The Thermodynamics of Aqueous Electrolyte Solutions

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 medium of lower dielectric constant than water, such as furfural, acetonitrile, alcohols, chloroacetic acid, dimethane, 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.

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

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

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

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

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

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

with

\[ \nu \equiv \nu_+ + \nu_- \quad (18.2) \]

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

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

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:

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

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[mole of \( i \)/1000g 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[mole of \( i \)/1000g 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 \( K_T \) in Equation 18.4 is equal to unity.

\[ \mu_E^\theta = \nu_+ \mu_+^\theta + \nu_- \mu_-^\theta \]

Again here, the value of \( \mu_E^\theta \) 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

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

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

$$\gamma_\pm \equiv \gamma_+ \gamma_-$$  \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,
\[
d \ln a_w = -\frac{M_w \nu \tilde{m}}{1000} d\varphi - \frac{M_w \nu}{1000} \varphi d\tilde{m}
\]

Combining this expression with the Gibbs–Duhem equation, Equation 18.10, we get
\[
d \ln a_E = \nu d\varphi + \nu \varphi \frac{d\tilde{m}}{\tilde{m}}
\]

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

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.
NEED FOR CONSIDERING THE EXISTENCE OF INDIVIDUAL IONS

One natural question arising at this point is why, for the thermodynamic treatment of strong electrolytes, one should go through all the trouble of considering independent ions in solution instead of defining an activity coefficient for the electrolyte as such by the relation

\[ \hat{a}_E = \hat{m} \gamma_E \]

The idea here is not to ignore the real existence of ions, which is evident from conductivity measurements, but to explore whether it is absolutely necessary to consider their existence for the thermodynamic treatment when it would be much simpler to consider the electrolyte as a single entity. The answer to this question is found by observing the behavior of the solution of an electrolyte in the very dilute region.

If we ignore the presence of ions and consider only the presence of molecules, we get from the above relation, in the very dilute region, when \( \gamma_E \to 1 \) and \( \hat{a}_E^{dil} = \hat{m} \), the following relation:

\[ \frac{d \ln \hat{a}_E^{dil}}{d \hat{m}} = \frac{1}{\hat{m}} \]

In addition, using the Gibbs–Duhem equation, Equation 18.10, we can calculate the slope of \( \ln \hat{a}_W^{dil} \) plotted versus the molality of salt \( \hat{m} \):

\[ \frac{d \ln \hat{a}_W^{dil}}{d \hat{m}} = -\frac{M_W}{1000} \]

On the other hand, if the presence of the ions is considered for thermodynamic treatment, in the dilute region, that is, when \( \gamma_E \to 1 \), Equation 18.7 gives

\[ a_E^{dil} = \hat{m}^{\nu}(\nu_+^{\nu_+} \nu_-^{\nu_-}) \]

and from Equation 18.11 we obtain

\[ \frac{d \ln a_W^{dil}}{d \hat{m}} = -\frac{\nu M_W}{1000} \]

Figure 18.1 shows a plot of \( -\ln a_W \) versus \( \hat{m} \) in the dilute region for NaCl (\( \nu = 2 \)) in aqueous solution at 298.2 K, and the slope of the line is 0.036, as predicted by the consideration of the ions, and not 0.018, as would be the case ignoring the ions in the thermodynamic approach.
The Thermodynamics of Aqueous Electrolyte Solutions

BEHAVIOR OF THE ACTIVITY OF INDIVIDUAL IONS

At high dilution, the ions of one kind are not affected by any other ion present in the solution. One reasonable question is whether, as the solution gets concentrated, the activity coefficient of an ion in the presence of a particular counterion will be the same or different from the activity coefficient of the same ion with a different counterion, both solutions at the same concentration and temperature. This question can be stated more clearly considering Equation 18.8 for solutions at the same concentration of two salts with the same anion, but with different cation. Consider, for example, a solution of a sodium salt with an anion \( Y^- \) and a potassium salt with the same anion, both solutions at the same concentration and temperature. If the activity coefficients of the anion were independent of the cation present, we would have

\[
\frac{(\gamma_Z^2)_{NaY}}{(\gamma_Z^2)_{KY}} \equiv \frac{\gamma_{Na^+} \gamma_{Y^-}}{\gamma_{K^+} \gamma_{Y^-}} = \frac{\gamma_{Na^+}}{\gamma_{K^+}}
\]

If this were true, the ratio of the mean ionic activity coefficients of two electrolytes with a common ion would have the same value independent of the nature of the common ion.


The Thermodynamics of Aqueous Electrolyte Solutions

Figure 18.2 shows the values of the left-hand side of this equation for aqueous solutions of electrolytes of the same cation with different anions at 298.2 K. Figure 18.3 shows the values of the left-hand side of this equation for aqueous solutions of electrolytes of the same anion with different cations at 298.2 K. These results show that at the same concentration, the activity coefficient of an ion is strongly dependent on the nature of the counterion present. At high dilution, the activity coefficient of an ion tends to be independent of the counterion, but as the solution becomes more concentrated, the ion behaves differently depending on its counterion.

DEBYE–HÜCKEL THEORY FOR DILUTE AQUEOUS ELECTROLYTE SOLUTIONS

Up to this point, we have made a deliberate effort to avoid introducing models or theories that are not part of the mathematical structure of thermodynamics. Models and theories change with time; the mathematics supporting the thermodynamic treatment of fluid systems does not. However, as a tool to discuss equations useful in the thermodynamic treatment of aqueous electrolyte solutions, we introduce here the expressions obtained by Debye and Hückel [4] for the treatment of dilute electrolyte solutions. This theory has stood the test of time.

Debye and Hückel developed a model by considering the mathematics of inserting charged particles (ions) into a solvent. In their model, based on what is called the MacMillan–Mayer framework, the solvent is not a component of the mixture, but it is just a background media supporting the ions. This restriction presents a problem for the thermodynamic treatment of electrolyte solutions in mixed solvents, but for all practical purposes, it can be ignored in the work of aqueous solutions or other single-solvent systems. For the activity coefficient of a single ion in a single solvent, Debye obtained the expression

\[ \ln \gamma_i = -\frac{A_D Z_i^2 I^{1/2}}{1 + B_{Di} I^{1/2}} + b_i I \]  

(18.16)

where \( A_D \) is a theoretical parameter that depends on the solvent and the temperature of the system. Although in principle \( B_{Di} \) is a parameter related to the size of the ion, in practice it is usually set equal to unity. The parameter \( b_i \) is an adjustable parameter. The ionic strength \( I \), written in terms of (dimensionless) molality, is defined as

\[ I = \frac{1}{2} \sum_{j=1}^{\text{all ions}} \tilde{m}_j Z_j^2 \]  

(18.17)

For a single electrolyte in solution, the ionic strength is given by

\[ I = \frac{\tilde{m}}{2} \sum_{j=1}^{\text{all ions}} \nu_j Z_j^2 \]  

(18.17a)
For 1:1 electrolytes such as HCl or NaCl, the ionic strength is numerically equal to the (dimensionless) molality. The Debye–Hückel expression for the mean ionic activity coefficient of the electrolyte obtained from Equation 18.8, assuming the same value of $B_D$ for the cation and the anion, can be written as

\[
\ln \gamma_\pm = -\frac{A_D |Z_+ Z_-| I^{1/2}}{1 + B_D I^{1/2}} + bl
\]

With

\[
b = \frac{(\nu_+ b_+ + \nu_- b_-)}{\nu}
\]

The absolute value of the product of the charges of the ions in Equation 18.18 arises from the relation of electrical neutrality for the electrolyte, Equation 18.1d. From Equation 18.10, the activity coefficient for water in a single electrolyte aqueous solution obtained from the Debye–Hückel theory is

\[
\ln \gamma_w = \frac{2A_D M_w}{(10B_D)} \left[ (1 + B_D I^{1/2}) \frac{1}{(10B_D I^{1/2})} - 2 \ln(1 + B_D I^{1/2}) \right] + \ln \left[ 1 + \frac{\nu M_w \tilde{m}}{1000} \right] - \frac{\nu M_w \tilde{m}}{1000} \left( 1 + \frac{bl}{2} \right)
\]

(18.19)

**LIMITING VALUES OF THE MEAN IONIC ACTIVITY COEFFICIENT AND THE OSMOTIC COEFFICIENT AT HIGH DILUTION**

One immediate application of the Debye–Hückel equation is to obtain explicitly the limiting value of the osmotic coefficients as the ionic strength goes to zero. As it can be seen from the definition of the osmotic coefficient by Equation 18.11, and more clearly from the case of a single electrolyte in solution, as the molality of the solute goes to zero, the activity of water goes to unity and its logarithm goes to zero, so no clear limiting behavior for the osmotic coefficient is obtained. At high dilution, the limiting behavior obtained from the Debye–Hückel equation takes the form

\[
\ln \gamma_w^m = -A_D |Z_+ Z_-| I^{1/2}
\]

(18.20)

Thus, according to Equation 18.17a, for a single electrolyte in solution,

\[
\ln \gamma_w^m = -A_D |Z_+ Z_-| \left( \frac{1}{2} \right)^{1/2} \tilde{m}^{1/2} = -A_v \tilde{m}^{1/2}
\]

(18.20a)
We have indicated by a subscript $\gamma$ in the Debye–Hückel constant $A$ that for any electrolyte other than type 1:1, the value of this constant is modified in this step. This fact is normally ignored in texts. Inserting Equation 18.20a into Equation 18.15, we observe that in the dilute region the osmotic coefficient is given by

$$\varphi = \lim_{\bar{m} \to 0} \int_0^{\bar{m}} \frac{A_\gamma}{\bar{m}} d(\bar{m}^{1/2}) + 1 = -\frac{A_\gamma}{3} \bar{m}^{1/2} + 1$$

Hence,

$$\lim_{\bar{m} \to 0} \varphi = 1 \quad (18.21)$$

As discussed in Chapter 20, this limiting behavior of the osmotic coefficient is well known for the case of the osmotic pressure in the study of nonelectrolyte solutions, but it is not immediately obvious for aqueous electrolyte solutions. In addition, for electrolyte aqueous solutions, this limiting behavior seems to create a problem with the value of the integrand at the lower limit of the integral in Equation 18.14.

$$\ln \gamma_e = (\varphi - 1) + \int_0^{\bar{m}} \frac{(\varphi - 1)}{\bar{m}} d\bar{m} \quad (18.14)$$

Again in this case, at the limit of infinite dilution the integrand seems to be undefined. However, the behavior of the osmotic coefficient in the dilute region just obtained shows that

$$\lim_{\bar{m} \to 0} \left[ \frac{\varphi - 1}{\bar{m}^{1/2}} \right] = -\frac{A_\gamma}{3} \quad (18.22)$$

This result suggests that a change in the denominator of the integrand of Equation 18.14 from $\bar{m}$ to $\bar{m}^{1/2}$ would solve the problem. This is achieved noting that

$$\frac{d}{d\bar{m}} \left( \bar{m}^{1/2} \right) = \frac{1}{2} \bar{m}^{-1/2} = \frac{1}{2} \bar{m}^{1/2}$$

or

$$2 \frac{d(\bar{m}^{1/2})}{\bar{m}^{1/2}} = \frac{d\bar{m}}{\bar{m}}$$

Hence, Equation 18.14 is written as

$$\ln \gamma_e = (\varphi - 1) + 2 \int_0^{\bar{m}} \frac{(\varphi - 1)}{\bar{m}^{1/2}} d\bar{m}^{1/2} \quad (18.14a)$$
In this form, at the lower limit of integration the integrand has a well-defined value given by Equation 18.22. For this reason, experimentally measured values of the osmotic coefficient or of the mean ionic activity coefficient are fitted with advantage as a function of $\tilde{m}^{1/2}$ instead of $\tilde{m}$.

**INDIRECT MEASUREMENT OF THE MEAN IONIC ACTIVITY COEFFICIENT**

Equation 18.14a is the basic relation for calculating the mean ionic coefficient from the osmotic coefficient data. The vapor pressure of water (or solvent) is measured under isothermal conditions for different molalities of a single electrolyte in solution. The activity of water is then obtained from Equation 18.12, and the osmotic coefficient calculated from Equation 18.11a. The values of the osmotic coefficient are then correlated as a function of molality, usually in terms of $\tilde{m}^{1/2}$, and the smooth function is used with Equation 18.14a to obtain values of the mean ionic activity coefficient $\gamma_\pm$ as a function of molality.

**DIRECT ELECTROCHEMICAL MEASUREMENT OF THE MEAN IONIC ACTIVITY COEFFICIENT**

The mean ionic activity coefficient of an electrolyte in aqueous solution can be obtained measuring the potential difference between the responses of an ion-selective electrode (ISE) sensitive to the cation and an ISE sensitive to the anion. These ISEs, of which the pH meter is a precursor, are commercially available for most ions of practical interest. The voltage response $E_{i,k}$ of an ISE sensitive to ion $i$ at molality $\tilde{m}_{i,k}$ in aqueous solution is given by the Nernst equation:

$$E_{i,k} = E_{i,0} + \frac{RT}{Z_iF} \ln(a_{i,k})$$  \hspace{1cm} (18.23)

In this equation, other than the usual symbols $R$, $T$, $Z_i$, and $a_{i,k}$ for the gas constant, the absolute temperature, the charge of the ion, and the activity of ion $i$ at molality $\tilde{m}_{i,k}$, $F$ is the Faraday constant and $E_{i,0}$ is the standard electrode potential. As the ISEs are transient instruments, the standard electrode potential has a constant value only over relatively short lapses of time. If an ISE is immersed in the same solution on different days, the standard electrode potential will have different values. Hence, either measurements are carried out in continuous runs in short periods of time, or if carried out on different days, the electrodes should be recalibrated as explained below. For clarity, we write the Nernst equation for the cation and for the anion as

$$E_{+,k} = E_{+,0} + \frac{RT}{Z_+F} \ln(a_{+,k})$$

and

$$E_{-,k} = E_{-,0} - \frac{RT}{|Z_-|F} \ln(a_{-,k})$$
If both electrodes are immersed in the same solution at the same time and their responses are measured directly one against the other in a voltmeter, the voltage difference is

$$\Delta E_k = \Delta E_0 + \frac{RT}{F} \ln \left( \frac{1}{a_{+,k}} \frac{1}{a_{-,k}} \right)$$ \hspace{1cm} (18.24a)

Now, using Equations 18.1b and 18.1c, we write

$$\left[ \frac{1}{a_{+,k}} \frac{1}{a_{-,k}} \right] = \left[ a_{+,k} a_{-,k} \right]^{\nu, Z}$$

But, according to Equation 18.7,

$$a^\nu_+ a^-_-= \bar{m}^\nu \gamma^\nu_\pm (\nu^\nu_+ \nu^-)$$

so,

$$\Delta E_k = \Delta E_0 + \frac{RT}{(\nu, Z)} \ln \left[ \bar{m}^\nu \gamma^\nu_\pm \left( \nu^\nu_+ \nu^- \right) \right]$$ \hspace{1cm} (18.24b)

The only residual problem is the evaluation of $\Delta E$. This is usually done by measuring several points in the dilute region where the mean ionic activity coefficient can be obtained from Equation 18.18 approximated as

$$\ln \gamma^\text{dil}_\pm = - \frac{A_D |Z_+ Z_-| I^{1/2}}{1 + I^{1/2}}$$

The rewarding result is that the mean ionic activity coefficient values for different electrolytes obtained by the direct electrochemical measurements agree with the values obtained by measurement of the osmotic coefficient.

**ELECTROCHEMICAL MEASUREMENT OF THE MEAN IONIC ACTIVITY COEFFICIENT WITH INDEPENDENT MEASUREMENTS FOR THE CATION AND THE ANION**

Although, as discussed above, the mean ionic activity coefficient can be measured connecting both ISEs, for the cation and for the anion, directly to a voltmeter, it is also instructive to consider the case of measuring each voltage response separately against a single-junction reference electrode, as shown in Figure 18.4. The reference electrode is immersed in an internal standard solution that leaks into the sample solution, creating a liquid junction potential at the surface of contact between the two solutions. This contact between the sample solution and the reference solution is...
necessary to close the electric circuit. In this case, the voltage response of the electrodes for an ion \( i \) takes the form

\[
E_{i,k}^R = E_{i,0}^R + \frac{RT}{Z_i F} \ln(a_{i,k}) + E_{J,k}
\]  

(18.25)

Thus, we write for the cation and for the anion

\[
E_{+k}^R = E_{+0}^R + \frac{RT}{Z_+ F} \ln(a_{+k}) + E_{J,k}
\]

\[
E_{-k}^R = E_{-0}^R - \frac{RT}{|Z_-| F} \ln(a_{-k}) + E_{J,k}
\]

We have used a superscript \( R \) to indicate that in this case, the voltage response is measured against a reference electrode and its value will be different from the value obtained in the previous experimental setup. The additional term, \( E_{J,k} \), is due to the junction potential generated by the contact of the sample solution with the reference solution that happens at the tip of the reference electrode. This junction potential will have the same value for the responses of both ISEs connected to the same reference electrode in simultaneous measurements. Taking the difference of both independent readings, we obtain

\[
\Delta E_k^R = \Delta E_0^R + \frac{RT}{F} \ln \left[ \frac{1}{a_{+k}^{Z_+}} \frac{1}{a_{-k}^{Z_-}} \right]
\]  

(18.24c)
Equation 18.24c is formally identical to Equation 18.24a and by calibration of the value of $\Delta E_0^E$ will yield values for the mean ionic activity coefficients of the electrolyte. Again, the rewarding result is that the mean ionic activity coefficient values for different electrolytes obtained by this approach agree with the values obtained by the direct electrochemical procedure and with the values obtained from measurements of the osmotic coefficient.

**ACTIVITY OF A SECOND SOLUTE IN AN AQUEOUS ELECTROLYTE SOLUTION**

The direct measurement of the mean ionic activity coefficient of an electrolyte using ISEs opens the possibility of determining the activity of a water-soluble solute dissolved in an electrolyte aqueous solution. According to Equation 7.11, for a solute $A$ in an aqueous solution with an electrolyte $E$,

$$\left[ \frac{\partial \mu_A}{\partial \tilde{m}_A} \right]_{T, \tilde{m}_E} = \left[ \frac{\partial \mu_E}{\partial \tilde{m}_A} \right]_{T, \tilde{m}_E}$$

Considering

$$\mu_A = \mu_A^0 + RT \ln(\tilde{m}_A \gamma_A)$$

and

$$\mu_E = \mu_E^0 + RT \ln(\tilde{m}_E^0 \gamma_A^0 \gamma_v^+ \gamma_v^-)$$

we obtain

$$\left[ \frac{\partial \ln \gamma_A}{\partial \tilde{m}_E} \right]_{T, \tilde{m}_A} = \nu \left[ \frac{\partial \ln \gamma_v^+}{\partial \tilde{m}_A} \right]_{T, \tilde{m}_E}$$

Thus, integrating between 0 and $\tilde{m}_E$, at constant $m_A$,

$$\ln \left( \frac{\gamma_A^{(2)}}{\gamma_A^{(1)}} \right) = \nu \int_0^{\tilde{m}_E} \left[ \frac{\partial \ln \gamma_v^+}{\partial \tilde{m}_A} \right]_{T, \tilde{m}_E} d\tilde{m}_E \quad (18.26)$$

In this expression, the superscripts (1) and (2) indicate the value of the activity coefficient of the solute $A$ in the absence of electrolyte and in the presence of electrolyte, respectively, both at the same molality of solute $A$. The former value should be available from independent measurements, usually from the isopiestic method in the case of nonelectrolytes. In order to obtain the activity coefficient of the solute $A$ in the presence of the electrolyte, measurements are made of the mean ionic activity coefficient of the electrolyte at fixed values of the molality of the electrolyte.
changing the concentration of the solute \( A \). These results are then correlated by a function of the form

\[
\ln \left[ \frac{\gamma^{(2)}_E}{\gamma^{(1)}_E} \right] = \sum_{k=1}^{C_k} m^k_A
\]

Usually, no more than three or four terms are required in the right-hand side of this equation. Again here, the superscripts (1) and (2) indicate the value of the activity coefficient of the electrolyte in the absence of solute \( A \) and in the presence of solute \( A \), respectively, both at the same molality of the electrolyte. The former value should be available from independent measurements. The values of the coefficients \( C_k \) are correlated as a function of the molality of the electrolyte.

\[
C_k = \sum_{j=1}^{c_j} m^j_E
\]

The rest is simple algebra necessary to obtain the value of the right-hand side of Equation 18.26 and get values of \( \gamma^{(2)}_E \).

**AQUEOUS SOLUTIONS OF WEAK ELECTROLYTES**

For weak electrolytes, only a fraction \( \alpha \) of the electrolyte added to the solution will ionize so that the activity of the electrolyte that can be obtained from the activity of water, by means of the Gibbs–Duhem equation, is an effective value. In this case, with a degree of dissociation \( \alpha \), the molality of the ion \( j \) in solution would be \( \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \nu \n
contain the cation or the anion of the weak electrolyte is added to the solution, the ionic strength will increase, and thus the value of the mean ionic activity coefficient will decrease, resulting in an increase of the degree of dissociation $\alpha$. If the added electrolyte contains either the cation or the anion of the weak electrolyte, the activity of the common ion will increase, and as the dissociation constant does not change, the activity of the undissociated electrolyte must increase; that is, the degree of dissociation decreases. This is the so-called common ion effect.

**CHARGED ORGANIC MOLECULES**

Amino acids are organic compounds having an amino group, $\text{–NH}_2$, and a carboxylic group, $\text{–COOH}$, attached to a hydrocarbon chain. Without going into the chemistry of amino acids, with the sole interest in their behavior in aqueous electrolyte solutions, we observe that most of the common amino acids at pH above 9.4 have the carboxyl group negatively charged, $\text{–COO}^-$, and at pH below 2.2, the amino group is positively charged, $\text{–NH}_3^+$. At a pH between 2.2 and 9.4, the amino acid has both a negative carboxyl group and a positive amino group. This state with zero net charge is known as the zwitterionic form from the German word *zwitter*, meaning “hybrid.” At the midpoint between the two limiting values of pH, the amino acid has a weak positive charge in the amino group and a weak negative charge in the hydroxyl group that closely compensate. This state is known as the isoelectric point, and the pH is designated as the pI of the amino acid. The interesting point is that at the isoelectric point the amino acid presents a minimum in its solubility in water. Amino acids associate in chains known as peptides, and peptides associate in larger molecules known as proteins, of which enzymes are a special kind presenting catalytic properties. In aqueous solutions, the presence of electrolytes, such as $(\text{NH}_4)_2\text{SO}_4$, for example, affects the solubility of proteins. In a dilute electrolyte solution, the protein is more soluble than in pure water, but if the concentration of the electrolyte is increased beyond a certain point, the protein is less soluble than in pure water. These behaviors are known as the salting in and salting out of the protein by changing the concentration of the electrolyte.

Different kinds of charged organic molecules are the so-called ionic liquids. These are organic salts that are in liquid phase at temperatures below the boiling point of water. This temperature limit is rather arbitrary, but it comes from the possibility of using these ionic liquids as solvents for green chemistry synthesis. Although ionic liquids are rather viscous, they have low volatility and high thermal stability properties that make them recyclable.

**EXPERIMENT TO DETERMINE THE CHARGE OF A PROTEIN**

The molecules of proteins behave as polyions in aqueous solutions and are too large to pass through some membranes, while other ions can. When one such polyelec- trolyte is in an aqueous solution on one side of a membrane and some electrolyte formed by small ions, NaCl, for example, and water can freely pass through the membrane, we are in the presence of the Donnan equilibrium described in Chapter 10. Due to the condition of electroneutrality on both sides of the membrane...
and the inability of a polyanion to migrate, ions are at different concentrations on each side of the membrane. This causes a difference in electric potential to arise between the two phases. As an illustration of the chemical equilibrium between ionic species separated by a permeable membrane, we discuss here an experiment designed for the determination of the charge of the sodium salt of an anionic protein. There are many kinds of membranes. Thus, the first step is to decide what kind of membrane is appropriate for the purpose. Some membranes are permeable only to the solvent; some are more permeable to cations than to anions or vice versa. It is known that biological membranes behave differently when they are part of a living tissue than when they are not. For this reason, the consideration of equilibrium in living biological systems may be a very poor assumption. As a general rule, it has been observed that single charged ions, such as Na\(^+\) or Cl\(^-\), permeate through membranes more easily than polycharged ions, such as Ba\(^{2+}\) or SO\(_4^{2-}\); hence, for this experiment NaCl is chosen as the electrolyte. The membrane is chosen to be permeable to both the sodium and the chloride ions. Figure 18.5a presents the experimental setup in which the same weight of deionized water is charged on both sides of the membrane, a molality \(m_p\) of the protein is charged to the left side of the cell, and a molality \(m\) of sodium chloride is charged to the right side. After equilibration, a molality \(m_{\text{eq}}\) of Cl\(^-\) is measured by titration of the solution in the right-hand side of the membrane (Figure 18.5b).

The dissociation equilibrium of the sodium salt of the anionic protein \(P\) with a negative charge \(|Z_p|\) is given by

\[
PNa_{[\xi_P]} = P^{[\xi_P]} + |Z_p|Na^+ \]

The charge balance of the solution in the left side of the membrane where there is the polyanion plus chloride and sodium ions is

\[
|Z_p| m_p + m_{-,L} = m_{+,L} \quad (18.28)
\]

**FIGURE 18.5** The system protein + electrolyte separated by an electrolyte-permeable membrane: (a) immediately after loading and (b) after the equilibrium is established.
or

$$|Z_P| = \frac{m_{+L} - m_{-L}}{m_P}$$  \hspace{1cm} (18.28a)

The molality of chloride ions on the right-hand side of the membrane after \(m_{-L}\) moles of chloride ion migrated to the left-hand side of the membrane is

$$m_{-R} = m - m_{-L}$$

Hence, the charge balance on the right-hand side of the membrane gives

$$m_{+R} = m_{-R} = m - m_{-L}$$ \hspace{1cm} (18.29)

In order to obtain the molality of sodium in the left-hand side of the membrane, we apply the expression for the Donnan equilibrum,

$$\left[ \frac{a_{+L}}{a_{-R}} \right]^{v_+} = \left[ \frac{a_{-R}}{a_{-L}} \right]^{v_-}$$

For NaCl, \(v_+ = v_- = 1\), so we write

$$\left[ \frac{m_{+L} \gamma_{+L}}{m_{+R} \gamma_{+R}} \right] = \left[ \frac{m_{-R} \gamma_{-R}}{m_{-L} \gamma_{-L}} \right]$$

Although in complete thermodynamic rigor the dimensionless molalities should be used for activities, in order to simplify the nomenclature, we are ignoring this requirement here. Thus, using the definition of the mean ionic activity coefficient,

$$m_{v,L} = \left[ \frac{m_{+R}}{m_{-L}} \right] \left[ \frac{\gamma_{z,R}}{\gamma_{z,L}} \right]^2$$

Replacing in this expression the molalities of sodium and chloride in the right-hand side of the membrane given by Equation 18.29, we write

$$m_{+L} = \left( \frac{m - m_{-L}}{m_{-L}} \right)^2 \left[ \frac{\gamma_{z,R}}{\gamma_{z,L}} \right]^2$$ \hspace{1cm} (18.30)

Thus, \(|Z_P|\) is directly obtained from Equation 18.28a. The mean ionic activity coefficient of sodium chloride in the right-hand side of the membrane can be obtained using the Debye–Hückel expression at low concentrations of NaCl or more complex correlations for concentrated solutions. On the other hand, the mean ionic activity coefficient of sodium chloride in the protein side of the membrane is not easily
evaluated because the charged protein increases the ionic strength of the solution on that side of the membrane. If we assume that the mean activity coefficients of NaCl have the same value on both sides of the membrane, from Equation 18.30,

\[ m_{+L} m_{-L} = (m - m_{-L})^2 \]

Replacing back \( m_{+L} \) from Equation 18.28,

\[ (|Z_p|m_p + m_{-L})m_{-L} = (m - m_{-L})^2 \]

and expanding and rearranging,

\[ m_{-L} = \frac{m}{2 + |Z_p|m_p/m} \]

From this approximate expression, it can be seen that less than half of the NaCl added to the right-hand side permeated to the left-hand side. Thus, the contribution to the ionic strength of the charged protein on the left-hand side is compensated to some extent by the smaller concentration of NaCl, and the ratio of the activity coefficients in Equation 18.30 can be set to unity as a good approximation.

**CONCLUSIONS**

In this chapter, we have presented a general view and the main concepts necessary for the understanding of the behavior of aqueous electrolyte solutions. This is just the starting point for more detailed studies. One case of interest, for example, is the measurement of the activity of individual ions, which is discussed in Chapter 27.

**REFERENCES**