substance on a molality basis is defined by Eq. 9.7.8:

$$\mu_{\mathrm{B}} = \mu_{m,\mathrm{B}}^\circ + RT \ln a_{m,\mathrm{B}} \tag{10.2.9}$$

Here $\mu_{m,\mathrm{B}}^\circ$ is the chemical potential of the solute in its standard state, which is the solute reference state at the standard pressure. By equating the expressions for μ_{B} given by Eqs. 10.2.8 and 10.2.9 and solving for the activity, we obtain

$$a_{m,\mathrm{B}} = \Gamma_{m,\mathrm{B}}(\gamma_\pm)^2 \left(\frac{m_{\mathrm{B}}}{m^\circ}\right)^2 \tag{10.2.10}$$
$$(\nu=2)$$

where $\Gamma_{m,\mathrm{B}}$ is the pressure factor defined by

$$\Gamma_{m,\mathrm{B}} \overset{\mathrm{def}}{=} \exp\left(\frac{\mu_{m,\mathrm{B}}^{\mathrm{ref}} - \mu_{m,\mathrm{B}}^\circ}{RT}\right) \tag{10.2.11}$$

We can use the appropriate expression in Table 9.6 to evaluate $\Gamma_{m,\mathrm{B}}$ at an arbitrary pressure p':

$$\Gamma_{m,\mathrm{B}}(p') = \exp\left(\int_{p^\circ}^{p'} \frac{V_{\mathrm{B}}^\infty}{RT}\, \mathrm{d}p\right) \approx \exp\left[\frac{V_{\mathrm{B}}^\infty (p' - p^\circ)}{RT}\right] \tag{10.2.12}$$

The value of $\Gamma_{m,\mathrm{B}}$ is 1 at the standard pressure, and close to 1 at any reasonably low pressure. For this reason it is common to see Eq. 10.2.10 written as $a_{m,\mathrm{B}} = \gamma_\pm^2 (m_{\mathrm{B}}/m^\circ)^2$, with $\Gamma_{m,\mathrm{B}}$ omitted.

Equation 10.2.10 predicts that the activity of HCl in aqueous solutions is proportional, in the limit of infinite dilution, to the *square* of the HCl molality. In contrast, the activity of a *non*electrolyte solute is proportional to the *first* power of the molality in this limit. This predicted behavior of aqueous HCl is consistent with the data plotted in Fig. 10.1, and is confirmed by the data for dilute HCl solutions shown in Fig. 10.2(a). The dashed line in Fig. 10.2(a) is the extrapolation of the ideal-dilute behavior given by $a_{m,\mathrm{B}} = (m_{\mathrm{B}}/m^\circ)^2$. The extension of this line to $m_{\mathrm{B}} = m^\circ$ establishes the hypothetical solute reference state based on molality, indicated by a filled circle in Fig. 10.2(b). (Since the data are for solutions at the standard pressure of 1 bar, the solute reference state shown in the figure is also the solute standard state.)

The solid curve of Fig. 10.2(c) shows how the mean ionic activity coefficient of HCl varies with molality in approximately the same range of molalities as the data shown in Fig. 10.2(b). In the limit of infinite dilution, $\gamma_\pm$ approaches unity. The slope of the curve approaches $-\infty$ in this limit, quite unlike the behavior described in Sec. 9.5.4 for the activity coefficient of a nonelectrolyte solute.

For a symmetrical strong electrolyte, $\gamma_\pm$ is the geometric average of the single-ion activity coefficients γ_+ and γ_-. We have no way of evaluating γ_+ or γ_- individually, even if we know the value of $\gamma_\pm$. For instance, we cannot assume that γ_+ and γ_- are equal.