

PRINCIPLE AND PROCEDURE

INVOLVED IN CONDUCTOMETRY



INTRODUCTION

- Conductometric analysis is based on the measurement of the electrical conductivity of the solution due to the mobility of cations and anions towards respective electrodes.
- The electrical conductivity is entirely due to the movement of ions.
- The ability of any ion to transport charge depends on the mobility of the ion.

The mobility of an ion is affected by factors such as:

- ♣ Number of ions
- ♣ Charge of ions
- ♣ Size of ions
- ♣ Temperature



PRINCIPLE

The main principle involved in this method is that the movement of the ions creates the electrical conductivity. The movement of the ions is mainly depended on the concentration of the ions.



where A^+B^- is the solution of strong electrolyte; C^+D^- is the solution of the reagent.

Here the ionic concentration of A^+ is determined by reacting the electrolyte solution with the reagent solution so that the A^+ ions are replaced by the C^+ ions. This replacement of the ions with the other ions shows the conductance increase or decrease. This is done mainly by the replacement of the hydrogen ion with other cation.

DEFINITIONS AND RELATIONS

' **Ohms law:** According to this law, the strength of current (I) flowing through a conductor is directly proportional to the potential difference (E) applied across the conductor and inversely proportional to the resistance (R) of the conductor.

$$I = E/R$$

' **Conductance:** It implies the ease with which the current flows through conductor, thus the conductance is reciprocal to resistance.

$$C = I/R$$



DEFINITIONS AND RELATIONS

- ' **Specific resistance:** (ρ) is the resistance offered by a substance of 1cm length and 1sq.cm surface area

$$R = \rho l/a$$

Where, ρ is the specific resistance or resistivity; l is the length; a is the cross-sectional area of the homogenous material.

Unit of measurement is **ohm cm**.

- ' **Specific conductivity:** (k_v) is the conductivity offered by a substance of 1cm length and 1sq.cm surface area,

Unit of measurement is **mhos cm⁻¹**

- ' **Equivalent conductivity:** (λ_v) is the conductivity of a solution containing equivalent weight of the solute between electrodes 1cm apart and 1sq cm surface area

Unit of measurement is **mhos cm⁻¹**



DEFINITIONS AND RELATIONS

- ' **Molecular conductance:** This may be defined as “the conductance of a solution containing 1gm mole of electrolyte when placed between two sufficiently large electrodes placed 1cm apart”
- ' It is denoted by μ_v and is measured in **mhos**



RELATION

Relation between specific conductance and equivalent conductance:

Consider a rectangular metallic vessel with opposite sides exactly 1cm apart.



If 1 c.c. of the solution is now placed in this vessel the area of the opposite faces of the cube covered by the solution will be 1sq.cm



If 1 c.c. of the solution is placed in the above vessel containing 1gm equivalent of the electrolyte, then the measured conductance will be equal to the equivalent conductance.

$$\lambda = k$$



RELATION

- ' Now dilute this 1 c.c. of the solution to 10 c.c. by adding 9 c.c. of pure solvent . The equivalent conductance however will be 10 times as specific conductance.

$$\lambda = k \times 10$$

- ' If the solution containing 1gm equivalent of the electrolyte is dissolved in V c.c. of the solution then

$$\lambda = k \times V$$

hence

equivalent conductance(λ) = specific conductance(k) x volume of solution in c.c. containing 1gm equivalent of the electrolyte(V).



RELATION

' **Relation between molecular conductance and specific conductance:**

' The relation which exists between molecular conductance and specific conductance is quite similar to the relation between equivalent conductance and specific conductance. Thus,

$$\mu_v = k \times V$$

' Molecular conductance = specific conductance \times volume of solution in c.c. containing 1gm mole of the electrolyte.



DETERMINATION OF CELL CONSTANT

- 'The electrodes in the cell are not exactly one cm apart and may not have surface area of one sq.cm.
- 'Thus, the value of observed conductivity is not equal to specific conductivity but proportional to it.
- 'It is important to calculate a factor for the conductivity cell, known as **cell constant**
- 'The cell constant when multiplied by the observed conductivity gives the value for specific conductivity.
- 'It is already mentioned that

$$R = \rho \frac{l}{a}$$



DETERMINATION OF CELL CONSTANT

$$R = \rho x \text{ [where } x=1/a= \text{ cell constant]}$$

$$X = \text{cell constant} = \frac{R}{\rho}$$

$$\text{cell constant} = \frac{1}{\frac{\text{observed conductivity}}{\text{specific conductivity}}}$$

$$\text{Specific conductivity} = \text{cell constant} \times \text{observed conductivity}$$



DETERMINATION OF CELL CONSTANT

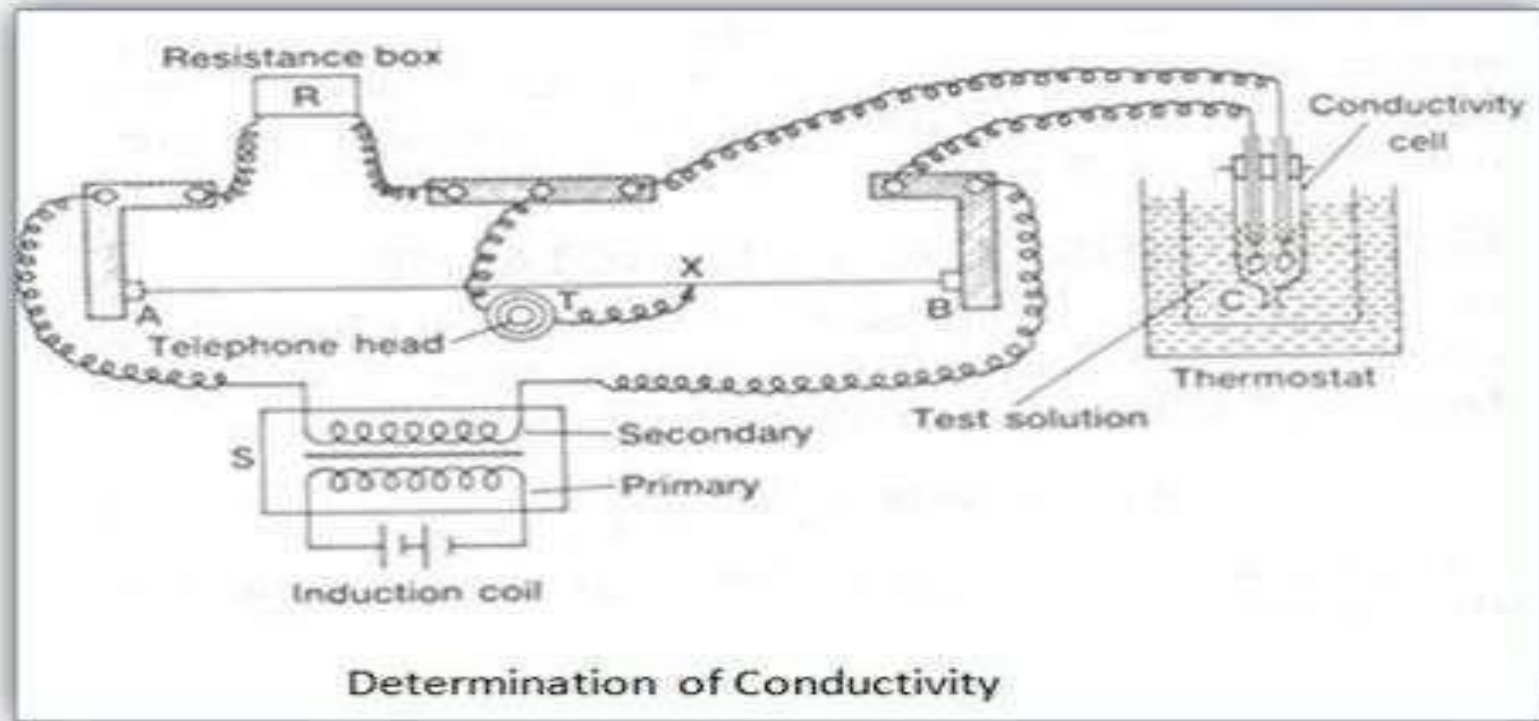
- 'The cell constant is determined by substituting the value of specific conductivity of N/50 KCl solution at 25°C.
- 'This value as determined by Kohlrausch was found to be 0.002765 mhos.
- 'The value of conductivity is then observed with the given cell using N/50 KCl solution.
- 'The cell constant is then calculated by using the following relation:

$$\text{cell constant} = \frac{0.002765}{\text{observed conductivity}}$$



MEASUREMENT OF CONDUCTANCE

It has already been seen that the measurement of conductance is a measurement of resistance, the **Wheatstone bridge** method can, therefore, be used for its measurement.

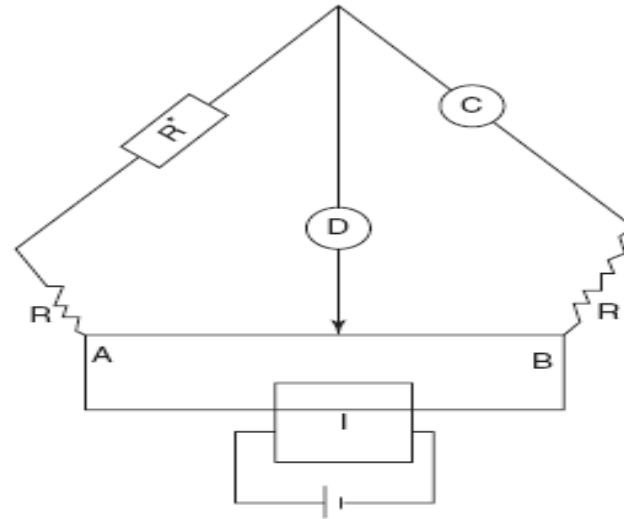


The following are the different bridges used for the measurement of the conductance:

(i) Kohlrausch bridge: It consists of a meter bridge wire AB with a fixed resistance R on both the ends. To increase the length of the wire, it is connected to the resistance box R^* , conductance cell C and the head phone D and a small induction coil I . All these are operated by the battery.

Headphone is used for the detection of the conductance difference.

Kohlrausch bridge



(ii) Direct reading conductance bridges: head phone replace by magic eye which is an electronic device

METHOD OF MEASUREMENT

- ' The solution whose conductance is to be measured is taken in the conductivity cell. It is known that conductance varies with temperature. It is therefore, necessary to keep the temperature of the solution constant throughout the experiment.
- ' This is achieved by placing the conductivity cell in the thermostat.
- ' The cell is connected to a resistance box R on one side and to a long thin wire AB stretched along a scale on the other side
- ' Now some known resistance R is taken out of the resistance box
- ' An alternating current is passed through the solution with the help of an induction coil.
- ' the sliding contact d is moved on the wire AB so that minimum or no sound is heard in the head phone.



METHOD OF MEASUREMENT

At this point, the following relationship holds good:

$$\frac{\text{Resistance of solution}}{\text{Resistance R}} = \frac{\text{length Bd}}{\text{length Ad}}$$

that knowing R, Ad and Bd, the resistance of the solution can be calculated.

Since conductivity of the solution = $\frac{1}{\text{Resistance of the solution}}$

Therefore knowing resistance of the solution, the conductivity of the solution can be calculated.



INSTRUMENTATION

'The instrument used for measurement of conductance are known as conductometers.

'It consists of :

'**1. current source**

– Alternating current

'**2. conductivity cells**

– Type-A

– Type-B

– Type-C

'**3. electrodes**



CURRENT SOURCE

- '1. Mechanical high frequency AC generator by washburn.
 - '2. Taylor and Acree suggest used of oscillator for producing AC current.
 - '3. Vacuum tube oscillator by hall and adams.
- ⊗ When electrical potential is applied across electrodes two process occurs.
 - Ions accumulate near the electrodes.
 - Transfer of charge through the interface.
 - Note: DC current is not employed in conductance measurement because
 - Electrodes becomes polarised leading to high cell resistance.

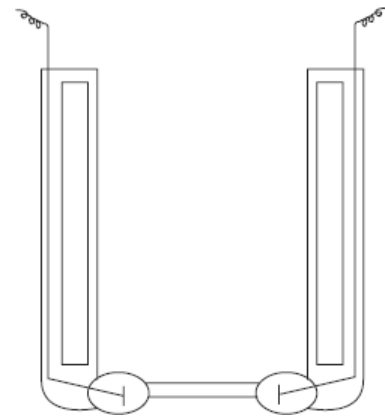
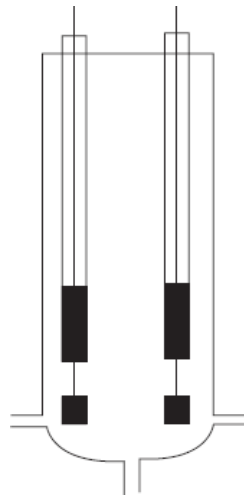
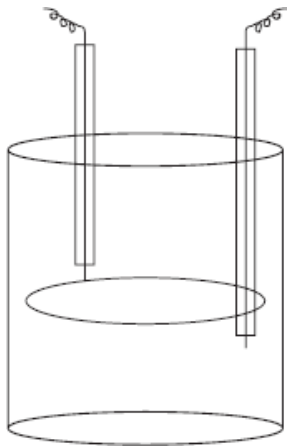


CONDUCTIVITY CELLS

- ' Made of pyrex or quartz and are fitted with two platinum electrodes.
- ' Should be placed in vessel containing water to maintain constant temperature.
- ' Types:
 - ' 1. Type-A
 - ' 2. Type-B
 - ' 3. Type-C



CONDUCTIVITY CELLS



ELECTRODES

- 'Platinum sheets each of 1cm^2 are fixed at distance of 1cm.
- 'The surface is coated with platinum black to avoid polarization effect and increase effective surface area.
- 'Platinisation of electrodes is done by coating solution 3% chlorplatinic acid and lead acetate on it to get uniform coating.
- 'Electrodes usage depends on conductivity and concentration.
- 'If concentration is low then electrodes should be largely and closely packed.



CONDUCTOMETRIC TITRATIONS:

⌘ Determination of end point of a titration with the help of conductivity measurements is termed as **conductometric titrations**.

– In a conductometric titration the titrant is added.



– The values of conductivity are then plotted against the volumes of the titrant in c.c.

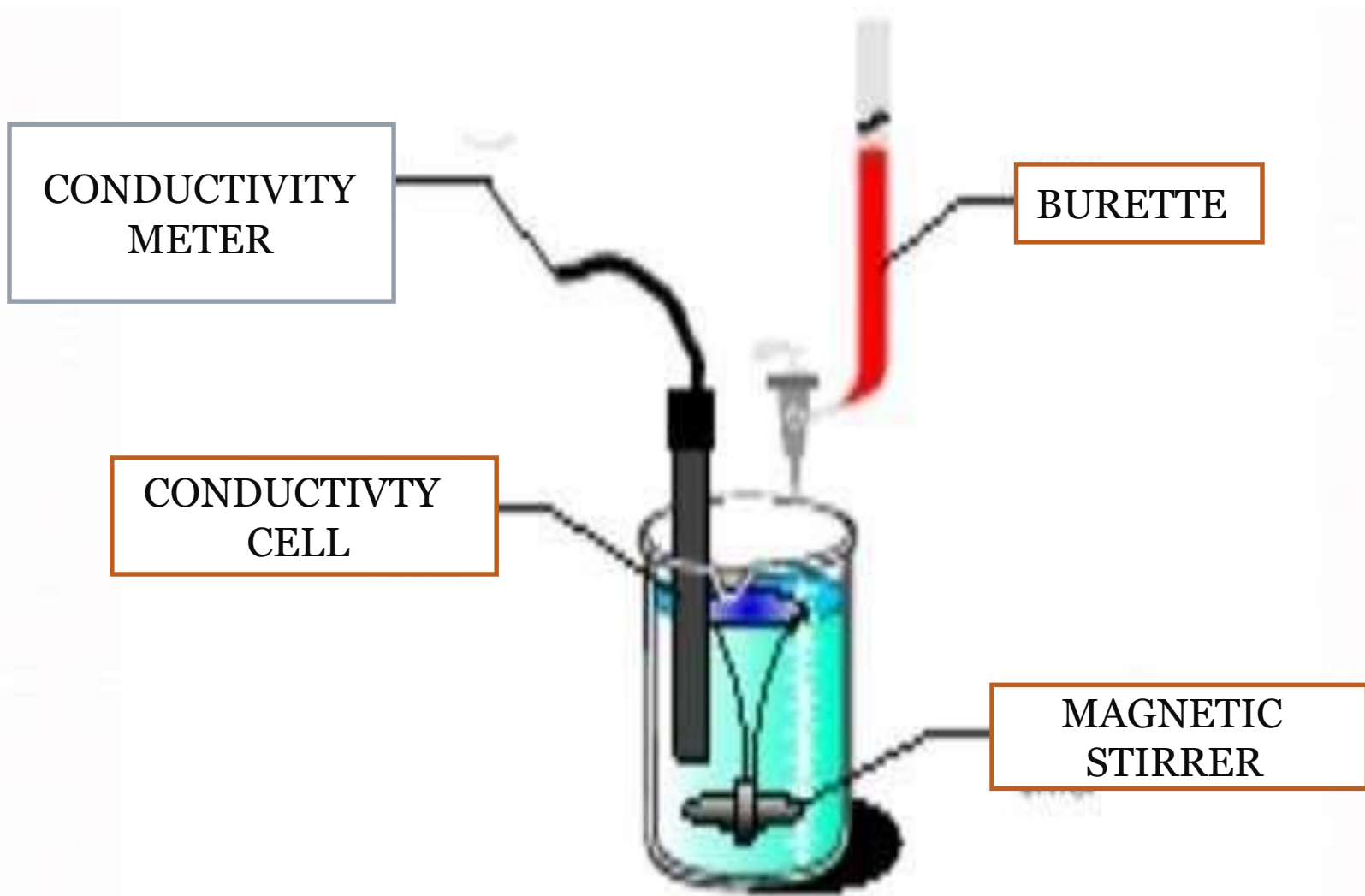


– Since the measured conductivity is a linear function of the concentration of ions present, two lines will be obtained which will intersect each other at a point, known as “**End point**” or “**Equivalence point**”



CONDUCTOMETER





TYPES OF CONDUCTOMETRIC TITRATIONS

Acid-base or neutral
Titration

Replacement Titration

Redox Titration

Complexometric Titration

Precipitation Titration



ACID-BASE OR NEUTRAL TITRATIONS

→ STRONG ACID- STRONG BASE

• Eg. **HCl vs NaOH**

→ STRONG ACID – WEAK BASE

• Eg. **HCl vs NH₄OH**

→ WEAK ACID – STRONG BASE

• Eg. **CH₃COOH vs NaOH**

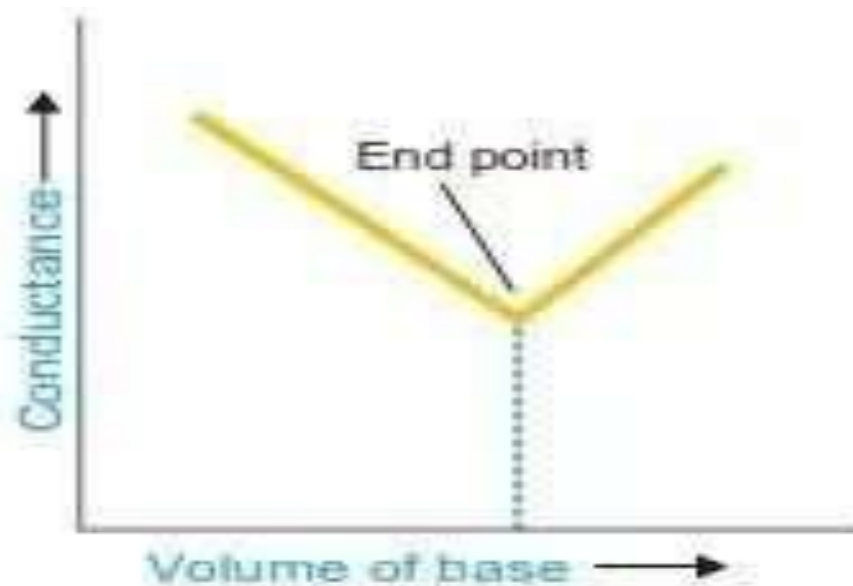
→ WEAK ACID – WEAK BASE

• Eg. **CH₃COOH vs NH₄OH**



STRONG ACID- STRONG BASE

- 'Fall in conductance due to replacement of high conductivity hydrogen ions by poor conductivity of sodium ions.
- 'Rise in conductance due to increase in hydroxyl ions.



■ **Figure**
Conductometric titration curve
for strong acid and strong base.



STRONG ACID – WEAK BASE

- 'Fall in conductance due to replacement of hydrogen by ammonium ions
- 'Conductance remain constant due to suppression of NH_4OH by NH_4Cl .

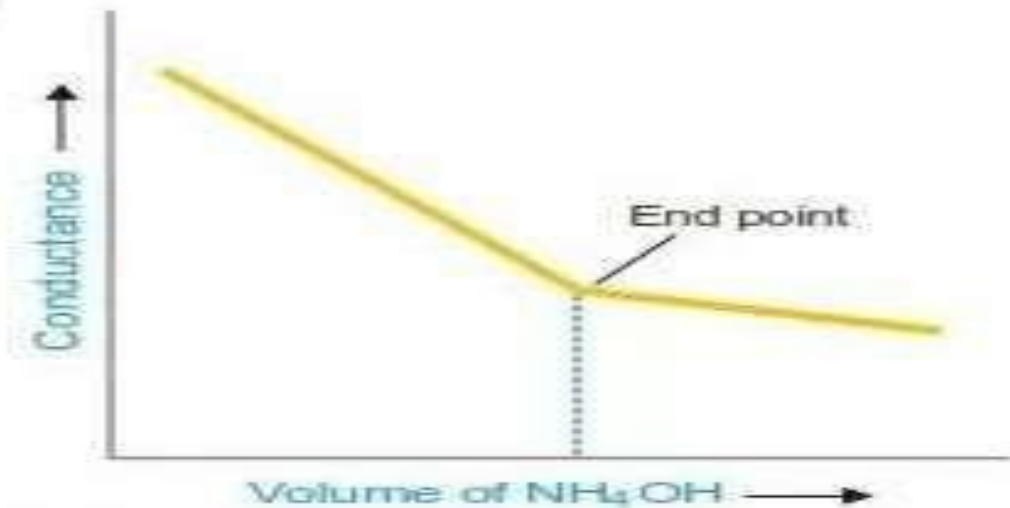
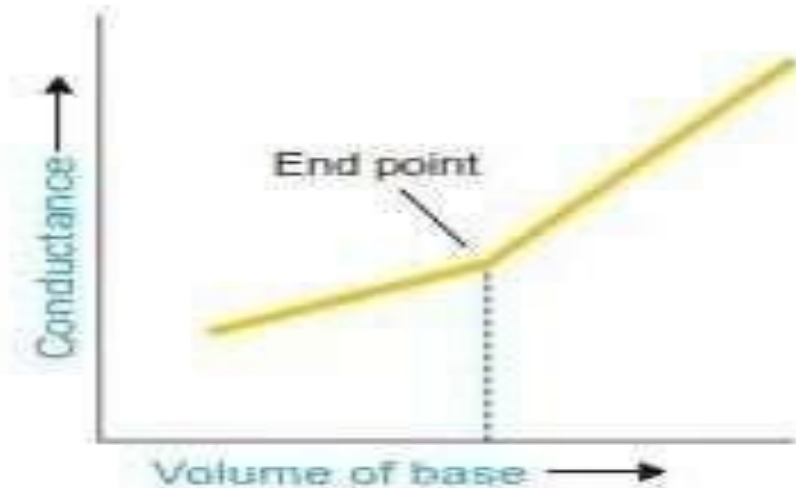


Figure
Curve for titration of a strong acid against a weak base.



WEAK ACID – STRONG BASE:

- 'Initial decrease in conductance followed by increase due to NaOH
- 'Steep rise due to excess of NaOH

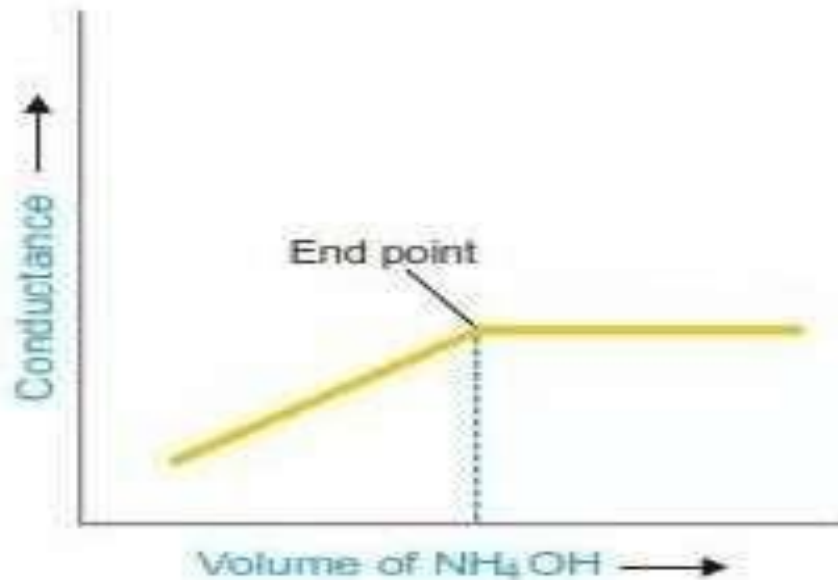


■ **Figure**
Curve for titration of a weak acid against a strong base.



WEAK ACID – WEAK BASE

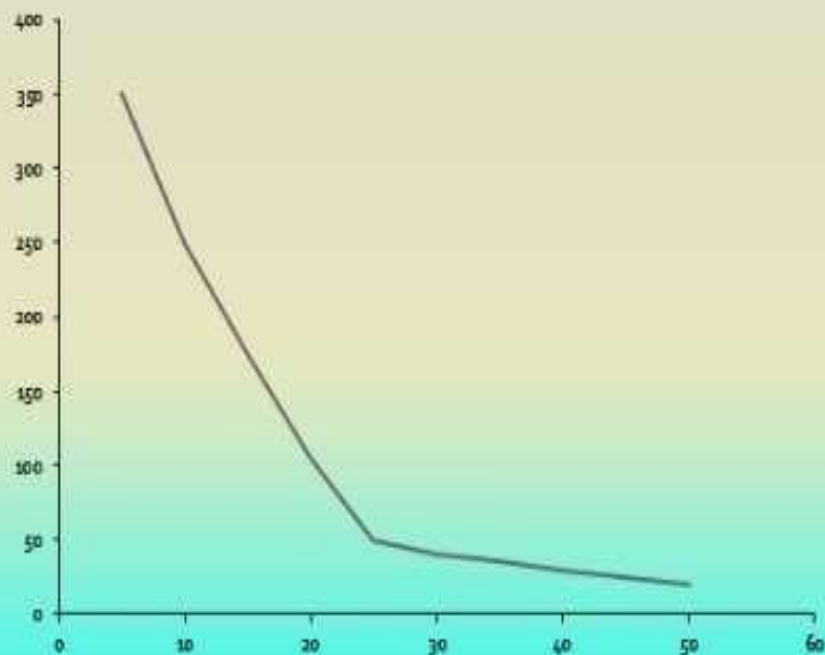
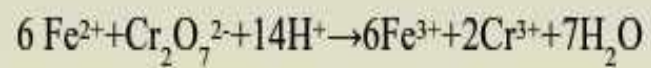
- ' Increase in conductance due to excess of CH_3COOH
- ' Constant conductance due to suppression of NH_4OH by CH_3COOH



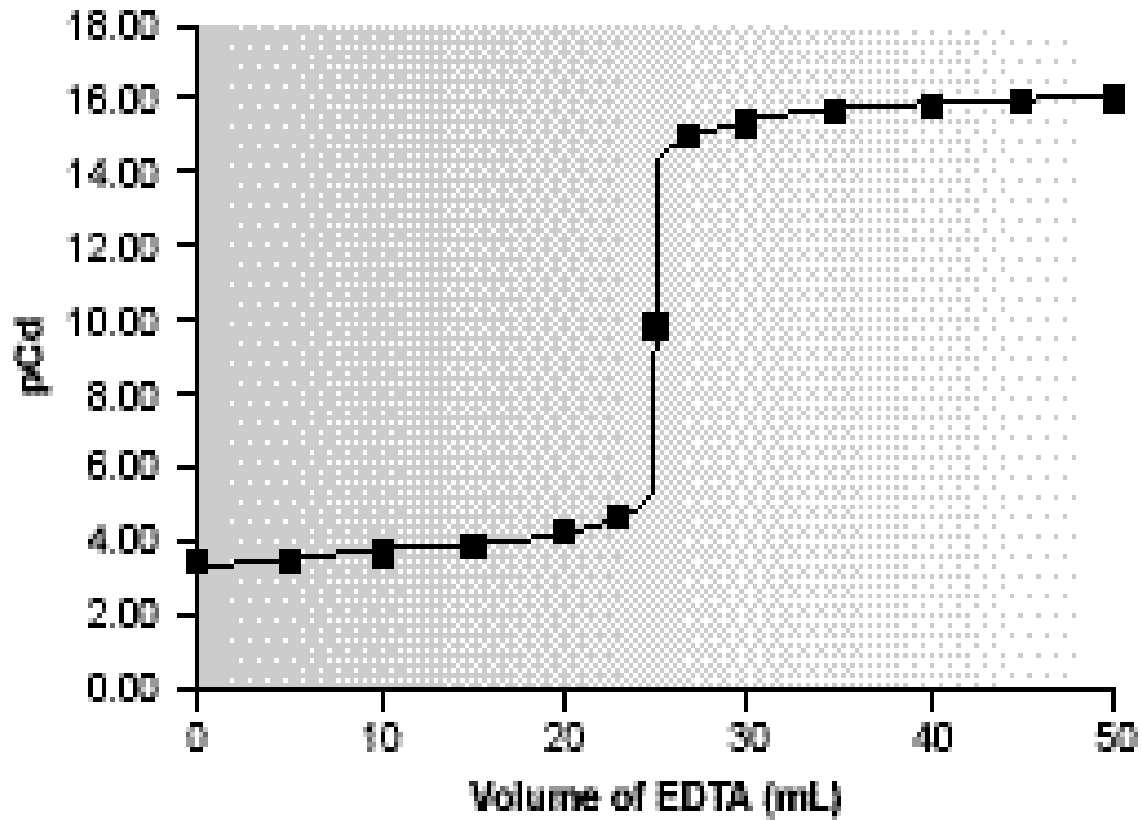
■ **Figure**
Curve for titration of acetic acid against ammonium hydroxide.



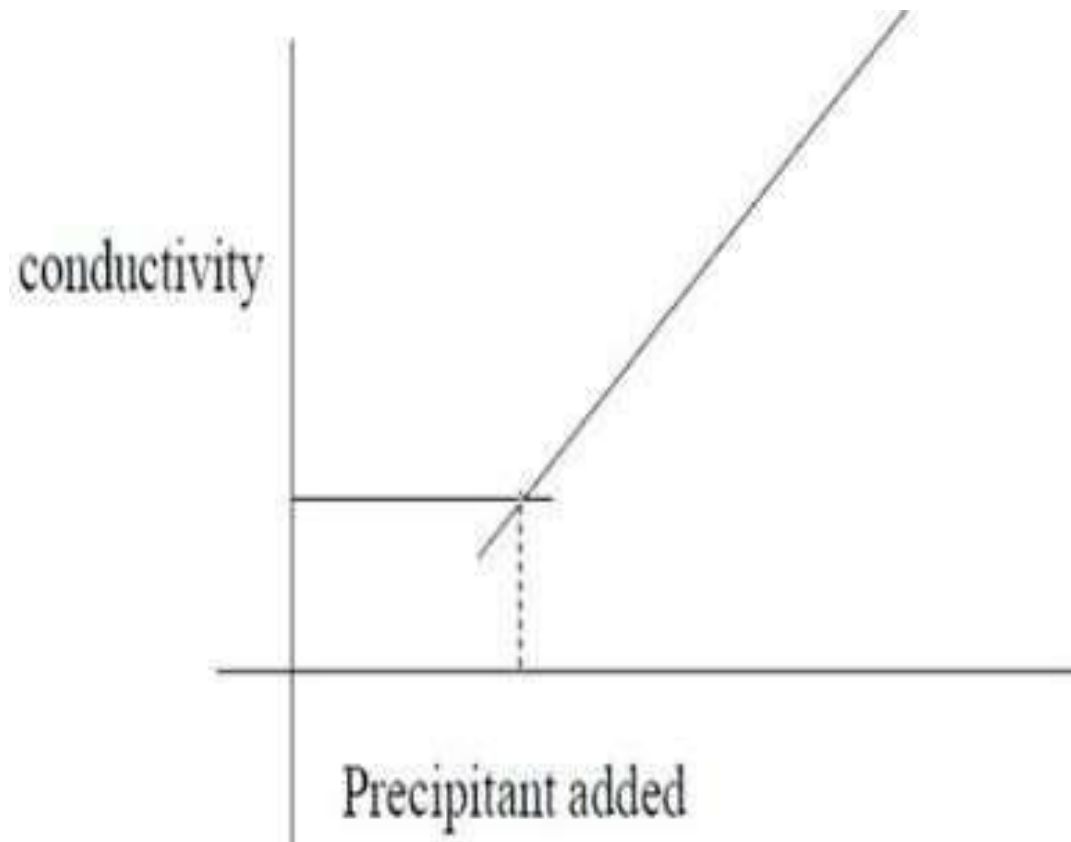
REDOX TITRATIONS



COMPLEXOMETRIC TITRATIONS



PRECIPITATION TITRATIONS



ADVANTAGES OF CONDUCTOMETRIC TITRATIONS

- ' Does not require indicators since change in conductance is measured by conductometer.
- ' Suitable for coloured solutions.
- ' Since end point is determined by graphically means accurate results are obtained with minimum error.
- ' Used for analysis of turbid suspensions, weak acids, weak bases, mix of weak and strong acids.
- ' Temperature is maintained constant throughout the titration.
- ' This method can be used with much diluted solutions.

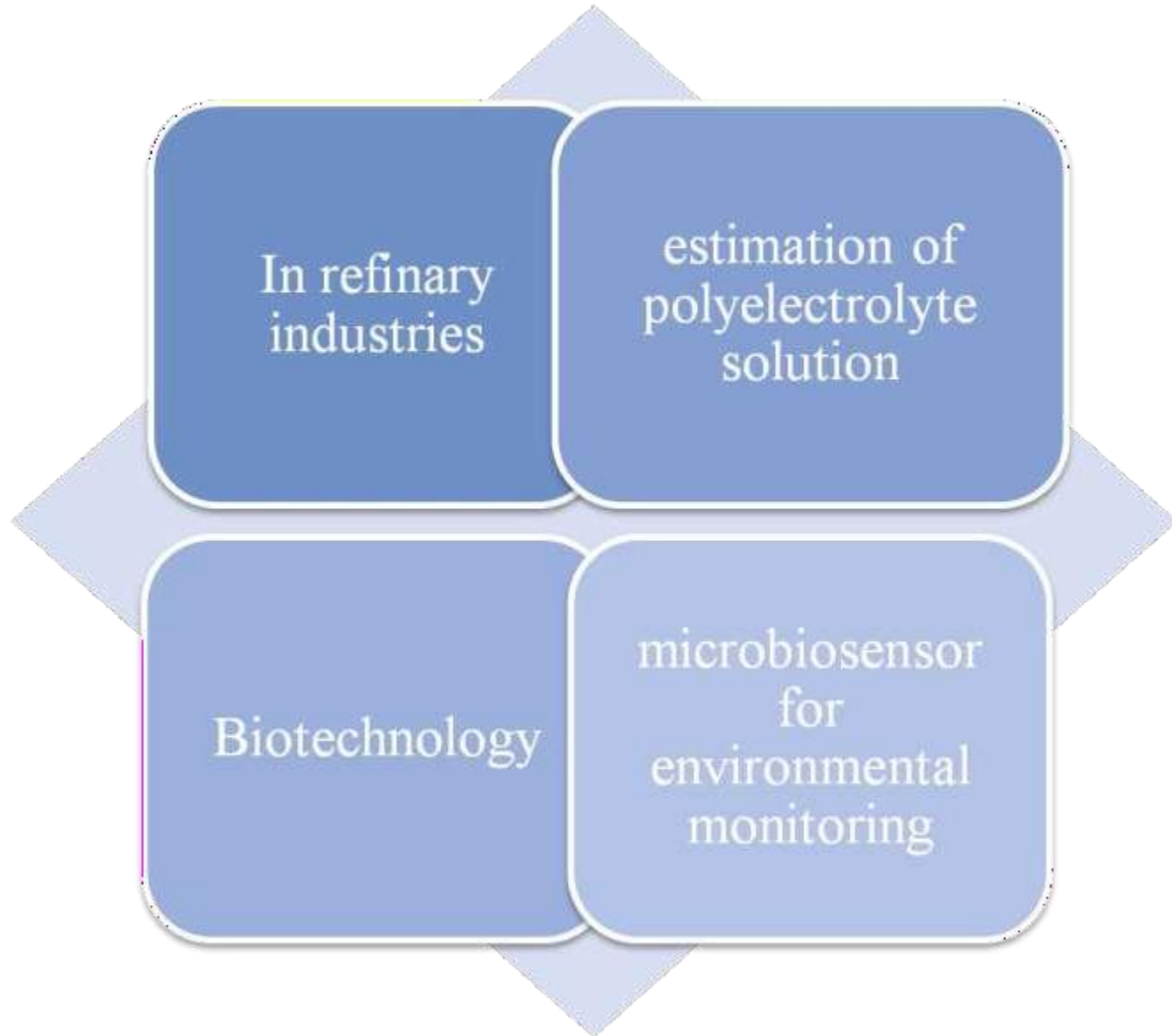


DISADVANTAGES

- ' Increased levels of salt in solutions masks the conductivity changes in such cases it does not give accurate results.
- ' Applications of conductometric titrations to redox systems is limited because, high concentration of hydronium ions in the solutions tends to mask the change in conductance.



RECENT DEVELOPMENTS



APPLICATIONS

Degree of dissociation of weaker electrolytes:

'The degree of dissociation of weak electrolyte is given by

$$\alpha = \lambda_v / \lambda_\infty$$

Where

λ_v = equivalent conductance at a given dilution V

λ_∞ = equivalent conductance at an infinite dilution

' λ_v can be found experimentally.

' Hence the degree of ionisation of weak electrolyte can be calculated.



APPLICATIONS

- 'Determination of sulphur dioxide in air pollution studies
- 'Determination of soap in oil
- 'Determination of accelerators in rubber
- 'Determination of total soap in latex
- 'Specific conductance of water
- 'Check water solubility in rivers and lakes
- 'Alkalinity of fresh water
- 'Salinity of sea water
- 'Deuterium ion concentration in water- deuterium mixture
- 'Food microbiology for tracing micro-organisms
- 'Tracing antibiotics



APPLICATIONS

- ' Estimation ash content in sugar juices
- ' Purity of distilled and de-ionised water can determined
- ' Solubility of sparingly soluble salts like AgCl, can be detected
- estimation of vanillin in vanilla flavour
- ' Determination of atmospheric SO₂
- ' Basicity of organic acids
- ' Ionic product of water
- ' Degree of hydrolysis



CONCLUSION

- ' By using conductometric titrations we can estimate the endpoint by plotting two straight lines using the usual graphical method. End point of the titration process is determined by means of measuring conductivity. This theory is used for colloids that have ionisable functional groups like latexes. This titration process can be used for either turbid or coloured liquids in cases when you cannot detect the endpoint by using indicators that are normal.



REFERENCES

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'Instrumental methods of chemical analysis by **B.K.Sharma**.

'Instrumental approach of chemical analysis by **A.K.Srivastava** and **P.C.Jain**



THANK YOU

