

Physical Chemistry

Electrochemistry

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1. Conduction in Metals and in Electrolyte Solutions

Conductors can be divided broadly into two categories:

- (i) Metallic or electronic conductors
- (ii) Electrolytic conductors

(i) *Metallic Conductors*

Metals are the best conductor and it remains unchanged with the passage of current. A metallic conductor behaves as if it contains electrons which are relatively free to move. So electrons are considered as charge carrier in metals. Therefore, these conductors are also called *electronic conductors*. Metallic conduction or electronic conduction is the property possessed by pure metals, most alloys, carbon and certain solid salts and oxides.

(ii) *Electrolytic Conductors*

Conductors, through which passage of an electric current through them results in actual transfer of matter or brings about a chemical change in them, are called *electrolytic conductors or electrolytes*. Electrolytic conductors are of two types: -

- (a) In the first category are electrolytic conductors, which conduct electrolytically in the pure state, such as acids, bases and salt in water. e.g. NaCl, NaNO₃, K₂SO₄ etc.
- (b) In second category are generally put electrolytic conductors which consists of solutions of one or more substances. Electrochemistry is mainly concerned with this type of electrolytic conductor.

Generally electrolytic solutions are prepared by dissolving a salt, acid or base in water or other solvents. 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.

1.1 Conduction in Electrolyte Solutions

The passage of current through solutions of salts of metals such as zinc, iron, nickel, cadmium, lead, copper, silver and mercury results in the liberation of these metals at the cathode and from solutions of salts of the metals. If the anode consists of an attackable metal, the flow of the current is accompanied by the passage of the metal into solution. When the anode is made of an inert metal, e.g., platinum, an element is generally set free at this electrode; from solutions of nitrates, sulphates, phosphates, etc., oxygen gas is liberated, whereas from halide solutions, other than fluorides, the free halogen is produced. The decomposition of solutions by the electric current, resulting in the liberation of gases or metals, is known as *electrolysis*.

1.2 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.

- (i) Strong electrolytes
- (ii) Weak electrolytes

1.2.1 Strong 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 i.e., aqueous solutions of these substances have high value of molar conductance and on dilution the increase in their molar conductance is very small. This is due to the fact that such electrolytes are completely ionized at all dilutions therefore on further dilution the number of current carrying particles does not increase in the solution. Thus, solutions of electrolytes that have high molar conductance, and increases very slowly on dilution has a high degree of dissociation is called *strong electrolyte*.

During the passage of an electric current through solutions, flow of electricity is associated with the movement of particles, which are called *ions*. The ions carrying positive charges and moving in the direction of the current, i.e., towards the cathode, are referred to as *cations* and those carrying a negative charge and moving in the opposite direction, i.e., towards the anode, are called *anions*.

1.2.2 Weak Electrolytes

Weak acids and weak bases, e.g., amines, phenols, most carboxylic acids and some inorganic acids and bases, such as hydrocyanic acid and ammonia, and a few salts, e.g., mercuric chloride and cyanide, are dissociated only to a small extent at reasonable concentration; this group of compounds in general are called as *weak electrolytes*.

The molar conductance of the solutions of these electrolytes increases rapidly on dilution. The reason of this is that more molecules ionize on dilution inspite of this they are never completely ionized. For these electrolytes, the nature of the solvent is also important; a particular compound may be strong electrolyte, being dissociated to large extent, in one solvent, but may behave as weak electrolyte in other solvent due to low degree of dissociation.

Q. Which of the following are strong electrolytes?

(a) CH_3COOH

(b) H_2SO_4

(c) NH_4Cl

(d) NaCl

(e) HNO_3

(f) NH_3

➤ (c) & (d) are soluble hydroxides; (b) and (e) are first proton.

2. Specific Conductance and Molar Conductance

Conductance

Consider a uniform bar of conductor of length ' l ' cm and cross-sectional area ' a ' sq. cm and the cross section is rectangular and that the whole body is placed into cubes of one cm. side, as shown in Figure 1.

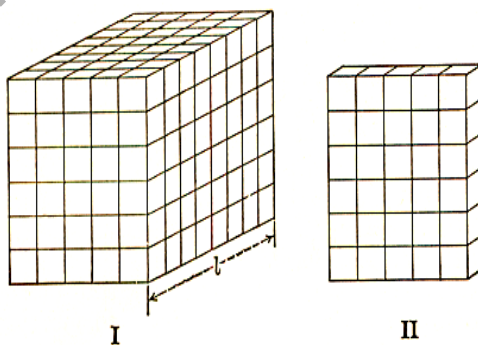


Fig. 1

Ohm's law states that 'The magnitude of current (I) passing through a conductor is directly proportional to the potential difference (E) applied across it and inversely proportional to the resistance (R) of the conductor'.

Q. The molar conductivity of a solution containing 2.54 g of CuSO_4/L is $91.0 \text{ cm}^2/\Omega\cdot\text{mole}$. What is the resistance of a cm^3 of this solution when placed between two electrodes 1.00 cm apart, each having an area of 1.00 cm^2 .

$$\kappa = \frac{C}{C^\circ}, \text{ where } C = \frac{N}{1000} = \text{mole}/\text{cm}^3$$

$$\left(\frac{2.54 \text{ g of } \text{CuSO}_4}{\text{L}} \right) \left(\frac{1 \text{ mol}}{159.5 \text{ g}} \right) \left(\frac{2 \text{ mol}}{\text{mol}} \right) = 0.0318 \text{ M } \text{CuSO}_4$$

$$\kappa = \left(\frac{91 \text{ cm}^2}{\Omega \text{ mol}} \right) \left(\frac{0.0318 \text{ mol}}{1000 \text{ cm}^3} \right) = 2.89 \times 10^{-3} \text{ S cm}^{-1}$$

We know that,

$$R = \frac{1}{\kappa} \cdot \frac{1}{A} = \left(\frac{1}{2.89 \times 10^{-3} \text{ S cm}^{-1}} \right) \left(\frac{1.00 \text{ cm}}{1.00 \text{ cm}^2} \right) = 346 \Omega$$

$$i = \frac{E}{R} \quad (1)$$

Thus, metallic conductor and electrolytes obey Ohm's law. Conductance is the reciprocal of resistance and is expressed in Siemen (S).

$$\text{Conductance} = \frac{1}{R} \quad (2)$$

2.1 Specific Conductance or Conductivity

The resistance of the bar (Fig.1) to the passage of electricity through it is proportional to its length 'l' (cm) and inversely proportional to the area of cross section 'a', therefore, the resistance 'R' is given by the relationship.

$$R \propto \frac{l}{a} \text{ or } R = \rho \frac{l}{a} \text{ ohms} \quad (3)$$

Where, 'ρ' is a constant known as specific resistance or resistivity.

If, $l = 1 \text{ cm}$, $a = 1 \text{ cm}^2$

Then, $\rho = R \text{ ohm cm}$

Specific conductance of any conducting material is defined as the reciprocal of its specific resistance. It is given the symbol 'κ' and is stated in reciprocal ohm cm^{-1} , nowadays called "Scm⁻¹".

Conductance 'G' is then defined as

$$G = \kappa \frac{a}{l} \text{ S} \quad (4)$$

$$G = \frac{1}{R} \quad (5)$$

The conductance (G) is the reciprocal of resistance, i.e. $G = \frac{1}{R}$

2.2 Molar Conductance

Molar conductivity of a solution 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 Λ_m .

Suppose 1 mole of an electrolyte is dissolved in $\Lambda_m \text{ cm}^3$ of a solution. Such a solution will cover an area of $v \text{ cm}^2$ of the electrodes kept 1 cm apart. The conductance of this system, which is the molar conductance Λ_m , may be derived from equation $R = \frac{l}{\kappa a}$, where 'a' is equal to $v \text{ cm}^2$ and 'l' is 1 cm; thus

$$\Lambda_m = \kappa v \quad (6)$$

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

$$\Lambda_m = 1000 \frac{\kappa}{c} \quad (7)$$

However if 'c' is expressed the equivalent conductance of any solution can thus be readily derived from its specific conductance and concentration. Since the units of κ are S cm^{-1} , those of Λ_m comes out from eq. (6) or (7) to be $\text{Scm}^2 \text{mol}^{-1}$.

If one uses SI units then the units for 'ρ' is $\Omega \text{ m}^{-1}$ for κ is Sm and for Λ_m is $\text{Sm}^2 \text{mol}^{-1}$. In earlier the term equivalent conductance Λ was used. It is defined as the conductance of 1gram equivalent of electrolyte in solution with a given concentration.

3. Measurement of Molar Conductance

Conductance is the reciprocal of resistance and the resistance can be determined by a Wheatstone bridge circuit in which the conductivity cell forms one arm of the bridge, this method is known as *Null Method (Kohlrausch conductance bridge)*.

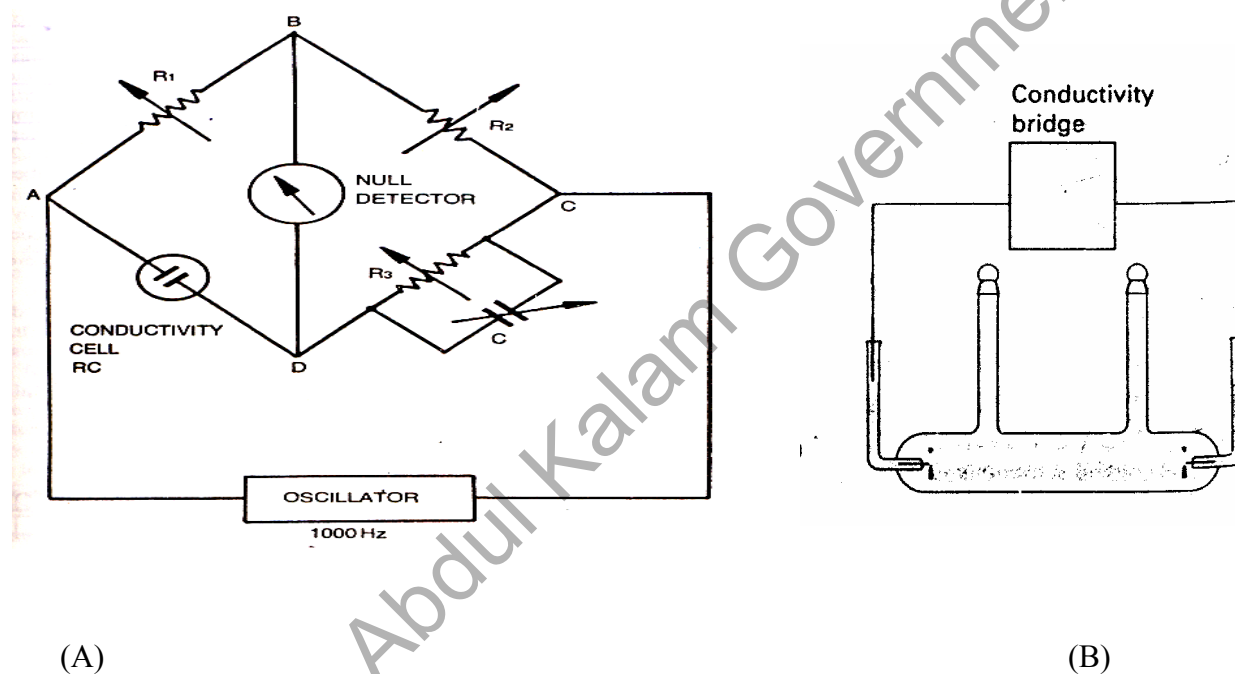


Fig. 2: (A) Wheatstone bridge circuit for measurement of conductivity, (B) Conductivity cell with one arm of a resistance bridge for measurement of conductivity of an electrolyte.

The arms AB and BC represented by resistance R_1 and R_2 are usually in the form of a single calibrated slide wire resistor with a sliding contact connected to the null detector. The solution whose conductance is to be determined is placed in conductivity cell. When the bridge is balanced, assuming that the conductivity cell behaves as a pure resistance, then the voltage between 'B' and 'D' is equal to zero.

$$R_{\Lambda} = \left(\frac{R_1}{R_2} \right) \times R_3 \quad (8)$$

By adjustment of the ratio R_1/R_2 , a wide range of resistances can be measured. However, whenever possible, this ratio should not deviate too far away from unity. The cell capacitance is balanced out by providing a variable capacitor in parallel with resistance R_3 . It is so adjusted that the detector gives a sharply defined balance point. The null detector is not an ordinary galvanometer as it is not sensitive to alternating current at the frequency, which is employed to excite the bridge. The most popular detector in use is the magic eye, or the cathode ray oscilloscope.

The problem in determining the resistance of the solution of an electrolyte by the above method is that electrolysis of the solution also occurs simultaneously with the conduction of the current and due to this: -

- a) Polarisation sets in and causes the resistance to vary.
- b) The concentration of the solution changes.

In order to avoid these complications an alternating source of power with frequency ~ 1000 Hz is used.

3.1 Determination of Cell Constant

The electrodes in the cell are not exactly 1 cm apart and may not have surface area of 1 sq. cm (1cm^2). Thus the value of observed conductivity is not equal to specific conductance but is proportional to it.

$$R = \rho \frac{1}{a} \text{ or } R = \rho x \text{ or } x = \frac{R}{\rho} \quad (9)$$

Where, $x = l/a = \text{cell constant}$

Cell constant, $x = \kappa/G$ or

Specific conductance, $\kappa = \text{cell constant 'a' X observed conductance 'G'}$.

Taking an example of N/50 KCl solution, the specific conductance at 25°C is $0.002765 \text{ Scm}^{-1}$.

We know that,

Cell constant, $x = 0.002765/\text{observed conductance (G)}$

By putting the value of observed conductance in the above expression, one can calculate cell constant. Once the value of cell constant has been determined, great care must be taken not to change the distance between the electrodes during further measurements in any way.

4. Variation of Molar and Specific Conductance with Dilution

4.1 Effect of Dilution on Molar Conductance

With dilution following variations on molar conductance are observed:

- (i) The value of molar conductance increases on dilution. The increase is due to the fact that molar conductance is the product of specific conductance (κ) and the volume (V) of the solution containing 1 mole of the electrolyte. As the decreasing value of specific conductance is more than compensated by the increasing value of ' V ', thus the value of molar conductance (Λ_m) will increase

with dilution. The variation of molar conductance at different dilutions of some common electrolytes are shown Table 1:

Table 1: Molar Conductance of some common electrolytes at 25°C in Scm^2 .

Concentration (mole/L)	NaOH	KCl	HCl	CH ₃ COOH	AgNO ₃
0.0005	246	147.81	422.74	-	131.36
0.001	245	146.95	421.36	48.63	130.51
0.005	240	143.55	415.80	22.80	127.20
0.01	237	141.27	412.00	16.20	124.76
0.02	233	138.34	407.24	11.57	121.41
0.05	227	133.37	399.09	7.36	115.24
0.10	221	128.96	391.32	5.20	109.14

(ii) Effect of dilution on molar conductance is shown in the Figure.4, where the molar conductance at different dilutions is plotted against concentration (M).

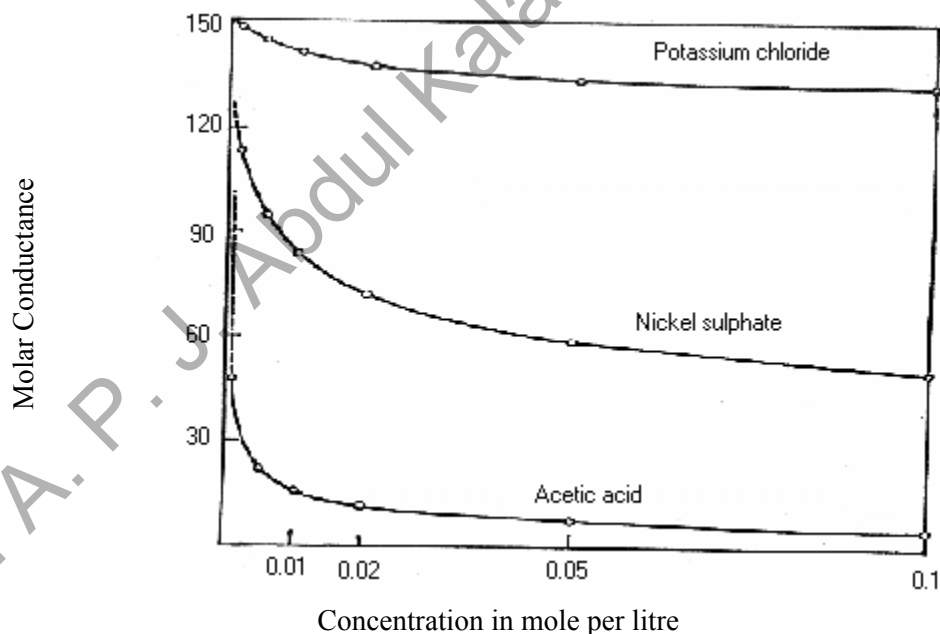


Fig. 3: Variation of equivalent conductance with concentration

From Figure 3 it is clear that strong electrolytes such as KCl, can have limiting value at zero concentration obtained by extrapolation (i.e. at infinite dilution) whereas for weak electrolyte such as acetic acid, there is no indication that a limiting value can be obtained by the extrapolation of the graph to zero concentration. It means we cannot experimentally determine molar conductivity of weak electrolytes at infinite dilution.

(iii) The maximum value of the molar conductivity is termed as the molar conductivity at zero concentration (or infinite dilution) and is termed \wedge_m^∞ .

4.2 Effect of Dilution on Specific Conductance

The specific conductance depends on the number of ions present per unit volume of the solution. Since on dilution the degree of dissociation increases but the number of ions per unit volume decreases, therefore it is expected that the specific conductance of a solution decrease on dilution (Table.2).

Table 2: Specific Conductance of NaCl Solution at 25° C:

Concentration	Molar Conductance (Scm ²)
0.000	0.012645
0.0005	0.012450
0.001	0.012374
0.01	0.011851
0.100	0.010674

5. Kohlrausch's Law of Independent Migration of 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 \wedge_m^∞ .

Kohlrausch made a systematic study of \wedge_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. Consider the values in Table.3 to appreciate the law:

Table.3: Values of Λ_0 for different electrolytes

Electrolyte		Λ_0 at 25° (Scm ²)	Difference (Scm ²)
I.	KCl	130.16	21.17
	NaCl	108.99	
II.	KNO ₃	126.50	21.17
	NaNO ₃	105.33	
III.	KCl	130.16	3.66
	KNO ₃	126.50	
IV.	NaCl	108.99	3.66
	NaNO ₃	105.33	

Electrolytes in set I and II have a common anion so that the difference can only be due to the difference in contribution to Λ by K^+ and Na^+ ions. In the same way in sets III and IV the constant difference may be attributed to the difference in contribution to Λ_m^∞ made by the Cl^- and NO_3^- ions. These observations can be explained by Kohlrausch's law of independent migration of ions which states that:

At infinite dilution, where the electrolytes are fully dissociated and free from interionic effects, each ion migrates independently of its co-ion. As such each ion contributes its definite share to the total equivalent conductivity of the electrolyte, which depends only on the nature of the contributing ions and not at all on the ion with which it is associated as a part of the electrolyte. In other words, the molar conductivity at infinite dilution of an electrolyte is equal to the sum of the ionic conductances of the ions composing it, provided the solvent and temperature are the same.

$$\Lambda_m^\infty = \nu_+ \Lambda_m^\infty + \nu_- \Lambda_m^\infty \quad (10)$$

Where, Λ_a and Λ_c are the ionic conductances of the anion and cation respectively at infinite dilution and ν_+ and ν_- is the number of cations and anions in which one molecule of the electrolyte. For anion and cation this value is constant at a fixed temperature and in a given solution. It is expressed in Scm²mol⁻¹ or Sm²mole⁻¹.

Q. The limiting molar conductivities of KCl, KNO₃, and AgNO₃ are 14.99 mSm²mol⁻¹, 14.50 mSm²mol⁻¹ and 13.34 mSm²mol⁻¹ respectively at 25°C. Calculate 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.

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

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

$$\Lambda_m^\infty(\text{KNO}_3) = \lambda(K^+) + \lambda(\text{NO}_3^-) = 14.50 \text{ mSm}^2\text{mol}^{-1}$$

$$\Lambda_m^\infty(\text{AgNO}_3) = \lambda(\text{Ag}^+) + \lambda(\text{NO}_3^-) = 13.34 \text{ mSm}^2\text{mol}^{-1}$$

$$\begin{aligned}\text{Hence } \Lambda_m^\infty(\text{AgCl}) &= \Lambda_m^\infty(\text{AgNO}_3) + \Lambda_m^\infty(\text{KCl}) - \Lambda_m^\infty(\text{KNO}_3) \\ &= 13.34 + 14.99 - 14.50 \text{ mSm}^2\text{mol}^{-1} \\ &= 13.83 \text{ mSm}^2\text{mol}^{-1}\end{aligned}$$

5.1 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 Λ_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:

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

$$\Lambda_m^\infty \text{CH}_3\text{COONa} = \Lambda_m^\infty \text{Na}^+ + \Lambda_m^\infty \text{CH}_3\text{COO}^- \quad \text{-----(12)}$$

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

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

$$\Lambda_m^\infty \text{HCl} + \Lambda_m^\infty \text{CH}_3\text{COONa} - \Lambda_m^\infty \text{NaCl} = \Lambda_m^\infty \text{H}^+ + \Lambda_m^\infty \text{Cl}^- + \Lambda_m^\infty \text{Na}^+ + \Lambda_m^\infty \text{CH}_3\text{COO}^- - \Lambda_m^\infty \text{Na}^+ - \Lambda_m^\infty \text{Cl}^-$$

$$x + y - z = \Lambda_m^\infty \text{H}^+ + \Lambda_m^\infty \text{CH}_3\text{COO}^- = \Lambda_m^\infty \text{CH}_3\text{COOH}$$

$$\Lambda_m^\infty \text{CH}_3\text{COOH} = x + y - z$$

5.1.2 Calculation of Degree of Dissociation of Weak Electrolytes

The degree of dissociation of weak electrolyte such as NH_4OH , 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 (α_c) of a weak electrolyte at the concentration C mole per liter may be given by the following relation:

$$\alpha_c = \frac{\Lambda_c}{\Lambda_\infty} \quad (14)$$

Where, Λ_c is the equivalent conductance of electrolyte at concentration 'c' and Λ_∞ is the equivalent conductance of the same electrolyte at infinite dilution. Hence, measurement of Λ_c permits evaluation of ' α_c ' if Λ_∞ is known.

5.1.3 Determination of Solubility of Sparingly Soluble Salts

Salts like AgCl , BaSO_4 , CaCO_3 , Ag_2CrO_4 , PbSO_4 , PbS , $\text{Fe}(\text{OH})_3$ 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,

$$\Lambda_m^\infty = \kappa \cdot V \quad (15)$$

Where, V is the volume in cm^3 containing 1 mole of salt while Λ_m^∞ , can be calculated using Kohlraush's law.

Substituting the values of κ and Λ_m^∞ in eq. 15; below the value of V can be calculated:

$$V = \Lambda_m^\infty / \kappa \approx (\nu_+ \Lambda_+ + \nu_- \Lambda_-) / \kappa \quad (16)$$

But $V \text{ cm}^3$ of saturated solution contains = 1 mole of salt

1000 cm^3 of saturated solution contains = $1000 / V$ mole of salt

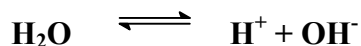
Hence, solubility of salt,

$$S = 1000/V \text{ M}$$

$$= 1000/V \times \text{M. Wt.} = \text{g/L}$$

5.1.4 Determination of ionic product of water

With the help of specific conductivity of water, the ionic product of water can be determined. The ionization of water may be represented as,



The product of the concentrations of H^+ and OH^- ions expressed in mol/L is called ionic product of water and is represented by K_w .

i.e. $[H^+][OH^-] = K_w$

The measured specific conductivity of the purest form of water is $0.055 \times 10^{-6} \text{ S cm}^{-1}$. The molar conductance is given by

$$\Lambda_m = K_v \times 18 \quad (17)$$

Thus,
$$\begin{aligned} &= 0.055 \times 10^{-6} \times 18 \\ &= 0.990 \times 10^{-6} \text{ Scm}^2\text{mol}^{-1} \end{aligned}$$

The molar conductance of water at infinite dilution can be obtained by

$$\Lambda_m^\infty (\text{H}_2\text{O}) = \Lambda (H^+) + \Lambda (OH^-)$$

Therefore,
$$\Lambda_\infty (\text{H}_2\text{O}) = 349.8 + 198.5 = 548.30 \text{ Scm}^2\text{mol}^{-1}$$

and for water,
$$\alpha = \Lambda_m / \Lambda_\infty$$

$$= 0.055 \times 10^{-3} \times 18 / 548.3$$

$$C_{H^+} = C_{OH^-} = 0.055 \times 10^{-3} \times 18 / 548.3$$

(Concentration of water = $1000/18 = 55.55 \text{ M}$)

$$C_{H^+} = C_{OH^-} = \alpha \times 55.55 \times 10^{-9}$$

$$= 1.806 \times 55.55 = 1.003 \times 10^{-7}$$

$$K_w = (1.003 \times 10^{-7})$$

$$= (1.006 \times 10^{-14})$$

Q. Calculate the value of K_w for water in 0.100 M NaCl solution. The experimental value is 1.65×10^{-14} .

➤ The thermodynamic value of the equilibrium constant for the dissociation of water



$$K_w = \frac{a_{\text{H}_3\text{O}^+} \cdot a_{\text{OH}^-}}{(a_{\text{H}_2\text{O}})} \\ = 1.01 \times 10^{-14}$$

Water is a liquid acting as a solvent, & its activity is its mole fraction, here $55.3/55.4 \approx 1$. Then

$$K_w^0 = [\text{H}_3\text{O}^+] [\text{OH}^-] \cdot f_{\text{H}_3\text{O}^+} \cdot f_{\text{OH}^-}$$

$$K_w^0 = K_w \cdot f_{\text{H}_3\text{O}^+} \cdot f_{\text{OH}^-}$$

Where K_w is the constant in terms of concentration activity coefficients from the extended Debye-Huckel eqn., $f_{\text{H}_3\text{O}^+} = 0.825$ and $f_{\text{OH}^-} = 0.753$.

Using these values, we obtain

$$K_w = \frac{1.01 \times 10^{-14}}{0.825 \times 0.753}$$

$$K_w = 1.61 \times 10^{-14}$$

5.1.5 Determination of Ionic Mobility of an Ion

Ionic mobility of an ion is defined as the speed of the ion in centimeters per second, when a potential of one volt is applied between two electrodes kept 1 cm apart. 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.

$$\lambda = zuF \quad (18)$$

where F is the Faraday constant ($F = N_A e$)

Equation (18) applies to the cations and to the anions and can be deduced to equation (18a) for solution in limit of zero concentration when there are no interionic interactions.

$$\Lambda_m^\infty = (z_+ u_+ \nu_+ + z_- u_- \nu_-) F \quad (18a)$$

For a symmetrical $z : z$ electrolyte this equation simplifies to

$$\Lambda_m^\infty = z(u_+ + u_-)F \quad (19)$$

6. Migration of Ions

As in a solution of an electrolyte the electricity is conducted by migration of ions and the ions move in solution independently towards the oppositely charged electrodes. This fact can be illustrated by following simple experiments:

(i) Lodge's moving boundary evidence

A glass tube of the shape as shown in the Figure 4 is taken and its middle portion between two arms is filled with a jelly of agar-agar. A trace of sodium hydroxide (or any alkali) and phenolphthalein are added during the preparation of the jelly. It becomes red due to phenolphthalein in alkaline medium. The jelly is allowed to set. After that dilute sulphuric acid is added to the left arm containing the anode and sodium sulphate solution to the right arm in which the cathode is placed. On passing the current, hydrogen ions migrate along the solution towards the cathode and their movement can be monitored by observing the gradual fading of red colour in the jelly due to the neutralization of the alkali by the hydrogen ions and the movement of the original boundary. Experiment clearly shows that positively charged hydrogen ions (H^+) are moving towards negatively charged cathode.

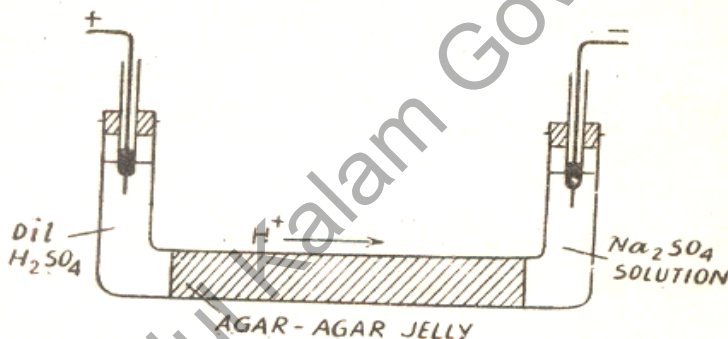


Fig. 4: Lodge's moving boundary experiment

(ii) Movement of coloured ions

A U shaped glass tube is taken and its middle portion is filled with an aqueous solution of 5% agar-agar and a mixture of copper sulphate and potassium dichromate in distilled water. This dark green-coloured solution after cooling forms a jelly and sets. The position of the surface of green solution in both the arms of the U-tube is marked by placing small amount of charcoal on it as shown in the Figure 5(A).

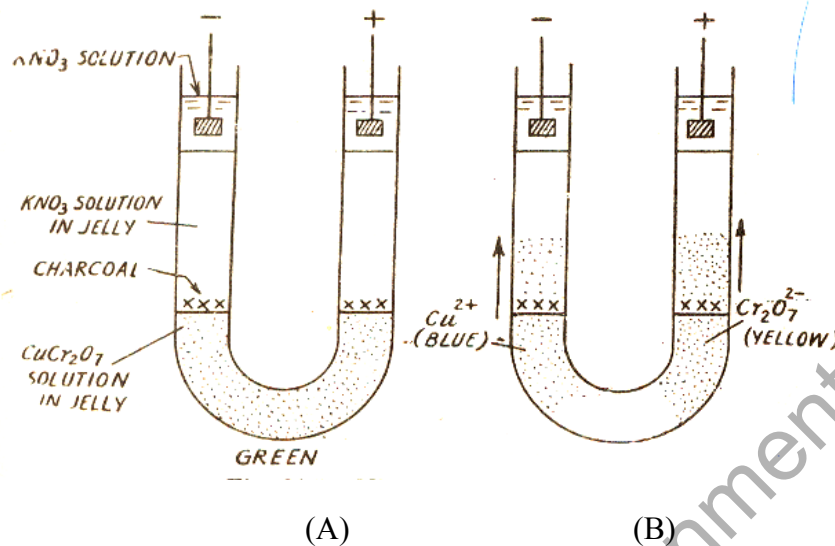


Fig. 5: Migration of ions

In both the arms then a solution of potassium nitrate and agar-agar is filled. This on cooling also set as jelly. Over this jelly, solution of potassium nitrate in distilled water is added and the electrodes are immersed in it. With the application of potential difference across the electrode the blue colour of copper ions rises in to the jelly towards the cathode. The reddish yellow dichromate ions move up in the other arm of the tube towards the anode. In this experiment two types of ions can be clearly seen moving with well-defined boundaries {Figure 5(B)}.

6.1 Speeds of migration of ions during electrolysis

During electrolysis ions are liberated according to Faraday's law at cathode and anode but their relative rate of movement towards the electrodes may be different.

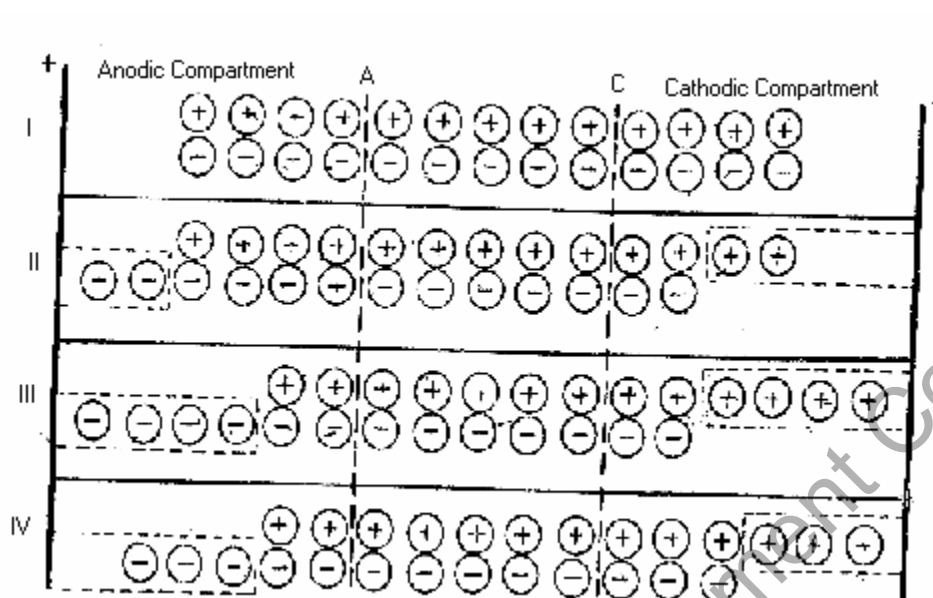


Fig. 6: Anodic and Cathodic compartments showing speeds of migration of ions during electrolysis

In the Figure. 6 'A' and 'C' are two porous diaphragms, which prevent convection currents but allow the passage of ions. The cell is divided into an anodic and cathodic compartment. Suppose initially 13 molecules were present. The number of molecules in each anode and cathode compartment is equal i.e. 4 and 5 molecules are present between the two segment in ac {Fig.6(I)}.

Consider the following possibilities in reference to the above experiment.

- {Fig.6(II)} shows the movement of two anions alone, here only anions are capable of movement.
- Both anions and cations move at the same rate towards the opposite charged electrodes, the condition as shown in {Fig.6 (III)}.
- In another situation cations move at twice the rate of the anions (Fig.6 (IV)).

In all the above conditions ions are always liberated in equivalent amounts; the effect of difference in their rate only cause a change of concentration around electrodes. Further, from the above experiment the following expression can be deduced.

$$\frac{\text{Reduction in number of anions around anode}}{\text{Reduction in number of cations around cathode}} = \frac{\text{Speed of cation towards cathode}}{\text{Speed of anion towards anode}}$$

Q. At 25°C the molar ionic conductivities of Li^+ , Na^+ , and K^+ are $3.87 \text{ mSm}^2\text{mol}^{-1}$, $5.01 \text{ mSm}^2\text{mol}^{-1}$, and $7.35 \text{ mSm}^2\text{mol}^{-1}$ respectively. Calculate their mobilities.

➤ We have, $u = \frac{\lambda}{zF}$

$$\begin{aligned} \text{(i) } u(\text{Li}^+) &= \frac{3.87 \text{ mSm}^2\text{mol}^{-1}}{96485 \text{ Cmol}^{-1}} \\ &= 4.01 \times 10^{-5} \text{ mSC}^{-1}\text{m}^2 \\ &= 4.01 \times 10^{-8} \text{ m}^2\text{V}^{-1}\text{s}^{-1} \quad (1\text{C}\Omega = 1\text{As}\Omega = 1\text{Vs}) \end{aligned}$$

$$\begin{aligned} \text{(ii) } u(\text{Na}^+) &= \frac{5.01 \text{ mSm}^2\text{mol}^{-1}}{96485 \text{ Cmol}^{-1}} \\ &= 5.19 \times 10^{-8} \text{ m}^2\text{V}^{-1}\text{s}^{-1} \end{aligned}$$

$$\begin{aligned} \text{(iii) } u(\text{K}^+) &= \frac{7.35 \text{ mSm}^2\text{mol}^{-1}}{96485 \text{ Cmol}^{-1}} \\ &= 7.62 \times 10^{-8} \text{ m}^2\text{V}^{-1}\text{s}^{-1} \end{aligned}$$

7. Arrhenius Theory of Electrolytic Dissociation

Arrhenius (1887) put forward the theory of electrolytic dissociation, as a more explicit form of one he had proposed in 1883, which forms the basis of the modern treatment of electrolytes. The assumption made was that when an acid, base or salt is dissolved in water, a considerable portion becomes spontaneously dissociated into positive and negative ions. Considering an electrolyte

$A_{\nu+} B_{\nu-}$, which might undergo complete dissociation to form ν_+ positive ions and ν_- negative ions according to the equation



We must calculate the net number of particles that result from a degree of dissociation α . If m is the molality of the electrolyte, α is the degree of dissociation, the concentration of undissociated electrolyte will be $m - \alpha m = m(1 - \alpha)$. In addition, the concentration of A^{z+} and B^{z-} will be $\nu_+ \alpha m$ and $\nu_- \alpha m$, respectively.

Here the concentration of particles is $m(1 - \alpha) + (\nu_+) \alpha m + (\nu_-) \alpha m$ and let ν be the total number of ions yielded by complete dissociation of the electrolyte, i.e., $\nu = \nu_+ + \nu_-$. With this notation the molality of particles for the partially dissociated electrolyte is $m(1 - \alpha) + \alpha \nu m$ rather than the value of 'm' expected for no dissociation.

The van't Hoff 'I' factor can be written as

$$= \frac{m(1 - \alpha) + \alpha \nu m}{m} = 1 - \alpha + \alpha \nu \quad (21)$$

From this interpretation of i , one obtains

$$\alpha = \frac{i-1}{\nu-1} \quad (22)$$

This relation can also be used in spite of the relation $\alpha = \frac{\Lambda}{\Lambda_m^\infty}$, for calculating the degree of dissociation of an electrolyte.

8. Ostwald's Dilution Law

The weak electrolyte ionizes to a very small extent and their molar conductivity doesn't attain a limiting value at high dilution. In such solutions there is equilibrium between free ions and undissociated molecules. The equilibrium can be written in the form:



Where $\text{M}^+ = \text{A}^- =$ free ions

MA = undissociated portion of the electrolyte including both nonionized molecules and ion pairs.

By law of equilibrium,

$$K = \frac{a_{\text{M}^+} \times a_{\text{A}^-}}{a_{\text{MA}}} \quad (24)$$

Where, a 's = activities of indicated species

K = the equilibrium constant called dissociation constant of the electrolyte

Equation (24) can be written as the product of concentration C , in g ions or moles per litre, and the activity coefficient f , above equation becomes;

$$K = \frac{c_{\text{M}^+} \times c_{\text{A}^-}}{c_{\text{MA}}} \cdot \frac{f_{\text{M}^+} \times f_{\text{A}^-}}{f_{\text{MA}}} \quad (25)$$

Here, ' α ' is the degree of dissociation of electrolyte, i.e., the fraction of the electrolyte in the form of free ions and c is its total concentration, (M). Both c_{M^+} and c_{A^-} are equal to αC while c_{MA} is equal to $c(1-\alpha)$ then eq. (25) can be written as,

$$K = \frac{\alpha^2 c}{(1-\alpha)} - \frac{f_{M^+} \times f_{A^-}}{f_{MA}} \quad (26)$$

In sufficiently dilute solution the activity coefficient is approximately unity, then eq. (26) takes the form:

$$K = \frac{\alpha^2 c}{(1-\alpha)} \quad (27)$$

This is the expression of the dilution law, first derived by W. Ostwald in 1888.

For weak electrolytes like acetic acid (CH_3COOH) or ammonium hydroxide (NH_4OH) the value of degree of dissociation is very small, i.e., $(1-\alpha) \approx 1$

eq. (27) can be written as;

$$K = \alpha^2 c \quad (28)$$

$$\alpha^2 = \frac{K}{c} \quad (29)$$

$$\alpha = \sqrt{\frac{K}{c}} \quad (30)$$

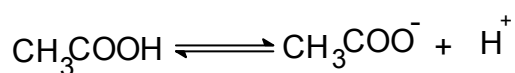
8.1 Verification of the Dilution Law

The degree of dissociation ' α ', is determined by conductivity measurements and is obtained by dividing the molar conductance at a certain dilution, Λ_v by the equivalent conductivity at infinite dilution Λ_∞ , and is given by eq. (31).

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\infty} \quad (31)$$

8.1.1 Determination of Dissociation Constant of Acetic Acid (CH_3COOH)

Acetic acid is a weak electrolyte and when it dissolves in water it dissociates as



If c g moles of acetic acid are dissolved per liter of the solution and α is the degree of dissociation, then the dissociation constant K is given by

$$K = \frac{\alpha^2 c}{(1 - \alpha)} \quad (32)$$

If ' \wedge_m^c ' is the equivalent conductance of the CH_3COOH solution at the given dilution and \wedge_m^∞ at infinite dilution, then

$$\alpha = \frac{\wedge_m^c}{\wedge_m^\infty} \quad (33)$$

The value of \wedge_m^c is determined by conductivity measurement at concentration C . The value of \wedge_m^∞ for acetic acid can be calculated with Kohlrausch's law i.e.,

$$\begin{aligned} \Lambda_\infty \text{ for } (\text{CH}_3\text{COOH}) &= \Lambda (\text{CH}_3\text{COO}^-) + \Lambda \text{ for } (\text{H}^+) \\ &= 40.9 + 349.8 \\ &= 390.7 \text{ mhos} \end{aligned} \quad (34)$$

The value of K can be calculated by substituting the values of \wedge_m^c , \wedge_m^∞ and c .

Q. At 25°C , the molar conductance of propanoic acid at infinite dilution is $386.6 \text{ S cm}^2\text{mol}^{-1}$. If its ionization constant is 1.4×10^{-5} . Calculate molar conductance of 0.05 M propanoic acid solution at 25°C ?

$$\text{➤} \quad K_a = \frac{cx^2}{(1-x)} \quad \text{If } x \ll 1 \text{ then } K_a = cx^2$$

$$K_a = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.4 \times 10^{-5}}{0.05}} = 0.0167$$

$$x = \frac{\wedge_m^c}{\wedge_m^\infty}$$

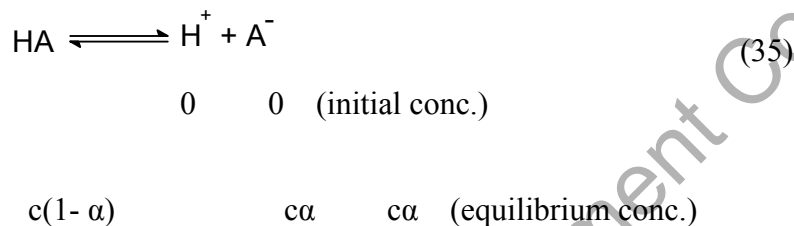
$$\begin{aligned} \wedge_m^c &= x \times \wedge_m^\infty \\ &= 0.0167 \times 386.6 \\ &= 6.47 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

9.2 Applications of Ostwald's Dilution Law

Applications of Ostwald's dilution law are many. Some of them are discussed below: -

9.2.1 Dissociation constant of monobasic acid

Dissociation constant of weak electrolytes such as weak acids, weak bases can be determined with the help of Ostwald's dilution law. Consider the solution of a weak acid HA with concentration 'c'. If α is the degree of dissociation at equilibrium, then



By applying the law of mass action,

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (36)$$

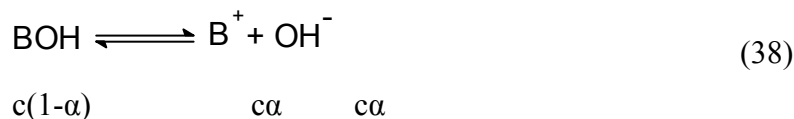
where K_a is the dissociation or ionization constant of the acid.

Substituting $[\text{H}^+]$, $[\text{A}^-]$ and $[\text{HA}]$ in eq. (36), we get

$$K_a = \frac{\alpha^2 c}{(1-\alpha)} \quad (37)$$

9.2.2 Dissociation constant of a weak base

Let us consider a weak base BOH dissolved in water. With concentration 'c'. Let ' α ' be the degree of dissociation at equilibrium, the following ionic equilibrium exist in solution,



The dissociation or ionization constant is given by

$$K_b = \frac{[B^+][OH^-]}{[BOH]} = \frac{\alpha^2 c}{(1-\alpha)} \quad (39)$$

(i) Experimental determination of dissociation constant

We have already shown that the dissociation constant of weak acids and weak base can be represented by

$$K_a = \frac{\alpha^2 c}{(1-\alpha)} \quad (40)$$

Here 'α' can be determined from the expression,

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

$$K_a = \frac{c \left(\frac{\Lambda_m^c}{\Lambda_m^\infty} \right)^2}{\left(1 - \frac{\Lambda_m^c}{\Lambda_m^\infty} \right)} \quad (41)$$

$$= \frac{c \Lambda_m^{c^2}}{\Lambda_m^\infty (\Lambda_m^\infty - \Lambda_m^c)} \quad (42)$$

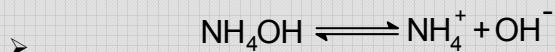
The value of Λ_m^c of the solution is determined from its specific conductivity. Λ_m^∞ of this solution is calculated from 'Kohlrausch law' i.e.

$$\Lambda_m^\infty = \Lambda_a^\infty + \Lambda_c^\infty \quad (43)$$

Where, Λ_a^∞ and Λ_c^∞ are ionic conductance of anion and cation of weak acids or bases.

By knowing the value of Λ_m^c and Λ_m^∞ values of α can be calculated. The dissociation constant can also be calculated using equation (40).

Q. Molar conductivities at infinite dilution at 25°C of NH_4Cl , NaOH and NaCl are 129.8, 217.4 & 108.9 $\text{S cm}^2\text{mol}^{-1}$. For 0.01 M NaOH molar conductance is 9.33 $\text{S cm}^2\text{mol}^{-1}$. Calculate ionization constant of NH_4OH .



By Ostwald's dilution law, ionization constant K_b of weak base is

$$K_b = \frac{cx^2}{(1-x)}$$

$$X = \text{degree of ionization} = \frac{\Lambda_m^c}{\Lambda_m^\infty}$$

$$\Lambda_m^c(0.01\text{N}) = 9.33 \text{ S cm}^2 \text{ mol}^{-1}$$

By Kohlrausch's law

$$\begin{aligned}\Lambda_m^\infty(\text{NH}_4\text{OH}) &= \Lambda_m^\infty(\text{NH}_4\text{Cl}) + \Lambda_m^\infty(\text{NaOH}) - \Lambda_m^\infty(\text{NaCl}) \\ &= 129.8 + 217.4 - 108.9 \\ &= 238.3 \text{ S cm}^2\text{mol}^{-1}\end{aligned}$$

$$x = \frac{9.33}{238.3} = 0.0392$$

$$K_b = \frac{cx^2}{(1-x)}$$

$$\begin{aligned}&= \frac{0.01 \times (0.0392)^2}{(1 - 0.0392)} \\ &= 1.6 \times 10^{-5}\end{aligned}$$

10. Debye-Huckel-Onsagar Equation

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 neighbouring 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 Onsagar and is known as Debye-Huckel-Onsagar (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

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. The quantitative formulation of these effects is far from simple, but the Debye-Huckel-Onsager theory is an attempt to obtain quantitative expression at about the same level of sophistication as the Debye-Huckel-theory itself. The theory leads to a Kohlrausch like expression in which

$$\kappa = A + B \wedge_m^\infty \quad (44)$$

$$\text{with } A = \frac{z^2 e F^2}{3\pi\eta} \left(\frac{2}{\epsilon RT} \right)^{1/2} \quad B = \frac{qz^3 e F}{24\pi\epsilon RT} \left(\frac{2}{\epsilon RT} \right)^{1/2} \quad (45)$$

Where, η = flux of momentum

ϵ = electric permittivity of the solvent and

$q = 0.586$ for a 1,1-electrolyte (Table 4)

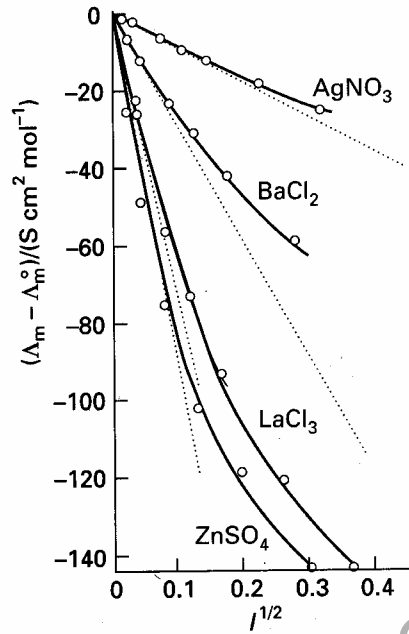


Fig. 7. The dependence of molar conductivities on the square root of the ionic strength, and comparison (shown by dotted lines) with the dependence predicted by the Debye-Huckel-Onsager theory.

Figure 7 shows the dependence of molar conductivities on the square root of the ionic strength and comparison with the dependence predicted by the Debye – Huckel – theory. The agreement is quite good at very low molar concentrations (less than about 10^{-3} M, depending on the charge type).

Green – Kubo relationship can be applied on electric conduction, which expresses a transport properly in terms of the fluctuations in microscopic properties of a system. The electrical conductivity is related to the fluctuations in the sample that arises from variations in the velocities of the ions.

$$\kappa = \frac{1}{KTV} \int_0^\infty \langle j(0)j(t) \rangle dt \quad (46)$$

$$j = \sum_i^N z_i e v_i \quad (47)$$

where v_i is the velocity of the ion i at a given instant and the angular brackets denote an average over the sample. If the ions are very mobile, there will be large fluctuations in the instantaneous currents in the same, and the conductivity of the medium will be high. If the ions are locked into position, as in an ionic solid, there will be no instantaneous currents, and the ionic conductivity will be zero. The velocities of the ions are calculated explicitly in a molecular dynamics simulation, so the correlation function, the quantity $\langle j(0)j(t) \rangle$, can be evaluated reasonably simply.

11. Transport Numbers

The transport number (t) is defined as the fraction of total current carried by the particular ionic species in the solution. In a simple case of a single electrolyte yielding the ions designated by the suffixes (+) and (-), the corresponding transference numbers are given as follows:

$$t_+ = \frac{q_+}{Q} \quad (48)$$

Where q_+ is the quantity of electricity carried by the cation and Q is the total quantity of electricity carried by all the ions through the solution. Similarly, the anion transport number t_- is defined as:

$$t_- = \frac{q_-}{Q} \quad (49)$$

Where q_- is the quantity of electricity carried by the anion, equations (48) and (49) can be expressed as

$$t_+ = \frac{c_+ u_+}{c_+ u_+ + c_- u_-} \quad (50)$$

$$t_- = \frac{c_- u_-}{c_+ u_+ + c_- u_-} \quad (51)$$

The quantities c_+ and c_- which represent the concentrations of the ions, are equal and therefore for this type of the electrolyte.

$$t_+ = \frac{u_+}{u_+ + u_-} \quad (52)$$

$$t_- = \frac{u_-}{u_+ + u_-} \quad (53)$$

$$\text{and } t_+ + t_- = 1$$

u_+ and u_- are the mobilities of the ions in the same solution and we know that the speed of an ion in a solution at any concentration is proportional to the conductance of the ion at that concentration and therefore the transference number may be represented in the form;

$$t_+ = \frac{\Lambda_+}{\Lambda_m} \text{ and } t_- = \frac{\Lambda_-}{\Lambda_m} \quad (54)$$

Where the values of Λ_+ and Λ_- (ion conductance) and Λ_m (molar conductance) of the solution, are at that particular concentration at which the transference numbers are applicable.

11.1 Determination of Transport Number

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.

11.1.1 Hittorf's Method

This method of determining transport numbers was described as long ago as 1901.

Apparatus

To understand the principle involved consider the overall description of the method given below. The apparatus consists of two separated compartments joined by a substantial middle compartment and may be of any of the shape as shown in figure 8(A) and (B). Let us take silver nitrate solution in a cell having silver electrodes. Before the experiment begins, the concentration of AgNO_3 is the same throughout the cell. The experiment involves passage of a direct electric current from a power source through the cell.

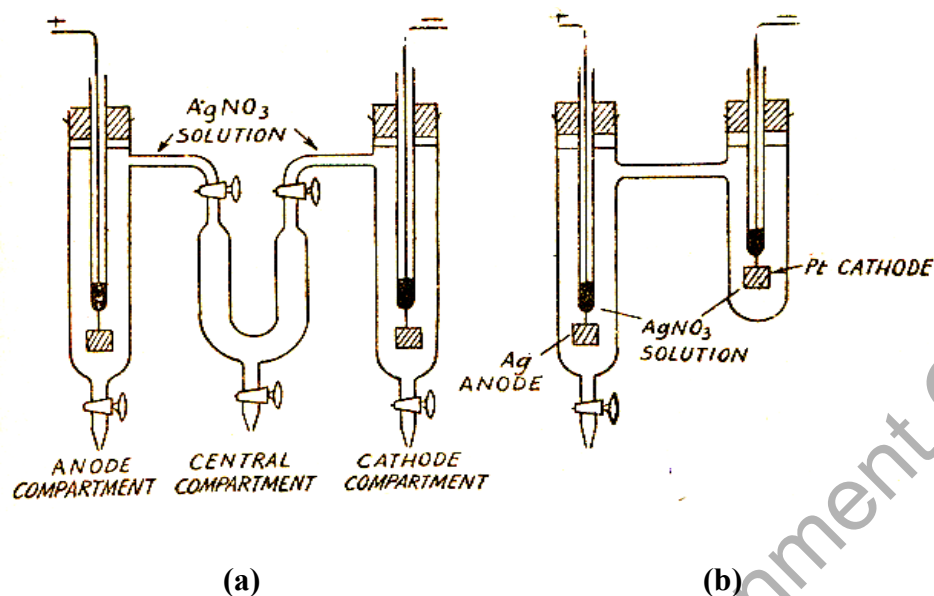


Fig.8: Hittorf's cell

At the left-hand electrode, Ag dissolves and increases the AgNO_3 concentration in its compartment. In the right-hand compartment, Ag^+ ions deposits so the AgNO_3 concentration decreases in the solution. Measurement of the changes in concentration in each compartment after a 2-3 h passage of current yields the transport number of the anion (since $t_+ + t_- = 1$, it also gives that of the cation). The current is passed for a fixed time. Thereafter, the anolyte (Figure 9) has an increased concentration c_1 and the catholyte a decreased concentration c_3 . The middle compartment does not change its concentration of silver nitrate, which will be designated c_2 .

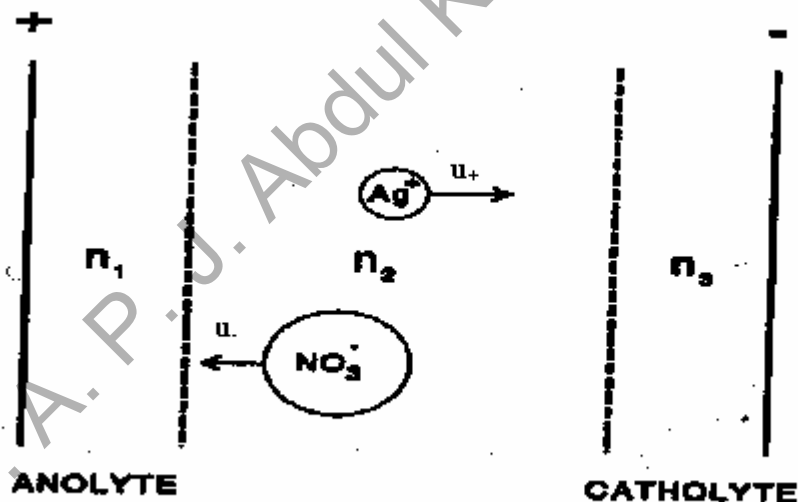


Fig. 9: The Principle of Hittorf's experiment (Adapted from J.O.M. Bockris and A.K.N. Reddy, *Modern Electrochemistry*, volume I, 2nd edition, Plenum Press, N.Y. (1998)).

After t seconds (s) at current I , the number of moles of Ag introduced into the anolyte is

$$N = \frac{It}{F} \quad (55)$$

Where F is the faraday or electrical charge on one 1 mole of Ag^+ .

In the central compartment, in which the concentration is shown by experiment to remain constant, current is given by the equation:

$$I = Ac_2F (u_{+2} + u_{-2}) \quad (56)$$

Where ' A ' is the cross sectional area of the central compartment and ' u_{+2} ' and ' u_{-2} ' are the ionic mobilities, respectively, of Ag^+ and NO_3^- . Therefore, from eq. (55) and (56),

$$N = Ac_2 (u_{+2} + u_{-2})t \quad (57)$$

In the *left*- hand compartment, Ag^+ ions are produced and also moved out. Hence,

$$\frac{dN_1}{dt} = \frac{1}{F} - Ac_1u_{+1} \quad (58)$$

According to principle of electroneutrality the concentration of both positive and negative ions in the left -hand compartment should be the same. Therefore,

$$\frac{dN_1}{dt} = Ac_2u_{-2} \quad (59)$$

which represents the rate at which anions introduced by dissolution from the silver electrode move into the left – hand compartment to join the cation. Integrating eq. (59) gives

$$N_1 - N_1^0 = Ac_2u_{-2}t \quad (60)$$

Where N_1^0 is the number of moles of AgNO_3 in the compartment before the current I was switched on.

In the catholyte compartment, Ag^+ ions are removed by deposition and transported from the middle compartment,

$$\frac{dN_3}{dt} = -Ac_2u_{+2} - \frac{1}{F} \quad (61)$$

NO_3^- moves out to allow electroneutrality to be maintained. It must move out at the same rate as Ag^+ disappears. Thus

$$\frac{dN_3}{dt} = -Ac_3u_{-3} \quad (62)$$

Integration of eq. (62) gives

$$N_3^0 - N_3 = Ac_3u_{-3}t \quad (63)$$

It has been assumed that the central compartment keeps a constant concentration while the AgNO_3 is increasing on the anolyte and decreasing in the catholyte.

Hence,
$$N_1 - N_1^0 = N_3^0 - N_3 \quad (64)$$

Now from eq. (57) and (60),

$$t_- = \frac{u_{-2}}{u_{+2} + u_{-2}} = \frac{N_1 - N_1^0}{N} = \frac{\text{Gain in weight in anolyte}}{\text{Loss of weight in anode}} \quad (65)$$

Again from eq. (57) and (63),

$$\frac{N_3^0 - N_3}{N} = \frac{\text{Loss of weight of silver in catholyte}}{\text{Gain in weight of cathode}} \quad (66)$$

Q. A solution containing 0.00739g of AgNO_3 per gram of water was electrolyzed between silver electrodes. During the experiment 0.0078g of silver was deposited in a silver coulometer placed in series. At the end of experiment, the anodic solution contains 23.14g of water and 0.236g of AgNO_3 . What are the transport number of Ag^+ and NO_3^- ions?

- **Before electrolysis:** Mass of water = 1g
Mass of AgNO_3 = 0.00739g
Number of gram equivalent of Ag = $\frac{0.00739}{170} = 4.347 \times 10^{-5}$
- **After electrolysis:** Mass of water = 23.14 g
Mass of AgNO_3 = 0.236g
Number of gram equivalent of Ag in 1g of water
= $\frac{0.236}{23.14} \times \frac{1}{170}$
= 5.992×10^{-5}

Increase in concentration of Ag^+ in the anodic compartment where no silver ions migrate = $\frac{0.0078}{170} = 4.588 \times 10^{-5}$

Increase in concentration of Ag^+ in the anodic compartment when Ag^+ ions migrate.
= Concentration of Ag after electrolysis – Concentration of Ag before electrolysis
= $5.992 \times 10^{-5} - 4.347 \times 10^{-5}$
= 1.645×10^{-5}

Fall in concentration of Ag^+ in anodic compartment
= $4.588 \times 10^{-5} - 1.645 \times 10^{-5}$
= 2.943×10^{-5}

$$\begin{aligned} \text{Transport number of } \text{Ag}^+ \text{ ions} &= \frac{\text{Fall in conc. around anode}}{\text{Silver deposited on Ag electrode}} \\ &= \frac{2.943 \times 10^{-5}}{4.588 \times 10^{-5}} = 0.641 \end{aligned}$$

Also transport number of NO_3^- ions can be calculated as

$$\begin{aligned} &= 1 - t_{\text{Ag}^+} \\ &= 1 - 0.641 \\ &= 0.359 \end{aligned}$$

11.1.2 Moving boundary method

The moving boundary method is based on measuring the rate of migration of one or both of the ionic species of the electrolyte, away from the similarly charged electrodes and by this method we can directly observe the migration of ions under the influence of an applied potential unlike the Hittrof's method in which concentration changes at the electrodes are observed. This method is very accurate and has been used in recent years for precision measurements.

In the practical application of the moving boundary method one boundary only is observed, and so the necessity of finding two indicator solutions is obviated; the method of calculation is as follows. If one faraday of electricity passes through the system, 't₊' equiv. of the cation must pass at any given point in one direction; if 'c' mole of the unit volume is the concentration of the solution in the vicinity of the boundary formed by the 'M' ions, this boundary must pass through a volume t₊ / c while one faraday is passing. The volume ϕ taken out by the cations for the passage of Q coulombs is thus

$$\Phi = Q t_+ / F c \quad (67)$$

Where F is one faraday, i.e., 96,500 coulombs. If the cross section of the tube in which the boundary moves is α sq. cm., and the distance through which it moves during the passage of Q coulombs is l cm., then Φ is equal to l α , and therefore from eq. (65)

$$t_+ = l \alpha F c / Q \quad (68)$$

Since the number of coulombs passing can be determined, the transference number of the ion may be calculated from the rate of movement of one boundary.

The apparatus used for the determination of the transport number by this method, consist a long vertical tube of uniform bore fitted with two electrodes at the two ends as shown in figure 10.

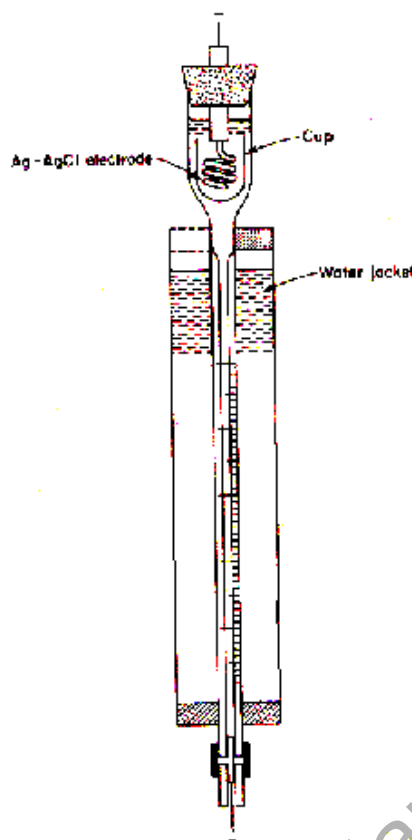


Fig.10: Cell for the determination of transport number by moving boundary method

Let us consider the electrolyte AgNO_3 the transport number of whose cation (Ag^+) is to be determined. A layer of a solution of AgNO_3 is introduced above the solution of another suitable electrolyte KNO_3 having the common anion NO_3^- . The electrolyte KNO_3 is selected so that the velocity of K^+ ions is less than those of Ag^+ ions. Under the circumstances, there will be a clear-cut boundary between the two electrolytes, even if the two solutions are colourless. On passing current between the two electrodes, both Ag^+ and K^+ ions move upward towards the negative electrode while NO_3^- ions move downward towards the positive electrode as shown in Figure 10. Since K^+ ions have a lower velocity than Ag^+ ions, a sharp boundary is always maintained between the two solutions. Also the K^+ ions are not far behind for if it so happens the solution below the boundary would get diluted and its increasing resistance causes an increased potential drop thereby increasing the velocity of K^+ ions. Thus the boundary moves slowly in the upward direction. On passing n faraday of current, $n \times t_{\text{Ag}^+}$ will be carried by Ag^+ ions and a corresponding amount ($n \times t_{\text{Ag}^+}$) mole of it moves up. If c represents the original concentration of Ag^+ ions in mole ml^{-1} and the boundary moves through a distance l cm in the tube of cross-section $S \text{ cm}^2$, the number of mole of Ag^+ moving upward is given by $S \times l \times c$. Thus:

$$n \times t_{\text{Ag}^+} = S \times l \times c \quad (69)$$

$$\text{or } t_{\text{Ag}^+} = \frac{S \times l \times C}{n} \quad (70)$$

Knowing the experimental values of S , l , C and n , the value of t_{Ag^+} the transport number of Ag^+ ions can be calculated.

- Q. In a moving boundary experiment 0.01 M HCl solution was treated on a lithium chloride solution. The tube used had a diameter of 1 cm. when a current of 11.0 milliampere was passed for 20 min., the H^+ ions – Li^+ ions boundary moved through 13.9 cm. Calculate the transport number of H^+ , Cl^- ions in HCl solution used?

$$\text{➤ We have, } t_{\text{H}^+} = \frac{s \times l \times F \times C}{Q}$$

$$\begin{aligned} \text{Also } s &= \pi r^2 \\ &= \frac{22}{7} \times 0.5 \times 0.5 \end{aligned}$$

$$l = 13.9 \text{ cm, } F = 96500 \text{ coulomb, } C = 0.01 \text{ N}$$

$$\begin{aligned} Q &= \text{quantity of current passed} \\ &= 11 \times 10^{-3} \times 20 \times 60 \end{aligned}$$

$$\begin{aligned} t_{\text{H}^+} &= \frac{22 \times 0.5 \times 0.5 \times 13.9 \times 96500 \times 0.01}{11 \times 10^{-3} \times 20 \times 60} \\ &= 0.7988 \end{aligned}$$

$$\begin{aligned} \text{and } t_{\text{Cl}^-} &= 1 - t_{\text{H}^+} \\ &= 1 - 0.7984 \\ &= 0.2012 \end{aligned}$$

12. Applications of Conductivity Measurements

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

12.1 Determination of degree of Dissociation

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

$$\alpha = \frac{\wedge_m}{\wedge_m^\infty} \quad (71)$$

Where ' \wedge_m ' is the molar conductance of the solution and can be obtained experimentally \wedge_m 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 .

$$\begin{aligned}
 \Lambda_m^\infty (\text{H}_3\text{PO}_4) &= \Lambda_m^\infty (\text{HCl}) + \Lambda_m^\infty (\text{NaH}_2\text{PO}_4) - \Lambda_m^\infty (\text{NaCl}) \\
 &= 378.3 + 70.0 - 109.0 \\
 &= 339.3
 \end{aligned}$$

The measured value of Λ_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.

12.3 Determination of Solubility Product of a Sparingly Soluble Salt

If a slightly soluble electrolyte such as AgCl , BaSO_4 , 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 ' κ ' is the specific conductance of the saturated solution, then its molar conductance ' Λ ' is given by the relation

$$\begin{aligned}
 \Lambda_m &= 1000 \frac{k}{s} \\
 \text{i.e. } s &= 1000 \frac{k}{\Lambda_m} \quad (72)
 \end{aligned}$$

At infinite dilution,

$$s = 1000 \frac{k}{\Lambda_m^\infty} \quad (73)$$

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 . First the salt is repeatedly washed with conductivity water to remove any soluble impurities. After that it is suspended in conductivity water, warm and cooled to 25°C . A very minute quantity of salt will pass in solution and the rest will settle down. The conductance of the solution and water used in the preparation of solution is determined in the usual way by placing the conductivity cell in the thermostat maintained at 25°C .

The value of Λ_0 for AgCl is given by

$$\Lambda_m^\infty (\text{AgCl}) = \Lambda_m^\infty \text{Ag}^+ + \Lambda_m^\infty \text{Cl}^- = 61.92 + 76.34 = 138.3 \text{ S cm}^2 \text{ mol}^{-1} \text{ at } 25^\circ\text{C}.$$

The specific conductance of a saturated solution of AgCl in water is $3.41 \times 10^{-6} \text{ S cm}^{-1}$ at 25°C and if 1.60×10^{-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 by putting the values in eq. (71).

$$\begin{aligned}
 s &= 1000 \frac{k}{\Lambda_m^\infty} \\
 &= 1000 \times 1.81 \times 10^{-6} / 138.3
 \end{aligned}$$

$$= 1.31 \times 10^{-5} \text{ mole/L at } 25^\circ \text{C.}$$

12.4 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 and interpretation of their curves are given in following paragraphs. In all cases, the equivalence points are located at the intersection of lines of differing slope. One of the requirements of these titrations is that the titrant should be at least ten times as concentrated as the solution being titrated, in order to keep the volume change small.

12.4.1 Acid-Base Titration

(i) Strong Acid with a Strong Base

When a strong alkali, e.g., sodium hydroxide is added to a solution of a strong acid, e.g., hydrochloric acid, the following reaction occurs:



In this type of reaction, the conductance first falls, due to the replacement of the H^+ ($\wedge_m^\infty = 350$) by the added cation Na^+ ($\wedge_m^\infty = 40-80$) and after the equivalence point has been reached, the conductance rapidly rises with further addition of strong alkali due to large \wedge_m^∞ value of the hydroxyl ion ($\wedge_m^\infty = 198$). The two branches of the curve are straight lines provided the volume increase is negligible and their intersection gives the endpoint. At the neutral point the conductance of the system will have a minimum value, from which the equivalence point of the reaction can be determined.

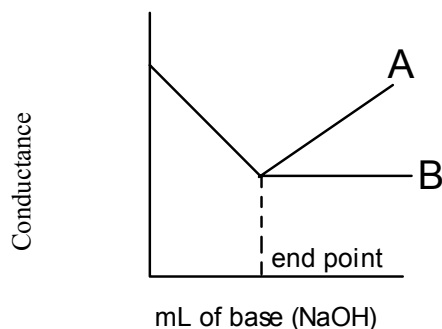
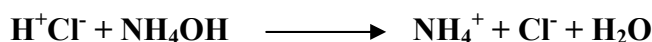


Fig. 11.(A)

In actual practice the lines may be slightly curved due to variation in temperature, heat of neutralization, interionic effect and slight increase in the volume of the solution because of the addition of titrant. In spite of this, the inflection is sharp enough to get the end point.

(ii) Strong Acid with a Weak Base

The titration of a strong acid with a weak base may be illustrated by the neutralization of dilute HCl by dilute NH_4OH .



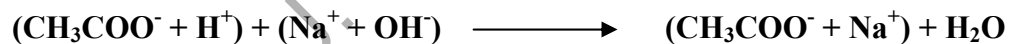
The first branch of the graph (Figure.11B) represents the neutralization of the acid and its (i.e., replacement of fast moving H^+ ions by slow moving NH_4^+ ions). After the neutralization (end point) is completed, the graph becomes almost horizontal, since the excess aqueous NH_4OH is not appreciably ionized in the presence of NH_4Cl . As NH_4OH is a weakly ionized electrolyte it has a very small conductivity compared with that of the acid or its salt.



Fig. 11 (B)

(iii) Weak Acid with a Strong Base

Consider the titration of the weak acid like CH_3COOH with strong base NaOH .



In this titration, the shape of the curve will depend upon the concentration and the K_a of the acid ($K_a \sim 1.8 \times 10^{-5}$). The sodium acetate salt formed during the titration tends to suppress the ionization of the acetic acid due to common ion effect and therefore its conductance decreases. The rising salt concentration will however tend to result in an increase in conductance. When the neutralization of acid is complete, further addition of alkali produces excess of OH^- ions. This excess OH^- ion increases the conductance of the solution more rapidly. Finding an accurate end point is difficult in this type of titration.

For moderately strong acids, the influence of the rising salt concentration is less pronounced. Difficulty is also experienced in locating the end point accurately and generally titration of weak acid and moderately strong acids with a strong base are not recommended for conductometric titration.

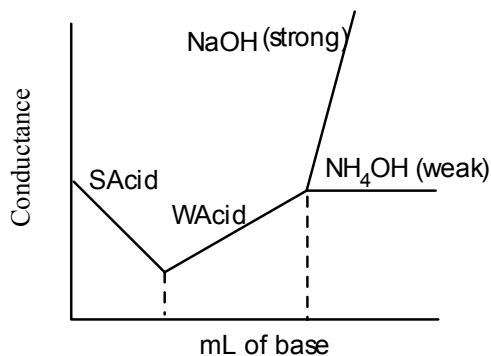
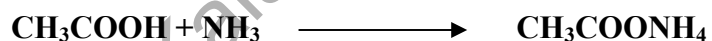


Fig. 12 (a)

(iv) Weak Acid with Weak Base

When a weak acid is titrated with a weak base the initial portion of the conductance titration curve is similar to that for a strong base, since the salt is a strong electrolyte inspite of the fact that the acid and base are weak.

Consider the titration curve of CH_3COOH and NH_3



Conductivity decreases as the anion formed suppresses the ionization, passes through a minimum and then increases up-to the end point. This is because of the conversion of non-conducting weak acid into its conducting salt.

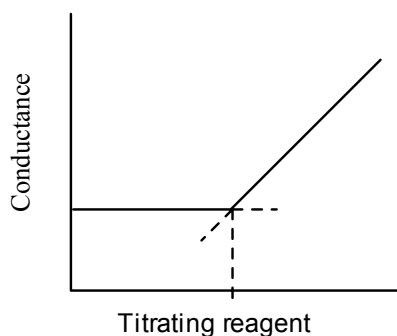
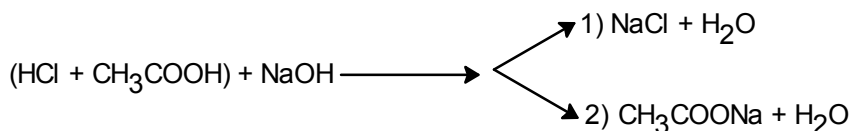


Fig. 12 (b)

It is observed that such titrations curves are generally curved because the incompleteness of reaction permits extra hydroxide ions (or hydrogen ions if a weak base is being titrated) to be present. This causes an increase in conductivity. It is observed that with more incompleteness of the reaction, the more curvature is observed in the graph.

(v) Mixture of a Strong Acid and a Weak Acid with a Strong Base



In such titration, the conductance decreases until the strong acid is neutralized and after that it rises as the weak acid is converted into its salt. Finally the conductance rises more steeply as excess alkali is introduced. The three branches of the curve will be straight lines except as: (i) increasing dissociation of the weak acid results in a rounding off at the first end point. (ii) hydrolysis of the salt of the weak acid causes a rounding off at the second end point. In case of rounding one can extrapolate to get a sharp end point.

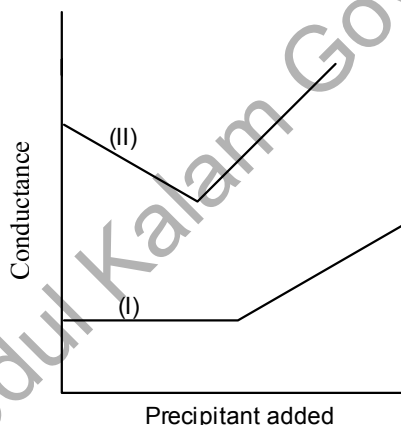


Fig. 13

12.4.2 Displacement Reactions

When a strong acid reacts with sodium or potassium salts of weak acids, the weaker acid will be displaced by the strong acid e.g.



In this reaction the highly ionized sodium acetate is replaced by highly ionized sodium chloride and almost unionized acetic acid. Only a slight increase in conductance is observed up-to the end point because chloride ion has slight by higher conductance than the acetate ion. After the end point is passed, however, the free strong acid produces a marked increase, and its position can be determined by the intersection of the two straight lines. (Figure 14).

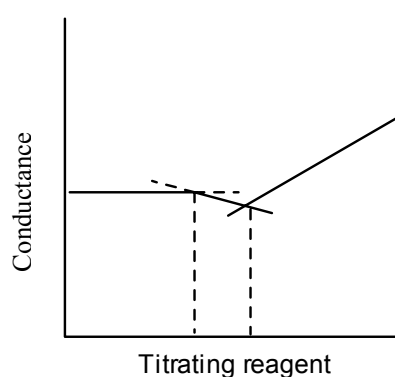
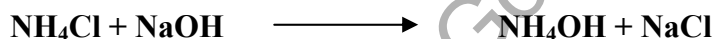


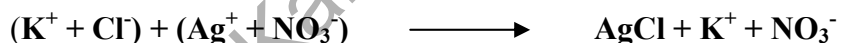
Fig. 14

Another example of such type of reactions is the salt of a weak base and a strong acid when titrated by a strong base in an analogous manner.

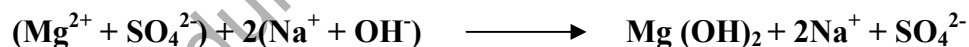


12.4.3 Precipitation Reactions

Precipitation titration may also be carried out by conductometric methods. In reactions of the type,

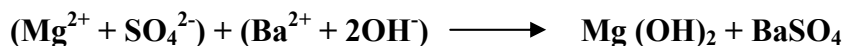


and



Where a precipitate is formed, one salt is replaced by an equivalent amount of another, e.g. potassium chloride by KNO_3 and here the conductance remains almost constant before the end point. After the equivalence point is passed, however, the excess KNO_3 causes a sharp rise in the conductance (Fig. 15, I); the end point of the reaction can thus be determined.

In another example, if both products of the reaction are sparingly soluble, the curve obtained takes up the form as shown in (Fig.15, II), e.g.,



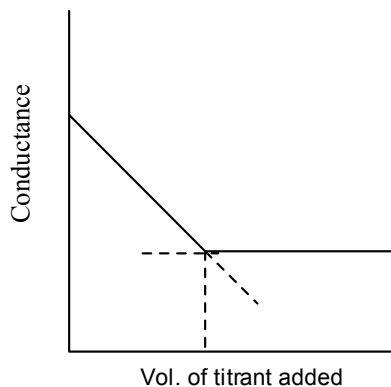


Fig. 15

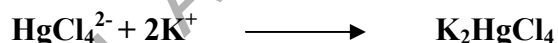
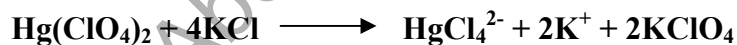
First, the conductance of the solution decreases but increases after the end point has passed. Precipitation reactions, however, cannot be carried out accurately using conductance measurement due to the following reasons.

- (a) Slow separation of the precipitate,
- (b) Removal of titrated solute by adsorption on precipitate

The best results are obtained by doing titration with dilute solutions in the presence of a relatively large amount of alcohol, the presence of alcohol decreases the solubility of the precipitate and also lesser adsorption.

(IV) Complexometric Titration Reactions

Conductometric titrations have also been employed in the determination of stoichiometry of complex compounds. For example, Job titrated roseo-cobaltic sulphate $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]_2(\text{SO}_4)_3$ with $\text{Ba}(\text{OH})_2$ and obtained two breaks in the titration curve (Figure 16). Also consider the complexometric titrations of KCl with $\text{Hg}(\text{ClO}_4)_2$, where two breaks are obtained in the curve as shown in Figure 16.



The first break is due to the formation of HgCl_4^{2-} and the second is due to the formation of K_2HgCl_4 at the end of the reaction.