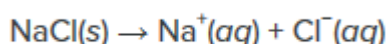


Electrolyte Solutions

Electrolytes are salts or molecules that ionize in solution. As a result, electrolyte solutions readily conduct electricity. This is because when a salt dissolves, its dissociated ions can move freely in solution, allowing a charge to flow.



There are two types of electrolyte solutions which are strong and weak electrolytes

Strong electrolytes will easily produce ions when dissolved. For example: Sodium Chloride, Chloride Acid and Sodium Hydroxide



[Ionic compound]

[Strong electrolyte]

(6-29).

weak electrolytes produce only a few ions, the rest will be neutral molecules. equilibrium between the molecules and the ions is established. for example : Acetic Acid, Carbonic Acid.



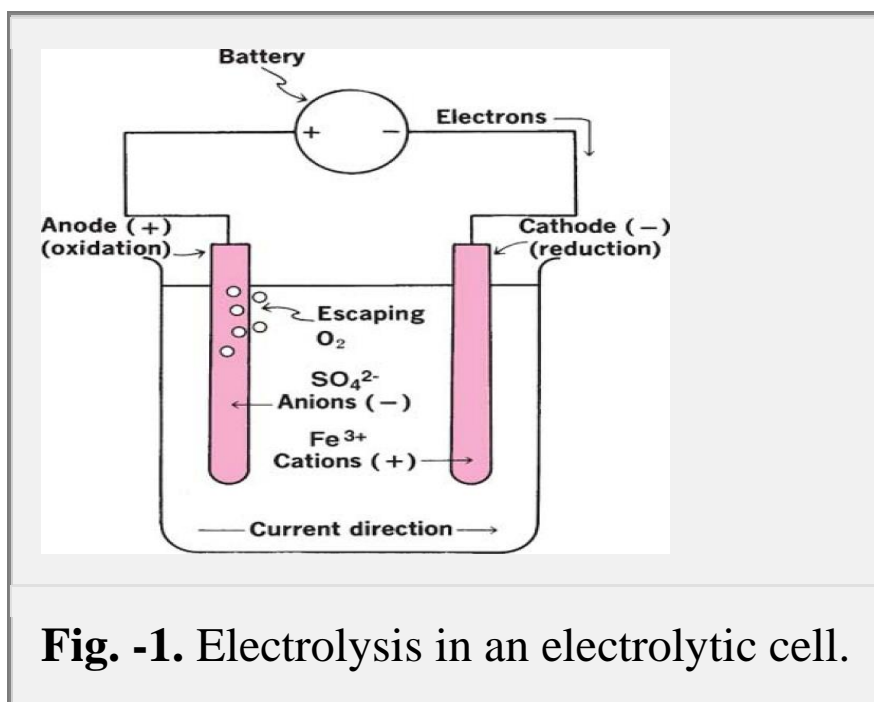
[Covalent
compound]

[Weak electrolyte]

(6-31)

Properties of Solutions of Electrolytes (Electrolysis)

under a potential of several volts, a direct electric current (dc) flows through an electrolytic cell (Fig. -1), a chemical reaction occurs. The process is known as **electrolysis**.



Electrons enter the cell from the battery or generator at the *cathode*; they combine with *cations* in the solution, and the cations are accordingly reduced. The *anions* carry electrons through the solution and discharge them at the *anode* and the anions are accordingly oxidized.

Reduction is the addition of electrons to a chemical species, Reduction occurs at the cathode

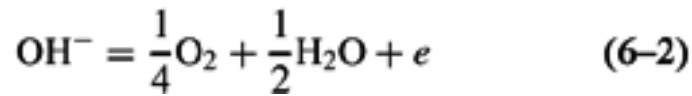
Oxidation is removal of electrons from a species. Oxidation occurs at the anode

The current in a solution consists of a flow of positive and negative ions toward the electrodes where the electrons are removed from a chemical species in solution and go into the external circuit.

In the electrolysis of a solution of ferric sulfate in a cell containing platinum electrodes, a ferric ion migrates to the cathode and is reduced:



hydroxyl ions of the water are converted into molecular oxygen,. The oxidation reaction at the anode is



Transference Numbers

The flow of electrons through the solution from right to left in Figure 1 is accomplished by the movement of cations to the right as well as anions to the left. The fraction of total current carried by the cations or by the anions is known as the **transport or transference number t_+ or t_-** :

$$t_+ = \frac{\text{Current carried by cations}}{\text{Total current}} \quad (6-4)$$

$$t_- = \frac{\text{Current carried by anions}}{\text{Total current}} \quad (6-5)$$

The sum of the two transference numbers is obviously equal to unity:

$$t_+ + t_- = 1 \quad (6-6)$$

The transference numbers are related to the **velocities** of the ions, the faster-moving ion carrying the greater fraction of current. The velocities of the ions in turn depend on **hydration** as well as ion **size** and **charge**.

Electrical Units

According to **Ohm's law**, the strength of an electric current (I) in amperes flowing through a metallic conductor is related to the difference in applied potential or voltage (E) and the resistance (R) in ohms, as follows:

$$I = \frac{E}{R} \quad (6-7)$$

The **current strength** (I) is the rate of flow of current or the quantity of electricity Q (electronic charge) in coulombs flowing per unit time:

$$I = \frac{Q}{t} \quad (6-8)$$

The quantity of electric charge is expressed in coulombs (1 coulomb = 3×10^9 electrostatic units of charge, or esu), the current in amperes, and the electric potential in volts

$$\text{Electric energy} = E \times Q \quad (6-10)$$

Faraday's laws

Faraday's laws can be summarized by

$$m = \left(\frac{Q}{F} \right) \left(\frac{M}{z} \right)$$

where:

- m is the mass of the substance liberated at an electrode in gms
- Q is the total electric charge passed through the substance in coulombs
- $F = 96485.332 \text{ C mol}^{-1}$ is the [Faraday constant](#)
- M is the molar mass of the substance in grams per mol
- z is the valency number of [ions](#) of the substance (electrons transferred per ion).

Note that M/z is the same as the [equivalent weight](#) of the substance altered.

$$m = \left(\frac{It}{F}\right) \left(\frac{M}{z}\right)$$

and then to

$$n = \left(\frac{It}{F}\right) \left(\frac{1}{z}\right)$$

n is the amount of substance ("number of moles")
liberated: $n = m/M$

Electrolytic Conductance

The resistance, R , in ohms of any uniform metallic or electrolytic conductor is directly proportional to its length, l , in cm and inversely proportional to its cross-sectional area, A , in cm^2 ,

$$R = \rho \frac{l}{A} \quad (6-13)$$

where ρ (specific resistance) is the resistance between opposite faces of a 1-cm cube of the conductor and is known as the .

The conductance, C , is the reciprocal of resistance,

$$C = \frac{1}{R} \quad (6-14)$$

conductance, C can be considered as a measure of the ease with which current can pass through the conductor. It is expressed in reciprocal ohms or mhos. From equation (6-13):

$$C = \frac{1}{R} = \frac{1}{\rho} \frac{A}{l} \quad (6-15)$$

The specific conductance κ is the reciprocal of specific resistance and is expressed in mhos/cm:

$$\kappa = \frac{1}{\rho} \quad (6-16)$$

The relationship between specific conductance and conductance or resistance is obtained by combining equations (6-15) and (6-16):

$$\kappa = C \frac{l}{A} = \frac{l}{R A} \quad (6-17)$$

the cell constant, K . Equation (6-17) thus can be written as

$$\kappa = KC = K/R \quad (6-19)$$

It would be difficult to measure l and A , but it is a simple matter to determine the cell constant experimentally. The specific conductance of several standard solutions has been determined in carefully calibrated cells.

Example 6-1

Calculating K

A 0.1-decimal solution of KCl was placed in a cell whose constant K was 0.012856 mho/cm. The resistance R was found to be 34.69 ohms at 25°C.

$$\begin{aligned} K &= \kappa R = 0.012856 \text{ mho/cm} \times 34.69 \text{ ohms} \\ &= 0.4460 \text{ cm}^{-1} \end{aligned}$$

Example 6-2

Calculating Specific Conductance

When the cell described in Example 6-1 was filled with a 0.01 N Na_2SO_4 solution, it had a resistance of 397 ohms. What is the specific conductance? We write

$$\kappa = \frac{K}{R} = \frac{0.4460}{397} = 1.1234 \times 10^{-3} \text{ mho/cm}$$

Equivalent Conductance

Equivalent conductance Λ is defined as the conductance of a solution of sufficient volume to contain 1 g equivalent of the solute when measured in a cell in which the electrodes are spaced 1 cm apart.

$$V = \frac{1000 \text{ cm}^3/\text{liter}}{c \text{ Eq/liter}} = \frac{1000}{c} \text{ cm}^3/\text{Eq} \quad (6-20)$$

The equivalent conductance Λ_c is obtained when the specific conductance κ is multiplied by V ,

$$\begin{aligned}\Lambda_c &= \kappa \times V \\ &= \frac{1000 \kappa}{c} \text{ mho cm}^2/\text{Eq}\end{aligned}\quad (6-21)$$

the equivalent conductance expressed in units of **mho cm²/Eq**

Example 6-3

Specific and Equivalent Conductance

The measured conductance of a 0.1 N solution of a drug is 0.0563 ohm at 25°C. The cell constant at 25°C is 0.520 cm⁻¹. What is the specific conductance and what is the equivalent conductance of the solution at this concentration?

$$\kappa = 0.0563 \times 0.520 = 0.0293 \text{ mho/cm}$$

$$\Lambda_c = 0.0293 \times 1000/0.1$$

$$= 293 \text{ mho cm}^2/\text{Eq}$$

Equivalent Conductance of Strong and Weak Electrolytes

As the solution of a strong electrolyte is diluted, the *specific conductance* κ decreases because the number of ions per unit volume of solution is reduced.

Conversely, the *equivalent conductance* Λ of a solution of a strong electrolyte steadily *increases* on dilution.

The expression for Λ_c , the equivalent conductance at a concentration c (Eq/L), is

$$\Lambda_c = \Lambda_0 - b\sqrt{c}\quad (6-22)$$

where Λ_0 is the intercept on the vertical axis and is known as the *equivalent conductance at infinite dilution*. The constant b is the slope of the line for the strong electrolytes shown in Figure 2.

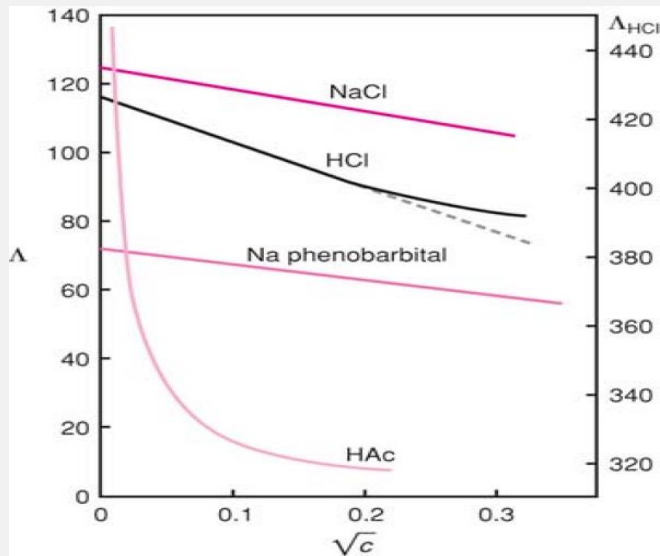


Fig. 6-4. Equivalent conductance of strong and weak electrolytes.

Λ_0 is the sum of the equivalent conductance's of the cations i_c^0 and the anions i_a^0 at infinite dilution

$$\Lambda_0 = i_c^0 + i_a^0 \quad (6-23)$$

Example 6-4

Equivalent Conductance of Phenobarbital

What is the equivalent conductance at infinite dilution of the weak acid phenobarbital? The Λ_0 of the strong electrolytes HCl, sodium phenobarbital (NaP), and NaCl are obtained from the experimental results shown in Figure 6-4. The values are $\Lambda_{0,\text{HCl}} = 426.2$, $\Lambda_{0,\text{NaP}} = 73.5$, and $\Lambda_{0,\text{NaCl}} = 126.5 \text{ mho cm}^2/\text{Eq}$.

Now, by Kohlrausch's law of the independent migration of ions,

$$\Lambda_{0,\text{HP}} = i_{\text{H}^+}^0 + i_{\text{P}^-}^0$$

and

$$\Lambda_{0,\text{HCl}} + \Lambda_{0,\text{NaP}} - \Lambda_{0,\text{NaCl}} = i_{\text{H}^+}^0 + i_{\text{Cl}^-}^0 + i_{\text{Na}^+}^0 + i_{\text{P}^-}^0 - i_{\text{Na}^+}^0 - i_{\text{Cl}^-}^0$$

which, on simplifying the right-hand side of the equation, becomes

$$\Lambda_{0,\text{HCl}} + \Lambda_{0,\text{NaP}} - \Lambda_{0,\text{NaCl}} = i_{\text{H}^+}^0 + i_{\text{P}^-}^0$$

Therefore,

$$\Lambda_{0, \text{HP}} = \Lambda_{0, \text{HCl}} + \Lambda_{0, \text{NaP}} - \Lambda_{0, \text{NaCl}}$$

and

$$\begin{aligned}\Lambda_{0, \text{HP}} &= 426.2 + 73.5 - 126.5 \\ &= 373.2 \text{ mho cm}^2/\text{Eq}\end{aligned}$$

Colligative Properties of Electrolytic Solutions and Concentrated Solutions of Nonelectrolytes

van't Hoff observed that the osmotic pressure, π , of dilute solutions of nonelectrolytes, such as sucrose and urea, could be expressed satisfactorily by the equation

$$\pi = RTC$$

van't Hoff found, however, that solutions of electrolytes gave **osmotic pressures** approximately two, three, and more times larger than expected from this equation, depending on the electrolyte investigated. Introducing a correction factor i to account for the irrational behavior of ionic solutions,

$$\pi = iRTC \quad (6-24)$$

The van't Hoff factor can also be expressed as the ratio of any colligative property of a real solution (electrolyte solution) to that of an ideal solution of a nonelectrolyte solution because i represents the number of times greater that the colligative effect is for a real solution (electrolyte or nonelectrolyte) than for an ideal nonelectrolyte.

The i factor is plotted against the molal concentration of both electrolytes and nonelectrolytes in Figure 6-5. For nonelectrolytes, it is seen to approach unity, and for strong electrolytes, it tends toward a value equal to the number of ions formed upon dissociation. For example, i approaches the value of 2 for solutes such as NaCl and CaSO₄, 3 for K₂SO₄ and CaCl₂, and 4 for K₃Fe(C)₆ and FeCl₃.

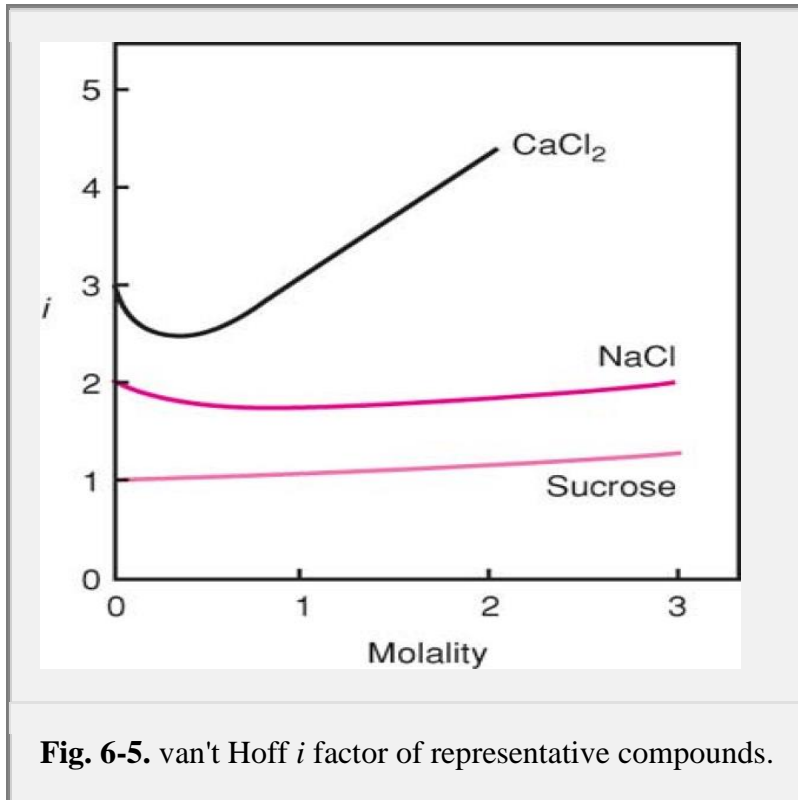


Fig. 6-5. van't Hoff *i* factor of representative compounds.

The colligative properties in dilute solutions of electrolytes are expressed on the molal scale by the equations

$$\Delta p = 0.018ip_1^\circ m \quad (6-25)$$

$$\pi = iRTm \quad (6-26)$$

$$\Delta T_f = iK_f m \quad (6-27)$$

$$\Delta T_b = iK_b m \quad (6-28)$$

Equation (6-25) applies only to aqueous solutions, whereas (6-26) through (6-28) are independent of the solvent used.

Example 6-5

Osmotic Pressure of Sodium Chloride

What is the osmotic pressure of a 2.0 *m* solution of sodium chloride at 20°C?

The *i* factor for a 2.0 *m* solution of sodium chloride as observed in Figure 6-5 is about 1.9. Thus,

$$\pi = 1.9 \times 0.082 \times 293 \times 2.0 = 91.3 \text{ atm}$$

Drugs and Ionization

Some drugs, such as anionic and cationic antibacterial and antiprotozoal agents, are more active when in the ionic state.

Other compounds, such as the hydroxyl benzoate esters (parabens) and many general anesthetics, bring about their biologic effects as nonelectrolytes. Still other compounds, such as the sulfonamides, are thought to exert their drug action both as ions and as neutral molecules.

Degree of Dissociation

degree of dissociation, α :- the fraction of solute molecules ionized, or the degree of dissociation, was expressed by the following equation

$$\alpha = \frac{\Lambda_c}{\Lambda_0} \quad (6-32)$$

where Λ_c/Λ_0 is known as the *conductance ratio*.

A strong electrolyte has high ***degree of dissociation, α*** and a weak electrolyte has low ***degree of dissociation***.

$$\alpha = \frac{i-1}{v-1} \quad (6-35)$$

The cryoscopic method is used to determine i from the expression

$$\Delta T_f = iK_f m \quad (6-36)$$

or

$$i = \frac{\Delta T_f}{K_f m} \quad (6-37)$$

Example 6-6

Degree of Dissociation of Acetic Acid

The equivalent conductance of acetic acid at 25°C and at infinite dilution is 390.7 ohm cm²/Eq. The equivalent conductance of a 5.9 × 10⁻³ M solution of acetic acid is 14.4 ohm cm²/Eq. What is the degree of dissociation of acetic acid at this concentration?

$$\alpha = \frac{14.4}{390.7} = 0.037 \text{ or } 3.7\%$$

Example 6-7

Degree of Ionization of Acetic Acid

The freezing point of a 0.10 *m* solution of acetic acid is -0.188°C. Calculate the degree of ionization of acetic acid at this concentration. Acetic acid dissociates into two ions, that is, $\nu = 2$.

$$i = \frac{0.188}{1.86 \times 0.10} = 1.011$$

$$\alpha = \frac{i - 1}{\nu - 1} = \frac{1.011 - 1}{2 - 1} = 0.011$$

Example 6-8

Degree of Dissociation

The freezing point depression for a 0.01 *m* solution of ammonium chloride is 0.0367°C. Calculate the “degree of dissociation” of this electrolyte.

$$i = \frac{\Delta T_f}{K_f m} = \frac{0.0367^\circ\text{C}}{1.86 \times 0.010} = 1.97$$

$$\alpha = \frac{1.97 - 1}{2 - 1} = 0.97$$

Theory of Strong Electrolytes

The Arrhenius theory is accepted for describing the behavior only of weak electrolytes. The degree of dissociation of a weak electrolyte can be calculated satisfactorily from the conductance ratio Λ_c/Λ_0 or obtained from the van't Hoff *i* factor.

For solutions of strong electrolytes. In dilute and moderately concentrated solutions, they dissociate almost completely into ions, and it is not satisfactory to write an equilibrium expression relating the concentration of the ions and the minute amount of un dissociated molecules, as is done for weak electrolytes. Moreover, a discrepancy exists between α calculated from the *i* value and α calculated from

the conductivity ratio for strong electrolytes in aqueous solutions having concentrations greater than about 0.5 M.

For these reasons, one does not account for the deviation of strong electrolyte from ideal nonelectrolyte behavior by calculating a degree of dissociation. It is more convenient to consider a strong electrolyte as completely ionized and to introduce a factor that expresses the deviation of the solute from 100% ionization. The activity and osmotic coefficient,

Activity and Activity Coefficients

Because of the electrostatic attraction and ion association in moderately concentrated solutions of strong electrolytes, the values of the freezing point depression and the other colligative properties are less than expected for solutions of unhindered ions. Consequently, a strong electrolyte may **be completely ionized, yet incompletely dissociated** into free ions.

The solution as having an “effective concentration” or, as it is called, an *activity*. The activity, in general, is less than the actual or stoichiometric concentration of the solute, not because the strong electrolyte is only partly ionized, but rather because some of the ions are effectively by the electrostatic forces of interaction.

At infinite dilution, in which the ions are so widely separated that they do not interact with one another, the activity a of an ion is equal to its concentration, expressed as molality or molarity.

$$a = m \quad (6-38)$$

$$\frac{a}{m} = 1 \quad (6-39)$$

As the concentration of the solution is increased, the ratio becomes less than unity because the effective concentration or activity of the ions becomes less than the stoichiometric or molal concentration. This ratio is known as the **practical activity coefficient, γ_m** , on the molal scale, and the formula is written, for a particular ionic species, as

$$\frac{a}{m} = \gamma_m \quad (6-40)$$

or

$$a = \gamma_m m \quad (6-41)$$

On the molarity scale, another *practical activity coefficient*, γ_c , is defined as

$$a = \gamma_c c \quad (6-42)$$

and on the mole fraction scale, a *rational activity coefficient* is defined as

$$a = \gamma_x X \quad (6-43)$$

A cation and an anion in an aqueous solution may each have a different ionic activity.

a_+ the activity of a cation

a_- the activity of an anion.

a_{\pm} the activity of the electrolyte

The activity of an electrolyte is defined by its **mean ionic activity**, which is given by the relation

$$a_{\pm} = (a_+^m a_-^n)^{1/(m+n)} \quad (6-44)$$

where the exponents m and n give the stoichiometric numbers of given ions that are in solution. Thus, an NaCl solution has a mean ionic activity of

$$a_{\pm} = (a_{\text{Na}^+} a_{\text{Cl}^-})^{1/2}$$

whereas an FeCl₃ solution has a mean ionic activity of

$$a_{\pm} = (a_{\text{Fe}^{+3}} a_{\text{Cl}^{-3}})^{1/4}$$

The **mean ionic activity coefficient** for the electrolyte can be defined by

$$\gamma_{\pm} = (\gamma_+^m \gamma_-^n)^{1/(m+n)} \quad (6-47)$$

And the mean ionic activity is equal:

$$a_{\pm} = \gamma_{\pm} (c_+^m c_-^n)^{1/(m+n)} \quad (6-49)$$

Example 6-9

Mean Ionic Activity of FeCl₃

What is the mean ionic activity of a 0.01 M solution of FeCl₃?

$$\begin{aligned} a_{\pm} &= \gamma_{\pm} (c_+ c_-^3)^{1/4} = \gamma_{\pm} [(0.01)(3 \times 0.01)^3]^{1/4} \\ &= 2.3 \times 10^{-2} \gamma_{\pm} \end{aligned}$$

Activity of the Solvent

When a solution is made infinitely dilute, it can be considered to consist essentially of pure solvent. The solvent behaves ideally in conformity with Raoult's law.

$$a = X_1 = 1 \quad (6-52)$$

As the solution becomes more concentrated in solute, the activity of the solvent ordinarily becomes less than the mole fraction concentration, and the ratio can be given, as for the solute, by the rational activity coefficient,

$$\frac{a}{X_1} = \gamma_x \quad (6-53)$$

or

$$a = \gamma_x X_1 \quad (6-54)$$

The activity of a volatile solvent can be determined rather simply. The ratio of the vapor pressure, p_1 , of the

solvent in a solution to the vapor pressure of pure solvent, p_1° , is approximately equal to the *activity* of the solvent at ordinary pressures:

$$a_1 = p_1/p^\circ.$$

Reference State

A **reference state** must be established in which each component behaves ideally. The reference state can be defined as the solution in which the concentration (mole fraction, molal or molar) of the component is equal to the activity,

Activity = Concentration

or, what amounts to the same thing, the activity coefficient is unity,

$$\gamma_i = \frac{\text{Activity}}{\text{Concentration}} = 1$$

Standard State

The **standard state** of a component in a solution is the state of the component at unit activity. The relative activity in any solution is then the ratio of the activity in that state to the value in the standard state. When defined in these terms, activity is a dimensionless number.

Ionic Strength

In dilute solutions of nonelectrolytes, activities and concentrations are considered to be practically identical because electrostatic forces do not bring about deviations from ideal behavior in these solutions. Likewise, for weak electrolytes that are present alone in solution, the differences between the ionic concentration terms and activities are usually disregarded in ordinary calculations because the

number of ions present is small and the electrostatic forces are negligible.

However, for strong electrolytes and for solutions of weak electrolytes together with salts and other electrolytes, such as exist in buffer systems, it is important to use activities instead of concentrations. The activity coefficient, and hence the activity, can be obtained by using one of the forms of the Debye-Hückel equation. the concept of **ionic strength, μ** , to relate interionic attractions and activity coefficients. The ionic strength is defined on the molar scale as

$$\mu = \frac{1}{2}(c_1 z_1^2 + c_2 z_2^2 + c_3 z_3^2 + \cdots + c_j z_j^2) \quad (6-55)$$

or, in abbreviated notation,

$$\mu = \frac{1}{2} \sum_1^j c_i z_i^2 \quad (6-56)$$

c_i is the concentration in moles/liter of any of the ions and z_i is its valence. Ionic strengths represent the contribution to the electrostatic forces of the ions of all types. It depends on the total number of ionic charges and not on the specific properties of the salts present in the solution.

The importance of the principle of ionic strength in biochemistry. In the study of the influence of pH on biologic action,

Example 6-11

Calculating Ionic Strength

What is the ionic strength of (a) 0.010 M KCl, (b) 0.010 M BaSO₄, and (c) 0.010 M Na₂SO₄, and (d) what is the ionic strength of a solution containing all three electrolytes together with salicylic acid in 0.010 M concentration in aqueous solution?

(a) KCl:

$$\begin{aligned} \mu &= \frac{1}{2}[(0.01 \times 1^2) + (0.01 \times 1^2)] \\ &= 0.010 \end{aligned}$$

(b) BaSO₄:

$$\begin{aligned}\mu &= \frac{1}{2}[(0.01 \times 2^2) + (0.01 \times 2^2)] \\ &= 0.040\end{aligned}$$

(c) Na₂ SO₄:

$$\begin{aligned}\mu &= \frac{1}{2}[(0.02 \times 1^2) + (0.01 \times 2^2)] \\ &= 0.030\end{aligned}$$

(d) The ionic strength of a 0.010 M solution of salicylic acid is 0.003 as calculated from a knowledge of the ionization of the acid at this concentration (using the equation $[H_3O^+] = \sqrt{K_a c}$). Unionized salicylic acid does not contribute to the ionic strength.

The ionic strength of the mixture of electrolytes is the sum of the ionic strength of the individual salts. Thus,

$$\begin{aligned}\mu_{\text{total}} &= \mu_{\text{KCl}} + \mu_{\text{BaSO}_4} + \mu_{\text{Na}_2\text{SO}_4} + \mu_{\text{HSal}} \\ &= 0.010 + 0.040 + 0.030 + 0.003 \\ &= 0.083\end{aligned}$$

Example 6-12

Ionic Strength of a Solution

A buffer contains 0.3 mole of K₂HPO₄ and 0.1 mole of KH₂PO₄ per liter of solution. Calculate the ionic strength of the solution.

The concentrations of the ions of K₂HPO₄ are $[K^+] = 0.3 \times 2$ and $[HPO_4^{2-}] = 0.3$. The values for KH₂PO₄ are $[K^+] = 0.1$ and $[H_2PO_4^-] = 0.1$. Any contributions to μ by further dissociation of $[HPO_4^{2-}]$ and $[H_2PO_4^-]$ are neglected. Thus,

$$\begin{aligned}\mu &= \frac{1}{2}[(0.3 \times 2 \times 1^2) + (0.3 \times 2^2) + (0.1 \times 1^2) + (0.1 \times 1^2)] \\ \mu &= 1.0\end{aligned}$$

The Debye-Hückel Theory

Debye and Hückel derived an equation based on the principles that strong electrolytes are completely ionized in dilute solution and that the deviations of electrolytic solutions from ideal behavior are due to the electrostatic effects of the oppositely charged ions.

The equation relates the activity coefficient of a particular ion or the mean ionic activity coefficient of an electrolyte to the valence of the ions, the ionic strength of the solution, and the characteristics of the solvent.

The equation can be used to calculate the activity coefficients of drugs whose values have not been obtained experimentally and are not available in the literature.

According to the theory of Debye and Hückel, the activity coefficient, γ_i , of an ion of valence z_i is given by the expression

$$\log \gamma_i = -Az_i^2 \sqrt{\mu} \quad (6-57)$$

Equation (6-57) yields a satisfactory measure of the activity coefficient of an ion species up to an ionic strength, μ , of about 0.02. For water at 25°C, A , a factor that depends only on the temperature and the dielectric constant of the medium, is approximately equal to 0.51. The values of A for various solvents of pharmaceutical importance are found in Tables. The form of the Debye-Hückel equation for a binary electrolyte consisting of ions with valences of z_+ and z_- and present in a dilute solution ($\mu < 0.02$) is

$$\log \gamma_{\pm} = -Az_+z_- \sqrt{\mu} \quad (6-58)$$

The symbols z_+ and z_- stand for the valences or charges, ignoring algebraic signs, on the ions of the electrolyte whose mean ionic activity coefficient is sought. the activity coefficient of a strong electrolyte in dilute solution depends on the total ionic strength of the solution, the valence of the ions of the drug involved, the nature of the solvent, and the temperature of the solution. the z_+z_- terms apply only to the drug whose activity coefficient is being determined.

The activity of elements and compounds in their pure state are considered as one for example :-

$$a_{\text{Na(s)}}=1$$

$$a_{\text{H}_2\text{O(l)}}=1$$

$$a_{\text{AgCl(s)}}=1$$

Example 6-13

Mean Ionic Activity Coefficient

Calculate the mean ionic activity coefficient for 0.005 M atropine sulfate (1:2 electrolyte) in an aqueous solution containing 0.01 M NaCl at 25°C. Because the drug is a uni-bivalent electrolyte, $z_1z_2 = 1 \times 2 = 2$. For water at 25°C, A is 0.51.

$$\mu \text{ for atropine sulfate} = \frac{1}{2}[(0.005 \times 2 \times 1^2) + (0.005 \times 2^2)] = 0.015$$

$$\mu \text{ for NaCl} = \frac{1}{2}[(0.01 \times 1^2) + (0.01 \times 1^2)] = 0.01$$

$$\text{Total } \mu = 0.025$$

$$\log \gamma_{\pm} = -0.51 \times 2 \times \sqrt{0.025}$$

$$\log \gamma_{\pm} = -1.00 + 0.839 = -0.161$$

$$\gamma_{\pm} = 0.690$$

Coefficients for Expressing Colligative Properties

The L Value

The van't Hoff expression $\Delta T_f = iK_f m$ probably provides the best single equation for computing the colligative properties of nonelectrolytes, weak electrolytes, and strong electrolytes. It can be modified slightly for convenience in dilute solutions by substituting molar concentration c and by writing iK_f as L , so that

$$\Delta T_f = Lc \quad (6-62)$$

L from experimental data for a number of drugs. It varies with the concentration of the solution. At a concentration of drug that is isotonic with body fluids, $L = iK_f$ is designated here as L_{iso} . It has a value equal to about

1.9 (actually 1.86) for nonelectrolytes,

2.0 for weak electrolytes,

3.4 for uni-univalent electrolytes, and larger values for electrolytes of high valences.

A plot of iK_f against the concentration of some drugs is presented in Figure 3, where each curve is represented as a band to show the variability of the L values within each ionic class. The approximate L_{iso} for each of the ionic classes can be obtained from the dashed line running through the figure.

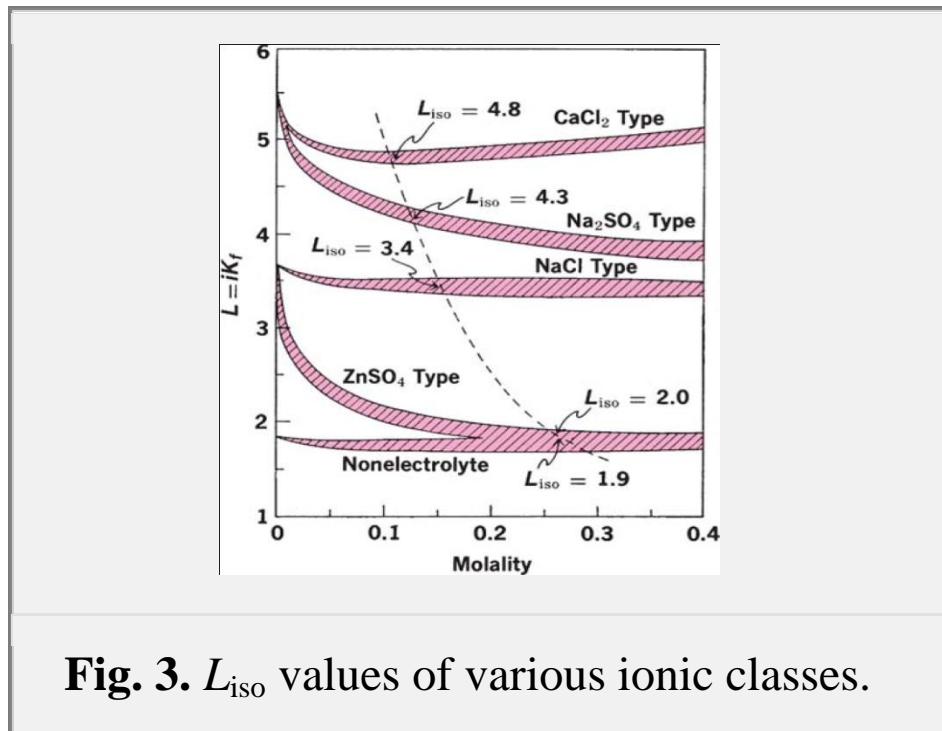


Fig. 3. L_{iso} values of various ionic classes.

Osmotic Coefficient

Other methods of correcting for the deviations of electrolytes from ideal colligative behavior have been suggested. One of these is based on the fact that as the solution becomes more dilute, i approaches v , the number of ions into which an electrolyte dissociates,

and **at infinite dilution, $i = v$, or $i/v = 1$.**

Proceeding in the direction of more concentrated solutions, i/v becomes less (and sometimes greater) than unity.

The ratio i/v is designated as g and is known as the **practical osmotic coefficient** when expressed on a molal basis.

In the case of a weak electrolyte, it provides a measure of the degree of dissociation.

For strong electrolytes, g is equal to unity for complete dissociation, and the departure of g from unity,

that is, $1 - g$, in moderately concentrated solutions is an indication of the interionic attraction. Osmotic coefficients, g , for electrolytes and nonelectrolytes are plotted against ionic concentration, νm , in Figure 4. Because $g = 1/v$ or $i = gv$ in a dilute solution, the cryoscopic equation can be written as

$$\Delta T_f = g \nu K_f m \quad (6-63)$$

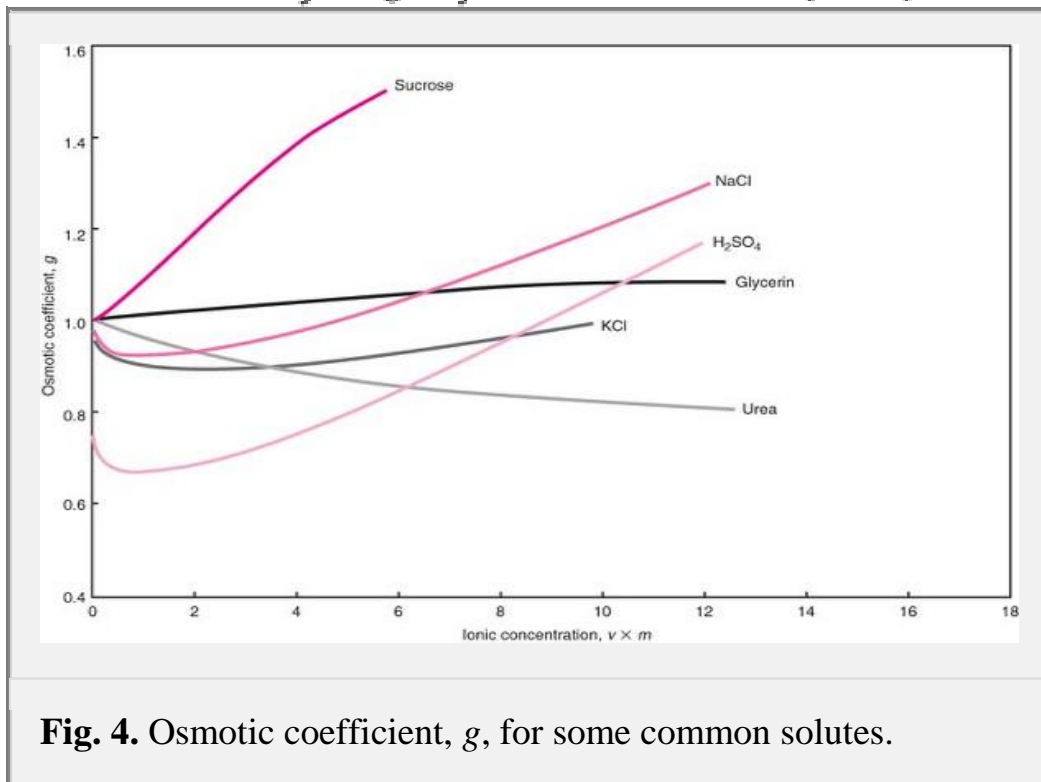


Fig. 4. Osmotic coefficient, g , for some common solutes.

Example 6-15

Molality and Molarity

The osmotic coefficient of LiBr at $0.2\ m$ is 0.944 and the L_{iso} value is 3.4 . Compute ΔT_f for this compound using g and L_{iso} . Disregard the difference between molality and molarity.

$$\begin{aligned}\Delta T_f &= gvK_fm = 0.944 \times 2 \times 1.86 \times 0.2 \\ &= 0.70^\circ \\ \Delta T_f &= L_{iso}c = 3.4 \times 0.2 = 0.68^\circ\end{aligned}$$

Osmolality

Osmolality measures the total number of particles dissolved in 1 kg of water, that is the osmols per kilogram of water, and depends on the electrolytic nature of the solute.

. For an electrolyte that dissociates into ions in a dilute solution, osmolality or milliosmolality can be calculated from

$$\text{Milliosmolality (mOsm/kg)} = i \cdot mm \quad (6-64)$$

where i is approximately the number of ions formed per molecule and mm is the millimolal concentration. If no ionic interactions occurred in a solution of sodium chloride, i would equal 2.0. In a typical case, for a 1:1 electrolyte in dilute solution, i is approximately 1.86 rather than 2.0, owing to ionic interaction between the positively and negatively charged ions.

osmolarity is used more frequently than osmolality in labeling parenteral solutions in the hospital. Yet, osmolarity cannot be measured and must be calculated from the experimentally determined osmolality of a solution.

$$\begin{aligned}\text{Osmolarity} &= (\text{Measured osmolality}) \\ &\quad \times (\text{Solution density in g/mL}) \\ &\quad - \text{Anhydrous solute concentration in g/mL} \quad (6-65)\end{aligned}$$

According to Streng et al. osmolality is converted to osmolarity using the equation

$$\begin{aligned}\text{mOsm/liter solution} &= \text{mOsm/(kg H}_2\text{O)} \\ &\quad \times [d_1^\circ(1 - 0.001 \bar{v}_2^\circ)] \quad (6-66)\end{aligned}$$

where d_1° is the density of the solvent and $[\bar{v}]_2^\circ$ is the partial molal volume of the solute at infinite dilution.

osmolarity differs from osmolality by only 1% or 2%.

Whole blood, plasma, and serum are complex liquids consisting of proteins, glucose, nonprotein nitrogenous materials, sodium, potassium, calcium, magnesium, chloride, and bicarbonate ions. The serum electrolytes, constituting less than 1% of the blood's weight, determine the osmolality of the blood. Sodium chloride contributes a milliosmolality of 275, whereas glucose and the other constituents together provide about 10 mOsm/kg to the blood.

Colligative properties such as freezing point depression are related to osmolality through equations

$$\Delta T_f \cong K_f im \quad (6-67)$$

where $i = gv$ and $im = gvm$ is osmolality.

(b) Glucose is a nonelectrolyte, producing only one particle for each of its molecules in solution, and for a nonelectrolyte, $i = v = 1$ and $g = i/v = 1$. Therefore, the freezing point depression of a 0.154 *m* solution of glucose is approximately

which is nearly one half of the freezing point depression provided by sodium chloride, a 1:1 electrolyte that provides two particles rather than one particle in solution.

The osmolality of a nonelectrolyte such as glucose is identical to its molal concentration because osmolality = $i \times$ molality, and i for a nonelectrolyte is 1.00. The milliosmolality of a solution is 1000 times its osmolality or, in this case, 154 mOsm/kg.

Although the osmolality of blood and other body fluids is contributed mainly by the content of sodium chloride, the osmolality and milliosmolality of these complex solutions by convention are calculated on the basis of i for nonelectrolytes, that is, i is taken as unity, and osmolality becomes equal to molality.