6 Electrolyte Solutions

Chapter Objectives

At the conclusion of this chapter the student should be able to:

1. Understand the important properties of solutions of electrolytes.
2. Understand and apply Faraday's law and electrolytic conductance.
3. Calculate the conductance of solutions, the equivalent conductance, and the equivalent conductance of electrolytes.
4. Compare and contrast the colligative properties of electrolytic solutions and concentrated solutions of nonelectrolytes.
5. Apply the Arrhenius theory of electrolytic dissociation.
6. Apply the theory of strong electrolytes; for example, calculate degree of dissociation, activity coefficients, and so on.
7. Calculate ionic strength.
8. Calculate osmotic coefficients, osmolality, and osmolarity.
9. Understand the differences between osmolality and osmolarity.

The first satisfactory theory of ionic solutions was that proposed by Arrhenius in 1887. The theory was based largely on studies of electric conductance by Kohlrausch, colligative properties by van't Hoff, and chemical properties such as heats of neutralization by Thomsen. Arrhenius1 was able to bring together the results of these diverse investigations into a broad generalization known as the theory of electrolytic dissociation.

Although the theory proved quite useful for describing weak electrolytes, it was soon found unsatisfactory for strong and moderately strong electrolytes. Accordingly, many attempts were made to modify or replace Arrhenius's ideas with better ones, and finally, in 1923, Debye and Hückel put forth a new theory. It is based on the principles that *strong electrolytes* are completely dissociated into ions in solutions of moderate concentration and that any deviation from complete dissociation is due to interionic attractions. Debye and Hückel expressed the deviations in terms of activities, activity coefficients, and ionic strengths of electrolytic solutions. These quantities, which had been introduced earlier by Lewis, are discussed in this chapter together with the theory of interionic attraction. Other aspects of modern ionic theory and the relationships between electricity and chemical phenomena are considered in following chapters.

This chapter begins with a discussion of some of the properties of ionic solutions that led to the Arrhenius theory of electrolytic dissociation.

Properties of Solutions of Electrolytes

Electrolysis

When, under a potential of several volts, a direct electric current (dc) flows through an electrolytic cell (Fig. 6-1), a chemical reaction occurs. The process is known as*electrolysis*. Electrons enter the cell from the battery or generator at the *cathode* (road down); they combine with positive ions or *cations* in the solution, and the cations are accordingly reduced. The negative ions, or *anions*, carry electrons through the solution and discharge them at the *anode* (road up), and the anions are accordingly oxidized. *Reduction* is the addition of electrons to a chemical species, and *oxidation* is removal of electrons from a species. The current in a solution consists of a flow of positive and negative ions toward the electrodes, whereas the current in a metallic conductor consists of a flow of free electrons migrating through a crystal lattice of fixed positive ions. Reduction occurs at the cathode, where electrons enter from the external circuit and are added to a chemical species in solution. Oxidation occurs at the anode, 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, where it picks up an electron and is reduced:

$$Fe^{3+} + e = Fe^{2+} \qquad (6\text{–}1)$$

The sulfate ion carries the current through the solution to the anode, but it is not easily oxidized; therefore, hydroxyl ions of the water are converted into molecular oxygen, which escapes at the anode, and sulfuric acid is found in the solution around the electrode. The oxidation reaction at the anode is

$$OH^- = \frac{1}{4}O_2 + \frac{1}{2}H_2O + e \qquad (6\text{–}2)$$

Platinum electrodes are used here because they do not pass into solution to any extent.

When *attackable* metals, such as copper or zinc, are used as the anode, their atoms tend to lose electrons, and the metal passes into solution as the positively charged ion.

In the electrolysis of cupric chloride between platinum electrodes, the reaction at the cathode is

$$\frac{1}{2}Cu^{2+} + e = \frac{1}{2}Cu \qquad (6\text{–}3)$$

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whereas at the anode, chloride and hydroxyl ions are converted, respectively, into gaseous molecules of chlorine and oxygen, which then escape. In each of these two examples, the net result is the transfer of one electron from the cathode to the anode.

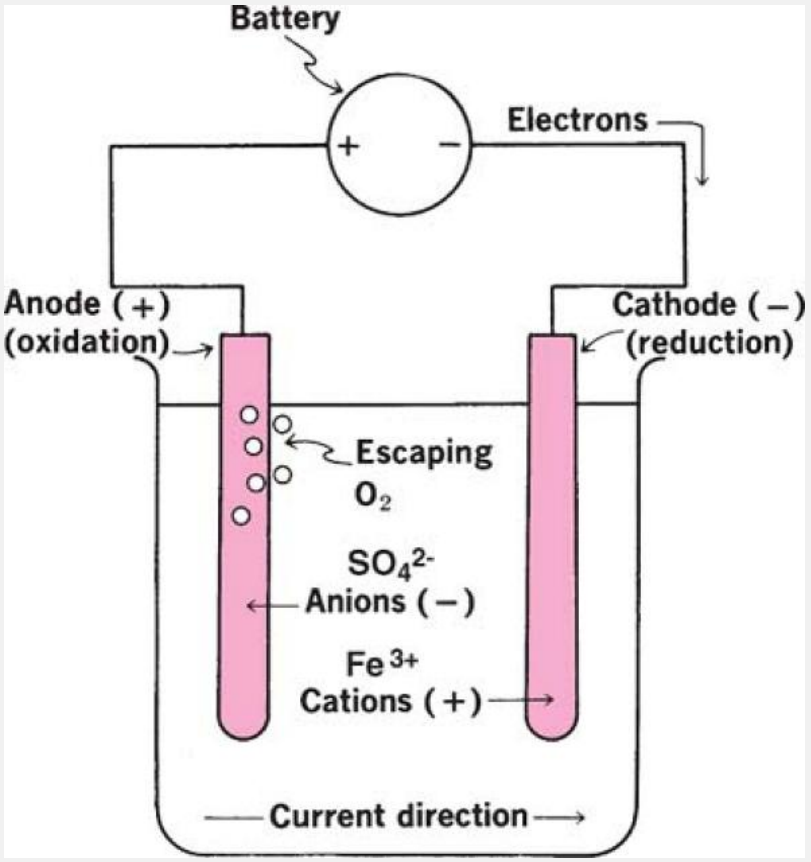


Fig. 6-1. Electrolysis in an electrolytic cell.

Transference Numbers

It should be noted that the flow of electrons through the solution from right to left in Figure 6-1 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_-:

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

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

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

$$t_+ + t_- = 1 \qquad (6\text{–}6)$$

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. Hence, the speed and the transference numbers are not necessarily the same for positive and for negative ions. For example, the transference number of the sodium ion in a 0.10 M solution of NaCl is 0.385. Because it is greatly hydrated, the lithium ion in a 0.10 M solution of LiCl moves more slowly than the sodium ion and hence has a lower transference number, 0.317.

Key Concept

Faraday's Laws

In 1833 and 1834, Michael Faraday announced his famous laws of electricity, which may be summarized in the statement, *the passage of 96,500 coulombs of electricity through a conductivity cell produces a chemical change of 1 g equivalent weight of any substance*. The quantity 96,500 is known as the faraday, F. The best estimate of the value today is 9.648456 × 10^4 coulombs/gram equivalent.

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:

$$I = \frac{E}{R} \qquad (6\text{–}7)$$

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

$$I = \frac{Q}{t} \qquad (6\text{–}8)$$

and

$$\text{Quantity of electric charge, } Q = \text{Current, } I \times \text{Time, } t \qquad (6\text{–}9)$$

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.

Electric energy consists of an intensity factor, electromotive force or voltage, and a quantity factor, coulombs.

$$\text{Electric energy} = E \times Q \qquad (6\text{–}10)$$

Faraday's Laws

A univalent negative ion is an atom to which a valence electron has been added; a univalent positive ion is an atom from which an electron has been removed. Each gram equivalent of ions of any electrolyte carries Avogadro's number (6.02 × 10^{23}) of positive or negative charges. Hence, from Faraday's laws, the passage of 96,500 coulombs of electricity results in the transport of 6.02 × 10^{23} electrons in the cell. One faraday is an Avogadro's number of electrons, corresponding to the mole, which is an Avogadro's number of molecules. The passage of 1 faraday of electricity causes the electrolytic deposition of the following number of gram atoms or “moles” of various ions: 1 Ag^+, 1 Cu^+, ½ Cu^{2+}, ½ Fe^{2+}, 1/3 Fe^{3+}. Thus, the number of positive charges carried by 1 g equivalent of Fe^{3+} is 6.02 × 10^{23}, but the number of positive charges carried by 1 g atom or 1 mole of ferric ions is 3 × 6.02 × 10^{23}.

Faraday's laws can be used to compute the charge on an electron in the following way. Because 6.02×10^{23} electrons are associated with 96,500 coulombs of electricity, each electron has a charge e of

$$e = \frac{96{,}500 \text{ coulombs}}{6.02 \times 10^{23}}$$

$$= 1.6 \times 10^{-19} \text{ coulomb} \qquad \textbf{(6–11)}$$

and because 1 coulomb $= 3 \times 10^{9}$ esu,

$$e = 4.8 \times 10^{-10} \text{ electrostatic unit of charge} \qquad \textbf{(6–12)}$$

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,

$$R = \rho \frac{l}{A} \qquad \textbf{(6–13)}$$

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

The *conductance*, ***C***, is the reciprocal of resistance,

$$C = \frac{1}{R} \qquad \textbf{(6–14)}$$

and hence 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):

$$C = \frac{1}{R} = \frac{1}{\rho}\frac{A}{l} \qquad \textbf{(6–15)}$$

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

$$\kappa = \frac{1}{\rho} \qquad \textbf{(6–16)}$$

It is the conductance of a solution confined in a cube 1 cm on an edge as seen in Figure 6-2. The relationship between specific conductance and conductance or resistance is obtained by combining equations (6-15) and (6-16):

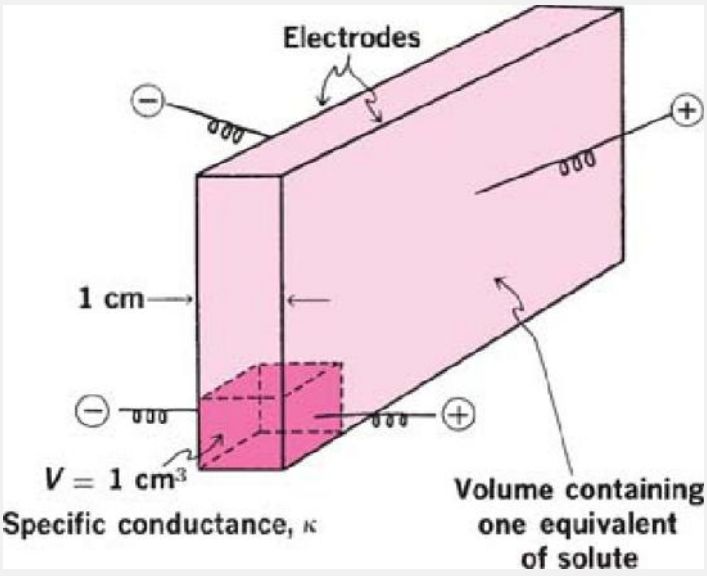


Fig. 6-2. Relationship between specific conductance and equivalent conductance.

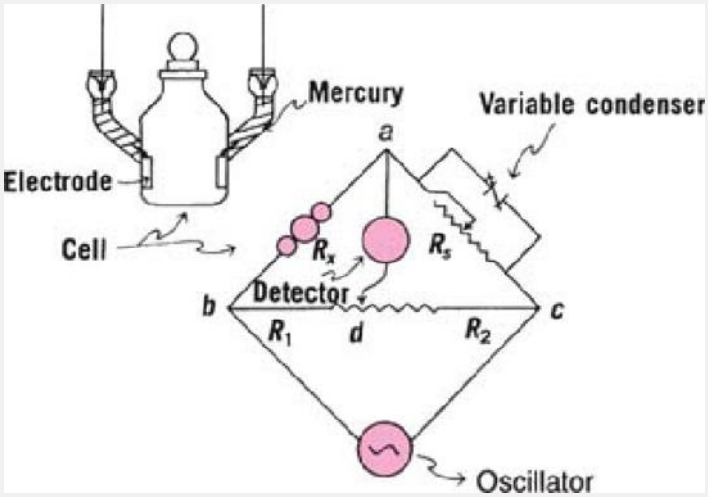


Fig. 6-3. Wheatstone bridge for conductance measurements.

$$\kappa = C\frac{1}{A} = \frac{1}{R}\frac{1}{A} \qquad (6\text{–}17)$$

Measuring the Conductance of Solutions

The Wheatstone bridge assembly for measuring the conductance of a solution is shown in Figure 6-3. The solution of unknown resistance R_x is placed in the cell and connected in the circuit. The contact point is moved along the slide wire *bc* until at some point, say *d*, no current from the source of alternating current (oscillator) flows through the detector (earphones or oscilloscope). When the bridge is balanced, the potential at *a* is equal to that at *d*, the sound in the earphones or the oscillating pattern on the oscilloscope is at a minimum, and the resistances R_s, R_1, and R_2 are read. In the balanced state, the resistance of the solution R_x is obtained from the equation

$$R_x = R_s\frac{R_1}{R_2} \qquad (6\text{–}18)$$

The variable condenser across resistance R_s is used to produce a sharper balance. Some conductivity bridges are calibrated in conductance as well as resistance values. The electrodes in the cell are platinized with platinum black by electrolytic deposition so that catalysis of the reaction will occur at the platinum surfaces and formation of a nonconducting gaseous film will not occur on the electrodes. Water that is carefully purified by redistillation in the presence of a little permanganate is used to prepare the solutions. Conductivity water, as it is called, has a specific conductance of about 0.05×10^{-6} mho/cm at 18°C, whereas ordinary distilled water has a value somewhat greater than 1×10^{-6} mho/cm. For most conductivity studies, "equilibrium water" containing CO_2 from the atmosphere is satisfactory. It has a specific conductance of about 0.8×10^{-6} mho/cm.

The specific conductance, κ, is computed from the resistance, R_x, or conductance, C, by use of equation (6-17). The quantity *l*/*A*, the ratio of distance between electrodes to the area of the electrode, has a definite value for each conductance

cell; it is known as the *cell constant, K*. Equation (6-17) thus can be written as

$$\kappa = KC = K/R \qquad (6\text{–}19)$$

(The subscript *x* is no longer needed on R and is therefore dropped.) 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. For example, a solution containing 7.45263 g of potassium chloride in 1000 g of water has a specific conductance of 0.012856 mho/cm at 25°C. A solution of this concentration contains 0.1 mole of salt per

cubic decimeter (100 cm^3) of water and is known as a 0.1-*demal* solution. When such a solution is placed in a cell and the resistance is measured, the cell constant can be determined by use of equation (6-19).

Example 6-1
Calculating *K*

A 0.1-demal solution of KCl was placed in a cell whose constant *K* was desired. The resistance *R* was found to be 34.69 ohms at 25°C. Thus,

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

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

To study the dissociation of molecules into ions, independent of the concentration of the electrolyte, it is convenient to use equivalent conductance rather than specific conductance. All solutes of equal normality produce the same number of ions when completely dissociated, and equivalent conductance measures the current-carrying capacity of this given number of ions. Specific conductance, on the other hand, measures the current-carrying capacity of all ions in a unit volume of solution and accordingly varies with concentration.

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. The equivalent conductance Λ_c at a concentration of *c* gram equivalents per liter is calculated from the product of the specific conductance κ and the volume *V* in cm^3 that contains 1 g equivalent of solute. The cell may be imagined as having electrodes 1 cm apart and to be of sufficient area so that it can contain the solution. The cell is shown in Figure 6-2. We have

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

The equivalent conductance is obtained when κ, the conductance per cm^3 of solution (i.e., the specific conductance), is multiplied by *V,* the volume in cm^3 that contains 1 g equivalent weight of solute. Hence, the equivalent conductance, Λ_c, expressed in units of mho cm^2/Eq, is given by the expression

$$\Lambda_c = \kappa \times V$$
$$= \frac{1000\,\kappa}{c} \text{ mho cm}^2/\text{Eq} \qquad (6\text{–}21)$$

If the solution is 0.1 N in concentration, then the volume containing 1 g equivalent of the solute will be 10,000 cm^3, and, according to equation (6-21), the equivalent conductance will be 10,000 times as great as the specific conductance. This is seen in the following example.

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? We write

$$\kappa = 0.0563 \times 0.520 = 0.0293 \text{ mho/cm}$$
$$\Lambda_c = 0.0293 \times 1000/0.1$$
$$= 293 \text{ mho cm}^2/\text{Eq}$$

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. It sometimes goes through a maximum before

decreasing. Conversely, the *equivalent conductance* Λ of a solution of a strong electrolyte steadily *increases* on dilution. The increase in Λ with dilution is explained as follows. The quantity of electrolyte remains constant at 1 g equivalent according to the definition of equivalent conductance; however, the ions are hindered less by their neighbors in the more dilute solution and hence can move faster. The equivalent conductance of a weak electrolyte also increases on dilution, but not as rapidly at first.

Kohlrausch was one of the first investigators to study this phenomenon. He found that the equivalent conductance was a linear function of the square root of the concentration for strong electrolytes in dilute solutions, as illustrated in Figure 6-4. The expression for Λ_c, the equivalent conductance at a concentration *c* (Eq/L), is

$$\Lambda_c = \Lambda_0 - b\sqrt{c} \qquad \textbf{(6–22)}$$

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 6-4.

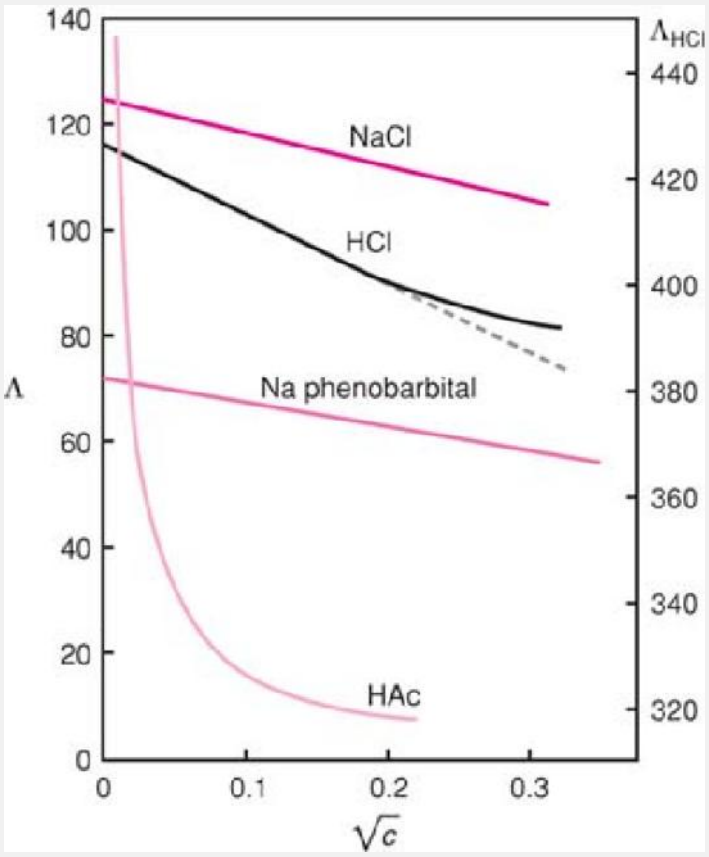


Fig. 6-4. Equivalent conductance of strong and weak electrolytes.

When the equivalent conductance of a weak electrolyte is plotted against the square root of the concentration, as shown for acetic acid in Figure 6-4, the curve cannot be extrapolated to a limiting value, and Λ_0 must be obtained by a method such as is described in the following paragraph. The steeply rising curve for acetic acid results from the fact that the dissociation of weak electrolytes increases on dilution, with a large increase in the number of ions capable of carrying the current. Kohlrausch concluded that the ions of all electrolytes begin to migrate independently as the solution is diluted; the ions in dilute solutions are so far apart that they do not interact in any way. Under these

conditions, Λ_0 is the sum of the equivalent conductances of the cations l_c^o and the anions l_a^o at infinite dilution

$$\Lambda_0 = l_c^o + l_a^o \qquad (6\text{–}23)$$

Based on this law, the known Λ_0 values for certain electrolytes can be added and subtracted to yield Λ_0 for the desired weak electrolyte. The method is illustrated in the following example.

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 $\Lambda_{0,HCl}$ = 426.2, $\Lambda_{0,NaP}$ = 73.5, and $\Lambda_{0,NaCl}$ = 126.5 mho cm^2/Eq.

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

$$\Lambda_{0,\,HP} = l^o_{H+} + l^o_{P}$$

and

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

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

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

Therefore,

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

and

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

Colligative Properties of Electrolytic Solutions and Concentrated Solutions of Nonelectrolytes

As stated in the previous chapter, 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 $\pi = RT_c$ [equation (5-34)], where R is the gas constant, T is the absolute temperature, and c is the concentration in moles/liter. 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, he wrote

$$\pi = iRTc \qquad (6\text{–}24)$$

By the use of this equation, van't Hoff was able to obtain calculated values that compared favorably with the experimental results of osmotic pressure. Van't Hoff recognized that i approached the number of ions into which the molecule dissociated as the solution was made increasingly dilute.

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 $CaSO_4$, 3 for K_2SO_4 and $CaCl_2$, and 4 for $K_3Fe(C)_6$ and $FeCl_3$.

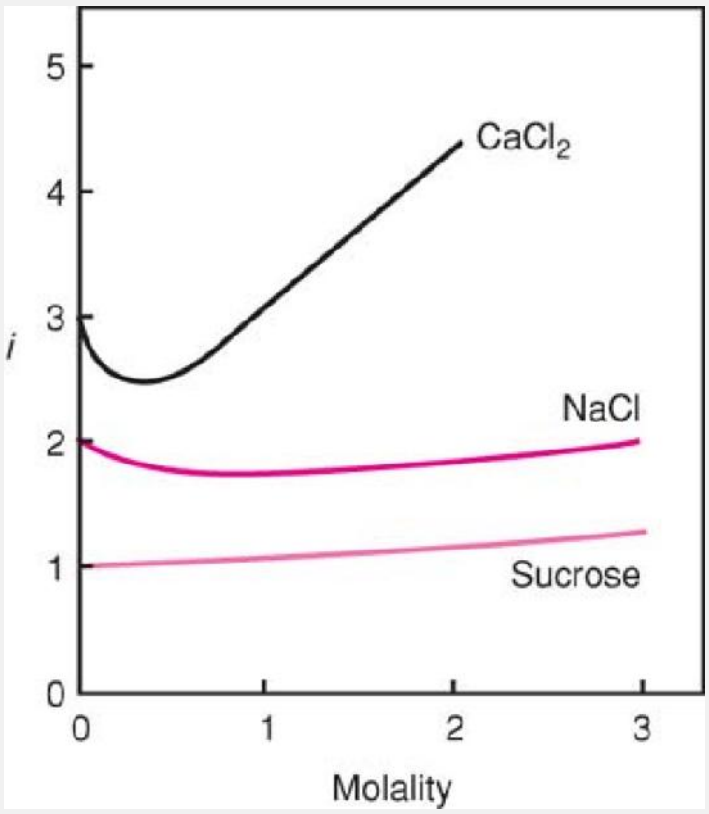


Fig. 6-5. van't Hoff *i* factor of representative compounds.

The van't Hoff factor can also be expressed as the ratio of any colligative property of a real solution to that of an ideal solution of a nonelectrolyte 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 colligative properties in dilute solutions of electrolytes are expressed on the molal scale by the equations

$$\Delta p = 0.018 i p_1^\circ m \qquad (6\text{–}25)$$

$$\pi = iRTm \qquad (6\text{–}26)$$

$$\Delta T_f = iK_f m \qquad (6\text{–}27)$$

$$\Delta T_b = iK_b m \qquad (6\text{–}28)$$

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,

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

Theory of Electrolytic Dissociation

During the period in which van't Hoff was developing the solution laws, the Swedish chemist Svante Arrhenius was preparing his doctoral thesis on the properties of electrolytes at the University of Uppsala in Sweden. In 1887, he published the results of his investigations and proposed the now classic theory of dissociation.1 The new theory resolved many of the anomalies encountered in the earlier interpretations of electrolytic solutions. Although the theory was viewed with disfavor by some influential

scientists of the nineteenth century, Arrhenius's basic principles of electrolytic dissociation were gradually accepted and are still considered valid today. The theory of the existence of ions in solutions of electrolytes even at ordinary temperatures remains intact, aside from some modifications and elaborations that have been made through the years to bring it into line with certain stubborn experimental facts.

Key Concept

van't Hoff Factor *i*

The factor *i* may also be considered to express the departure of concentrated solutions of nonelectrolytes from the laws of ideal solutions. The deviations of concentrated solutions of nonelectrolytes can be explained on the same basis as deviations of real solutions from Raoult's law, considered in the preceding chapter. They included differences of internal pressures of the solute and solvent, polarity, compound formation or complexation, and association of either the solute or the solvent. The departure of electrolytic solutions from the colligative effects in ideal solutions of nonelectrolytes may be attributed—in addition to the factors just enumerated—to dissociation of weak electrolytes and to interaction of the ions of strong electrolytes. Hence, the van't Hoff factor *i* accounts for the deviations of real solutions of nonelectrolytes and electrolytes, regardless of the reason for the discrepancies.

The original Arrhenius theory, together with the alterations that have come about as a result of the intensive research on electrolytes, is summarized as follows. When electrolytes are dissolved in water, the solute exists in the form of ions in the solution, as seen in the following equations:

$$H_2O + \underset{\text{[Ionic compound]}}{Na^+Cl^-} \rightarrow Na^+ + Cl^- + H_2O$$

$$H_2O + \underset{\text{[Covalent compound]}}{HCl} \xrightarrow{\text{[Strong electrolyte]}} H_3O^+ + Cl^- \qquad (6\text{–}29)$$

$$H_2O + \underset{\text{[Covalent compound]}}{CH_3COOH} \xrightleftharpoons{\text{[Strong electrolyte]}} H_3O^+ + CH_3COO^- \qquad (6\text{–}30)$$

$$\xrightarrow{\text{[Weak electrolyte]}} \qquad (6\text{–}31)$$

The solid form of sodium chloride is marked with plus and minus signs in reaction (6-29) to indicate that sodium chloride exists as ions even in the crystalline state. If electrodes are connected to a source of current and are placed in a mass of fused sodium chloride, the molten compound will conduct the electric current because the crystal lattice of the pure salt consists of ions. The addition of water to the solid dissolves the crystal and separates the ions in solution.

Hydrogen chloride exists essentially as neutral molecules rather than as ions in the pure form and does not conduct electricity. When it reacts with water, however, it ionizes according to reaction [equation (6-30)]. H_3O^+ is the modern representation of the hydrogen ion in water and is known as the *hydronium or oxonium* ion. In addition to H_3O^+, other hydrated species of the proton probably exist in solution, but they need not be considered here.2

Sodium chloride and hydrochloric acid are *strong electrolytes* because they exist almost completely in the ionic

form in moderately concentrated aqueous solutions. Inorganic acids such as HCl, HNO_3, H_2SO_4, and HI; inorganic bases as NaOH and KOH of the alkali metal family and $Ba(OH)_2$ and $Ca(OH)_2$ of the alkaline earth group; and most inorganic and organic salts are highly ionized and belong to the class of strong electrolytes.

Acetic acid is a *weak electrolyte*, the oppositely directed arrows in equation **(**6-31**)** indicating that equilibrium between the molecules and the ions is established. Most organic acids and bases and some inorganic compounds, such as H_3BO_3, H_2CO_3, and NH_4OH, belong to the class of weak electrolytes. Even some salts (lead acetate, $HgCl_2$, HgI, and HgBr) and the complex ions $Hg(NH_3)_2^+$, $Cu(NH_3)_4^{2+}$, and $Fe(CN)_6^{3-}$ are weak electrolytes.

Faraday applied the term *ion* (Greek: "wanderer") to these species of electrolytes and recognized that the cations (positively charged ions) and anions (negatively charged ions) were responsible for conducting the electric current. Before the time of Arrhenius's publications, it was believed that a solute was not spontaneously decomposed in water but rather dissociated appreciably into ions only when an electric current was passed through the solution.

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 hydroxybenzoate 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.3

Degree of Dissociation

Arrhenius did not originally consider strong electrolytes to be ionized completely except in extremely dilute solutions. He differentiated between strong and weak electrolytes by the fraction of the molecules ionized: the *degree of dissociation*, *α*. A strong electrolyte was one that dissociated into ions to a high degree and a weak electrolyte was one that dissociated into ions to a low degree.

Arrhenius determined the degree of dissociation directly from conductance measurements. He recognized that the equivalent conductance at infinite dilution Λ_0 was a measure of the complete dissociation of the solute into its ions and that Λ_c represented the number of solute particles present as ions at a concentration *c*. Hence, the fraction of solute molecules ionized, or the degree of dissociation, was expressed by the equation4

$$\alpha = \frac{\Lambda_c}{\Lambda_0} \qquad \textbf{(6–32)}$$

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

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 cm^2/Eq. The equivalent conductance of a 5.9×10^{-3} M solution of acetic acid is 14.4 ohm cm^2/Eq. What is the degree of dissociation of acetic acid at this concentration? We write

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

The van't Hoff factor, *i*, can be connected with the degree of dissociation, *α*, in the following way.

The *i* factor equals unity for an ideal solution of a nonelectrolyte; however, a term must be added to account for the particles produced when a molecule of an electrolyte dissociates. For 1 mole of calcium chloride, which yields three ions per molecule, the van't Hoff factor is given by

$$i = 1 + \alpha(3 - 1) \qquad \textbf{(6–33)}$$

or, in general, for an electrolyte yielding *v* ions,

$$i = 1 + \alpha(v - 1) \qquad \textbf{(6–34)}$$

from which we obtain an expression for the degree of dissociation,

$$\alpha = \frac{i - 1}{v - 1} \qquad \textbf{(6–35)}$$

The cryoscopic method is used to determine *i* from the expression

$$\Delta T_f = iK_f m \qquad \textbf{(6–36)}$$

or

$$i = \frac{\Delta T_f}{K_f m} \qquad \textbf{(6–37)}$$

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, $v = 2$. We write

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

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

In other words, according to the result of Example 6-7, the fraction of acetic acid present as free ions in a 0.10 *m* solution is 0.011. Stated in percentage terms, acetic acid in 0.1 *m* concentration is ionized to the extent of about 1%.

Theory of Strong Electrolytes

Arrhenius used α to express the degree of dissociation of both strong and weak electrolytes, and van't Hoff introduced the factor *i* to account for the deviation of strong and weak

electrolytes and nonelectrolytes from the ideal laws of the colligative properties, regardless of the nature of these discrepancies. According to the early ionic theory, the degree of dissociation of ammonium chloride, a strong electrolyte, was calculated in the same manner as that of a weak electrolyte.

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. We write

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

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

The Arrhenius theory is now 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.

Many inconsistencies arise, however, when an attempt is made to apply the theory to 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 undissociated molecules, as is done for weak electrolytes (Chapter 7). Moreover, a discrepancy exists between α calculated from the *i* value and αcalculated 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*, discussed in subsequent paragraphs, are used for this purpose.

Activity and Activity Coefficients

An approach that conforms well to the facts and that has evolved from a large number of studies on solutions of strong electrolytes ascribes the behavior of strong electrolytes to an electrostatic attraction between the ions.

Key Concept

Weak and Strong Electrolytes

The large number of oppositely charged ions in solutions of electrolytes influence one another through *interionic attractive forces*. Although this interference is negligible in dilute solutions, it

becomes appreciable at moderate concentrations. In solutions of weak electrolytes, regardless of concentration, the number of ions is small and the interionic attraction correspondingly insignificant. Hence, the Arrhenius theory and the concept of the degree of dissociation are valid for solutions of weak electrolytes but not for strong electrolytes.

Not only are the ions interfered with in their movement by the "atmosphere" of oppositely charged ions surrounding them, they can also associate at high concentration into groups known as *ion pairs* (e.g., Na^+Cl^-) and ion triplets ($Na^+Cl^-Na^+$). Associations of still higher orders may exist in solvents of low dielectric constant, in which the force of attraction of oppositely charged ions is large.

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.

One may think of 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 "taken out of play" 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. It is written on a molal basis at infinite dilution as

$$a = m \qquad \textbf{(6–38)}$$

or

$$\frac{a}{m} = 1 \qquad \textbf{(6–39)}$$

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

$$\frac{a}{m} = \gamma_m \qquad \textbf{(6–40)}$$

or

$$a = \gamma_m m \qquad \textbf{(6–41)}$$

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

$$a = \gamma_c c \qquad \textbf{(6–42)}$$

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

$$a = \gamma_x X \qquad \textbf{(6–43)}$$

One sees from equations **(**6-41**)** through **(**6-43**)** that these coefficients are proportionality constants relating activity to molality, molarity, and mole fraction, respectively, for an ion. The activity coefficients take on a value of unity and are thus identical in infinitely dilute solutions. The three coefficients usually decrease and assume different values as the concentration is increased; however, the differences among the three activity coefficients may be disregarded in dilute solutions, in which c [congruent] m < 0.01. The concepts of activity and activity coefficient were first introduced by Lewis and Randall5 and can be applied to solutions of nonelectrolytes and weak electrolytes as well as to the ions of strong electrolytes.

A cation and an anion in an aqueous solution may each have a different ionic activity. This is recognized by using the symbol a_+ when speaking of the activity of a cation and the symbol a_- when speaking of the activity of an anion. An electrolyte in solution contains each of these ions, however, so it is convenient to define a relationship between the activity of the electrolyte $a_\pm$ and the activities of the individual ions. The activity of an electrolyte is defined by its *mean ionic activity*, which is given by the relation

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

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

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

whereas an $FeCl_3$ solution has a mean ionic activity of

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

The ionic activities of equation (6-44) can be expressed in terms of concentrations using any of equations (6-41) to (6-43). Using equation (6-42), one obtains from equation (6-44) the expression

$$a_{\pm} = [(\gamma_+ c_+)^m (\gamma_- c_-)^n]^{1/(m+n)} \qquad \textbf{(6–45)}$$

or

$$a_{\pm} = (\gamma_+{}^m \gamma_-{}^n)^{1/(m+n)} (c_+{}^m c_-{}^n)^{1/(m+n)} \qquad \textbf{(6–46)}$$

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

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

and

$$\gamma_{\pm}^{m+n} = \gamma_+{}^m \gamma_-{}^n \qquad \textbf{(6–48)}$$

Substitution of equation (6-47) into equation (6-46) yields

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

In using equation (6-49), it should be noted that the concentration of the electrolyte *c* is related to the concentration of its ions by

$$c_+ = mc \qquad \textbf{(6–50)}$$

and

$$c_- = nc \qquad \textbf{(6–51)}$$

Example 6-9

Mean Ionic Activity of $FeCl_3$

What is the mean ionic activity of a 0.01 M solution of $FeCl_3$? We write

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

It is possible to obtain the *mean ionic activity coefficient*, $\gamma\pm$, of an electrolyte by several experimental methods as well as by a theoretical approach. The experimental methods include distribution coefficient studies, electromotive force measurements, colligative property methods, and solubility determinations. These results can then be used to obtain approximate activity coefficients for individual ions, where this is desired.6

Debye and Hückel developed a theoretical method by which it is possible to calculate the activity coefficient of a single ion as well as the mean ionic activity coefficient of a solute without recourse to experimental data. Although the theoretical equation agrees with experimental findings only in dilute solutions (so dilute, in fact, that some chemists have referred jokingly to such solutions as “slightly contaminated water”), it has certain practical value in solution calculations. Furthermore, the Debye-Hückel equation provides a remarkable confirmation of modern solution theory.

The mean ionic activity coefficients of a number of strong electrolytes are given in Table 6-1. The results of various investigators vary in the third decimal place; therefore, most of the entries in the table are recorded only to two places, providing sufficient precision for the calculations in this book. Although the values in the table are given at various molalities, we can accept these activity coefficients for problems involving molar concentrations (in which *m* $0.1) because, in dilute solutions, the difference between molality and molarity is not great.

The mean values of Table 6-1 for NaCl, $CaCl_2$, and $ZnSO_4$ are plotted in Figure 6-6 against the square root of the molality. The reason for plotting the square root of the concentration is due to the form that the Debye-Hückel equation takes. The activity coefficient approaches unity with increasing dilution. As the concentrations of some of the electrolytes are increased, their curves pass through minima and rise again to values greater than unity. Although the curves for different electrolytes of the same ionic class

coincide at lower concentrations, they differ widely at higher values. The initial decrease in the activity coefficient with increasing concentration is due to the interionic attraction, which causes the

activity to be less than the stoichiometric concentration. The rise in the activity coefficient following the minimum in the curve of an electrolyte, such as HCl and $CaCl_2$, can be attributed to the attraction of the water molecules for the ions in concentrated aqueous solution. This *solvation* reduces the interionic attractions and increases the activity coefficient of the solute. It is the same effect that results in the salting out of nonelectrolytes from aqueous solutions to which electrolytes have been added.

Table 6-1 Mean Ionic Activity Coefficients of Some Strong Electrolytes at 25°C On the Molal Scale

Molality (*m*)	HCl	NaCl	KCl	NaOH	$CaCl_2$	H_2SO_2	Na_2SO_2	$CuSO_2$	$ZnSO_2$
0.000	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
0.005	0.93	0.93	0.93	–	0.79	0.64	0.78	0.53	0.48
0.01	0.91	0.90	0.90	0.90	0.72	0.55	0.72	0.40	0.39
0.05	0.83	0.82	0.82	0.81	0.58	0.34	0.51	0.21	0.20
0.10	0.80	0.79	0.77	0.76	0.52	0.27	0.44	0.15	0.15
0.50	0.77	0.68	0.65	0.68	0.51	0.16	0.27	0.067	0.063
1.00	0.81	0.66	0.61	0.67	0.73	0.13	0.21	0.042	0.044
2.00	1.01	0.67	0.58	0.69	1.55	0.13	0.15	–	0.035
4.00	1.74	0.79	0.58	0.90	2.93	0.17	0.14	–	–

Activity of the Solvent

Thus far, the discussion of activity and activity coefficients has centered on the solute and particularly on electrolytes. It is customary to define the activity of the solvent on the mole fraction scale. When a solution is made infinitely dilute, it can be considered to consist essentially of pure solvent. Therefore, X_1 [congruent] 1, and the solvent behaves ideally in conformity with Raoult's law. Under this condition, the mole fraction can be set equal to the activity of the solvent, or

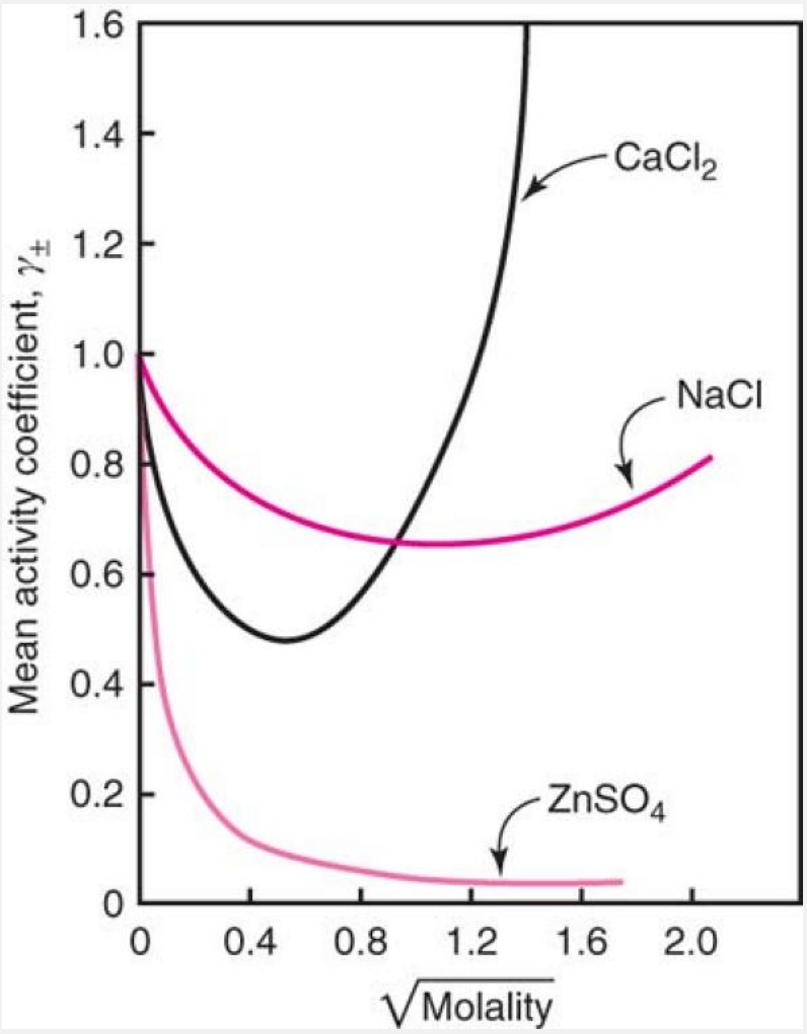


Fig. 6-6. Mean ionic activity coefficients of representative electrolytes plotted against the square root of concentration.

$$a = X_1 = 1 \qquad \textbf{(6–52)}$$

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,

$$\frac{a}{X_1} = \gamma_x \qquad \textbf{(6–53)}$$

or

$$a = \gamma_x X_1 \qquad \textbf{(6–54)}$$

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: $a_1 = p_1/p°$.

Example 6-10

Calculating Escaping Tendency

The vapor pressure of water in a solution containing 0.5 mole of sucrose in 1000 g of water is 17.38 mm and the vapor pressure of pure water at 20°C is 17.54 mm. What is the activity (or escaping tendency) of water in the solution? We write

$$a = \frac{17.38}{17.54} = 0.991$$

Reference State

The assignment of activities to the components of solutions provides a measure of the extent of departure from ideal solution behavior. For this purpose, 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

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

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

The reference state for a solvent on the mole fraction scale was shown in equation **(**6-52**)** to be the pure solvent.

The reference state for the solute can be chosen from one of several possibilities. If a liquid solute is miscible with the solvent (e.g., in a solution of alcohol in water), the concentration can be expressed in mole fraction, and the pure liquid can be taken as the reference state, as was done for the solvent. For a liquid or solid solute having a limited solubility in the solvent, the reference state is ordinarily taken as the infinitely dilute solution in which the concentration of the solute and the ionic strength (see the following) of the solution are small. Under these conditions, the activity is equal to the concentration and the activity coefficient is unity.

Standard State

The activities ordinarily used in chemistry are relative activities. It is not possible to know the absolute value of the activity of a component; therefore, a standard must be established just as was done in Chapter 1 for the fundamental measurable properties.

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.

The pure liquid at 1 atm and at a definite temperature is chosen as the standard state of a solvent or of a liquid solute miscible with the solvent because, for the pure liquid, $a = 1$. Because the mole fraction of a pure solvent is also unity, mole fraction is equal to activity, and the reference state is identical with the standard state.

The standard state of the solvent in a solid solution is the pure solid at 1 atm and at a definite temperature. The assignment of $a = 1$ to pure liquids and pure solids will be found to be convenient in later discussions on equilibria and electromotive force.

The standard state for a solute of limited solubility is more difficult to define. The activity of the solute in an infinitely dilute solution, although equal to the concentration, is not unity, and the standard state is thus not the same as the reference state. The standard state of the solute is defined as a hypothetical solution of unit concentration (mole fraction, molal or molar) having, at the same time, the characteristics of an infinitely dilute or ideal solution. For complete understanding, this definition requires careful development, as carried out by Klotz and Rosenberg.7

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 (considered later) if one knows the ionic strength of the solution. Lewis and Randall8 introduced the concept of *ionic strength*, μ, to relate interionic attractions and activity coefficients. The ionic strength is defined on the molar scale as

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

or, in abbreviated notation,

$$\mu = \frac{1}{2}\sum_{1}^{j} c_i z_i^2 \quad \textbf{(6–56)}$$

where the summation symbol indicates that the product of cz^2 terms for all the ionic species in the solution, from the first one to the jth species, is to be added together. The term 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. It was found that bivalent ions are equivalent not to two, but to four univalent ions; hence, by introducing the square of the valence, one gives proper weight to the ions of higher charge. The sum is divided by 2 because positive ion-negative ion pairs contribute to the total electrostatic interaction, whereas we are interested in the effect of each ion separately.

Example 6-11
Calculating Ionic Strength

What is the ionic strength of (*a*) 0.010 M KCl, (*b*) 0.010 M $BaSO_4$, and (*c*) 0.010 M Na_2SO_4, 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:

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

(b) $BaSO_4$:

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

(c) $Na_2 SO_4$:

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

(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,

$$\mu_{total} = \mu_{KCl} + \mu_{BaSO_4} + \mu_{Na_2SO_4} + \mu_{HSal} = 0.010 + 0.040 + 0.030 + 0.003 = 0.083$$

Example 6-12
Ionic Strength of a Solution

A buffer contains 0.3 mole of K_2HPO_4 and 0.1 mole of KH_2PO_4 per liter of solution. Calculate the ionic strength of the solution.

The concentrations of the ions of K_2HPO_4 are $[K^+] = 0.3 \times 2$ and $[HPO_4^{2-}] = 0.3$. The values for KH_2PO_4 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,

$$\mu = \frac{1}{2}[(0.3 \times 2 \times 1^2) + (0.3 \times 2^2) + (0.1 \times 1^2) + (0.1 \times 1^2)]$$

$$\mu = 1.0$$

It will be observed in Example 6-11 that the ionic strength of a 1:1 electrolyte such as KCl is the same as the molar concentration; μ of a 1:2 electrolyte such as Na_2SO_4 is three times the concentration; and μ for a 2:2 electrolyte is four times the concentration.

The mean ionic activity coefficients of electrolytes should be expressed at various ionic strengths instead of concentrations. Lewis showed the uniformity in activity coefficients when they are related to ionic strength:

a. The activity coefficient of a strong electrolyte is roughly constant in all dilute solutions of the same ionic strength, irrespective of the type of salts that are used to provide the additional ionic strength.
b. The activity coefficients of all strong electrolytes of a single class, for example, all uni-univalent electrolytes, are approximately the same at a definite ionic strength, provided the solutions are dilute.

The results in Table 6-1 illustrate the similarity of the mean ionic activity coefficients for 1:1 electrolytes at low concentrations (below 0.1 *m*) and the differences that become marked at higher concentrations. Bull9 pointed out the importance of the principle of ionic strength in biochemistry. In the study of the influence of pH on biologic action, the effect of the variable salt concentration in the buffer may obscure the results unless the buffer is adjusted to a constant ionic strength in each experiment. If the biochemical action is affected by the specific salts used, however, even this precaution may fail to yield satisfactory results. Further use will be made of ionic strength in the chapters on ionic equilibria, solubility, and kinetics.

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 mathematical derivation of the equation is not attempted here but can be found in Lewis and Randall's *Thermodynamics* as revised by Pitzer and Brewer.10 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

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

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 Table 6-2.

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

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

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 coefficient in equation (6-58) should

actually be γ_x, the rational activity coefficient (i.e., $\gamma\pm$ on the mole fraction scale), but in dilute solutions for which the Debye-Hückel equation is applicable, γ_x can be assumed without serious error to be equal also to the practical coefficients, γ_m and Λ_c, on the molal and molar scales.

Table 6-2 Values of *A* For Solvents at 25°C*

Solvent	Dielectric Constant, ε	A_{calc}
Acetone	20.70	3.76
Ethanol	24.30	2.96
Water	78.54	0.509

*$A_{calc} = (1.824 \times 10^6)/(\varepsilon \times T)^{3/2}$, where ε is the dielectric constant and T is the absolute temperature on the Kelvin scale.

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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. We have

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

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

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

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

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

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

With the present-day accessibility of the handheld calculator, the intermediate step in this calculation (needed only when log tables are used) can be deleted.

Thus, one observes that 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. Notice that although the ionic strength term results from the contribution of all ionic species in solution, the z_1z_2 terms apply only to the drug whose activity coefficient is being determined.

Extension of the Debye-Hückel Equation to Higher Concentrations

The limiting expressions (6-57) and (6-58) are not satisfactory above an ionic strength of about 0.02, and equation (6-58) is not completely satisfactory for use inExample 6-13. A formula that applies up to an ionic strength of perhaps 0.1 is

$$\log \gamma_{\pm} = -\frac{Az_+z_-\sqrt{\mu}}{1 + a_i B\sqrt{\mu}} \qquad (6\text{–}59)$$

The term a_i is the mean distance of approach of the ions and is called the *mean effective ionic diameter* or the *ion size parameter*. Its exact significance is not known; however, it is somewhat analogous to the *b* term in the van der Waals gas equation. The term *B*, like *A*, is a constant influenced only by the nature of the solvent and the temperature. The values of a_i for several electrolytes at 25°C are given in Table 6-3 and the values of *B* and *A* for water at various temperatures are shown in Table 6-4. The values of *A* for various solvents, as previously mentioned, are listed in Table 6-2.
Because a_i for most electrolytes equals 3 to 4 × 10^{-8} and *B* for water at 25°C equals 0.33 × 10^{8}, the product of a_i and *B* is approximately unity. Equation (6-59) then simplifies to

$$\log \gamma_{\pm} = -\frac{Az_+z_-\sqrt{\mu}}{1+\sqrt{\mu}} \qquad \textbf{(6–60)}$$

Table 6-3 Mean Effective Ionic Diameter for Some Electrolytes at 25°C

Electrolyte	a_i (cm)
HCl	5.3×10^{-8}
NaCl	4.4×10^{-8}
KCl	4.1×10^{-8}
Methapyrilene HCl	3.9×10^{-8}
$MgSO_4$	3.4×10^{-8}
K_2SO_4	3.0×10^{-8}
$AgNO_3$	2.3×10^{-8}
Sodium phenobarbital	2.0×10^{-8}

Example 6-14
Comparing Activity Coefficients
Calculate the activity coefficient of a 0.004 M aqueous solution of sodium phenobarbital at 25°C that has been brought to an ionic strength of 0.09 by the addition of sodium chloride. Use equations (6-58) through (6-60) and compare the results.

$$\textbf{Equation (6–58): } \log \gamma_{\pm} = -0.51\sqrt{0.09}; \gamma_{\pm} = 0.70$$

$$\textbf{Equation (6–59): } \log \gamma_{\pm} = \frac{0.51\sqrt{0.09}}{1+2[(2\times 10^{8})\times(0.33\times 10^{3})\times\sqrt{0.09}]}; \gamma_{\pm} = 0.75$$

$$\textbf{Equation (6 – 60): } \log \gamma_{\pm} = -\frac{0.51\sqrt{0.09}}{1+\sqrt{0.09}}; \gamma_{\pm} = 0.76$$

These results can be compared with the experimental values for some uni-univalent electrolytes in Table 6-1 at a molal concentration of about 0.1.

For still higher concentrations, that is, at ionic strengths above 0.1, the observed activity coefficients for some electrolytes pass through minima and then increase with concentration; in some cases, they become greater than unity, as seen in Figure 6-6. To account for the increase in $\gamma\pm$ at higher concentrations, an empirical term $C\mu$ can be added to the Debye-Hückel equation, resulting in the expression

$$\log \gamma_{\pm} = -\frac{Az_+z_-\sqrt{\mu}}{1 + a_i B\sqrt{\mu}} + C\mu \qquad \textbf{(6–61)}$$

This equation gives satisfactory results in solutions of concentrations as high as 1 M. The mean ionic activity coefficient

obtained from equation (6-61) is γ_x; however, it is not significantly different from γ_m and γ_c even at this concentration. Zografi et al.11 used the extended Debye-Hückel equation [(equation (6-61)] in a study of the interaction between the dye orange II and quarternary ammonium salts.

Table 6-4 Values of *A* and *B* for Water at Various Temperatures

Temperature (°C)	*A*	*B*
0	0.488	0.325×10^8
15	0.500	0.328×10^8
25	0.509	0.330×10^8
40	0.524	0.333×10^8
70	0.560	0.339×10^8
100	0.606	0.348×10^8

Investigations have resulted in equations that extend the concentration to about 5 moles/liter.12

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

$$\Delta T_f = Lc \qquad \textbf{(6–62)}$$

Goyan et al.13 computed 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 6-7, 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.

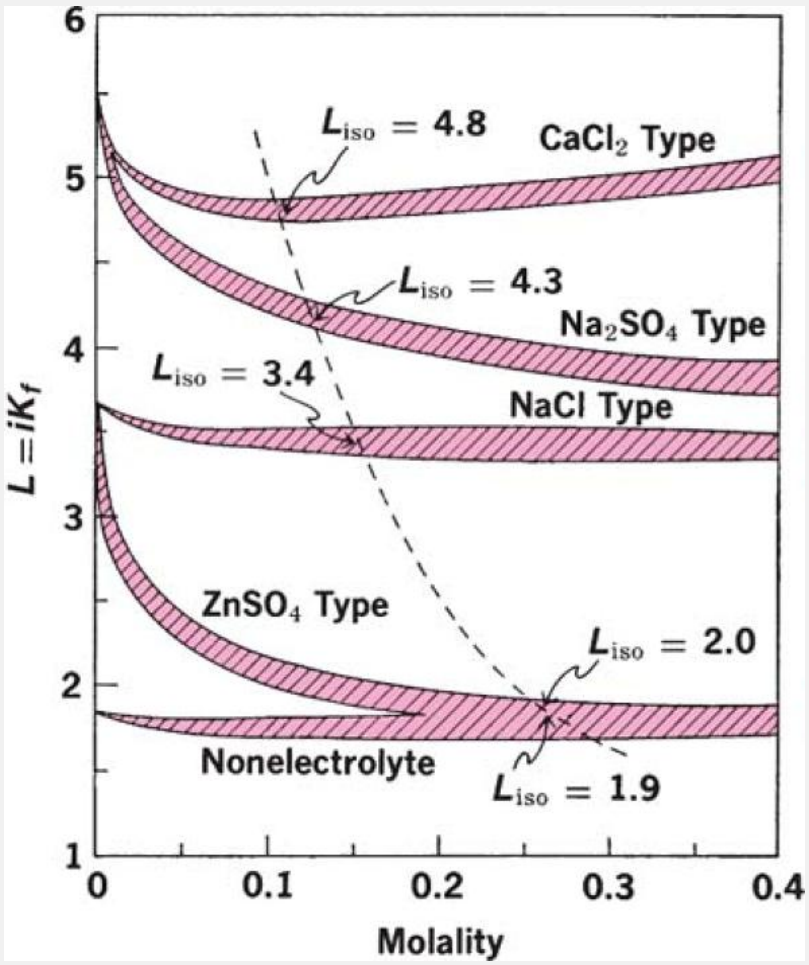


Fig. 6-7. L_{iso} values of various ionic classes.

Key Concept

Activities

Although activities can be used to bring the colligative properties of strong electrolytes into line with experimental results, the equations are complicated and are not treated in this book. Activities are more valuable in connection with equilibrium expressions and electrochemical calculations. The use of activities for calculating the colligative properties of weak electrolytes is particularly inconvenient because it also requires knowledge of the degree of dissociation.

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, *vm*, in Figure 6-8. Because $g = 1/v$ or $i = gv$ in a dilute solution, the cryoscopic equation can be written as

$$\Delta T_f = g\nu K_f m \qquad (6\text{–}63)$$

The molal osmotic coefficients of some salts are listed in Table 6-5.

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. We have

$$\Delta T_f = g\nu K_f m = 0.944 \times 2 \times 1.86 \times 0.2 = 0.70°$$

$$\Delta T_f = L_{iso} c = 3.4 \times 0.2 = 0.68°$$

Osmolality

Although osmotic pressure classically is given in atmospheres, in clinical practice it is expressed in terms of osmols (Osm) or milliosmols (mOsm). A solution containing 1 mole (1 g molecular weight) of a nonionizable substance in 1 kg of water (a 1 *m* solution) is referred to as a 1-osmolal solution. It contains 1 osmol (Osm) or 1000 milliosmols (mOsm) of solute per kilogram of solvent. 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. An ionic species dissolved in water will dissociate to form ions or “particles.” These ions tend to associate somewhat, however, owing to their ionic interactions. The apparent number of “particles” in solution, as measured by osmometry or one of the other colligative methods, will depend on the extent of these interactions. An un-ionized material (i.e., a nonelectrolyte) is used as the reference solute for osmolality measurements, ionic interactions being insignificant for a nonelectrolyte. For an electrolyte that dissociates into ions in a dilute solution, osmolality or milliosmolality can be calculated from

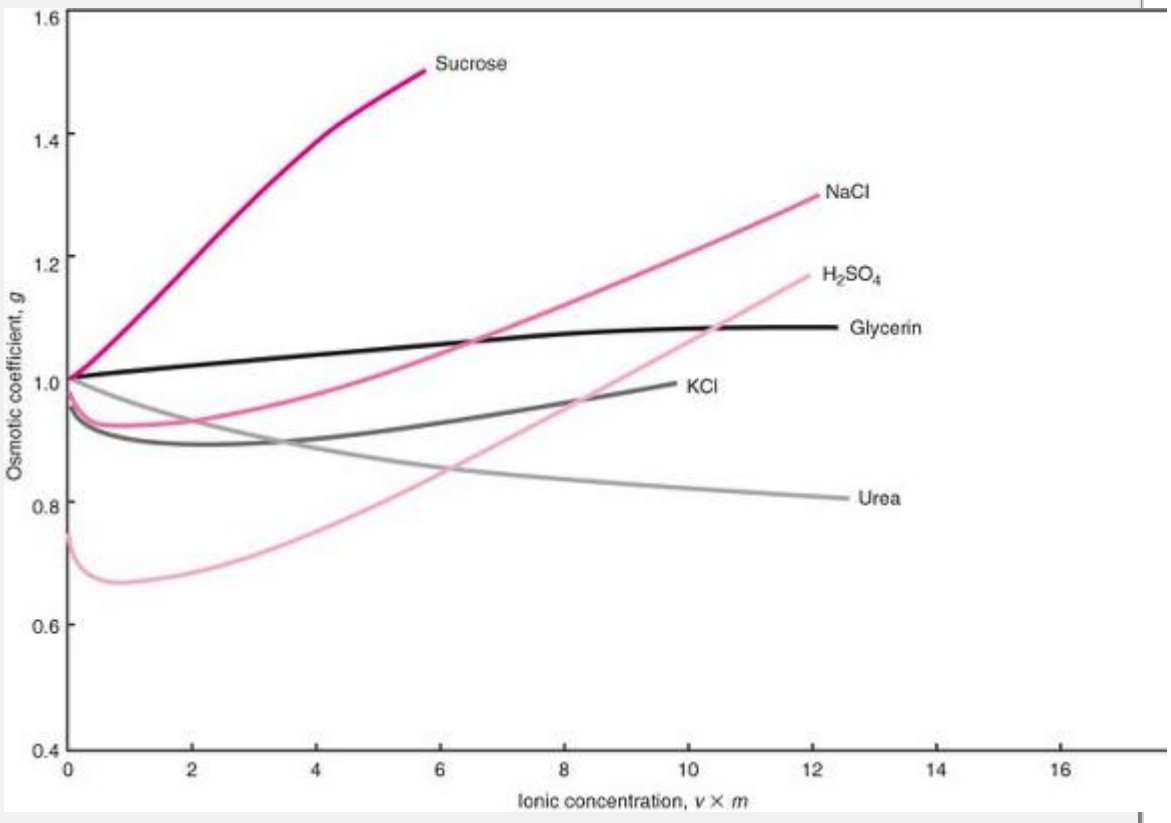


Fig. 6-8. Osmotic coefficient, *g*, for some common solutes. (From G. Scatchard, W.

Hamer, and S. Wood, J. Am. Chem. Soc.**60,** 3061, 1938. With permission.)

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

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.

Table 6-5 Osmotic Coefficient, *g*, at 25°C*

m	NaCl	KCl	H_2SO_4	Sucrose	Urea	Glycerin
0.1	0.9342	0.9264	0.6784	1.0073	0.9959	1.0014
0.2	0.9255	0.9131	0.6675	1.0151	0.9918	1.0028
0.4	0.9217	0.9023	0.6723	1.0319	0.9841	1.0055
0.6	0.9242	0.8987	0.6824	1.0497	0.9768	1.0081
0.8	0.9295	0.8980	0.6980	1.0684	0.9698	1.0105
1.0	0.9363	0.8985	0.7176	1.0878	0.9631	1.0128
1.6	0.9589	0.9024	0.7888	1.1484	0.9496	1.0192
2.0	0.9786	0.9081	0.8431	1.1884	0.9346	1.0230
3.0	1.0421	0.9330	0.9922	1.2817	0.9087	1.0316
4.0	1.1168	0.9635	1.1606	1.3691	0.8877	1.0393
5.0	1.2000	0.9900	–	1.4477	0.8700	1.0462

*From G. Scatchard, W. G. Hamer, and S. E. Wood, J. Am. Chem. Soc. **60**, 3061, 1938. With permission.

Example 6-16

Calculating Milliosmolality

What is the milliosmolality of a 0.120 *m* solution of potassium bromide? What is its osmotic pressure in atmospheres?

For a 120 millimolal solution of KBr:

$$\text{Milliosmolality} = 1.86 \times 120 = 223 \text{ mOsm/kg}$$

A 1-osmolal solution raises the boiling point 0.52°C, lowers the freezing point 1.86°C, and produces an osmotic pressure of 24.4 atm at 25°C. Therefore, a 0.223-Osm/kg solution yields an osmotic pressure of 24.4 × 0.223 = 5.44 atm.

Streng et al.14 and Murty et al.15 discuss the use of osmolality and osmolarity in clinical pharmacy. Molarity (moles of solute per liter of solution) is used in clinical practice more frequently than molality (moles of solute per kilogram of solvent). In addition, 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. As shown by Murty et al.,15 the conversion is made using the relation

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

According to Streng et al.,14 osmolality is converted to osmolarity using the equation

$$\begin{aligned}\text{mOsm/liter solution} = &\ \text{mOsm/(kg } H_2O) \\ &\times [d_1^\circ(1 - 0.001\,\bar{v}_2^\circ)] \quad \textbf{(6–66)}\end{aligned}$$

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.

Example 6-17

Converting Osmolality to Osmolarity

A 30-g/liter solution of sodium bicarbonate contains 0.030 g/mL of anhydrous sodium bicarbonate. The density of this solution was found to be 1.0192 g/mL at 20°C and its measured milliosmolality was 614.9 mOsm/kg. Convert milliosmolality to milliosmolarity. We have

$$\begin{aligned}\text{Milliosmolarity} = &\ 614.9\,\text{mOsm/kg } H_2O \\ &\times (1.0192\ \text{g/mL} - 0.030\,\text{g/mL}) \\ = &\ 608.3\,\text{mOsm/L solution}\end{aligned}$$

Example 6-18

Calculating Milliosmolarity

A 0.154 *m* sodium chloride solution has a milliosmolality of 286.4 mOsm/kg (see Example 6-19). Calculate the milliosmolarity, mOsm/liter solution, using equation (6-66). The density of the solvent—water—at 25°C is d_1° = 0.9971 g/cm^3 and the partial molal volume of the solute—sodium chloride—is $\bar{v}_2^\circ$ = 16.63 mL/mole.

$$\begin{aligned}\textbf{Milliosmolality} = &\ \textbf{(286.4 mOsm/kg } H_2O\textbf{)} \\ &\times [0.9971(1 - 0.001(16.63))] \\ = &\ \textbf{280.8 mOsm/L solution}\end{aligned}$$

As noted, osmolarity differs from osmolality by only 1% or 2%. However, in more concentrated solutions of polyvalent electrolytes together with buffers, preservatives, and other ions, the difference may become significant. For accuracy in the preparation and labeling of parenteral solutions, osmolality should be measured carefully with a vapor pressure or freezing point osmometer (rather than calculated) and the results converted to osmolarity using equation **(**6-65**)** or **(**6-66**)**.

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 (6-27) and (6-63):

$$\Delta T_f \cong K_f im \qquad (6\text{–}67)$$

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

Example 6-19

Calculate Freezing Point Depression

Calculate the freezing point depression of (*a*) 0.154 *m* solution of NaCl and (*b*) a 0.154 *m* solution of glucose. What are the milliosmolalities of these two solutions?

(a) From Table 6-5, *g* for NaCl at 25°C is about 0.93, and because NaCl ionizes into two ions, $i = vg = 2 \times 0.93 = 1.86$. From equation (6-64), the osmolality of a 0.154 *m* solution is $im = 1.86 \times 0.154 = 0.2864$. The milliosmolality of this solution is therefore 286.4 mOsm/kg. Using equation (6-67), with K_f also equal to 1.86, we obtain for the freezing point depression of a 0.154 *m* solution—or its equivalent, a 0.2864-Osm/kg solution—of NaCl:

$$\Delta T_f = (1.86)(1.86)(0.154)$$
$$= (1.86)(0.2864) = 0.53^\circ\text{C}$$

(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

$$\Delta T_f = K_f im = (1.86)(1.00)(0.154)$$
$$= 0.286^\circ\text{C}$$

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.

Ohwaki et al.16 studied the effect of osmolality on the nasal absorption of secretin, a hormone used in the treatment of duodenal ulcers. They found that maximum absorption through the nasal mucosa occurred at a sodium chloride milliosmolarity of about 860 mOsm/liter (0.462 M), possibly owing to structural changes in the epithelial cells of the nasal mucosa at this high mOsm/liter value.

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. This principle is best described by an example.

Example 6-20

Milliosmolarity of Blood

Freezing points were determined using the blood of 20 normal individuals and were averaged to -0.5712°C. This value of course is equivalent to a freezing point depression of +0.5712°C below the freezing point of water because the freezing point of water is taken as 0.000°C at atmospheric pressure. What is the average milliosmolality, *x*, of the blood of these subjects? Using equation (6-67) with the arbitrary choice of $i = 1$ for body fluids, we obtain

$$0.5712 = (1.86)(1.00)x$$
$$x = 0.3071 \text{ Osm/kg}$$
$$= 307.1 \text{ mOsm/kg}$$

It is noted in Example 6-20 that although the osmolality of blood and its freezing point depression are contributed mainly by NaCl, an *i* value of 1 was used for blood rather than $gv = 1.86$ for an NaCl solution.

The milliosmolality for blood obtained by various workers using osmometry, vapor pressure, and freezing point depression apparatus ranges from about 250 to 350 mOsm/kg.17 The normal osmolality of body fluids is given in medical handbooks18 as 275 to 295 mOsm/kg, but normal values are likely to fall in an even narrower range of 286 ± 4 mOsm/kg.19 Freezing point and vapor pressure osmometers are now used routinely in the hospital. A difference of 50 mOsm/kg or more from the accepted values of a body fluid suggests an abnormality such as liver failure, hemorrhagic shock, uremia, or other toxic manifestations. Body water and electrolyte balance are also monitored by measurement of milliosmolality.

Chapter Summary

In this chapter, solutions of electrolytes were introduced and discussed. Understanding the properties of electrolytes in solution is still very important today in the pharmaceutical sciences. You should be able to understand Faraday's law and calculate the conductance in solutions. The rationale for using the concept of activity rather than concentrations is important in many chemical calculations since solutions that contain ionic solutes do not behave ideally even at very low concentrations. The information provided establishes a framework for calculating ionic strength, osmolality, and osmolarity. The successful student will not only be able to do these calculations but will understand the differences between osmolality and osmolarity.

Practice problems for this chapter can be found at thePoint.lww.com/Sinko6e.

References

1. S. Arrhenius, Z. Physik. Chem. **1,** 631, 1887.
2. H. L. Clever, J. Chem. Educ. **40,** 637, 1963; P. A. Giguère, J. Chem. Educ. **56,** 571, 1979; R. P. Bell, *The Proton in Chemistry*, 2nd Ed., Chapman and Hall, London, 1973, pp. 13–25.
3. A. Albert, *Selective Toxicity*, Chapman and Hall, London, 1979, pp. 344, 373–384.
4. S. Arrhenius, J. Am. Chem. Soc. **34,** 361, 1912.
5. G. N. Lewis and M. Randall, *Thermodynamics*, McGraw-Hill, New York, 1923, p. 255.
6. S. Glasstone, *An Introduction to Electrochemistry*, Van Nostrand, New York, 1942, pp. 137–139.
7. I. M. Klotz and R. M. Rosenberg, *Chemical Thermodynamics*, 3rd Ed., W. A. Benjamin, Menlo Park, Calif., 1973, Chapter 19.
8. G. N. Lewis and M. Randall, *Thermodynamics*, McGraw-Hill, New York, 1923, p. 373.
9. H. B. Bull, *Physical Biochemistry*, 2nd Ed., Wiley, New York, 1951, p. 79.
10. G. N. Lewis and M. Randall, *Thermodynamics, Rev*. K. S. Pitzer and L. Brewer, 2nd Ed., McGraw-Hill, New York, 1961, Chapter 23.
11. G. Zografi, P. Patel, and N. Weiner, J. Pharm. Sci. **53,** 545, 1964.
12. R. H. Stokes and R. A. Robinson, J. Am. Chem. Soc. **70,** 1870, 1948; M. Eigen and E. Wicke, J. Phys. Chem. **58,** 702, 1954.
13. F. M. Goyan, J. M. Enright, and J. M. Wells, J. Am. Pharm. Assoc. Sci. Ed. **33,** 74, 1944.
14. W. H. Streng, H. E. Huber, and J. T. Carstensen, J. Pharm. Sci. **67,** 384, 1978; H. E. Huber, W. H. Streng, and H. G. H. Tan, J. Pharm. Sci. **68,** 1028, 1979.
15. B. S. R. Murty, J. N. Kapoor, and P. O. DeLuca, Am. J. Hosp. Pharm. **33,** 546, 1976.
16. T. Ohwaki, H. Ando, F. Kakimoto, K. Uesugi, S. Watanabe, Y. Miyake, and M. Kayano, J. Pharm. Sci. **76,** 695, 1987.
17. C. Waymouth, In Vitro **6,** 109, 1970.
18. M. A. Kaupp, et al. (Eds.), *Current Medical Diagnosis and Treatment*, Lange, Los Altos, Calif., 1986, pp. 27, 1113.
19. L. Glasser, D. D. Sternalanz, J. Combie, and A. Robinson, Am. J. Clin. Pathol. **60,** 695–699, 1973.

Recommended Readings

R. A. Robinson and R. H. Stokes, *Electrolyte Solutions: Second Revised Edition*, Dover Publications, Mineola NY, 2002.

Chapter Legacy

Fifth Edition: published as Chapter 6 (Electrolyte Solutions). Updated by Patrick Sinko.
Sixth Edition: published as Chapter 6 (Electrolyte Solutions). Updated by Patrick Sinko.