1-4 Conductivity Of Electrolytes

We have seen that electrolyte solutions conduct electric currents through them by movement of the ions to the electrodes. The power of electrolytes to conduct electric currents is termed

conductivity or **conductance.** Like metallic conductors, electrolytes obey Ohm's law. According to this law, the current *I* flowing through a metallic conductor is given by the relation.

$$I = \frac{E}{R}$$

where *E* is the potential difference at two ends (in volts); and *R* is the resistance measured in ohms (or Ω). The resistance *R* of a conductor is directly proportional to its length, *l*, and inversely proportional to the area of its cross-section, *A*. That is,

$$R \propto \frac{l}{A}$$

$$R = \rho \times \frac{l}{A} \quad ....(1)$$

The exact value of (*l/A*) is the **cell constant** (X $_{CELL)}$ that can be determined by measuring the distance between the electrodes (*l*) and their area of cross sections (*A*).

where ρ "rho" is a constant of proportionality and is called **resistivity** or **specific resistance.** Its value depends upon the material of the conductor. From (1) we can write

$$\rho = R \times \frac{A}{l}$$

If *l* = 1 cm and *A* = 1 sq cm, then

$$\rho = R$$

1-4-1 Specific Conductance

It is evident that a substance which offers very little resistance to the flow of current allows more current to pass through it. Thus the power of a substance to conduct electricity or conductivity is the converse of resistance.

L= 1/R

The reciprocal of specific resistance is termed **Specific conductance** or **Specific conductivity** It is defined as : **the conductance of one centimetre cube (cc) of a solution of an electrolyte.**

The specific conductance is denoted by the symbol κ (kappa). Thus,

$$\kappa = \frac{1}{\rho}$$

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A}$$

κ **= observed conductance × cell constant**

Units of Specific conductance

Specific conductance is generally expressed in **mhos** or **ohm**$^{-1}$. Its unit can be derived

$\frac{1}{\text{ohm}} \times \frac{\text{cm}}{\text{cm}^2}$ = **ohm**$^{-1}$**cm**$^{-1}$

The specific conductance increases with : (*i*) ionic concentration, and (*ii*) speeds of the ions concerned.

1-4-2 Equivalent Conductance

It is defined as **the conductance of an electrolyte obtained by dissolving one gram-equivalent of it in Vcc of water.**

The equivalent conductance is denoted by Λ . It is equal to the product of the specific conductance, к and the volume V in cubic centimeters (cc) containing one gram-equivalent of the electrolyte at the dilution V.

$$\Lambda = \frac{\kappa \times 1000}{N}$$

Unit of Equivalent conductance

$$\Lambda =$$

$$= \frac{1}{R} \times \frac{l}{A} \times V$$

$$= \frac{1}{ohm} \times \frac{cm}{cm^2} \times \frac{cm^3}{eqvt}$$

$$= ohm^{-1} \, cm^2 \, eqvt^{-1}$$

Variation of Equivalent conductance with Concentration (or Dilution)

 The equivalent conductance of a solution does not vary linearly with concentration. The effect of concentration on equivalent conductance can be studied by plotting Λ values against the square root of the concentration. It has been found that variation of equivalent conductance with C depends upon the nature of electrolyte. Fig. 3 shows the behaviour of strong and weak electrolytes with change of concentration.
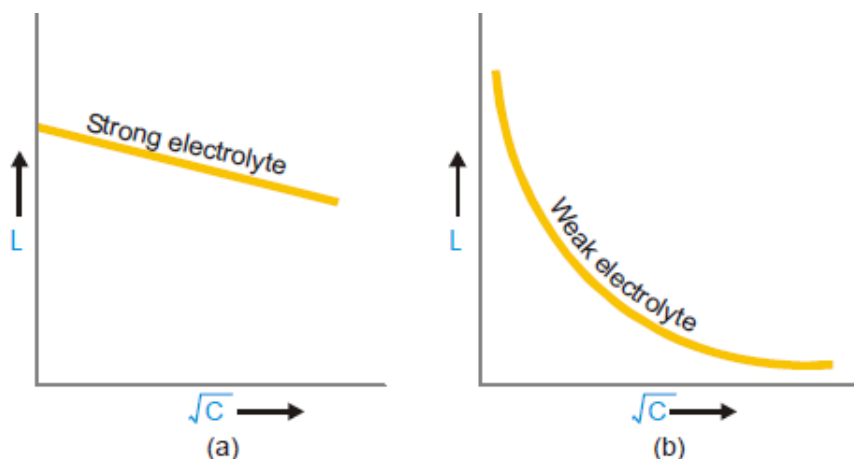
Figure 3 Variation of equivalent conductivity, with C : (a) for strong electrolyte;

(b) for weak electrolyte.

Strong electrolytes are completely ionised at all concentrations (or dilutions). The increase in equivalent conductance is not due to the increase in the number of current carrying species. This is, in fact, due to the decrease in forces of attraction between the ions of opposite charges with the decrease in concentration (or increase in dilution). At higher concentration, the forces of attraction between the opposite ions increase ($F \propto q1\ q2\ /\ r^2$). Consequently, it affects the speed of the ions with which they move towards oppositely charged electrodes. This phenomenon is called **ionic interference. As the solution becomes more and more dilute, the equivalent conductance increases, till it reaches a limitary value.** This value is known as equivalent conductance at infinite dilution (zero concentration) and is denoted by A.

Weak electrolytes have low ionic concentrations and hence interionic forces are negligible. Ionic speeds are not affected with decrease in concentration (or increase in dilution). The increase in

equivalent conductance with increasing dilution is due to the increase in the number of currentcarrier species. In other words, the degree of ionisation (α) increases. Thus **increase in equivalent conductance (Λ) in case of a weak electrolyte is due to the increase in the number of ions.**

In case of a weak electrolyte Λ_∞ is the equivalent conductance when ionisation is complete. So, the conductance ratio Λ/Λ_∞ is the degree of ionisation. That is,

$$\alpha = \frac{\Lambda}{\Lambda_\infty}$$

SOLVED PROBLEM 1. 0.5 Normal solution of a salt placed between two platinum electrodes, 20 cm apart and of area of cross-section 4.0 sq cm has a resistance of 25 ohms. Calculate the equivalent conductance of the solution.

SOLUTION

Calculation of specific conductance

$$l = 20 \text{ cm} \qquad A = 4.0 \text{ sq cm} \qquad R = 25 \text{ ohms}$$

$$\text{Specific conductance } \kappa = \frac{1}{R} \times \frac{l}{A}$$

$$= \frac{1}{25} \times \frac{20}{4}$$

$$= 0.2 \text{ ohm}^{-1} \text{ cm}^{-1}$$

Calculation of Equivalent conductance

$$\text{Equivalent conductance} = \kappa \times \frac{1000}{N} = \frac{0.2 \times 1000}{0.5}$$

$$= 400 \text{ ohm}^{-1} \text{ cm}^2 \text{ eqvt}^{-1}$$

1-4-3 Molar conductance

It is another quantity which helps in comparing the conductivities of electrolytes. It is defined as : **the conductance of all ions produced by one mole (one gram-molecular weight) of an electrolyte when dissolved in a certain volume V cc.** Molar conductance is denoted by

μ. Its value is obtained by multiplying the specific conductance, κ, by the volume in cc containing one mole of the electrolyte.

  Thus, Molar conductance,

$$\mu = \frac{\kappa \times 1000}{M}$$

where *M* is the number of moles of the electrolyte present in 1000 cc of solution.

Units of Molar conductance

Since

$$\kappa = \frac{1}{R} \times \frac{l}{A}$$

$$\mu = \frac{1}{R} \times \frac{l}{A} \times V$$

$$= \frac{1}{ohm} \times \frac{cm}{cm^2} \times \frac{cm^3}{mol}$$

$$= ohm^{-1} \, cm^2 \, mol^{-1}$$

1-5 Kohlrausch's Law of Independent Migration of Ions

1-For strong electrolytes

 1 It has been observed that the conductivity of solution increases with dilution until it reaches its limiting value at **infinite dilution** is represented as Λ^∞_m .

  Kohlrausch made a systematic study of Λ^∞_m 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.

$$\Lambda^\infty_m = \nu_+ + \lambda_+ + \nu_- \lambda_-$$

λ_+, λ_- : are the **limiting molar conductivities of cation and anion** respectively and $v+$ and $v-$ is the number of cations and anions in which one molecule of the electrolyte.

Example: the equivalent conductance of NaCl at infinite dilution at 25°C is found to be 126.45. The equivalent conductance of Na^+ and Cl^- ion is 50.11 ohm^{-1} and 76.34 ohm^{-1} respectively. Thus,

$$\Lambda\infty\ (NaCl) = \lambda_{Cl-} + \lambda_{Na+}$$

or   126.45 = 50.11 + 76.34

This is in conformity with the Kohlrausch's Law.

Q. The limiting molar conductivities of KCl, KNO$_3$, and AgNO$_3$ are 14.99 mSm^{2}mol^{-1}, 14.50 mSm^{2}mol^{-1} and 13.34 mSm^{2}mol^{-1} respectively at 25°C. Calculated the limiting molar conductivity of AgCl at this temperature?

➢   The basis for the solution is Kohlrausch's law of independent of ions. Switching counterions does not affect the mobility of the remaining other ion at infinite dilution.

$$\Lambda_m^\infty = V_+\lambda_+ + V_-\lambda_-$$

$$\Lambda_m^\infty (KCl) = \lambda(K^+) + \lambda(Cl^-) = 14.99 \text{ mSm}^2\text{mol}^{-1}$$

$$\Lambda_m^\infty (KNO_3) = \lambda(K^+) + \lambda(NO_3^-) = 14.50 \text{ mSm}^2\text{mol}^{-1}$$

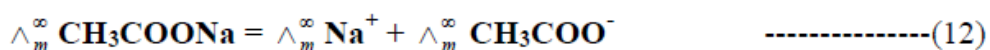$$\Lambda_m^\infty (AgNO_3) = \lambda(Ag^+) + \lambda(NO_3^-) = 13.34 \text{ mSm}^2\text{mol}^{-1}$$

Hence $\Lambda_m^\infty (AgCl) = \Lambda_m^\infty (AgNO_3) + \Lambda_m^\infty (KCl) - \Lambda_m^\infty (KNO_3)$

$$= 13.34 + 14.99 - 14.50 \text{ mSm}^2\text{mol}^{-1}$$
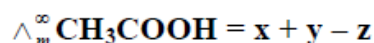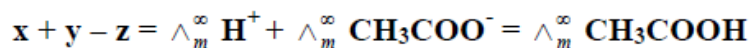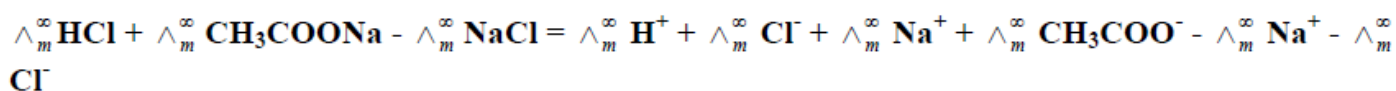$$= 13.83 \text{ mSm}^2\text{mol}^{-1}$$

Applications of Kohlrausch Law

5.1.1 Calculation of molar conductivity of a weak electrolyte at infinite dilution

It is not possible to determine the value of $\Lambda^{\infty}{}_m$ for weak electrolytes since we cannot obtain the limiting value of the molar conductivity for a weak electrolyte. This is done indirectly by the molar ionic conductance for the individual ions of the weak electrolyte as follows:

For e.g. molar conductance of acetic acid at infinite dilution can be calculated from the molar conductance at infinite dilution of hydrochloric acid, sodium acetate and sodium chloride as follows:

$$\Lambda_m^{\infty} \, HCl = \Lambda_m^{\infty} \, H^+ + \Lambda_m^{\infty} \, Cl^- \qquad \text{------------(11)}$$

$$\Lambda_m^{\infty} \, CH_3COONa = \Lambda_m^{\infty} \, Na^+ + \Lambda_m^{\infty} \, CH_3COO^- \qquad \text{---------------(12)}$$

$$\Lambda_m^{\infty} \, NaCl = \Lambda_m^{\infty} \, Na^+ + \Lambda_m^{\infty} \, Cl^- \qquad \text{------------- (13)}$$

Add eq. 11 and 12 and subtract 13 we get:

$$\Lambda_m^{\infty} HCl + \Lambda_m^{\infty} CH_3COONa - \Lambda_m^{\infty} NaCl = \Lambda_m^{\infty} H^+ + \Lambda_m^{\infty} Cl^- + \Lambda_m^{\infty} Na^+ + \Lambda_m^{\infty} CH_3COO^- - \Lambda_m^{\infty} Na^+ - \Lambda_m^{\infty} Cl^-$$

$$x + y - z = \Lambda_m^{\infty} H^+ + \Lambda_m^{\infty} CH_3COO^- = \Lambda_m^{\infty} CH_3COOH$$

$$\Lambda_m^{\infty} CH_3COOH = x + y - z$$

1-5-2 Calculation of Degree of Dissociation of Weak Electrolytes

The degree of dissociation of weak electrolyte such as NH4OH, acetic acid can be determined by measuring the molar conductivity Λ, of the solution of the electrolyte at any given dilution. For e.g. the degree of dissociation (αc) of a weak electrolyte at the concentration C mole per liter may be given by the following relation

$$\alpha_c = \frac{\Lambda_c}{\Lambda_{\infty}}$$

Where, Λc is the equivalent conductance of electrolyte at concentration 'c' and $\Lambda \infty$ is the

equivalent conductance of the same electrolyte at infinite dilution. Hence, measurement of Λc permits

evaluation of 'αc' if $\Lambda \infty$ is known.

1-5-3 Determination of Solubility of Sparingly Soluble Salts

Salts like AgCl, BaSO$_4$, CaCO$_3$, Ag$_2$CrO$_4$, PbSO$_4$, PbS, Fe(OH)3 etc. are ordinarily regarded as sparingly soluble and have a very small but definite solubility in water. The solubility of such sparingly soluble salts is obtained by determining the specific conductivity (κ) of a saturated salt solution. The molar conductivity at such high dilution can practically be taken as Λ^{∞}_m , i.e. for sparingly soluble salts,

$$\Lambda^{\infty}_m = \frac{\kappa \times 1000}{M}$$

Example/ The specific conductance of saturated solution of silver chloride is 2.28×10^{-4} **ohm^{-1} m^{-1}** after subtracting that of water. The molar conductance at **infinite dilution** of silver chloride is 0.0138 **ohm^{-1}m^2 mol^{-1}** . Calculate the solubility of silver chloride

1-6 CONDUCTOMETRIC TITRATIONS

Titrations in which conductance measurements are made use of in determining the end-point of acid-alkali reactions, some displacement reactions or precipitation reactions are called **Conductometric titrations.** In these titrations, advantage is taken of the fact that the **conductance of a solution at a constant temperature depends upon the number of ions present in it and their mobility.** For this purpose, the titrant is added from a burette into a measured volume of the solution to be titrated which is taken in a conductance cell and the conductance readings corresponding to the various additions are plotted against the volume of the titrant.

(1) Titration of a Strong acid against a Strong base

Consider the reaction in which hydrochloric acid solution is titrated against a solution of sodium hydroxide. Take 20 ml of the acid solution in the conductance cell placed in a thermostat and determine its conductance. Now add 1 ml sodium hydroxide solution from the burette at a time. After each addition, determine the conductance of the solution after through mixing and plot the conductanceof the solution against the volume of the alkali added. It will be observed that the points lie on two lines which are almost straight. The point of intersection of the interpolated lines will be the end point and the volume of alkali corresponding to this point is the volume of alkali required to neutralize 20 ml of the acid (Fig. 3). The reason for this is that before the addition of alkali, the conductance of the solution is due to presence of H+ and Cl– ions. Since hydrogen ions possess the greatest mobility of any ion, the greater part of the conductance is due to it. As alkali solution is added, the hydrogen ions are removed by combination with the hydroxyl ions forming

feebly ionised water molecules and their place is taken up by comparatively slow moving Na+ ions.

$H^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + H2O$
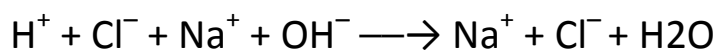
As a result of this, the conductance of the solution decreases and continues to fall with every subsequent addition of alkali till the end-point is reached. After the equivalence point, the further addition of sodium hydroxide solution results in an increase of conductance
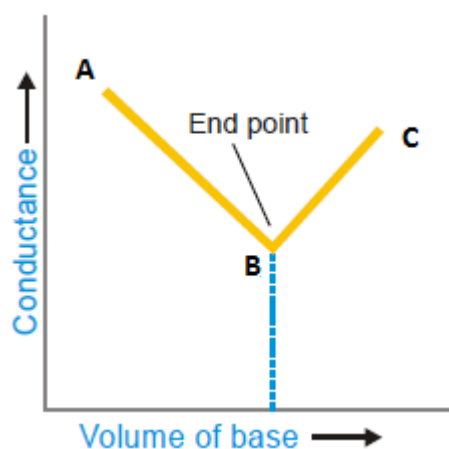

Fig.3: Conductometric titration curvefor strong acid and strong base.

(2) Titration of a Weak acid against a Strong alkali

When a weak acid like acetic acid is titrated against a strong alkali like sodium hydroxide, we geta curve of the type shown in Fig. 4. The initial conductance of the solution is low because of the poor dissociation of the weak acid. On adding alkali, highly ionised sodium acetate is formed. The acetate ions at first tend to suppress the ionisation of acetic acid still further due to **Common Ion Effect** but after a while the conductance begins to increase because the

conducting power of highly ionised salt exceeds that of the weak acid.

$$CH_3COOH + Na^+ + OH^- \longrightarrow CH_3COO^- + Na^+ + H_2O$$
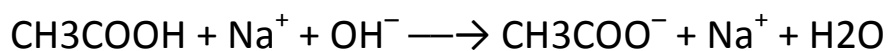
Immediately after the end point, further addition of sodium hydroxide introduces the fast moving hydroxyl ions. Thus, the *conductance value shows a sharp increase*. The point of intersection of the two curves, gives the end-point.
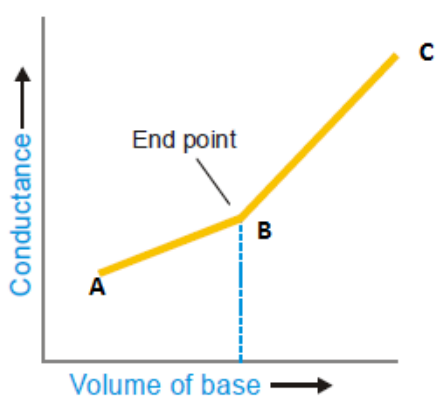

Fig.4: Curve for titration of a weakacid against a strong base.