

## Chapter one

### Electrolytic Solutions

#### 1.1. Introduction

**Electrochemistry** is the branch of physical chemistry that studies the relationship between electricity, as a measurable and quantitative phenomenon, and identifiable chemical change, with either electricity considered an outcome of a particular chemical change or vice versa. These reactions involve electric charges moving between electrodes and an electrolyte (or ionic species in a solution). Thus electrochemistry deals with the interaction between electrical energy and chemical change.

When a chemical reaction is caused by an externally supplied current, as in electrolysis, or if an electric current is produced by a spontaneous chemical reaction as in a battery, it is called an **electrochemical reaction**. Chemical reactions where electrons are transferred directly between molecules and/or atoms are called oxidation-reduction or (redox) reactions. In general, electrochemistry describes the overall reactions when individual redox reactions are separate but connected by an external electric circuit and an intervening electrolyte.

It is Study of chemical changes produced by electrical current and the production of electricity by chemical reactions.

#### 1.2. Electrolytic Solutions

Solution is a homogenous mixture which may a liquid, gas or solid formed by dissolving one or more substances. Depending on the amount of solute present, solution is divided into **saturated**, **unsaturated** and **super saturated** solutions. But based on dissociation into ions, solutions can be divided into **electrolytic** and **non-electrolytic** solutions.

**An electrolytic solution** is a solution that generally contains ions, atoms or molecules that have lost or gained electrons, and is electrically conductive. For this reason they are often called ionic solutions, however there are some cases where the electrolytes are not ions. For this discussion we will only consider solutions of ions. A basic principle of electrostatics is that opposite charges

attract and like charges repel. It also takes a great deal of force to overcome this electrostatic attraction.

An **electrolyte** is a substance that produces an electrically conducting solution when dissolved in a polar solvent, such as water. The dissolved electrolyte separates into cations and anions, which disperse uniformly through the solvent. Electrically, such a solution is neutral. If an electric potential is applied to such a solution, the cations of the solution are drawn to the electrode that has an abundance of electrons, while the anions are drawn to the electrode that has a deficit of electrons. The movement of anions and cations is in opposite directions within the solution.

### Classification of Conductors

All forms of matter appear to be able to conduct the electric current to some extent, but the conducting powers of different substances vary over a wide range; thus silver, one of the best conductors, is  $10^{24}$  times more effective than paraffin wax, which is one of the poorest conductors. It is not easy to distinguish sharply between good and bad conductors, but a rough division is possible; the systems studied in electrochemistry are generally good conductors.

These may be divided into two main categories; they are:

- a) **Metallic conductors:** Metals are the best conductors, in general, and the passage of current is not accompanied by any movement of matter; it appears, therefore, that the electricity is carried exclusively by the electrons, the atomic nuclei remaining stationary. This is in accordance with modern views which regard a metal as consisting of a relatively rigid lattice of ions together with a system of mobile electrons. Metallic conduction, or electronic conduction as it is often called, is not restricted to pure metals, for it is a property possessed by most alloys, carbon and certain solid salts and oxides.
- b) **Electrolytic conductors or Electrolyte solutions:** when a chemical compound (salt, acid, or base) when dissolved in a solvent dissociates into electrically charged ions and the solution that contains such electrically charged ions is known as **electrolytic solution**.

There is a special class of conductors, which conduct partly electronically and partly electrolytically, are known as *mixed conductors*. For example, solution of the alkali and alkaline

earth metals in liquid ammonia are mixed conductors. Fused cuprous sulphide conducts electronically, but a mixture with sodium or ferrous sulphide also shows electrolytic conduction.

#### Difference between electronic & electrolytic conductors

Electronic Conductors	Electrolytic Conductors
Flow of electricity take place without decomposition of substances	Flow of electricity takes place with decomposition of substances
Conduction is due to flow of electrons	Flow of electricity is due to movements of ions
Conduction decrease as temperature increases and resistance increases	Conduction increases with increase temperature due to decrease in resistance for mobility of ions
No transfer of mass	Transfer of mass

#### Electrical Conduction in Electrolyte Solutions

Electric currents in metallic conductors and semiconductors are due to the motions of electrons, whereas electric currents in electrolyte solutions are due to the motions of ions.

The materials, generally small sheets of metal, which are employed to pass an electric current through an electrolytic solution, are called electrodes; the one at which the positive current enters is referred to as the *positive electrode or anode*, whereas the electrode at which current leaves is called the *negative electrode, or cathode*.

#### Strong and Weak Electrolytes

Solutes giving conducting solution in a suitable solvent are called electrolytes. On the basis of degree of ionization, these electrolytes have been divided into two categories:

- ✓ Strong electrolytes
- ✓ Weak electrolytes.

Substances, which are highly dissociated and give solutions with high conductance in water, are called **strong electrolytes**. Due to the high degree of dissociation of strong electrolytes these substances are good conductor of electricity.

**Examples**

- ✓ strong acid ( $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ )
- ✓ Strong bases ( $\text{NaOH}$ ,  $\text{Ca}(\text{OH})_2$ , and  $\text{KOH}$ )
- ✓ Salts ( $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{MgCl}_2$ )

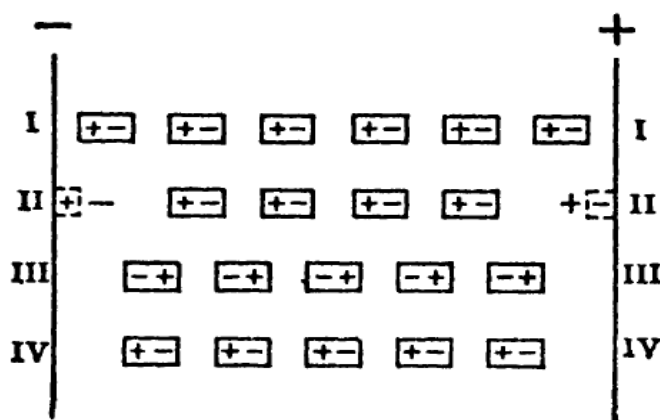
Substances that dissociated only to a small extent at reasonable concentration; this group of compounds in general are called as **weak electrolytes**.

**Examples**

- ✓ Weak acids and weak bases, e.g., amines, phenols, most carboxylic acids
- ✓ Some inorganic acids and bases, such as hydrocyanic acid and ammonia, and
- ✓ a few salts, e.g., mercuric chloride and cyanide

The mechanism of electrolytic conduction suggests that the dissolved substance consist of particles with positive and negative ends, these particles being distributed in a random manner throughout the solution. When a potential is applied it is believed that the particles (molecules) become oriented in the form of chains with the positive parts pointing in one direction and the negative parts in the opposite direction. The positive end of the particles will be attracted to the negative electrode, while the negative end of the particles is attracted to positive electrode.

**Figure 1** demonstrates this situation as:



Electrical conduction is a transport phenomenon in which electrical charge (carried by electrons or ions) moves through the system. The **electric current**  $I$  is defined as the rate of flow of charge

through the conducting material:  $I \equiv \frac{dQ}{dt}$  where  $dQ$  is the charge that passes through a cross section of the conductor in time  $dt$ .

The SI unit of current is the **ampere** (A) and equals one coulomb per second:

$$1A = 1C / s$$

Although the charge  $Q$  is more fundamental than the current  $I$ , it is easier to measure current than charge. The SI system therefore takes the ampere as one of its fundamental units.

The ampere is defined as the current that when flowing through two long, straight parallel wires exactly one meter apart will produce a force per unit length between the wires of exactly  $2 \times 10^{-7} N / m$ .

Charge flows because it experiences an electric force, so there must be an electric field  $\mathbf{E}$  in a current-carrying conductor.

The **conductivity** (formerly called the *specific conductance*)  $\kappa$  (kappa) of a substance is defined by

$$\kappa \equiv j / E \text{ or } j \equiv \kappa E.$$

Where  $E$  is the magnitude of the electric field. The higher the conductivity  $\kappa$ , the greater the current density  $j$  that flows for a given applied electric field.

The conductivity has the units  $\Omega^{-1} m^{-1}$ .

But  $\Omega^{-1} = S$ , where S is seimens

Therefore the conductivity has the units Siemens per meter ( $S m^{-1}$ ).

**Specific conductance or conductivity** may also be defined as *the conductance of one centimeter cube of a solution of an electrolyte*.

The reciprocal of the conductivity is the **resistivity** ( $\rho$ ):

$$\rho = 1 / \kappa$$

Current flows in a conductor only when there is a gradient of electric potential in the conductor. Such a gradient can be produced by attaching the ends of the conductor to the terminals of a battery.

In order to account for the phenomena observed during the passage of an electric current through solutions, Faraday assumed that the flow of electricity was associated with the movement of particles of matter carrying either positive or negative charges. These charged particles were called ions; the ions carrying positive charges and moving in the direction of the current, i.e., towards the cathode, and those carrying a negative charge and moving in the opposite direction, i.e., towards the anode.

The function of the applied E.M.F. is to direct the ions towards the appropriate electrodes where their charges are neutralized and they are set free as atoms or molecules. The direction of an electric current is defined as the direction of apparent motion of positive charges.

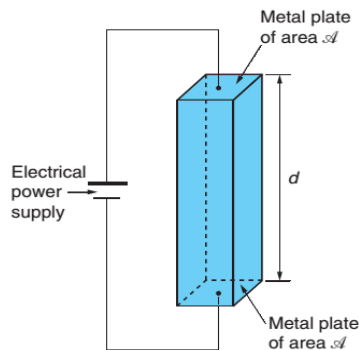
**The resistance (R)** of a conductor of uniform cross section is proportional to its length,  $\ell$  and inversely proportional to its cross-sectional area,  $a$ .

$R = \frac{\rho \times \ell}{a}$  or from Ohm's law as  $R = \frac{V}{I}$  where, V is the potential difference, I is the current in ampere.

We can also define the resistivity (specific resistance),  $\rho$  of a conducting object shaped as in **Figure 2** by:

$\rho = \frac{R \cdot a}{\ell}$  Where  $a$  is the cross sectional area of the object,  $\ell$  is the length of the object.

In other words, *specific resistance is the resistance of one centimeter cube of a solution of an electrolyte.*



**Figure 2:** A conducting metal plate

The SI unit of resistivity is the ohm .meter ( $\Omega.m$ ).

The specific resistance changes with the concentration, temperature, and pressure.

The **conductance**,  $C$  is the reciprocal of **resistance**, i.e.,  $C = \frac{1}{R}$ , and

$C = \kappa \frac{a}{\ell}$ , the SI unit  $\Omega^{-1}$ .

The physical meaning of the specific conductance may be understood by supposing an E.M.F. of one volt to be applied to a conductor; since  $V = 1$ , it follows, by Ohm's law, that the current  $I$  is equal to  $1/R$ , and hence to the conductance ( $C$ ).

For a centimeter cube  $a$  and  $\ell$  are unity, and so  $C$  is equal to  $\kappa$ . It is seen, therefore, that when a potential difference of **one volt** is applied to a centimeter cube of a conductor, the current in amperes flowing is equal in magnitude to the **specific conductance** in  $\Omega.cm^{-1}$  units.

**Example:** The resistance  $R = 100\Omega$  was measured in potassium chloride solution. Each of the electrodes had a surface area of  $4cm^2$ , and the distance between them was 2 cm. calculate the conductivity of the solution.

**Solution:**  $\rho = \frac{R.a}{\ell}$  and  $\kappa = 1 / \rho$  from these relations we obtain

$$\kappa = \ell / R.a = \frac{2 \times 10^{-2}}{100 \times 4 \times 10^{-4}} = 0.5 Sm^{-1}$$

### Conductivity cell constant (K)

Calculating conductivity from relations  $\rho = \frac{R.a}{\ell}$  and  $\kappa = 1 / \rho$  is impractical in electrolytes due to problems related to the determination of accurate values of the electrodes surface area,  $a$  and the distance between them,  $\ell$ . For this reason, conductivity is usually calculated using the relation

$\kappa = \frac{K}{R}$ , where the quantity **K** is called the **conductivity cell constant**, and it is determined by calibration. Its SI unit is  $\text{m}^{-1}$ .

### Example

The conductivity of a potassium chloride solution of the concentration  $0.1 \text{ mol dm}^{-3}$  is  $\kappa = 1.288 \text{ S m}^{-1}$ . The resistance of this solution was measured in a conductivity cell and the value  $R = 220 \text{ } \Omega$  was found. Calculate the conductivity cell constant.

### Solution

From equation  $\kappa = \frac{K}{R}$  we obtain

$$K = R \kappa = 220 \times 1.288 = \mathbf{540.9 \text{ m}^{-1}}$$

### Equivalent conductance and Molar conductance

**Equivalent Conductance:** is the conductance of one gram equivalent of the electrolyte dissolved in V cc of the solution. To understand the meaning of equivalent conductance, imagine a rectangular trough with two opposite sides made of metallic conductor (acting as electrodes) exactly 1 cm apart, If  $1 \text{ cm}^3$  (1 mL) solution containing 1 gram equivalent of an electrolyte is placed in this container is measured.

Equivalent conductance is represented mathematically by:

$$\Lambda = k\nu = k \frac{1000}{\text{Normality}}$$

Where,  $\kappa$  = Specific conductivity V = Volume of solution in cc. containing one gram equivalent of the electrolyte.

The unit of equivalent conductance is  $\text{ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$ .

**Molar conductance:** is the conductivity of that volume containing 1 mole of an electrolyte when placed between two sufficiently large electrodes, which are 1 cm apart. It is represented by  $\Lambda_m$ .

$$\Lambda_m = k\nu$$



Where  $v$  is the “dilution” of the solution in cc. per mole. If  $c$  is the concentration of the solution, in mol /L, then  $v$  is equal to  $1000/c$ , then it becomes:

$$\Lambda_m = 1000 \frac{k}{c}$$

### Factors Affecting Molar And Equivalent Conductances:

- ✓ Nature of electrolyte i.e, strong or weak
- ✓ Temperature
- ✓ Concentration of electrolyte
- ✓ Size of the ions produced

**1. Nature of electrolyte:** The conductance of an electrolyte depends upon the number of ions present in the solution. Therefore, the greater the number of ions in the solution the greater is the conductance. The number of ions produced by an electrolyte depends upon its nature. The strong electrolytes dissociate almost completely into ions in solutions and, therefore, their solutions have high conductance. On the other hand, weak electrolytes dissociate to only small extents and give lesser number of ions. Therefore, the solutions of weak electrolytes have low conductance.

**2. Concentration of the solution:** The molar conductance of electrolytic solution varies with the concentration of the electrolyte. In general, the molar conductance of an electrolyte increases with decrease in concentration or increase in dilution. The molar conductance of strong electrolyte (HCl, KCl, KNO<sub>3</sub>) as well as weak electrolytes (CH<sub>3</sub>COOH.NH<sub>4</sub>OH) increase with decrease in concentration or increase in dilution. The variation is however different for strong and weak electrolytes.

The variation of molar conductance with concentration can be explained on the basis of conducting ability of ions for weak and strong electrolytes.

**For weak electrolytes** the variation of  $\Lambda$  with dilution can be explained on the bases of number of ions in solution. The number of ions furnished by an electrolyte in solution depends upon the degree of dissociation with dilution. With the increase in dilution, the degree of dissociation increases and as a result molar conductance increases.

**For strong electrolytes**, there is no increase in the number of ions with dilution because strong electrolytes are completely ionised in solution at all concentrations. However, in concentrated solutions of strong electrolytes there are strong forces of attraction between the ions of opposite charges called **inter-ionic** forces. Due to these inter-ionic forces the conducting ability of the ions is less in concentrated solutions. With dilution, the ions become far apart from one another and inter-ionic forces decrease. As a result, molar conductivity increases with dilution. When the concentration of the solution becomes very-very low, the inter-ionic attractions become negligible and the molar conductance approaches the limiting value called molar conductance at infinite dilution. This value is characteristic of each electrolyte.

**3. Temperature:** The conductivity of an electrolyte depends upon the temperature. With increase in temperature, the conductivity of an electrolyte increases.

**4. Size of ions:** The velocity with which ions move under the influence of an electric field is inversely proportional to the mass and the size of the ions. But the size of ions should be defined carefully since ions possess higher charges or smaller sizes. The ions with smaller size exhibit lower conductance.

### 1.3. Activity and Activity Coefficients

**Activity ( $a$ )** is a measure of the “effective concentration” of a species in a mixture, in the sense that the species' chemical potential depends on the activity of a real solution in the same way that it would depend on concentration for an ideal solution.

By convention, activity is treated as a dimensionless quantity, although its value depends on customary choices of standard state for the species. The activity of pure substances in condensed phases (solid or liquids) is normally taken as unity (the number 1). Activity depends on temperature, pressure and composition of the mixture, among other things. For gases, the effective partial pressure is usually referred to as fugacity.

The difference between activity and other measures of composition arises because molecules in non-ideal gases or solutions interact with each other, either to attract or to repel each other. The activity of an ion is particularly influenced by its surroundings.

**Activity coefficient** ( $\gamma$ ) measures the degree of departure of substance,  $i$ 's behavior from ideal or ideally dilute behavior.

- ✓ Is a factor used in thermodynamics to account for deviations from ideal behavior in a mixture of chemical substances?

In an ideal mixture, the microscopic interactions between each pair of chemical species are the same (or macroscopically equivalent, the enthalpy change of solution and volume variation in mixing is zero) and, as a result, properties of the mixtures can be expressed directly in terms of simple concentrations or partial pressures of the substances present e.g. **Raoult's law** deviations from ideality are accommodated by modifying the concentration by an **activity coefficient**.

$$a = \gamma \frac{m_i}{m_0} \quad (1)$$

$m_0$  is the standard concentration, (e.g.: 1 mol kg<sup>-1</sup>),

$m_i$  the molality of  $i^{\text{th}}$  component of a solution,

$\gamma$  Is the concentration dependent activity coefficient

Both  $a$  and  $\gamma$  have no unit. On diluting the solution, i.e.

$$c \rightarrow 0 \quad \gamma \rightarrow 1 \quad \text{then} \quad a = c$$

activity becomes equal to the concentration. *In very dilute solution* interactions are insignificant and concentration and effective concentration are the same.

Though, activity and activity coefficient have no unit their magnitude depend on the *concentration units* used. E.g., concentration of the same solution can be given in units mol·kg<sup>-1</sup>, mol·dm<sup>-3</sup>, molar fraction and so on. The value of  $\gamma$  depends on:

- ✓ Concentration of ions and charge in the solution (**Ionic Strength**)
- ✓ Charge of the ion
- ✓ Diameter of the ion (**Hydrated Radius**)

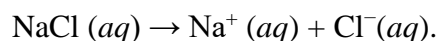
**Ion activity**

Activities of ionic solutions serve us for calculating accurate chemical potentials and accurate equilibrium constants

Taking into account that the activity has a greater importance in ionic solution than that of non-electrolytes. Interaction forces are greater among ions (Coulombic interaction).

**Ions in aqueous solution**

*Strong electrolytes* are the ionic compounds that completely dissociate into ions when they are dissolved.



*Weak electrolytes* are ionic compounds that partially dissociate

The chemical potentials for the formation of ions in aqueous solution

$$\mu_{\text{NaCl, aq}} = \mu_{\text{Na}^+, \text{aq}} + \mu_{\text{Cl}^-, \text{aq}} \quad (2)$$

which also implies that standard chemical potentials

$$\mu_{\text{NaCl, aq}}^0 = \mu_{\text{Na}^+, \text{aq}}^0 + \mu_{\text{Cl}^-, \text{aq}}^0$$

We also know that we can write Equation 2. Again with standard chemical potential and activity

$$\mu_{\text{NaCl, aq}} = \mu_{\text{NaCl, aq}}^0 + RT \ln a_{\text{NaCl, aq}}$$

When working with ionic solutions we would like to be a little more specific about the activities of the species in solution. It is customary to use units of molality,  $m$ , for ions and compounds in aqueous solution. If the solutions were *ideal* we could write for the activity of  $i^{\text{th}}$  component

$$a_i = \frac{m_i}{m_0}$$

and the chemical potential would be written

$$\mu_i = \mu_i^0 + RT \ln \frac{m_i}{m_i^0} \quad (3)$$

Two things must be said about Equation 3. First, it must be understood that there is an implied  $m_i^0$  dividing the  $m_i$  inside the logarithm, and second, the *standard state* is the solution at concentration  $m_i = m_i^0$ . Usually we set  $m_i^0 = 1 \text{ mol kg}^{-1}$ . However, ionic solutions are far from ideal so we must correct this expression for chemical potential for the non-idealities. As usual, we will use an activity coefficient,  $\gamma$ , and write the activity as

$$a_i = \gamma_i \cdot \frac{m_i}{m_0}$$

and consistent with what we have been doing, we will set  $m_i^0$  to 1 molal and not write it in the equation. The form of equation indicates that activity and activity coefficient are dimensionless, i.e. they have no unit. Thus the chemical potential will be written

$$\mu_i = \mu_i^0 + RT \ln m_i \gamma_i$$

The standard state for this equation is a **hypothetical standard state**.

We will also refer to the ionic compound simply as the "salt." With this notation we can rewrite former Equations as,

$$\mu_{\text{salt}} = \mu_+ + \mu_- \quad (4)$$

or 
$$\mu_{\text{salt}}^0 + RT \ln a_{\text{salt}} = \mu_+^0 + RT \ln m_+ \gamma_+ + \mu_-^0 + RT \ln m_- \gamma_-.$$

In a simplified form

$$\mu_{\text{salt}}^0 + RT \ln a_{\text{salt}} = \mu_+^0 + \mu_-^0 + RT \ln m_+ \gamma_+ \cdot m_- \gamma_- \quad (5)$$

The sum of standard chemical potentials is equal to that of the salt

$$\mu_{\text{salt}}^0 = \mu_+^0 + \mu_-^0$$

The logarithmic term in equ. (5) on the left is identical to the logarithmic term on the right,

$$RT \ln a_{\text{salt}} = RT \ln m_+ \gamma_+ \cdot m_- \gamma_-$$

from which we conclude that

$$a_{\text{salt}} = m_+ \gamma_+ \cdot m_- \gamma_-$$

The activity coefficients,  $\gamma_+$  and  $\gamma_-$  can't be measured independently because solutions must be electrically neutral. In other words, you can't make a solution which has just positive or just negative ions.

However, you can measure a "geometric mean" activity coefficient and, within limits, you can calculate it from theory.

### Geometric mean.

Numbers like  $x_1, x_2, \dots, x_n$  form a geometric mean which can be given as,  $\bar{m} = \sqrt[n]{x_1 \cdot x_2 \cdot \dots \cdot x_n}$

The actual form of the geometric mean depends on the number of ions produced by the salt. Right now we will define it for NaCl and then give more examples later. For NaCl we define,

$$\gamma_+ \cdot \gamma_- = \gamma_{\pm}^2 \quad \text{or} \quad (\gamma_+ \cdot \gamma_-)^{\frac{1}{2}} = \gamma_{\pm} \quad (6)$$

It turns from the form of Equation 6. that  $\gamma_+ = \gamma_-$  which says that equal amount of "activity coefficient property" is divided to positive and negative ions. So,

$$a_{\text{salt}} = m_+ \cdot m_- \cdot \gamma_{\pm}^2$$

But for a NaCl solution of molality,  $m$ , we have  $m_+ = m_- = m$  so that

$$a_{\text{salt}} = m^2 \cdot \gamma_{\pm}^2 \quad (7)$$

The chemical potential of salt given in terms of activity coefficient and molality

$$\mu_{\text{salt}} = \mu_{\text{salt}}^0 + RT \ln m^2 \gamma_{\pm}^2 \quad (8)$$

Keep in mind that this is for NaCl, but it is correct for any *one-to-one* ionic compound.

Try  $\text{MgCl}_2$ ,



$$\mu_{\text{salt}}^0 + RT \ln a_{\text{salt}} = \mu_{\text{Mg}^{2+}}^0 + RT \ln m_{\text{Mg}^{2+}} \gamma_+ + 2\mu_{\text{Cl}^-}^0 + 2RT \ln m_{\text{Cl}^-} \gamma_-$$

$$\mu_{\text{salt}}^0 + RT \ln a_{\text{salt}} = \mu_{\text{Mg}^{2+}}^0 + 2\mu_{\text{Cl}^-}^0 + RT \ln m_+ \gamma_+ \cdot m_-^2 \gamma_-^2$$

$$\text{So } a_{\text{salt}} = m_+ m_-^2 \cdot \gamma_-^2 \gamma_+$$

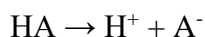
But for  $\text{MgCl}_2$  at molality,  $m$ , we know that  $m_+ = m$  and  $m_- = 2m$ . Further, we define the geometric mean activity coefficient by,

$$\gamma_{\pm} = (\gamma_-^2 \gamma_+)^{\frac{1}{3}} \quad \text{Then } a_{\text{salt}} = m \cdot (2m)^2 \cdot \gamma_{\pm}^3 = 4m^3 \gamma_{\pm}^3$$

### Relationship between $K_a$ and $K_m$

The equilibrium constant given in terms of activities is the *thermodynamic equilibrium constant*.

Use an example of dissociation equilibrium of a weak acid to show this relationship;



the equilibrium constant of the reaction, (introducing the standard concentration,  $m^0$  again)

$$K_a = \frac{a_+ a_-}{a_{\text{HA}}} = \frac{m_+ \gamma_+ m_- \gamma_-}{m_{\text{HA}} \cdot \gamma_{\text{HA}}} \cdot \frac{1}{m^0}$$

Knowing:  $\gamma_+ \cdot \gamma_- = \gamma_{\pm}^2$  and  $m_+ = m_- = m$

$$K_a = \frac{a_+ a_-}{a_{\text{HA}}} = \frac{m^2 \cdot \gamma_{\pm}^2}{m^0 \cdot m_{\text{HA}} \cdot \gamma_{\text{HA}}} \quad (9)$$

$$K_a = K_c \cdot K_{\gamma}$$

$$\text{Where } K_c = \frac{m^2}{m^0 \cdot m_{\text{HA}}} \quad K_{\gamma} = \frac{\gamma_{\pm}^2}{\gamma_{\text{HA}}}$$

**Debye-Hückel Limiting Law**

The theory of Peter Debye and Erich Hückel provides theoretical expressions for **single-ion activity coefficients** and **mean ionic activity coefficients** in electrolyte solutions.

Theoretical calculation of  $\gamma_{\pm}$ . The Debye Hückel limiting law gives the  $\gamma_{\pm}$  in terms of the *ionic strength*,  $I$ , defined as,.

$$I = \frac{1}{2} \sum_i m_i z_i^2$$

where  $z_i$  is the charge on ion  $i$ , and  $m_i$  is the molality of ion  $i$ . The ionic strength of a solution is a measure of the amount of ions present. The ionic strength is a measure of the *total concentration of charge* in the solution. A divalent ion (a 2+ or 2- ion, like  $\text{Ca}^{2+}$ ) does more to make the solution ionic than a monovalent ion (e.g.,  $\text{Na}^+$ ). The ionic strength, emphasizes the charges of ions because the charge numbers occur as their squares.

**Examples**

- a. What is the value of ionic strength of HCl solution with molality 0.010:

$$m_{\text{H}^+} = m_{\text{Cl}^-} = 0.01 \text{ mol/kg, and } z_{\text{H}^+}^2 = z_{\text{Cl}^-}^2 = 1$$

$$I = \frac{1}{2} (0.01 \cdot (+1)^2 + 0.01 \cdot (-1)^2) = 0.01 \text{ mol} \cdot \text{kg}^{-1}$$

Notice that for a simple salt of two monovalent ions, the ionic strength is just the concentration of the salt.

- b. the ionic strength of 0.10 molal  $\text{Na}_2\text{SO}_4$

$$I = \frac{1}{2} (0.20(+1)^2 + 0.10(-2)^2) = \frac{1}{2} (0.20 + 0.40) = 0.30 \text{ molal}$$

The chemical potential or activity of ions cannot be determined on a purely *thermodynamic basis*. This is due to the fact that the effects of an ion cannot be separated from the effects of the accompanying counter-ion, or in other terms, the electrochemical potential of the ion cannot be



separated into the chemical and the electrical component. Such a separation must necessarily be based on a non-thermodynamic convention.

The mean activity coefficient can be calculated at very low concentrations by the **Debye-Hückel Limiting Law**

$$\lg \gamma_{\pm} = -A \cdot |z_{+} \cdot z_{-}| \cdot I^{1/2}$$

Where  $A = 0.509 / (\text{mol kg}^{-1})^{1/2}$  for an aqueous solution at 25 °C, in general,  $A$  depends on the relative permittivity of solvent and the temperature.

$|z_{+} \cdot z_{-}|$  The  $\log_{10}$  of mean activity coefficient also depends on the product of the absolute value of cation and anion charge number.

When the ionic strength of the solution is too high for the limiting law to be valid, it is found that the activity coefficient may be estimated from the *extended Debye-Hückel law*.

$$\lg \gamma_{\pm} = \frac{-0.511 \cdot |z_{+} \cdot z_{-}| I^{1/2}}{1 + b \cdot I^{1/2}}$$

Where  $b$  is a measure of distance between ions.

In the limit of small concentration  $I^{1/2} \ll 1$ , and in the denominator of Eq. the term  $b \cdot I^{1/2}$  can be neglected, therefore we receive *Debye-Hückel Limiting Law* again.

Let's try to make sense of our equation for the mean activity coefficient by taking it apart\

$$\gamma_{\pm} = 10^{-0.511 \cdot A \cdot B}, \text{ where } A = |z_{+} \cdot z_{-}|; B = \frac{I^{1/2}}{1 + I^{1/2}}$$

A Greater charges produce more negative the argument for the exponential,  $\gamma_{\pm}$  is farther away from 1, its ideal value.

B The term  $B$  varies between 0 and 1. When  $I$  is small  $B \sim 0$ , and  $\gamma_{\pm} \sim 1$ .

**Example:** for  $A = 1$ ,  $B = 0.001$ , the argument for the exponential is -0.000511, and

$$\gamma_{\pm} = 10^{-0.000511} = 0.9988$$

## 1.4. Theory of Electrolytic conductance

### A) Kohlrausch's Theory of Independent Migration of Ions

In an extensive series of measurements during the nineteenth century, Friedrich Kohlrausch showed that at low concentrations the molar conductivities of strong electrolytes vary linearly with the square root of the concentration:

$$\Lambda_m = \Lambda_m^\infty - kC^{1/2}$$

This variation is called **Kohlrausch's law**. The constant  $\Lambda_m^\infty$  is the **limiting molar conductivity**, the molar conductivity in the limit of zero concentration (when the ions are effectively infinitely far apart and do not interact with one another) and  $k$  is constant.

Kohlrausch was also able to establish experimentally that  $\Lambda_m^\infty$  can be expressed as the sum of contributions from its individual ions. It has been observed that the conductivity of solution increases with dilution until it reaches its limiting value at infinite dilution is represented as  $\Lambda_m^\infty$

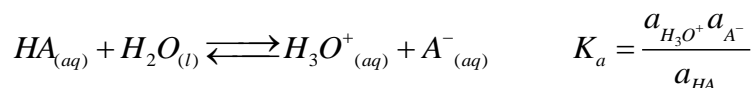
Kohlrausch made a systematic study of  $\Lambda_m^\infty$  for different electrolytes and concluded that each ion contributes a characteristic value of its own to molar conductivity at infinite dilution irrespective of the nature of the other ion present. It applies that:

$$\Lambda_m^\infty = \nu^+ \Lambda_{m,\infty}^+ + \nu^- \Lambda_{m,\infty}^-$$

Where  $\Lambda_{m,\infty}^+$  is the molar conductivity of the cation at infinite dilution and  $\Lambda_{m,\infty}^-$  is the molar conductivity of the anion at infinite dilution. The law expresses the fact that ions in an infinitely diluted solution do not influence each other.

### B) Ostwald's dilution law

Weak electrolytes are not fully ionized in solution. They include weak Brønsted acids and bases, such as  $\text{CH}_3\text{COOH}$  and  $\text{NH}_3$ . The marked concentration dependence of their molar conductivities arises from the displacement of the equilibrium towards products at low molar concentrations.



The conductivity depends on the number of ions in the solution, and therefore on the **degree of ionization**,  $\alpha$ , of the electrolyte; when referring to weak acids, we speak instead of the **degree of deprotonation**. It is defined so that, for the acid HA at a molar concentration  $c$ , at equilibrium.

$$[H_3O^+] = \alpha c \quad [A^-] = \alpha c \quad [HA] = (1 - \alpha)c$$

If we ignore activity coefficients, the acidity constant,  $K_a$ , is approximately

$$K_a = \left( \frac{\alpha^2 c}{1 - \alpha} \right) \quad (x)$$

From which it follows that:

$$\alpha = \frac{K_a}{2c} \left\{ \left( 1 + \frac{4c}{K_a} \right)^{1/2} - 1 \right\} \quad (y)$$

The acid is fully deprotonated at infinite dilution, and its molar conductivity is then  $\Lambda_m^\infty$ . Because only a fraction  $\alpha$  is actually present as ions in the actual solution, the measured molar conductivity  $\Lambda_m$  is given by:

$$\Lambda_m = \alpha \Lambda_m^\infty \quad (z)$$

Once we know  $K_a$ , we can use eqns (y) and (z) to predict the concentration dependence of the molar conductivity. More usefully, we can use the concentration dependence of  $\Lambda_m$  in measurements of the limiting molar conductance. First, we rearrange eqn (x) into:

$$\frac{1}{\alpha} = 1 + \frac{\alpha c}{K_a}$$

Then, by using eqn (z), we obtain **Ostwald's dilution law**:

$$\boxed{\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^\infty} + \frac{\Lambda_m c}{K_a (\Lambda_m^\infty)^2}}$$

This equation implies that, if  $\frac{1}{\Lambda_m}$  is plotted against  $c\Lambda_m$  then the intercept at  $c = 0$  will be  $\frac{1}{\Lambda_m^\infty}$

### 1.5. Transport properties or mobilities of ions

To interpret conductivity measurements we need to know why ions move at different rates, why they have different molar conductivities, and why the molar conductivities of strong electrolytes decrease with the square root of the molar concentration.

- ✓ In a transport process, some quantity is transported from one place to another. The principal transport processes are heat conduction, diffusion, and viscous flow.
- ✓ In heat conduction, energy in the form of heat is transported. In diffusion, substances are transported. In viscous flow, momentum is transported.

The central idea is that, although the motion of an ion remains largely random, the presence of an electric field biases its motion, and the ion undergoes net migration through the solution.

**A) Transport /Transference number, ( $t$ ):** During electrolysis, the electric charge is carried in the electrolyte by both cations and anions, but the amount of charge they transport is different.

Which is the fraction of current that is carried by the given type of ion.

$t_i = \frac{j_i}{j_{total}}$ , where  $j_i$  is the magnitude of the current density due to ions of type  $i$  and  $j_{total}$  is the magnitude of the total current density.

It can also be given by:  $t_i = \frac{Q_i}{Q}$ , where  $Q_i$  is the charge carried by species  $i$ ,  $Q$  is the total charge.

It is obvious that the sum of the transference numbers of the cations and anions is equal to unity, as:  $t_+ + t_- = 1$

The cations and anions in a given electrolyte will not generally have equal friction coefficients; the two kinds of ions will not necessarily carry the same amount of current.

The amount of the transported charge relates to the velocity with which the ions travel through the electrolyte.

$t_+ = \frac{v_+}{v_+ + v_-}$ ,  $t_- = \frac{v_-}{v_+ + v_-}$  Where  $v_+$  is the velocity of the cation and  $v_-$  is that of the anion.

The velocity of ions in a solution of a given concentration, temperature and pressure depends on the voltage between the two electrodes and on the distance between them. The higher the voltage and the closer the electrodes to each other, the higher is the ions velocity.

**B) The mobility,  $u_i$**  is defined as the velocity of an ion at a potential gradient of  $1\text{Vm}^{-1}$ .

It is given as:  $u_i = \frac{\ell}{E} v_i$ , where  $v_i$  is the magnitude of the mean drift velocity of the type of ion

and where  $E$  is the magnitude of the electric field and  $\ell$  is the distance between the electrodes.

The transport / transference number of a given type of ion can also be given by relation using ionic mobilities as:

$$t_i = \frac{u_i}{u}, \text{ where } u = u_+ + u_-$$

When there are more kinds of anions and cations in an electrolyte, the generalized equation becomes;  $\sum_i t_i^+ + \sum_j t_j^- = 1$

The usefulness of ionic mobilities is that they provide a link between measureable and theoretical quantities. Following equation shows the relationship between an ion's mobility and its molar conductivity.

$$\Lambda = zuF \quad \text{Where } z = \text{charge on the ion } F = \text{faradays constant}$$

Transport numbers and ionic mobilities depend on the concentration of the electrolyte, temperature and (to a small extent) pressure.

Three methods have been generally employed for the experimental determination of transference numbers:

- ✓ The first, based on the procedure originally proposed by Hittorf, involves measurement of changes of concentration in the vicinity of the electrodes;
- ✓ In the second, known as the “moving boundary” method, the rate of motion of the boundary between two solutions under the influence of current is studied;
- ✓ The third method is based on electromotive force measurements of suitable cells.

Therefore the methods are: Hittorf method

Moving boundary method

Electromotive force method

### C) Migrations of Ion

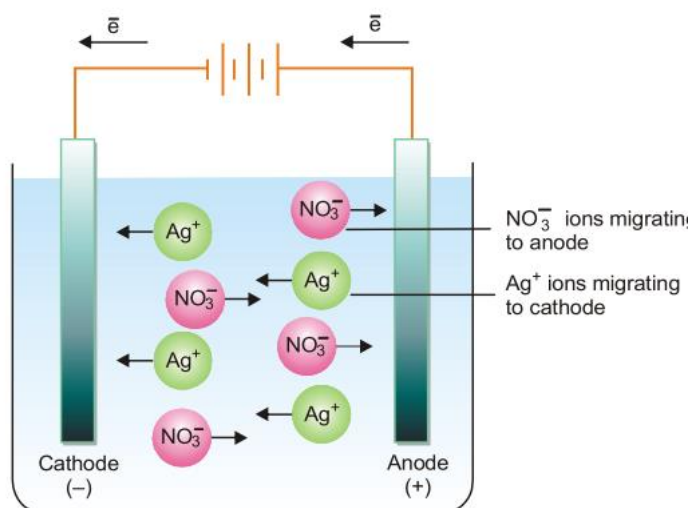
As in a solution of an electrolyte the electricity is conducted by migration of ions. The ions move in solution independently towards the oppositely charged electrodes.

This means that:-

- Anion moves towards Anode
- Cation moves towards Cathode

**Example:**  $\text{AgNO}_3 \longrightarrow \text{Ag}^+ + \text{NO}_3^-$

In the electrolytic solution of  $\text{AgNO}_3$ , the cations ( $\text{Ag}^+$ ) will move to the cathode and anions ( $\text{NO}_3^-$ ) will move to the anode. Usually different ions move with different rates.



**Figure 3:** Migration of ions through electrolytic solution to opposite electrodes.

### D) Conductivities and ion-ion interactions (Debye – Hückel – Onsager theory)

In order to explain the abnormal behaviour of strong electrolytes number of scientists worked in this field viz. Noyes (1904), Sutherland (1906), Bjerrum (1909) and Milner (1912), Debye and Huckel in 1923, and Onsagar in 1926 put forward the modern theory of strong electrolytes known as Debye- Huckel- Onsagar theory of strong electrolyte.

Debye-Huckel treatment deals with the distribution of ions around a given ion and the net effects of these neighboring ions have on the central ion. Debye and Huckel derived an equation based on the quantitative treatment of inter ionic attraction. This equation was later on modified by

Onsager and is known as Debye-Huckel-Onsager (DHO) equation for strong electrolyte. It shows how the potential energy of an ion in solution depends on the ionic strength of the solution. In the case of strong electrolytes the value of molar conductance at infinite dilution is much less than unity due to following effects:

**(i) Relaxation effect:**

Interionic forces are present and each ion has a tendency to be surrounded on the time average by ions of opposite charge called the ionic atmosphere. A negative ion is surrounded by the ions of opposite charge called the ionic atmosphere. When an EMF is applied, the negative ions migrate towards the anode where the ionic atmosphere of positive ions is left behind to disperse, at this time a new ionic atmosphere is under formation. The rate of formation of new ionic atmosphere is not the same at which the previous ionic atmosphere disperses and the later takes more time. This time is called the ‘relaxation time’. In the case of the moving ion there will always be an excess of ions of opposite charge. The ions will always be dragged back. This effect will decrease the mobility of the ions and is known as ‘relaxation effect or asymmetric factor’

**(ii) Electrophoretic effect:**

It is another factor that slows down the motions of ions at high concentrations. It arises from the tendency of ionic atmosphere associated with hydrated water dipoles, which moves in the opposite direction to that of central ions motions. The solvent molecules attach themselves to ionic atmosphere and the ions move in the direction opposite to that of central ion. It produces friction due to which the mobility of the central ion is retarded. This effect is called the electrophoretic effect. The electrophoretic effect reduces the mobility of the ions and hence also reduces their conductivities.

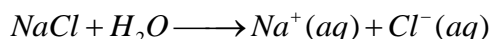
**(iii) Viscous Effect:**

This effect arises from the viscous drag of the solvent on the movement of ions. The ions moves as directed by the applied field and the electrical force on ions are opposed by the frictional viscous force exerted by solvent. For a given ion, more viscous the solvent, the greater the viscous pull, lesser the ionic mobility and thus decrease in conductance

## 1.6. Ionic Equilibria

The most commonly studied solution equilibria are ionic equilibria in aqueous solutions. Savante Arrhenius studied the conduction of current through water solutions of electrolytes. He came to believe that the conductivity of solutions was due to the presence of ions. He gave four main theory of ionization.

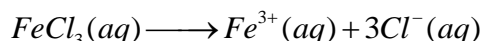
1. In solution or molten state, the molecules dissociate partly or usually into positively charged (cation) and negatively charged ions (anion).



2. The number of cations may not be equal to the number of anions produced. But the total positive charge carried by the cations is exactly equal to the negative charge carried by anions.

**Example:**  $NaCl(aq) \longrightarrow Na^+(aq) + Cl^-(aq)$

- ✓ Here, there is equal number of cation and anion (1:1) as well as equal number of charge (1:1). But in the dissociation of  $FeCl_3$ :



- ✓ 1 cation and 3 anions, the number of charge carried by both of them is equal (3 +ve charge and 3 -ve charge).
3. The ions are responsible for carrying of electricity through the electrolyte. When the electrodes are connected to the terminals of battery the positively charged cations move toward cathode and the negatively charged anions move toward positively charged electrode (anode).
  4. Apart from the solvent, the conducting power or conductance of electrolytic solution depend up on :
    - ✓ The charge carried by the ions
    - ✓ The number of ions
    - ✓ The velocity of the ions

Increase in temperature  $\longrightarrow$  increase in solubility  $\longrightarrow$  increase in number of charges  $\longrightarrow$  conductivity increases.



### 1.7. Applications of Conductivity Measurements

Some of the important applications of conductivity measurements are as follows:

#### A) Determination of degree of Dissociation

The degree of dissociation of a weak electrolyte is determined by the application of expression:

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\infty}$$

Where  $\Lambda_m$  ' is the molar conductance of the solution and can be obtained experimentally  $\Lambda_m^\infty$  is the molar conductance at infinite dilution and can be found from the literature. The method may be illustrated with special reference to the determination of the dissociation of phosphoric acid. Consider phosphoric acid, ionizing as a monobasic acid in to  $H^+$  and  $H_3PO_4^-$  ions, at 25 ° C.

$$\Lambda_m^\infty(H_3PO_4) = \Lambda_m^\infty(HCl) + \Lambda_m^\infty(NaH_2PO_4) - \Lambda_m^\infty(NaCl) = 378.3 + 70.0 + 109.0 = 339.3$$

The measured value of  $\Lambda_m$  for 0.1M phosphoric acid is  $96.5 \text{ Scm}^2 \text{ mol}^{-1}$  and the approximate degree of dissociation is  $96.5/339.3$  i.e., 0.285 and the concentration of the ions is approximately 0.0285 M.

#### B) Determination of Solubility Product of a Sparingly Soluble Salt

If a slightly soluble electrolyte such as  $AgCl$ ,  $BaSO_4$ , and  $PbSO_4$  dissociate in a simple manner, it is possible to determine the solubility of such salts by conductance measurements. If 's' is the solubility in mole/liter, of a sparingly soluble salt and ' $\kappa$ ' is the specific conductance of the saturated solution, then its molar conductance ' $\Lambda$ ' is given by the relation:

$$\Lambda_m = 1000 \frac{\kappa}{s} \quad \text{i.e. } s = 1000 \frac{\kappa}{\Lambda_m}$$

$$\text{At infinite dilution, } s = 1000 \frac{\kappa}{\Lambda_m^\infty}$$

The method for the determination of solubility products of a sparingly soluble salt may be explained by taking the example of solubility of silver chloride in water at 25°C. The value of  $\Lambda^\infty$  for  $AgCl$  is given by:

$$\Lambda_m^\infty(AgCl) = \Lambda_m^\infty Ag^+ + \Lambda_m^\infty Cl^- = 61.92 + 76.34 = 138.3 \text{ Scm}^2 \text{ mol}^{-1}$$

The specific conductance of a saturated solution of AgCl in water is  $3.41 \times 10^{-6} \text{ S cm}^{-1}$  at  $25^\circ \text{C}$  and if  $1.60 \times 10^{-6}$  is deducted for the conductance of the water, the value of  $k$  is  $1.81 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ . Hence solubility of AgCl may be determined

$$s = 1000 \frac{k}{\Lambda_m^\infty} = 1000 \times \frac{1.81 \times 10^{-6}}{138.3} = 1.31 \times 10^{-5} \text{ mol / L}$$

### C) Conductometric Titration

The determination of the end point of a titration by means of conductance measurements is known as conductometric titration. In these titrations measurement of actual specific conductance of the solution is not required, and any quantity proportional to it is sufficient.

The titrant is added by a burette and change of conductance as a function of added titrant is used to determine the equivalence point. A conductance cell, in which solution of substance to be titrated is taken, consists of two platinum electrodes of large surface area across which an alternating low-voltage potential is applied.

Generally, potential in the range 5-10V at 1000 – 3000 Hz is employed. The conductance cell, therefore, is incorporated into one arm of a Wheatstone bridge type of circuit and the conductance is measured by adjustment of a calibrated resistor to balance the bridge.

Some typical examples of conductometric titration are Acid-Base Titration, Displacement Reactions, Precipitation Reactions and Complexometric Titration Reactions.