

10.3: Electrolytes in General

The formula unit of a *nonsymmetrical* electrolyte solute has more than two ions. General formulas for the solute as a whole are more complicated than those for the symmetrical case treated in the preceding section, but are derived by the same reasoning.

Again we assume the solute dissociates completely into its constituent ions. We define the following symbols:

ν_+ = the number of cations per solute formula unit

ν_- = the number of anions per solute formula unit

ν = the sum $\nu_+ + \nu_-$

For example, if the solute formula is $\text{Al}_2(\text{SO}_4)_3$, the values are $\nu_+=2$, $\nu_-=3$, and $\nu=5$.

10.3.1 Solution of a single electrolyte

In a solution of a single electrolyte solute that is not necessarily symmetrical, the ion molalities are related to the overall solute molality by

$$m_+ = \nu_+ m_B \quad m_- = \nu_- m_B \quad (10.3.1)$$

From the additivity rule for the Gibbs energy, we have

$$\begin{aligned} G &= n_A \mu_A + n_B \mu_B \\ &= n_A \mu_A + \nu_+ n_B \mu_+ + \nu_- n_B \mu_- \end{aligned} \quad (10.3.2)$$

giving the relation

$$\mu_B = \nu_+ \mu_+ + \nu_- \mu_- \quad (10.3.3)$$

in place of Eq. 10.2.4. The cations and anions are in the same phase of electric potential ϕ . We use Eqs. 10.1.4 and 10.1.5 to obtain

$$\nu_+ \mu_+(\phi) + \nu_- \mu_-(\phi) = \nu_+ \mu_+(0) + \nu_- \mu_-(0) + (\nu_+ z_+ + \nu_- z_-) F \phi \quad (10.3.4)$$

Electrical neutrality requires that $(\nu_+ z_+ + \nu_- z_-)$ be zero, giving

$$\mu_B = \nu_+ \mu_+(0) + \nu_- \mu_-(0) \quad (10.3.5)$$

By combining Eq. 10.3.5 with Eqs. 10.1.10, 10.3.1, and 10.3.3, we obtain

$$\mu_B = \mu_B^{\text{ref}} + RT \ln \left[(\nu_+^{\nu_+} \nu_-^{\nu_-}) (\gamma_+^{\nu_+}) (\gamma_-^{\nu_-}) \left(\frac{m_B}{m^\circ} \right)^\nu \right] \quad (10.3.6)$$

where $\mu_B^{\text{ref}} = \nu_+ \mu_+^{\text{ref}} + \nu_- \mu_-^{\text{ref}}$ is the chemical potential of the solute in the hypothetical reference state at $\phi=0$ in which B is at the standard molality and behaves as at infinite dilution. Equation 10.3.6 is the generalization of Eq. 10.2.6. It shows that although μ_+ and μ_- depend on ϕ , μ_B does not.

The mean ionic activity coefficient γ_\pm is defined in general by

$$\gamma_\pm^\nu = (\gamma_+^{\nu_+}) (\gamma_-^{\nu_-}) \quad (10.3.7)$$

or

$$\gamma_\pm = (\gamma_+^{\nu_+} \gamma_-^{\nu_-})^{1/\nu} \quad (10.3.8)$$

Thus γ_\pm is a geometric average of γ_+ and γ_- weighted by the numbers of the cations and anions in the solute formula unit. With a substitution from Eq. 10.3.7, Eq. 10.3.6 becomes

$$\mu_B = \mu_B^{\text{ref}} + RT \ln \left[(\nu_+^{\nu_+} \nu_-^{\nu_-}) \gamma_\pm^\nu \left(\frac{m_B}{m^\circ} \right)^\nu \right] \quad (10.3.9)$$

Since $\mu_B - \mu_B^{\text{ref}}$ is a measurable quantity, so also is γ_\pm .

The solute activity, defined by $\mu_B = \mu_{m,B}^\circ + RT \ln a_{m,B}$, is

$$a_{m,B} = (\nu_+^{\nu_+} \nu_-^{\nu_-}) \Gamma_{m,B} \gamma_\pm^\nu \left(\frac{m_B}{m^\circ} \right)^\nu \quad (10.3.10)$$

where $\Gamma_{m,B}$ is the pressure factor that we can evaluate with Eq. 10.2.12. Equation 10.3.10 is the generalization of Eq. 10.2.10. From Eqs. 10.1.12, 10.1.13, and 10.2.11 and the relations $\mu_B^{\text{ref}} = \nu_+ \mu_+^{\text{ref}} + \nu_- \mu_-^{\text{ref}}$ and $\mu_B^\circ = \nu_+ \mu_+^\circ + \nu_- \mu_-^\circ$, we obtain the relation

$$\Gamma_{m,B} = \Gamma_+^{\nu_+} \Gamma_-^{\nu_-} \quad (10.3.11)$$

10.3.2 Multisolute solution

Equation 10.3.3 relates the chemical potential of electrolyte B in a binary solution to the single-ion chemical potentials of its constituent ions:

$$\mu_B = \nu_+ \mu_+ + \nu_- \mu_- \quad (10.3.12)$$

This relation is valid for each individual solute substance in a multisolute solution, even when two or more of the electrolyte solutes have an ion species in common.

As an illustration of this principle, consider a solution prepared by dissolving amounts n_B of BaI_2 and n_C of CsI in an amount n_A of H_2O . Assume the dissolved salts are completely dissociated into ions, with the I^- ion common to both. The additivity rule for the Gibbs energy of this solution can be written in the form

$$G = n_A \mu_A + n_B \mu_B + n_C \mu_C \quad (10.3.13)$$

and also, using single-ion quantities, in the form

$$G = n_A \mu_A + n_B \mu(\text{Ba}^{2+}) + 2n_B \mu(\text{I}^-) + n_C \mu(\text{Cs}^+) + n_C \mu(\text{I}^-) \quad (10.3.14)$$

Comparing Eqs. 10.3.13 and 10.3.14, we find the following relations must exist between the chemical potentials of the solute substances and the ion species:

$$\mu_B = \mu(\text{Ba}^{2+}) + 2\mu(\text{I}^-) \quad \mu_C = \mu(\text{Cs}^+) + \mu(\text{I}^-) \quad (10.3.15)$$

These relations agree with Eq. 10.3.12. Note that $\mu(\text{I}^-)$, the chemical potential of the ion common to both salts, appears in both relations.

The solute activity $a_{m,B}$ is defined by the relation $\mu_B = \mu_B^\circ + RT \ln a_{m,B}$ (Eq. 10.2.9). Using this relation together with Eqs. 10.1.7 and 10.1.14, we find that the solute activity is related to ion molalities by

$$a_{m,B} = \Gamma_{m,B} \gamma_{\pm}^{\nu} \left(\frac{m_+}{m^\circ} \right)^{\nu_+} \left(\frac{m_-}{m^\circ} \right)^{\nu_-} \quad (10.3.16)$$

where the pressure factor $\Gamma_{m,B}$ is defined in Eq. 10.2.11. The ion molalities in this expression refer to the constituent ions of solute B, which in a multisolute solution are not necessarily present in the same stoichiometric ratio as in the solute substance.

For instance, suppose we apply Eq. 10.3.16 to the solution of BaI_2 and CsI used above as an illustration of a multisolute solution, letting $a_{m,B}$ be the activity of solute substance BaI_2 . The quantities m_+ and m_- in the equation are then the molalities of the Ba^{2+} and I^- ions, and γ_{\pm} is the mean ionic activity coefficient of the dissolved BaI_2 . Note that in this solution the Ba^{2+} and I^- ions are not present in the 1:2 ratio found in BaI_2 , because I^- is a constituent of both solutes.

10.3.3 Incomplete dissociation

In the preceding sections of this chapter, the electrolyte solute or solutes have been assumed to be completely dissociated into their constituent ions at all molalities. Some solutions, however, contain *ion pairs*—closely associated ions of opposite charge. Furthermore, in solutions of some electrolytes (often called “weak” electrolytes), an equilibrium is established between ions and electrically-neutral molecules. In these kinds of solutions, the relations between solute molality and ion molalities given by Eq. 10.3.1 are no longer valid. When dissociation is not complete, the expression for μ_B given by Eq. 10.3.9 can still be used. However, the quantity γ_{\pm} appearing in the expression no longer has the physical significance of being the geometric average of the activity coefficients of the actual dissociated ions, and is called the **stoichiometric activity coefficient** of the electrolyte.

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