Conductometry

UNIT-V

- **Electrochemical methods of analysis**
  - **Conductometry**- Introduction, Conductivity cell, Conductometric titrations, applications.
  - **Potentiometry** - Electrochemical cell, construction and working of reference (Standard hydrogen, silver chloride electrode and calomel electrode) and indicator electrodes (metal electrodes and glass electrode), methods to determine end point of potentiometric titration and applications.
  - **Polarography** - Principle, Ilkovic equation, construction and working of dropping mercury electrode and rotating platinum electrode, applications

Conductometry

It is the measurement of conductivity of a solution due to the mobility of cation and anion towards respective electrode.

Principle

Conductometry is the ability of solution, a metal or gas to pass an electric current.

In solution : current is carried by cations and anions

In metals : current is carried by e^-

A solution conducts electricity depends on multiple factors like
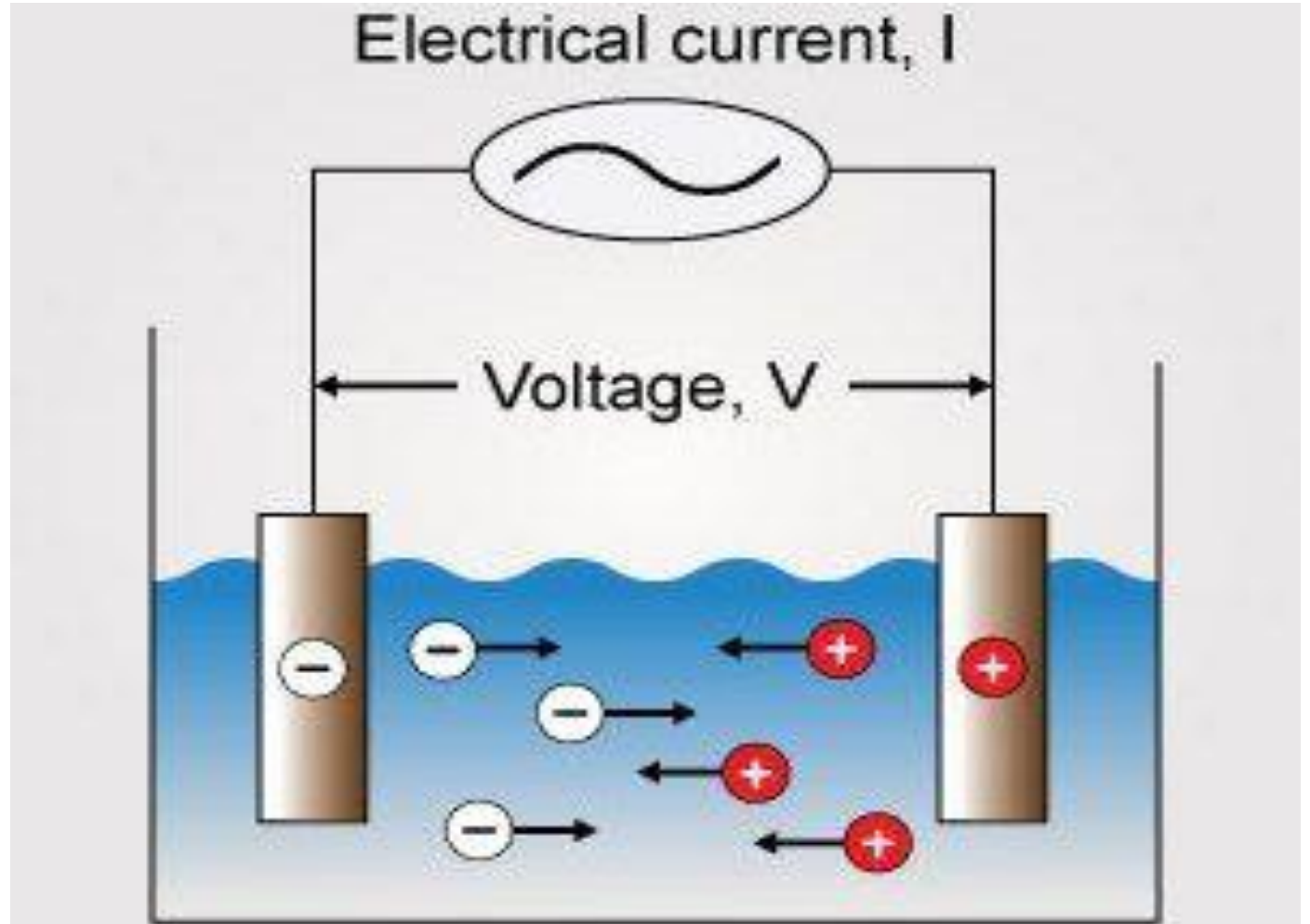
Concentration of solution

Mobility of ions

Temperature

Migration of ions in a solution

The solution of electrocyte conducts electric current like a metallic conductor. Thus, the electrolyte solution obeys ohm's law.

Ohm's Law

It states that current flows in conductor.

Is directly proportional to voltage

V ∝ I

Here, V:- voltage

I:- current

Hence, I = V/R

Inversely proportional to resistance of conductor

I ∝ 1/R

Here, I: current

R:- resistance

Conductance

- Reciprocal of resistance unit = ohm^{-1}
- Current flows through the conductor
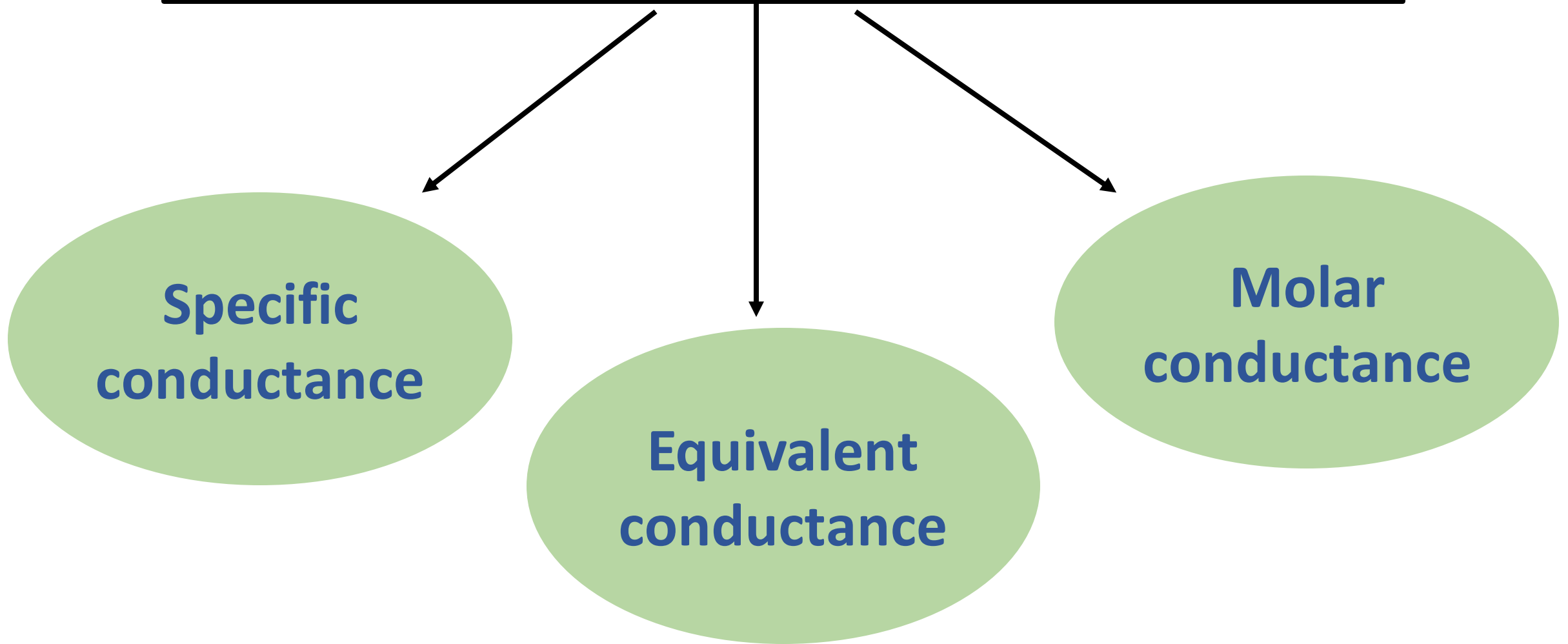- Reciprocal of resistance
  - Principle of conductance.

Movement of ions creates conductivity

Depends upon concentration of ions

Conductivity increases or decreases by replacement of ions

DEPTH OF BIOLOGY

Types of conductance

Specific conductance

Equivalent conductance

Molar conductance

1. Specific Conductance

- Denoted by (k) , k = kappa

- Reciprocal of specific resistance

$$R = \rho\,\frac{\ell}{a}$$

$$R = \frac{1}{k} \times \frac{\ell}{a}$$

$$k = \frac{1}{R} \times \frac{\ell}{a}\ \text{ohms}^{-1}\text{cm}^{-1}$$

$$k = \frac{1}{R} = \frac{1}{\rho}$$

- Resistance of a conductor is

- Directly proportional to length

- Inversely proportional to area.

$$R \propto l/a \ ; \ R = S \, l/a \ ;$$

$$S \rightarrow \text{specific resistance} \rightarrow \text{constant}$$

- Unit = ohm – centimetre

- It is also called resistivity.

2. Equivalent Conductance

o Conductance of a volume of solution containing one equivalent weight of dissolved substance.

o When placed between two parallel electrodes 1cm apart + large enough to contain all the solution between then.

3. Molar Conductance

Denoted by capital lambdr ($\wedge$)

Conductance of a solution containing one mole of the solute in 1000ml of the solution.

$\wedge$ = 1000/C ; C = concentration of solute.

Conductometer :- instrument used for measurement of conductance.

Current source :- Alternating current source is employed for conductometer.

High frequency A.C Generators are used when electrical potential is applied across electrode, leads to ion accumulation near the electrode.
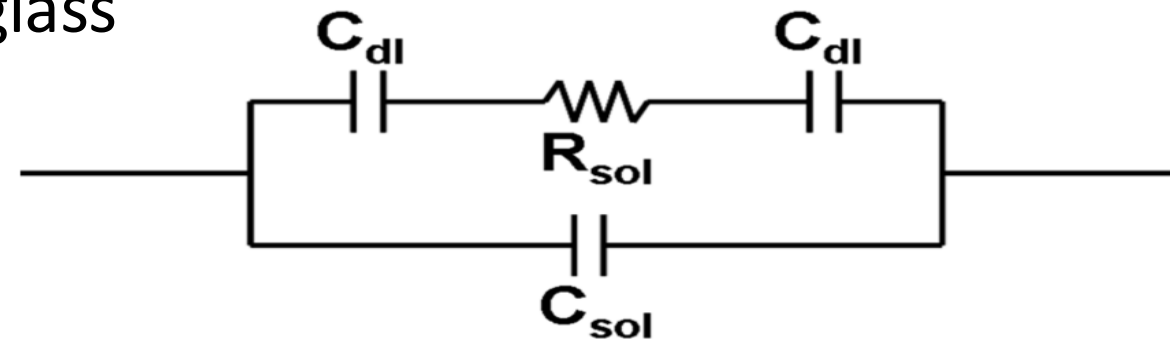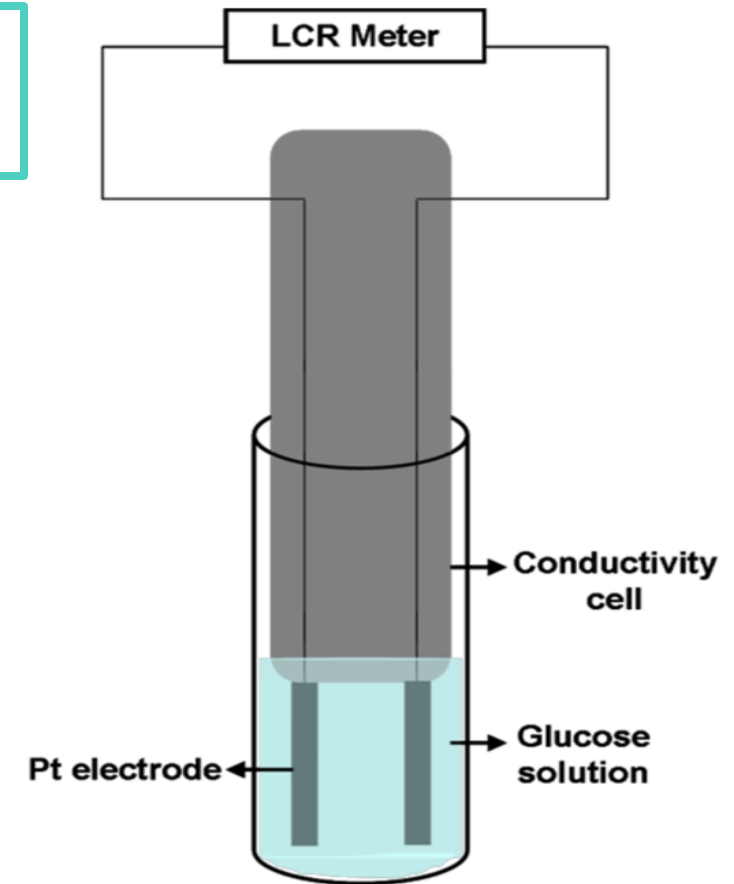
Conductivity Meter

- Measures the conductivity of solution.

- Wide mouthed cells are used in conductometer.

E.g. → a) Low conductance measurement cell

b) Diotype cell

A. Low conductance measurement cell.

- It is usually wide mouth borosilicate glass

- Battle directly filled with bark cork

- Apparatus wire is present

Electrode

- The electrode are generally made of two parallel sheets of Platinum foil which do not bend readily.

- The dipelectrode passing the current for about 15-20minutes.

Conductivity Cells

To measure conductance of electrolyte solution.

After connecting the conductivity cell to the instrument, measurement can be made.

1. Two types of conductivity cells:-

a) Conductivity cells with two electrodes :-

➢ These are conventional type of cells used very commonly.

b) Conductivity cells with four electrodes :-

➢ Used in dirty media with high conductance.

2. Induction type conductivity cells:-

Used for highly corrosive medium to measure very high conductance.

Electrode type conductivity cells

a) Two electrode conductivity cells :-

• This type of cells consists of two or more than two metal electrodes

• These two electrodes are usually $1cm^2$ metal plates and separated by 1cm distance.

• This setup is equivalent to a cell constant of $1cm^{-1}$

Cell Constant

- Intrinsic feature of a conductivity cell.

- Depending upon cell geometry.

- Expressed as cm^{-1}.

- Cell constant C of $1cm^{-1}$ is universally accepted one.

- Allows the measurement of conductance from low level to high level.

b) Conductivity cells with four electrodes:-

Consists of four electrodes

2

2

Force a uniform time varying electric field

Measure voltage

- o In this cell, this charge flows back and forth, results in reduction and oxidation reaction.

- o Double layer capacitive effects are caused by charging of the electrode solution at the interface.

Usage

- To reduce contact and interface interference in conductance measurement especially in water conductivity measurement.

- Due to high precision sensors, used good stability and an intrinsic capability to minimize error caused by polarization.

Inductive type conductivity cells:-

- These conductivity cells use inductive sensors or toroidal sensors.

- Inductive sensor contains 2 coils, sealed within a non-conductive housing.

- The first coil induces an electric current in water.

- The second coil detects the magnitude of the induce current & proportional to the conductivity of the solution.

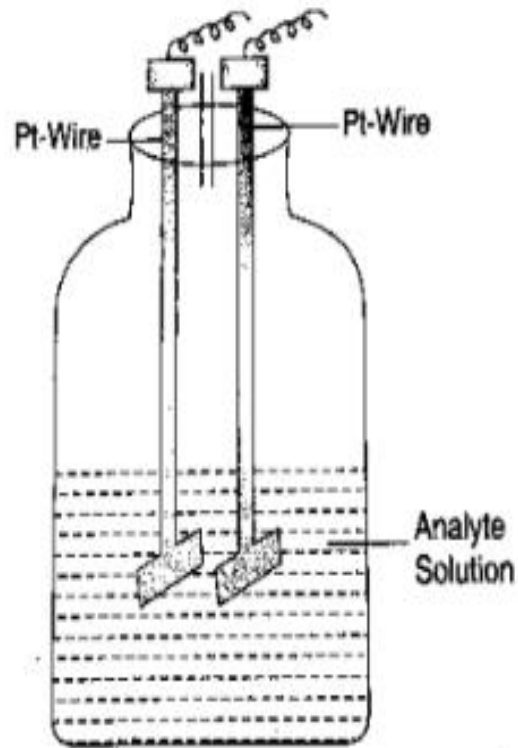Some common types of conventional conductivity cells are shown below:-

Fig. 16.8: A Low Conductance Measurement Cell

(A)
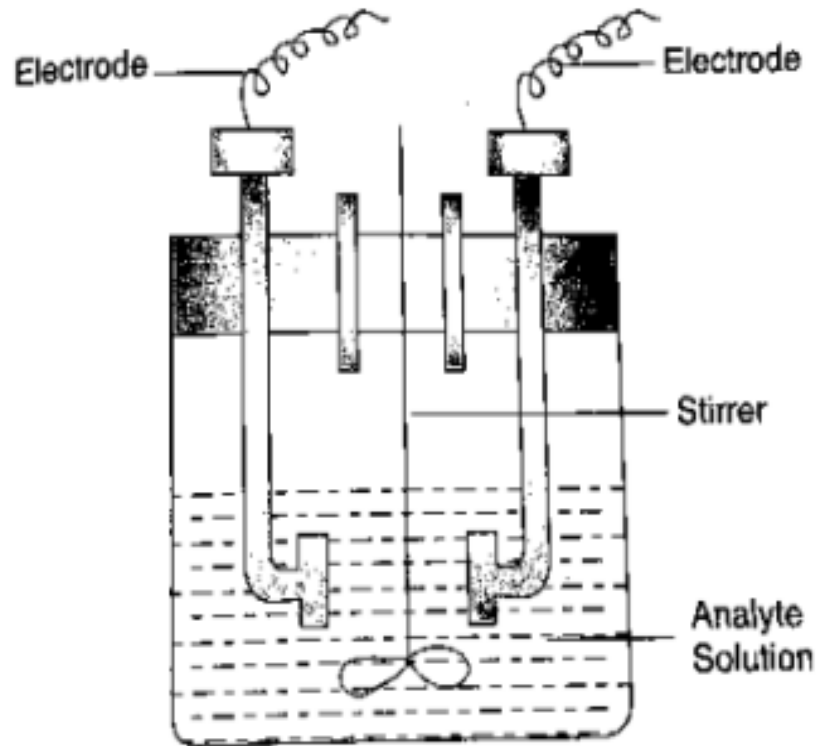
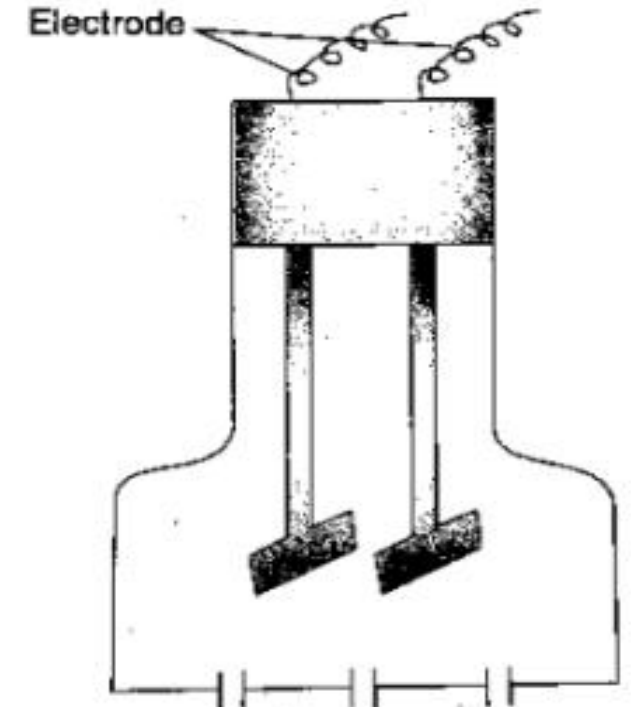Fig. 16.9: Conductivity Cell for Precipitating Type of Reaction

(B)

Fig. 16.10: A Dip Type Cell [or Electrode Type Cell]

(C)

- In type (A), wide mouth bottle with bark cork has holes for passing two platinum wires of 1cm^2 size is used.

- In type (B), the electrodes are firmly fixed in the Perspex lif which is provided with opening for the stirrer and the tip of the stirrer and the tip of the burette.

- The stir way be replaced by magnetic stirrer.

- This type of cell is more suitable for precipitate giving reaction. Since, the face of electrode plates are vertical and parallel.

- In type (C) or dip type copper wires are fixed in a wide bore coming glass tube, the tip of which have two platinum plates of 1cm2 in size fixed at 1cm apart.

$$K = Q/R$$

K = specific conductance

R = resistance of solution

Conductometric Titrations

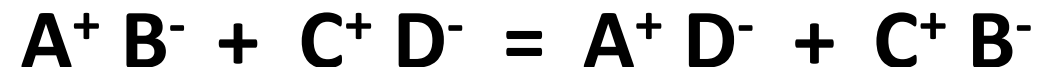Conductometry is the measure of conductivity of a solution.

Principle of conductometric titration :-

Conductivity is the ability of solution, a metal or a gas to pass electric current.

In solution :- Current is carried by cations and anions.

In metals :- Current is carried by electrons.

Principle is based upon substitution of ions of mobility by the ions of mobility.

$$A^+ B^- + C^+ D^- = A^+ D^- + C^+ B^-$$

The conductance will increase or decrease depending upon whether the mobility of C+ ion greater or lesser than that of ion A.

- The conductometry titrations, titrant is added in small volumes and conductivity is measured.

- The volume changes by addition of titrants should not be addition of titrants should not be appreciable. For this titrant of 10-20 times concentrated than is employed. A correction for dilution effect is made by multiplying the readings of conductivity by factor

  V + V / V

  V = original volume ;   V = volume of titrant added

- Conductance of weak electrolyte is largely dependent upon the degree of largely dependent upon the degree of ionization which in term dependent upon dilution and temperature.

- Solution of weak electrolyte diluted before titration carried out.

- To control temperature, thermostat arrangement may be employed.

Conductometric Titrations

Conductometry → used to carry out acid- alkali titrations leads to formation of conductometric graphs.

Various types of acid-alkali titrations are –

1. Strong acid with strong base

HCl with NaOH

Initially, fall in conductance (due to replacement of H^+ ions with Na^+ ions) then, end point conductance rises (due to excess of hydroxyl ions (199) being added)

Why H^+ gets replaced with Na+ ions?

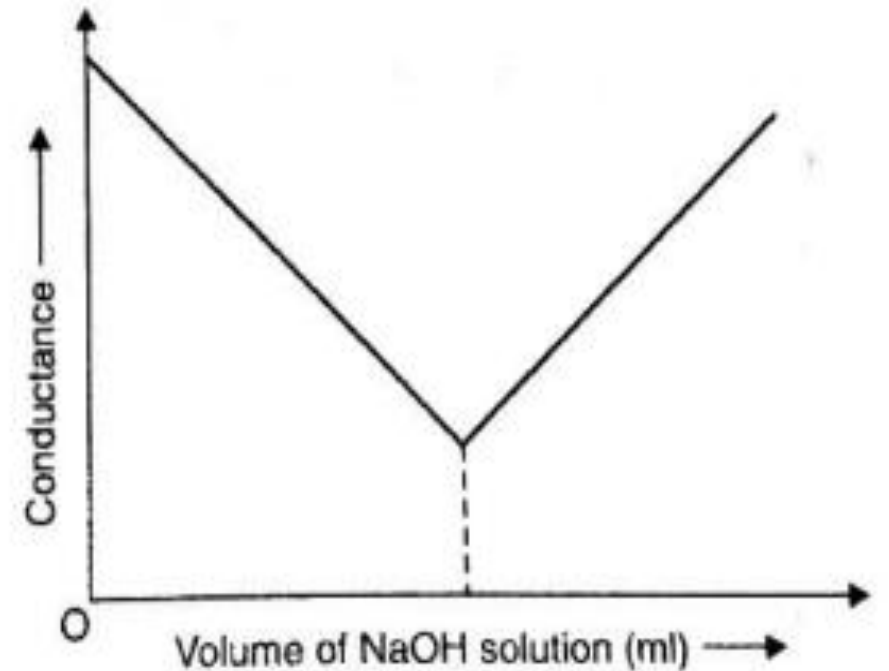H^+ has high ionic mobility (350) and Na+ has slow ionic mobility (50).

Fig. 11.5. Conductometric titration of a strong acid (HCl) vs strong base (NaOH).

2. Strong acid with weak base :- HCl or H_2SO_4 with NH_4OH

- Initially, progressive fall in conductance after end point graph becomes almost horizontal

- Progressive fall in conductance due to disappearance of H+ ions having high ionic mobility during Neutralization.

- Graph becomes horizontal to the end ionization of ammonia is prevented in presence of ammonium chloride/ ammonium sulphate.

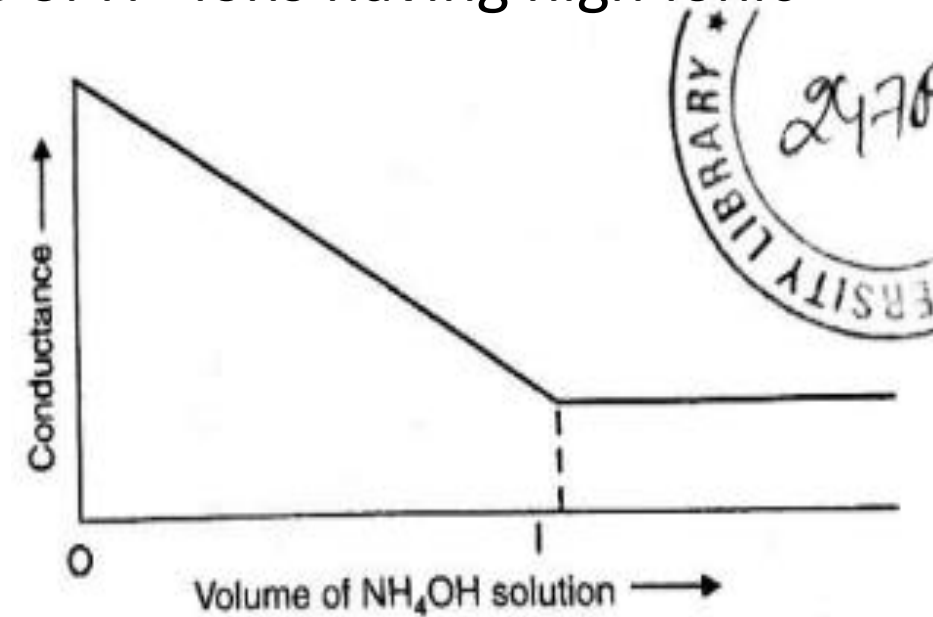- These are formed during Neutralization reaction.

Fig. 11.7. Conductometric titration of a strong acid (H_2SO_4) vs weak base (NH_4OH).

3. Weak acid with strong base :- CH_3COOH/ H_3BO_3 with NaOH

Shape of the graph depends upon concentration, dissociation constant of acid.

Initial conductance is due to ionization of small amount of acetic acid.

Progressive salt formation increases conductance. This intern repress the ionization of acetic acid.

These show fall → followed by rise in conductance.

After neutralization there is break indicating rise in conductance (due to hydroxyl ions)

0.1 M

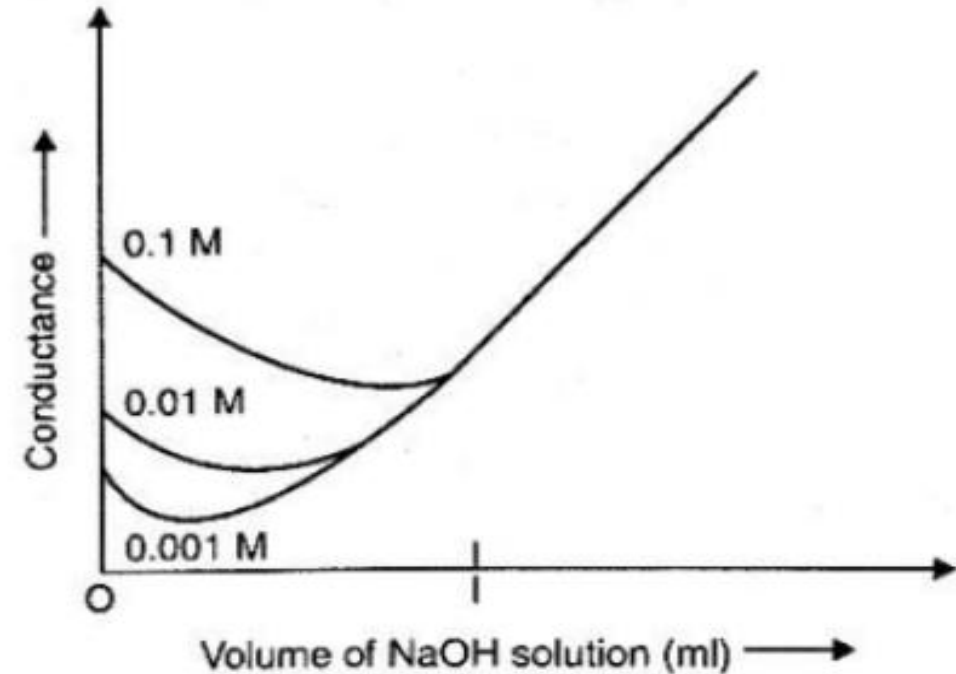0.01 M

0.001 M

Conductance

Volume of NaOH solution (ml) →

Fig. 11.6. Conductometric titration of a weak acid (acetic acid) vs strong base (NaOH)

4. Weak acid with weak base :- CH_3COOH / phenol with $NH_4OH(aq)$

• Neutralization curve upto end of weak acid is similar to obtained with NaOH.

• Conductance rises due to salt formation of weak acid

• After the equivalence point, excess of

NH$_4$OH solution has no effect upon

conductivity suppression of ionization

of ammonia by the sat above formed.
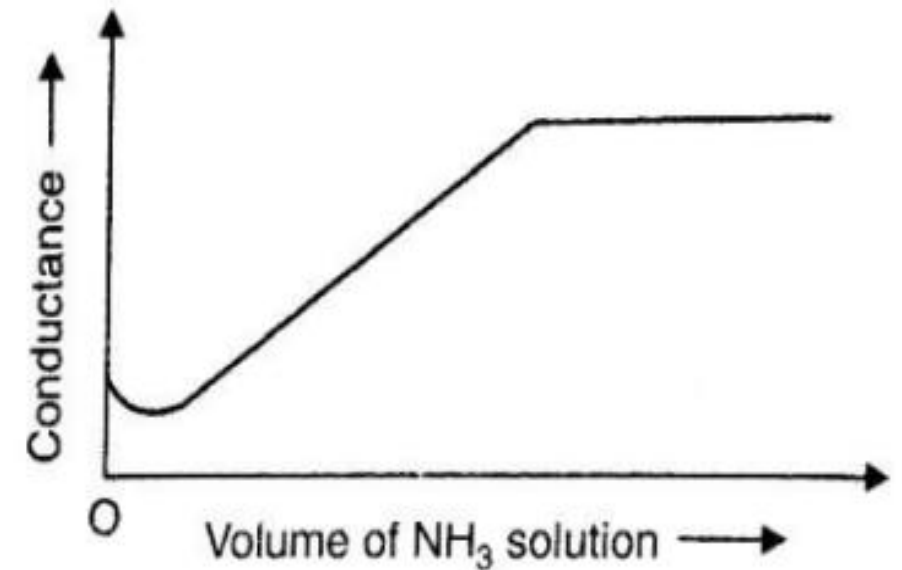
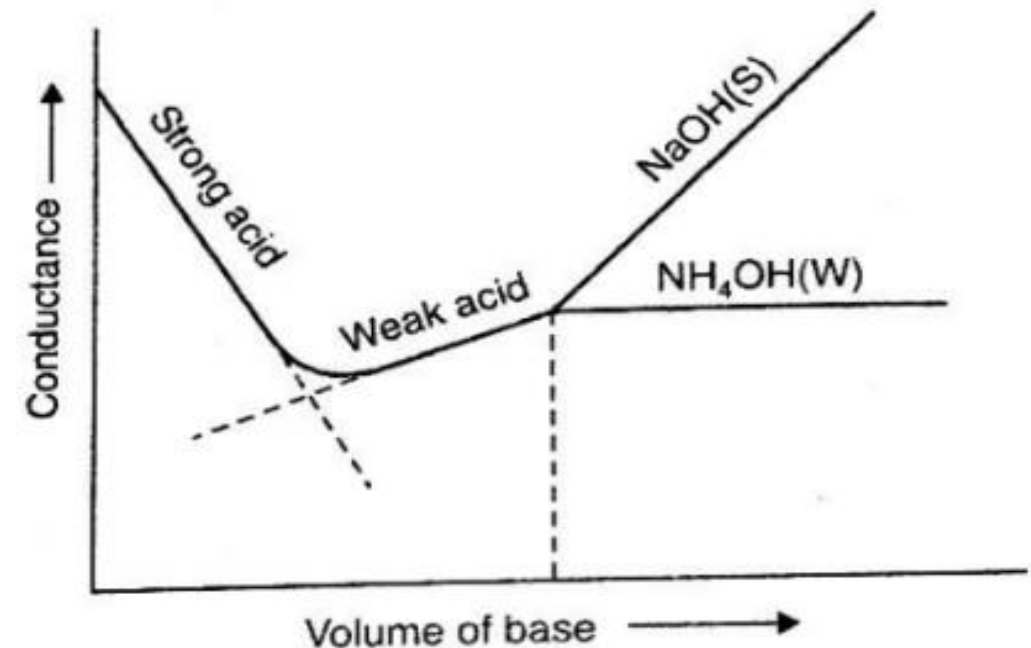Fig. 11.8. Conductometric titration of a weak acid (acetic acid) vs weak base (NH$_4$OH).

5. Very weak acid with strong base :- H$_3$BO$_3$ with NaOH (solution)

- Initially, conductance is very small increases progressively (as neutralization proceeds)

- Salt formation takes place which accounts for rise in conductance due to hydrolysis.

- After the equivalence point sharp rise in conductance due to excess hydroxide ion is added as titrant.


Fig. 11.9. Conductometric titration of a mixture of a strong acid (HCl) and a weak acid (CH$_3$COOH) vs a strong base (NaOH) or a weak base (NH$_4$OH).

6. Mixture of strong acid and weak acid with strong base.

HCl + CH$_3$COOH + Strong base

- Initially, conductance falls (due to neutralization of strong acid), then rises (weak acid is converted into salt).
- Conductance finally rises more sleepy
- After complete neutralization of both acids the excess of (OH) alkali ions are introduced.
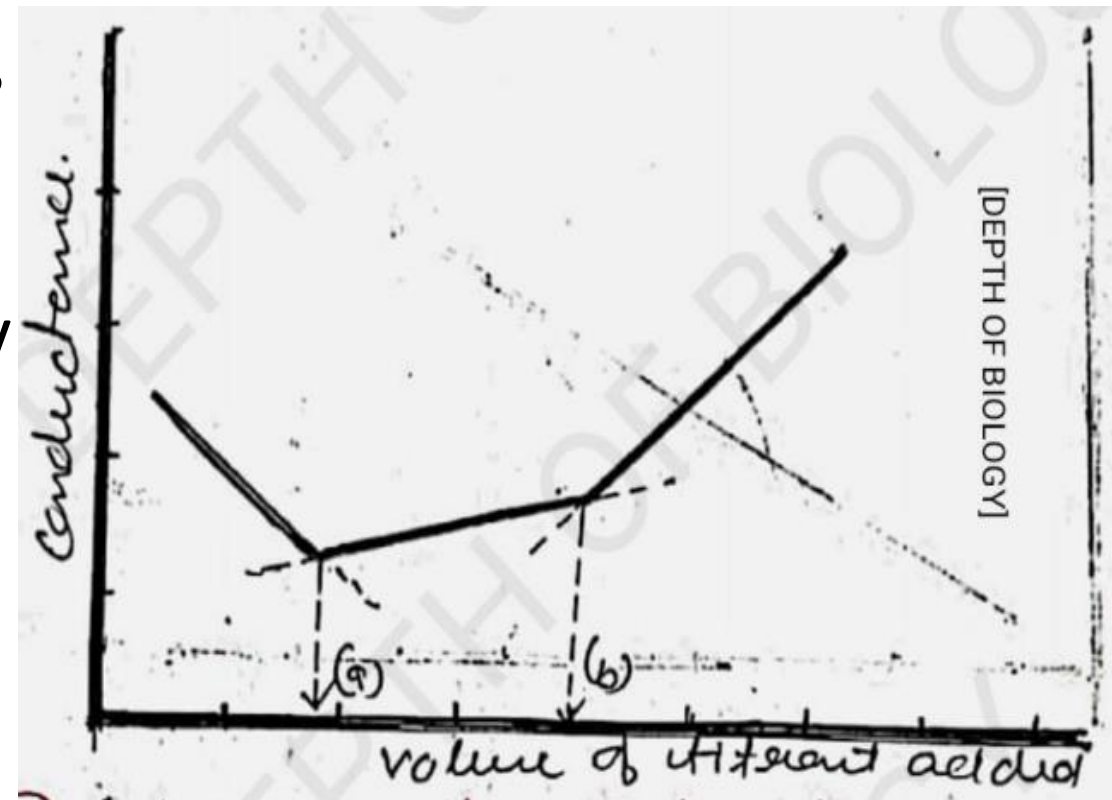
7. Displacement Titrations :-

Sodium acetate + HCl

a) Salt of weak base ammonium chloride

b) This can be followed by conductometry

- In CH_3COONa (sodium acetate) titration with HC

- Initial increase in conductivity
  (due to slightly great increase in ionic mobility
  of chloride ion than acetate ions)

- Until replacement is complete, solution contains
  sufficient sodium acetate to suppress the ionization of liberated acetic acid.

- Near equivalence point acetic acid sufficiently ionized give rise to conductance.

- Beyond equivalence point Excess of HCl → high conductance
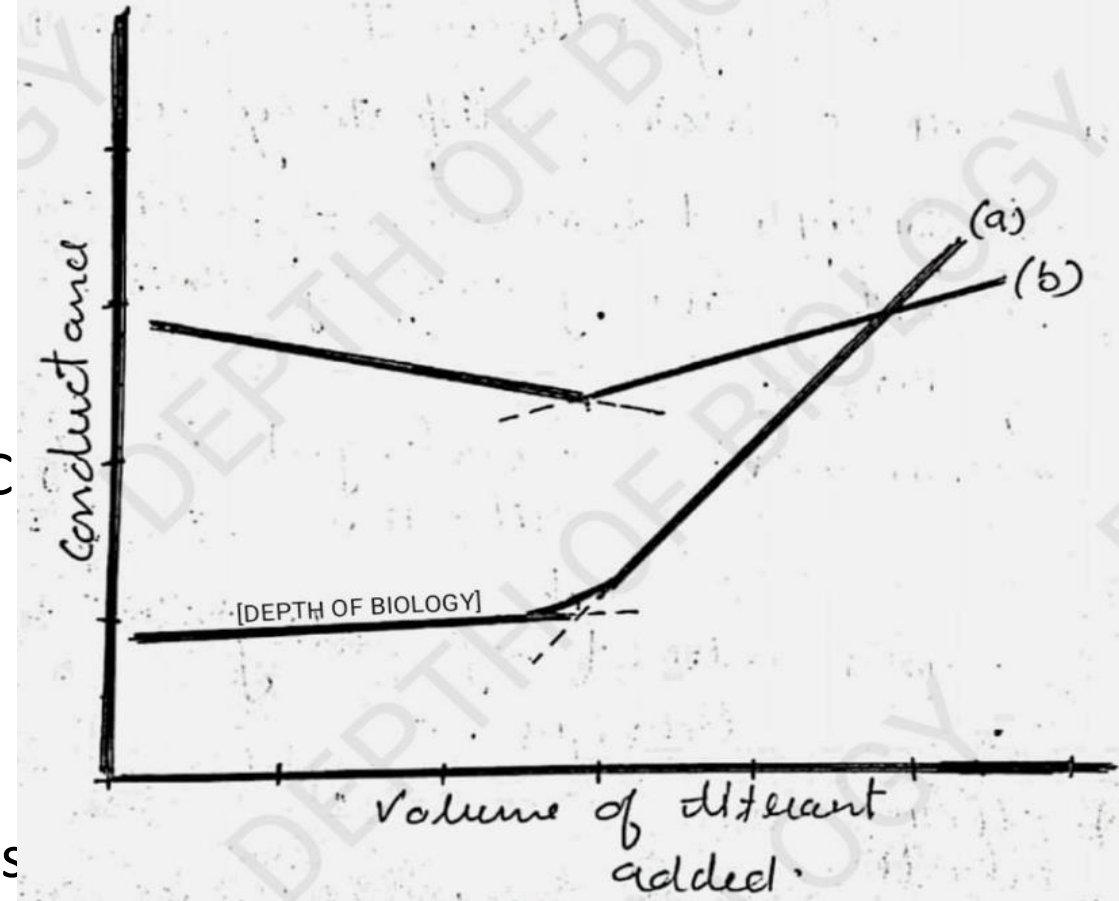
Application of Conductometry in Analysis

1.   Determination of solubility of sparingly soluble materials is solubility in /liter

By measuring specific conductance and limiting conductance of constituent ions of sparingly soluble salt solubility is determined.

2.   Kinetic studies:- based upon the measurement of conductivity before of chemical reaction during at the end.

In alkaline hydrolysis of ethyl acetate

Initial conductance → due to excess of alkali and ester.

During hydrolysis → conductance's is due to exchange of acetate (slow) ions by hydroxyl (very mobile) ions.

At the end, due to excess of base and acetate produced.

Conductance is mainly due to acetate ions produced and residual base.

3. Degree of dissociation of weaker electrolytes (alpha) can be found using

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

4. Basicity of organic acids (B) can be found by using empirical formula given by Ostwald .

$$B = \frac{\Lambda_{1024} - \Lambda_{32}}{10 \cdot 8}$$

- Here, Λ_{1024} & Λ_{32} = Equivalent conductance of salt at 25°C and dilution of 1024 liters and 32 liters per gram equivalent respectively.

- This method is not correct in case of very weak acids.

- Their salts are considerably hydrolysed in solution.

5. Determination of Concentration

- Based on determination of conductivity of solution at different concentrations,

- Series of solution with known content of electrolyte is prepared → determine their conductivities → plot the calibration curve of conductivity of solution against concentration of electrolyte.

- Determine conductivity of unknown solution and find concentration using calibration curve.