As discussed in Chapter 10, when a salt is dissolved in water or in other appropriate solvent, the molecules dissociate into ions. In aqueous solutions, strong electrolytes, that is, those formed from a strong acid neutralized with a strong base, will dissociate almost completely into ions, while weak electrolytes will dissociate only partially. In a media of lower dielectric constant than water, such as furfural, acetonitrile, alcohols, chloroacetic acid, dimethyle, acetone, acetic acid, or in their mixtures with water, conductivity measurements show that all electrolytes are increasingly weak; that is, they are partially associated, as the solvent moves down in the scale of dielectric constants. Thus, the classification of strong electrolytes as strong acids, bases, and their salts (chlorides, fluorides, sulfates of sodium, potassium, magnesium, copper, zinc, etc.) is only valid in aqueous media. On the other hand, weak electrolytes such as acetic acid or chloroacetic acid in concentrated aqueous solutions can associate to such a high degree as to change the properties of water as solvent. The dielectric constant of air is so low that there are no ions present in the vapor phase over a solution of a volatile electrolyte. All molecules are fully associated. In mercury or sodium lamps, ions exist in the vapor phase under a voltage difference and in the absence of air.

BASIC RELATIONS

With these considerations in mind, without specifying the extent of the actual dissociation in aqueous solution, for 1 mole of an electrolyte $E$ that in total dissociation would give $v_+ cations \ C^{z+}$ and $v_– anions \ A^{z–}$, we write

$$C_{v_+}A_{v_–} = v_+ C^{z+} + v_– A^{z–}$$

For a single electrolyte, the electroneutrality condition reduces to

$$v_+ Z_+ + v_– Z_– = 0 \quad (18.1)$$

In this equation, the sign of the charge is implicit in $Z_i$. For clarity, it is better to have the signs of the charges explicit and write

$$v_+ Z_+ = v_– |Z_–| \quad (18.1a)$$
Variations of this relation that are often used in the literature without further explanation may be confusing at first, so we write some of them in detail.

\[
\frac{1}{Z_+} = \frac{\nu_+}{\nu_+ |Z_-|} = \frac{\nu_+}{\nu_+ Z_+} \quad \text{(18.1b)}
\]

\[
\frac{1}{|Z_-|} = \frac{\nu_-}{\nu_+ Z_+} \quad \text{(18.1c)}
\]

One important form is obtained by multiplying Equation 18.1a first by \(|Z_-|\) to obtain

\[
\nu_+ |Z_+ Z_-| = \nu_- (Z_-)^2
\]

and then multiplying Equation 18.1a by \(Z_+\) to obtain

\[
\nu_+ (Z_+)^2 = \nu_- |Z_+ Z_-|
\]

Taking the difference of these two expressions and rearranging, we get

\[
|Z_+ Z_-| = \frac{\nu_+ (Z_+)^2 + \nu_- (Z_-)^2}{\nu_+ + \nu_-} \quad \text{(18.1d)}
\]

with

\[
\nu \equiv \nu_+ + \nu_-
\]

According to Equation 12.15, the equilibrium constant for the ionic dissociation in terms of activities takes the form

\[
K_T = \frac{a_+^{\nu_+} a_-^{\nu_-}}{a_E} \quad \text{(18.3)}
\]

For the dissociation of the electrolyte \(E\), according to Equation 12.16, the value of the equilibrium constant is obtained from the standard Gibbs energy change:

\[
K_T = \exp \left[ \frac{\mu_E^0 - \nu_+ \mu_+^0 - \nu_- \mu_-^0}{RT} \right] \quad \text{(18.4)}
\]

Some treatments of electrolyte solutions have proposed to use mole fractions as a measure of composition. For all practical purposes, the use of molality is simpler and gives a better range of values. As an example, the solubility of common salt (NaCl) in water at 298 K is 360 g kg\(^{-1}\) of water or 6.16 moles per 55.51 moles of water. Thus, at saturation, that is, the maximum concentration of salt possible at this temperature, the mole fraction of each ion is 0.100, while the molality is 6.16. Having decided to
use molality as the measure of concentration, the next step is to choose the standard states for the activity coefficients to be used in the evaluation of the activities by

\[ a_i = \tilde{m}_i \gamma_i = \nu_i \tilde{m} \gamma_i \]  

(18.5)

Thus, for the cation,

\[ a_+ = \tilde{m}_+ \gamma_+ = \nu_+ \tilde{m} \gamma_+ \]  

(18.5a)

and for the anion,

\[ a_- = \tilde{m}_- \gamma_- = \nu_- \tilde{m} \gamma_- \]  

(18.5b)

In this expression, as the activities are dimensionless, \( \tilde{m}_i \) is the dimensionless molality of the ion \( i \) and \( \tilde{m} \) is the dimensionless molality of the electrolyte solute; that is, the value of the molality divided by \( 1 [ \text{mole of } i / 1000 \text{g of solvent}] \). Similarly to the case of the use of molality for nonelectrolytes discussed in Chapter 15, the reference state for the activity coefficient of the ions is their state at infinite dilution, and their standard state is the ideal solution in Henry’s sense at \( 1 [ \text{mole of } i / 1000 \text{g of solvent}] \). At the reference state, the activity coefficient of an ion is normalized to unity.

\[ \lim_{\tilde{m}_i \to 0} \gamma_i = 1 \]  

(18.6)

**MEAN IONIC ACTIVITY COEFFICIENT**

At the standard state, the activity of an ion is equal to unity (dimensionless). This is so because in its standard state the ion is in an ideal solution at unit molality. The normalization of the activity coefficients of the ions to unity at their state in an infinitely dilute solution is of great importance. At this state, the presence of any other ion is immaterial, be it a co-ion or a counterion. Thus, the same condition is valid independently of the nature of the electrolyte generating the ion. With this normalization, although its value is not known, the standard state potential of an ion in solution is fixed and well defined, and it is independent where the ion came from. The standard state for the electrolyte is chosen so that the constant \( K_r \) in Equation 18.4 is equal to unity.

\[ \mu^\theta_E = \nu_+ \mu^\theta_+ + \nu_- \mu^\theta_- \]

Again here, the value of \( \mu^\theta_E \) for the electrolyte is not known, but we know that for each electrolyte it has a fixed and well-defined value depending only on the temperature and the pair of ions forming the electrolyte. Hence, from Equation 18.3 we write

\[ a_E = a_+ a_- = (\tilde{m}_+ \gamma_+) \nu_+ (\tilde{m}_- \gamma_-) \nu_- = \tilde{m} \gamma_{\pm} (\nu^\nu_+ \nu^\nu_-) \]  

(18.7)
where the mean ionic activity coefficient of the electrolyte $\gamma_\pm$ is defined as

$$\gamma_\pm^y \equiv \gamma^y_+ \gamma^y_-$$  \hspace{1cm} (18.8)

with $\nu \equiv \nu_+ + \nu_-$, as defined by Equation 18.2.

At infinite dilution, by normalization of the activity coefficients of the ions, we have

$$\lim_{m \to 0} \gamma_\pm = 1$$  \hspace{1cm} (18.9)

**OSMOTIC COEFFICIENT**

For a single electrolyte aqueous solution at constant temperature, neglecting pressure effects, the Gibbs-Duhem equation, which relates the changes in $a_E$ with the changes in the activity of water $a_w$, takes the form

$$n_E d \ln a_E + n_w d \ln a_w = 0$$

where $n_E = \tilde{m}$ and $n_w = 1000/M_w$ are the number of moles of salt and water, respectively.

$$\tilde{m} d \ln a_E + \frac{1000}{M_w} \phi \ln a_w = 0$$  \hspace{1cm} (18.10)

The activity of water is sometimes given in terms of the osmotic coefficient of the solution, defined as

$$\phi \equiv -\frac{1000}{M_w} \sum_{j} (\nu \tilde{m})_j \ln a_w$$  \hspace{1cm} (18.11)

For an aqueous solution of a nonvolatile electrolyte, the activity of water is obtained directly by measuring the vapor pressure, $P$, of the solution at the temperature of interest. From Equation 16.4, we write

$$a_w = x_w \gamma_w = \frac{P}{P^*[w]}$$  \hspace{1cm} (18.12)

Here, $P^*[w]$ is the vapor pressure of pure water at the temperature of the system. For work at high pressure, the correction factors included in Equation 16.2a should be included in Equation 18.12. It is of interest to obtain the relations between the osmotic coefficient of a single electrolyte solution, $\phi$, and the mean ionic activity coefficient of the electrolyte. For a single electrolyte in solution, Equation 18.11 takes the form

$$\ln a_w \equiv -\frac{M_w \nu \tilde{m}}{1000} \phi$$  \hspace{1cm} (18.11a)
Then,

\[ d \ln a_w \equiv -\frac{M_w \nu \tilde{m}}{1000} d\varphi - \frac{M_w \nu}{1000} \varphi d\tilde{m} \]

Combining this expression with the Gibbs–Duhem equation, Equation 18.10, we get

\[ d \ln a_E = \nu d\varphi + \nu \frac{d\tilde{m}}{\tilde{m}} \]

From Equation 18.7,

\[ d \ln a_E = \nu \frac{d\tilde{m}}{\tilde{m}} + \nu d \ln \gamma_\pm \]

Thus, equating these two expressions and rearranging, the relation between the osmotic coefficient of a single electrolyte solution and the mean ionic activity coefficient takes the form

\[ d \ln \gamma_\pm = d\varphi + \frac{(\varphi - 1)}{\tilde{m}} d\tilde{m} \]  (18.13)

This differential relation can be used to obtain the mean ionic activity coefficient in terms of the osmotic coefficient and vice versa. Integrating between the limit at infinite dilution, where the mean ionic activity coefficient and the osmotic coefficient tend to unity, and a molality \( m \),

\[ \ln \gamma_\pm = (\varphi - 1) + \int_0^{\tilde{m}} \frac{(\varphi - 1)}{m} d\tilde{m} \]  (18.14)

Because in Equation 18.14 the molality appears as a ratio, for simplicity, the tilde differentiating it from its dimensionless value is sometimes dropped. Rearranging Equation 18.13, we write

\[ \tilde{m} d \ln \gamma_\pm = \tilde{m} d\varphi + \varphi d\tilde{m} = d(\tilde{m}\varphi) - d\tilde{m} \]

or

\[ d(\tilde{m}\varphi) = \tilde{m} d \ln \gamma_\pm + d\tilde{m} \]

Integrating between the same limits as before and rearranging,

\[ \varphi = \frac{1}{\tilde{m}} \int_0^{\tilde{m}} \tilde{m} d \ln \gamma_\pm + 1 \]  (18.15)

Again, as the molality appears as a ratio in this expression, sometimes the difference between the molality and its dimensionless form is ignored.