Electrolyte Solutions

- **Electrolytes** are substances that form ions in solutions, conduct the electric current.

- Electrolytes may be subdivided further into strong electroytes (hydrochloric acid, sodium sulphate) and weak electrolytes (ephedrine, phenobarbital).

- **Strong electrolytes** are substances that are completely ionized when they are dissolved in water. They conduct electrical currents very efficiently. The classes of strong electrolytes include: (a) soluble salts e.g. $BaCl_2$, (b) strong acids e.g. HCl, HNO_3, H_2SO_4, (c) strong bases e.g. NaOH, KOH

- **Weak electrolytes** are substances that exhibit a small degree of ionization in water. That is, they produce relatively few ions when dissolved in water. Their solutions produce a small current. The most common weak electrolytes are weak acids (e.g. acetic acid) and weak bases (ammonium hydroxide – NH_4OH).

Properties of Solutions of Electrolytes

- *Electrolysis: When a direct electric current flows through an electrolytic cell, a chemical reaction occurs. This process is known as electrolysis.*

- *Electrons enter the cell from the battery or generator at the cathode, 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, and the anions are accordingly oxidized.*
- *Reduction is the addition of electrons to a chemical species*
- *oxidation* is removal of electrons from a species.
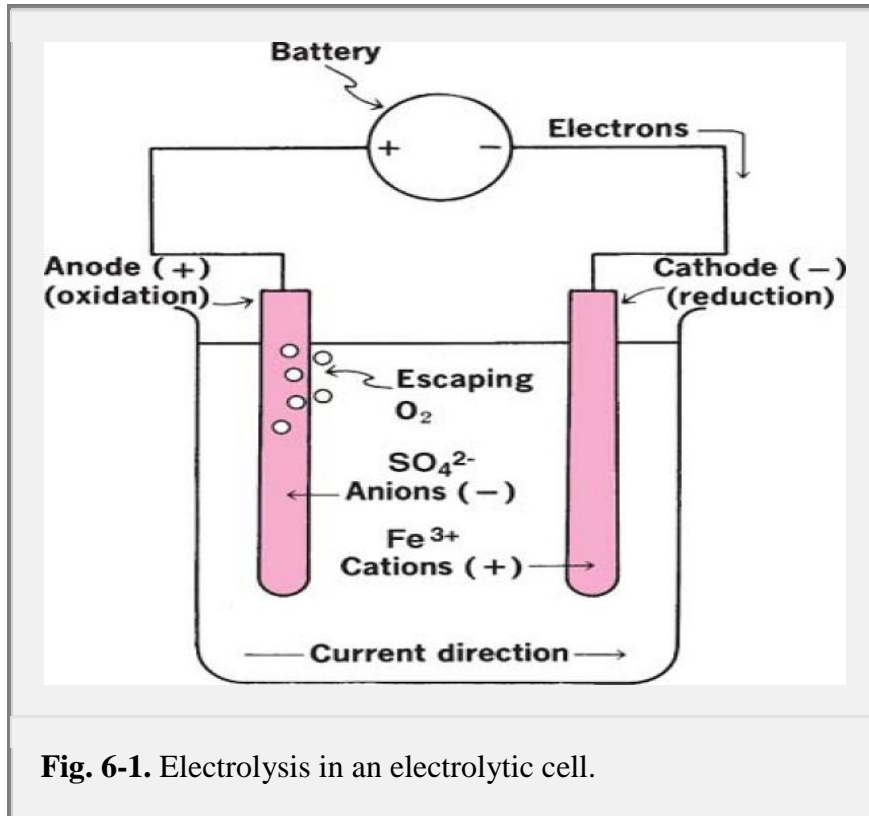- The current in a solution consists of a flow of positive and negative ions toward the electrodes,

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

Electrons enter the cell from the battery or generator at the *cathode* (road down); they combine *cations* in the solution, and the cations are accordingly reduced.

anions, carry electrons through the solution and discharge them at the *anode* (road up), and the anions are accordingly oxidized.

The current in a solution consists of a flow of positive and negative ions toward the electrodes.

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.

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

$$OH^- = \frac{1}{4}O_2 + \frac{1}{2}H_2O + e \qquad (6\text{–}2)$$
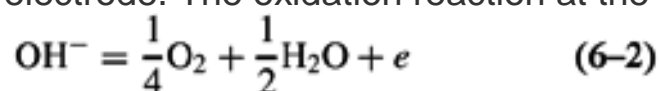
Platinum electrodes are used here because they do not pass into solution to any extent. When *attackable* metals, such as copper or zinc, are used as the anode, their atoms tend to lose electrons, and the metal passes into solution as the positively charged ion.

Transference Numbers

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.

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 of electricity Q (electronic charge) in coulombs flowing per unit time:

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

and

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.

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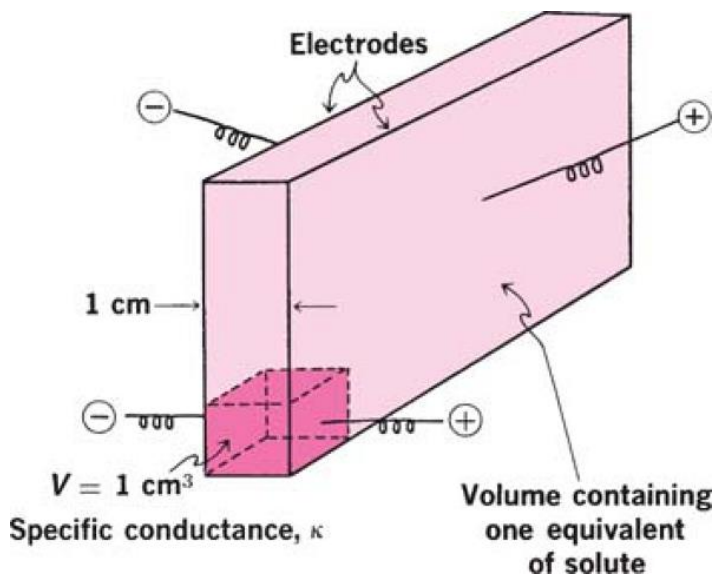
Electrolytic Conductance

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

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

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,

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

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)**:

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

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

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

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

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

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.

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

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

$$\Lambda_c = \kappa \times V$$

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

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.

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.

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

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

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.
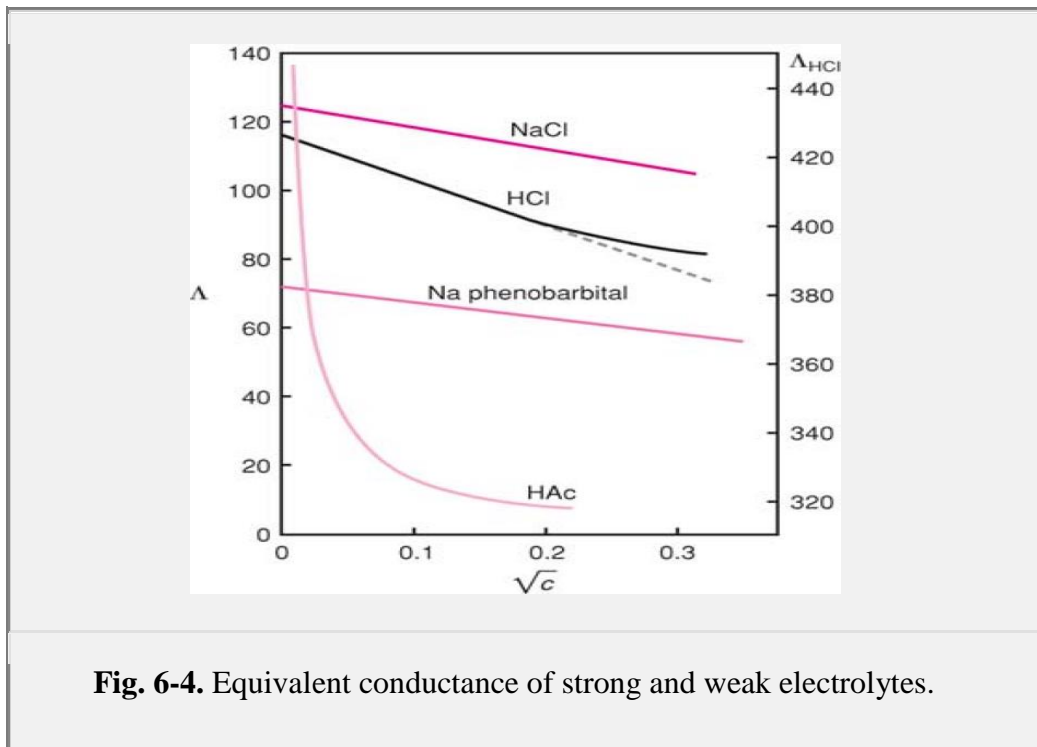

Fig. 6-4. Equivalent conductance of strong and weak electrolytes.

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

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

Colligative Properties of Electrolytic Solutions and Concentrated Solutions of Nonelectrolytes

- ■ *Van't Hoff introduced a correction factor i to account for the irrational behavior of ionic solutions.*

   $\pi = iRTc$

- ■ *i approached the number of ions into which the molecule dissociated as the solution was made increasingly dilute.*

- ■ ***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 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, since i represents the number of times greater that the colligative effect is for a real solution (electrolyte or nonelectrolyte) than for an ideal solution.

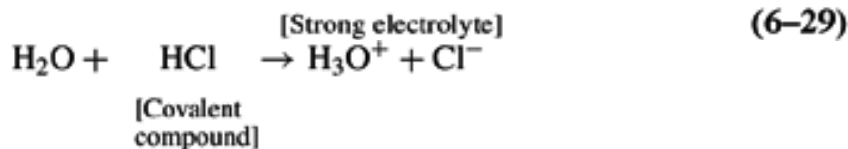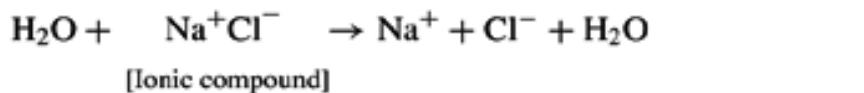$$\Delta p = 0.018 i p_1^0 m \text{ --------(1)} \qquad \pi = iRTm \text{ ------------(2)}$$
$$\Delta T_f = iK_f m \text{ -------------(3)} \qquad \Delta T_b = iK_b m \text{ -----------(4)}$$

Equation **(1)** applies only to aqueous solutions, whereas **(2)** through **(4)** are independent of the solvent used.
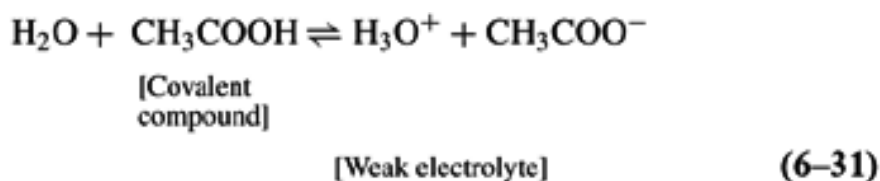
Theory of Electrolytic Dissociation

Arrhenius theory, 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:

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

$$\text{[Strong electrolyte]} \qquad (6\text{--}29)$$

$$H_2O + \underset{\substack{\text{[Covalent} \\ \text{compound]}}}{HCl} \rightarrow H_3O^+ + Cl^-$$

$$\text{[Strong electrolyte]} \qquad (6\text{--}30)$$

$$H_2O + \underset{\substack{\text{[Covalent} \\ \text{compound]}}}{CH_3COOH} \rightleftharpoons H_3O^+ + CH_3COO^-$$

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

- ■ In fact, Arrhenius did not consider strong electrolytes to be ionized completely except in extremely diluted solutions. He differentiated between strong and weak electrolytes by the fraction of the molecules ionized: the degree of dissociation α.

A strong electrolytes is one that dissociated into ions to a high degree and a weak electrolyte is one that dissociated into ions to a low degree

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

A strong electrolyte was one that dissociated into ions to a high **degree of dissociation, α**. and a weak electrolyte was one that dissociated into ions to a low degree.

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 1-the conductance ratio Λ_c/Λ_0 or 2- van't Hoff i factor

1- the degree of dissociation can be determined from conductance measurements. Equivalent conductance at infinite dilution Λ_o 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 concentration c.

Hence the fraction of solute molecules ionized, or the degree of dissociation, can be expressed by the equation

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

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

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

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

The cryoscopic method is used to determine i from the expression

$$\Delta T_f = iK_f m \qquad (6\text{--}36)$$

or

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

Theory of Strong Electrolytes

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.

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 .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.