

6.2 CONDUCTOMETRY

6.2.1 Introduction

Conductometry is an electrochemical method of analysis which is concerned with electrical conductance through an electrolyte solution.

It is defined as determination or measurement of the electrical conductance of an aqueous electrolyte solution by means of a conductometer. The electrical conductivity or conductance of an electrolyte solution depends on :

1. Type of ions (cations, anions, singly charged, doubly charged).
2. Concentration of the ions.
3. Temperature.
4. Mobility of the ions - Mobility of an ion is defined as its velocity (speed or rate of movement) through the solution. It is influenced by factors such as mass, charge, size and extent of solvation of electrolyte.

6.2.2 Principle

The principle involved in conductometry is based on the conductance of electrical current by aqueous electrolyte solutions in a manner similar to that of metallic conductors.

The electrical conductance is in accordance with the Ohm's law which states that the strength of current (i) passing through a conductor (in this case electrolyte solution) is directly proportional to the potential difference (V) applied across the electrodes, and inversely proportional to the resistance offered by the conductor.

$$\text{i.e., } i = \frac{V}{R}$$

where,

i - Current (amperes)

V - Potential difference (volts)

R - Resistance (ohms Ω)

Some Important Definitions & Relations :

- (i) **Conductance (G)** : It is defined as the ease with which the current flows per unit area of conductor per unit potential applied. It is the reciprocal of resistance (R).

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

Or

$$G = R^{-1}$$

The SI unit is Siemen ($S = 1 \Omega^{-1}$) formerly expressed as mhos or $\text{ohm}^{-1} (\Omega^{-1})$

- (ii) **Specific Conductance (k)** : Specific conductance of a homogenous body may be defined as the conductance of the body of uniform length (l) and uniform area of cross section (A).

The conductance of a homogenous body of uniform cross section is proportional to the cross section (A) and inversely proportional to the length (l).

i.e., $G \propto \frac{A}{l}$

$$G = k \frac{1}{A}$$

$$G = R^{-1}$$

$$k = G \frac{1}{A} \quad (\text{Or})$$

$$k = \frac{1}{R} \cdot \frac{1}{A}$$

Where,

k - Specific conductance.

Units :

$\text{ohm}^{-1} \text{cm}^{-1}$ or $S \cdot \text{cm}^{-1}$

Specific conductance is also defined as reciprocal of specific resistance.

- (iii) **Molar Conductance ($\wedge$)** : It is defined as the conductance of a solution containing 1 mole of the solute (electrolyte) in 1000 cm^3 (1 litre) of the solution which is placed between two parallel electrodes which are 1 cm apart.

$$\Lambda = \frac{1000k}{C}$$

Where,

k - Specific conductance ($\text{ohm}^{-1}, \text{cm}^{-1}$)

C - Molar concentration (moles/cm^3)

It is also equal to the product of specific conductance and volume of the solution containing 1 mole of the solute.

$$\Lambda = k \times V$$

Units :

$$\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$$

(iv) **Equivalent Conductance (Λ_{eq})** : It is defined as the specific conductance (k) of a solution containing 1 gm equivalent of solute (electrolyte) in 1000 cm^3 (1 litre) of solution. It is represented by :

$$\Lambda_{eq} = \frac{k}{C_{eq}}$$

$$\Lambda_{eq} = \frac{1000k}{C_{eq}}$$

Where,

k - Specific conductance ($\text{ohm}^{-1} \text{ cm}^{-1}$).

C_{eq} - Equivalent concentration (equiv/cm^3)

If a solution contains 1 gm equivalent of solute in $V \text{ cm}^3$ of solution, then equivalent conductance is given as :

$$\Lambda_{eq} = k \times V$$

Hence, equivalent conductance is equal to the product of specific conductance (k) and volume (in cm^3) of the solution containing 1 gm equivalent of the solute.

Units : $\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{equiv}^{-1}$

(v) **Resistance (R)** : It is defined as a measure of the conductors opposition to the flow of electric charge.

$$R = \frac{1}{G}$$

$$\text{(Or)} \quad R = G$$

Units : The SI unit is Siemen-1 ($1 \Omega = 1 \text{ S}^{-1}$) formerly expressed as ohm (Ω).

(vi) **Specific Resistance (ρ)** : Specific Resistance may be defined as the resistance offered by a conductor of unit length and having a unit area of cross section. Resistance of a conductor (of uniform cross section) is directly proportional to its length and inversely proportional to its area of cross section.

Thus,

$$R \propto l$$

$$\text{and, } R \propto \frac{1}{A}$$

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

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

$$\rho = \frac{RA}{l}$$

Where,

ρ – Specific resistance or resistivity.

R – Resistance (ohm).

A – Area of cross section of conductor (cm^2).

l – Length of the conductor (cm).

Units :

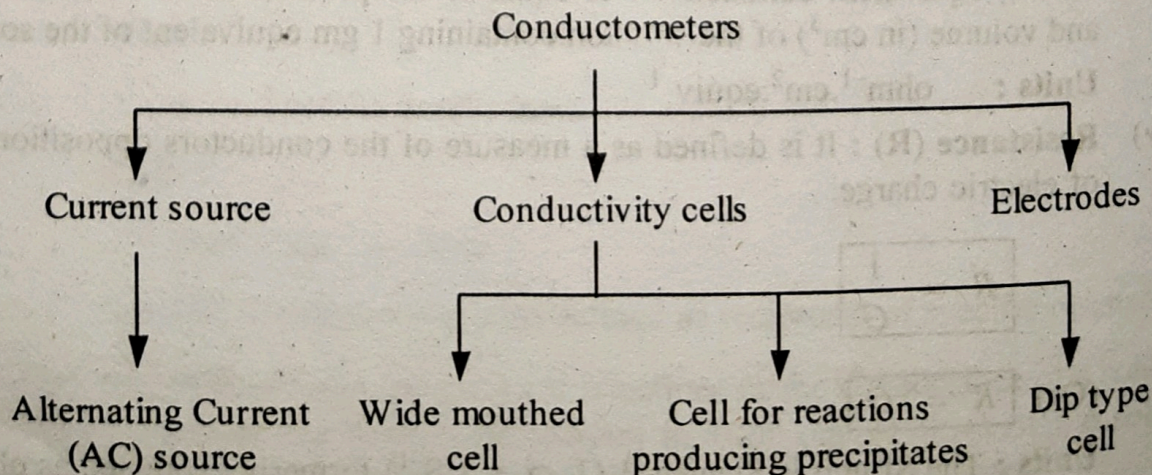
$$\text{As } \rho = \frac{R \cdot A}{l} = \text{ohm} \frac{\text{cm}^2}{\text{cm}}$$

$$\rho = \text{ohm.cm}$$

Hence, we can define specific resistance as “the resistance of a conductor of 1 cm length and area of cross section of 1 cm^2 ”.

6.2.3 Instrumentation

The instruments used for measurement of conductance are known as Conductometers. The conductometers consists of the following types :



1. **Current Source** : When electrical potential is applied across the electrodes, two processes occur :
- (a) Ions accumulate near the electrodes (creation of double layers), the sign of which is opposite to the sign of the corresponding electrodes.
 - (b) Transfer or diffusion of charge through the interface (Faradaic Reaction).

DC circuit is not employed in conductance measurement because, the electrodes quickly become polarised i.e., electrode reactions takes place which set up an electrochemical motive force (emf) opposing the applied emf (i.e., back emf), thereby leading to a high cell resistance.

The back emf can be prevented by :

- (i) Using a high frequency AC source (1000 - 4000 Hz), so that the current carried during one half of the cycle (alternate cycle) is sufficient to generate any polarization effects.
- (ii) By increasing the effective surface area of the electrodes. This can be done by coating the electrodes with a colloidal deposit of platinum black. This helps in adsorption of small quantities of reaction products which contributes to the back emf.

High voltage DC can be applied for measurement of conductance of non-aqueous solvents with low dielectric constants such as dioxane, benzene. Low voltage DC is used when reversible electrodes are used instead of platinum electrodes.

Examples of electrical power sources are :

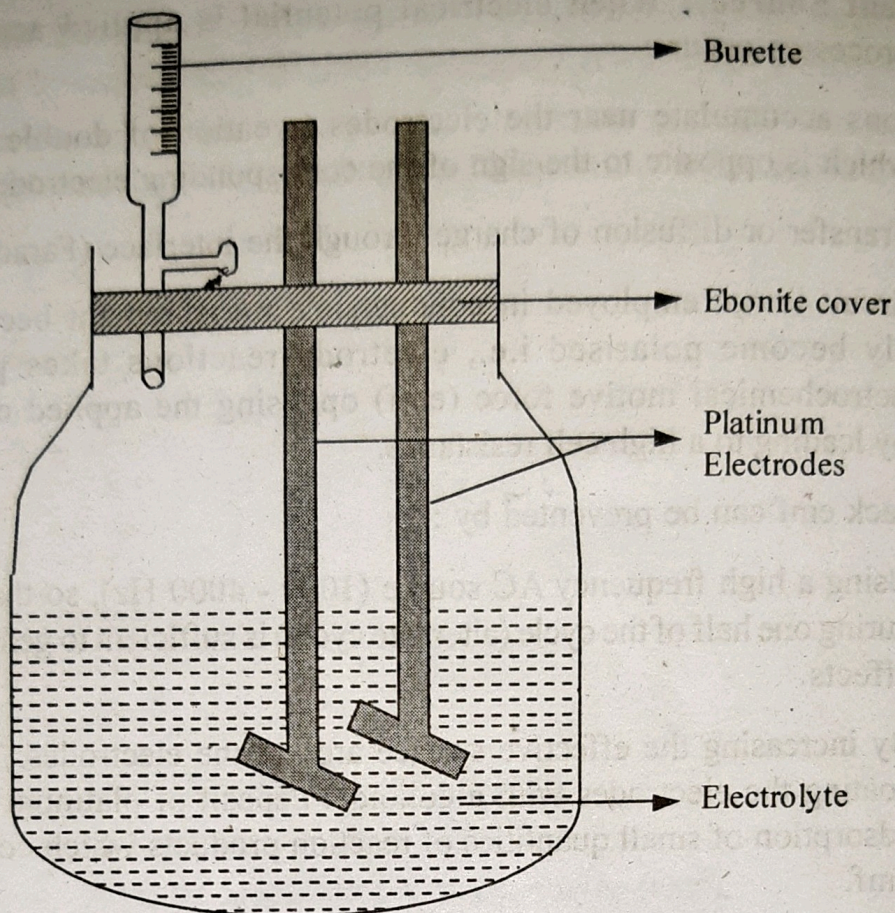
- (a) Mechanical high frequency AC generator by Washburn.
- (b) Vreeland oscillator by Taylor and Acree.
- (c) Vacuum tube oscillators by Hall and Adams.

2. **Conductivity Cells** : The cell which is used to measure the conductivity of a solution is called as conductivity cell. Conductivity cells are made up of pyrex or quartz and are fitted with two platinum electrodes. These cells should be placed in a large vessel containing water in order to maintain constant temperature.

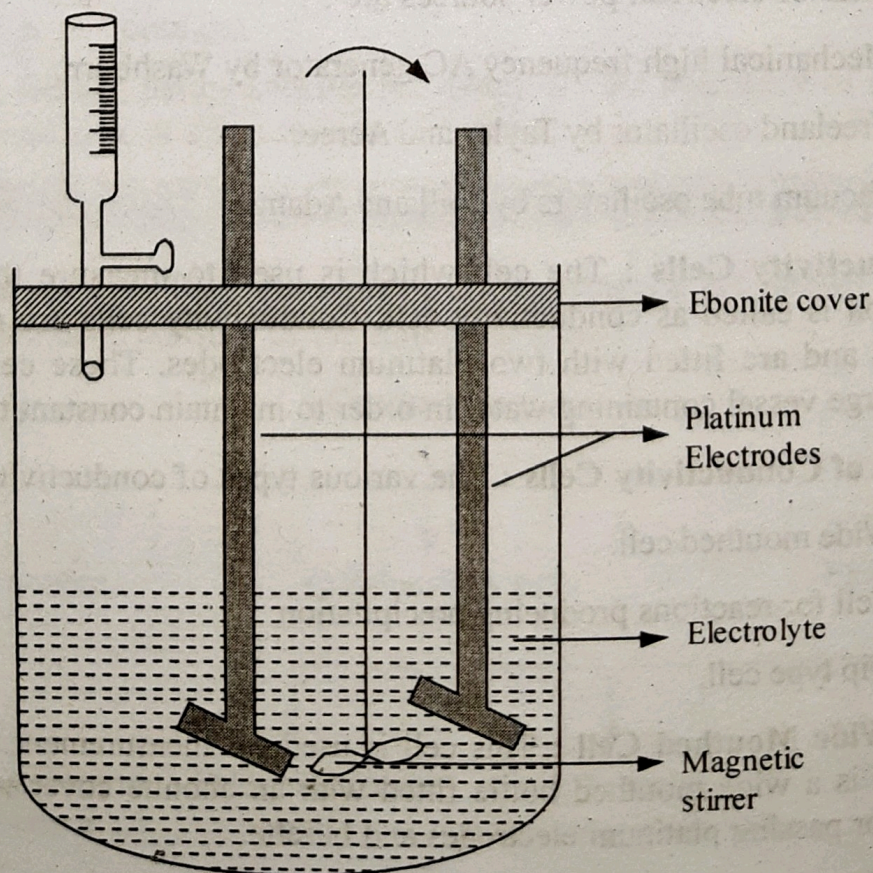
Types of Conductivity Cells : The various types of conductivity cells used are :

- (a) Wide mouthed cell.
- (b) Cell for reactions producing precipitation.
- (c) Dip type cell.

- (a) **Wide Mouthed Cell** : This cell is used for measurement of low conductance. It is a wide mouthed bottle fitted with an ebonite cover which has provisions for passing platinum electrodes and burette.

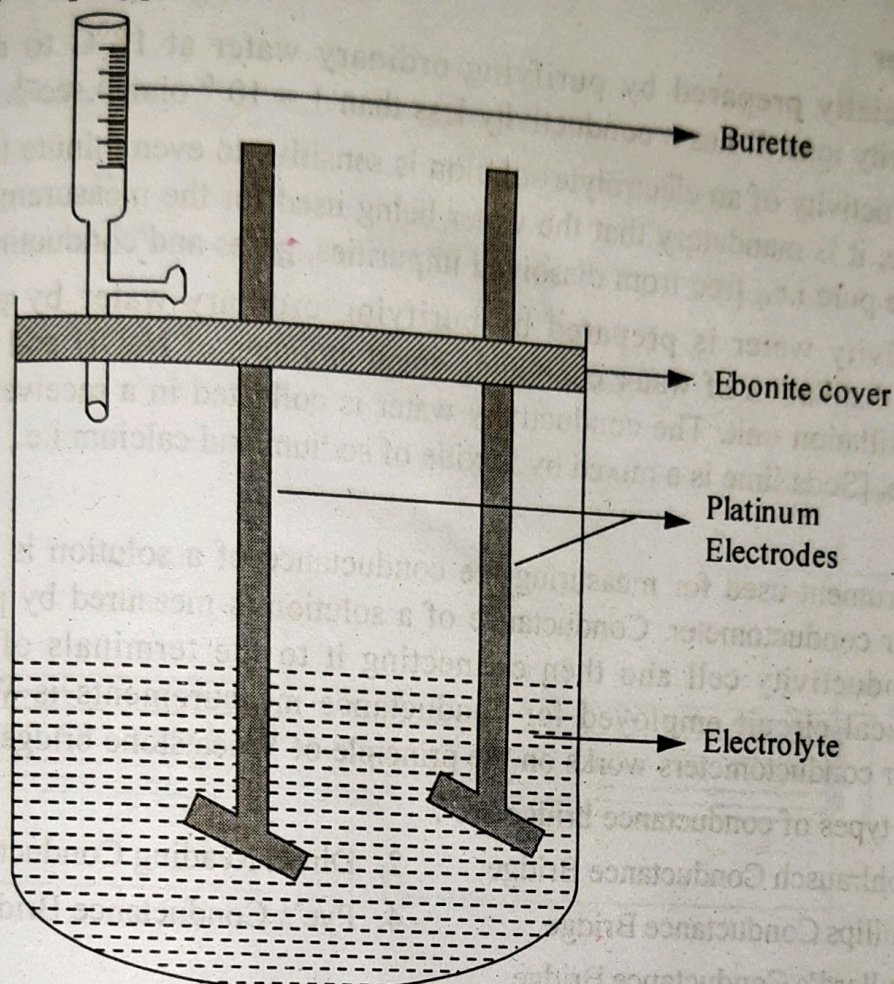


- (b) **Cell for Reactions producing Precipitates :** It is also a wide mouthed vessel fitted with an ebonite cover which has provisions for inserting platinum electrodes, burette tip and a stirrer. The stirrer may be either mechanical or magnetic. This type of cell is well suited for titration of those reagents which produce precipitates during the reaction.



(c) Dip Type Cell :

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It is the most commonly used cell. It also contains a wide glass tube with provisions for two platinum electrodes and burette tip.

Electrodes :

The electrodes used in the conductivity cells are essentially two platinum sheets, each of 1 cm^2 area fixed at a distance of 1 cm. The surface of the electrode is coated with platinum black (platinized electrodes) to increase their effective surface area and to prevent the polarization effects. Platinisation of electrodes also help in establishing a sharp balance.

Platinisation of electrodes is done by coating a solution of 3% chlorplatinic acid and 0.02 – 0.03 gm of lead acetate onto it in order to get a uniform coating. The amount of coating solution should be sufficient enough so that, the electrodes are immersed into it. Current is passed through this solution for about 15 - 20 minutes. This leads to electrolysis of chlorplatinic acid wherein the electrodes acquire a thin black velvety coating due to accumulation of finely divided platinum. After the coating is completed, electrodes are washed thoroughly with distilled water which is followed by conductivity water. To prevent drying or damage due to scratching during storage, the electrodes should be stored in water.

The usage of different electrodes depends on the conductivity and concentration of the electrolyte solution. If the electrolyte solution is less concentrated, then the electrodes used should be larger and closely placed. Electrodes used in precipitation titrations should be placed vertically in the electrolyte solution in order to prevent the accumulation of precipitate on the electrode surface.

Conductivity Water :

It is specially prepared by purifying ordinary water at 18°C to make it free from conductivity ions. It has a conductivity less than $1 \times 10^{-6} \text{ ohm}^{-1} \cdot \text{sec}^{-1}$.

The conductivity of an electrolyte solution is sensitive to even minute traces of impurities. Therefore, it is mandatory that the water being used for the measurement of conductance should be pure i.e., free from dissolved impurities, gases and conducting ions.

Conductivity water is prepared by purifying ordinary water by a technique which involves distillation of water containing small amounts of NaOH and KMnO_4 in a pyrex glass distillation unit. The conductivity water is collected in a receiver fitted with a soda lime tube. [Soda lime is a mixed hydroxide of sodium and calcium i.e., $\text{NaOH} + \text{Ca(OH)}_2$].

Conductometer :

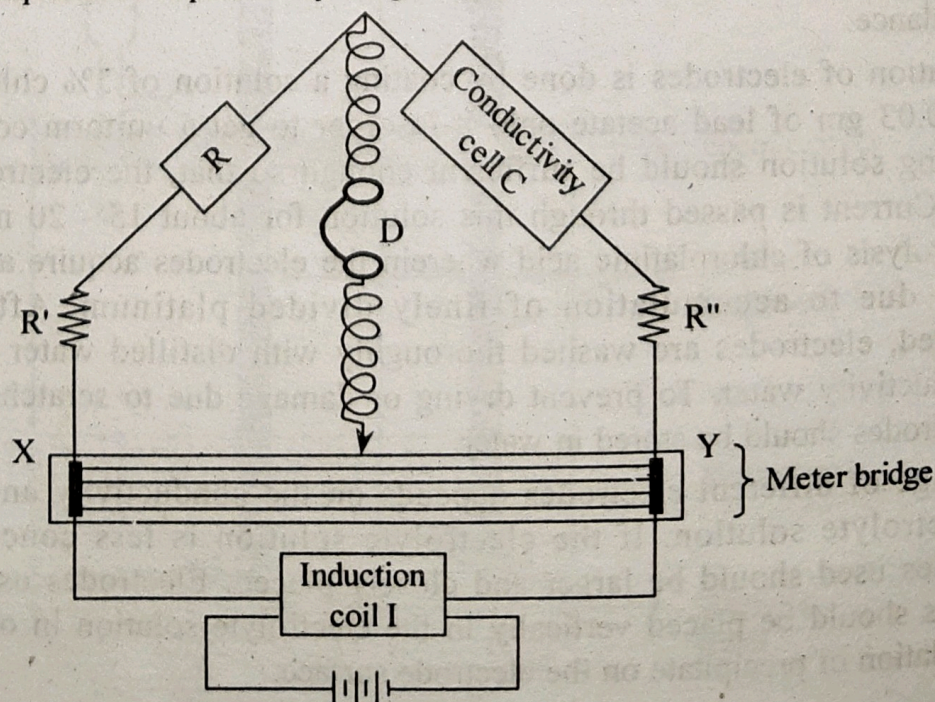
The instrument used for measuring the conductance of a solution is called conductance bridge or conductometer. Conductance of a solution is measured by placing the solution in a conductivity cell and then connecting it to the terminals of a conductometer. A classical circuit employed for conductance measurements is Wheatstone bridge. All other conductometers works on the principle of Wheatstone bridge.

Various types of conductance bridge are :

1. Kohlrausch Conductance Bridge
2. Direct Reading Conductance Bridge
3. Phillips Conductance Bridge
4. Pye's Conductance Bridge
5. Mullard's Conductance Bridge

1. **Kohlrausch Conductance Bridge :** This type of bridge consists of a meter bridge XY with fixed resistors R' and R'' at both the ends. One arm of the bridge consists of a resistance box ' R ' and the other arm contains conductivity cell ' C '. Detector D is a headphone while inductance coil ' I ' is AC source which is operated by means of a battery.

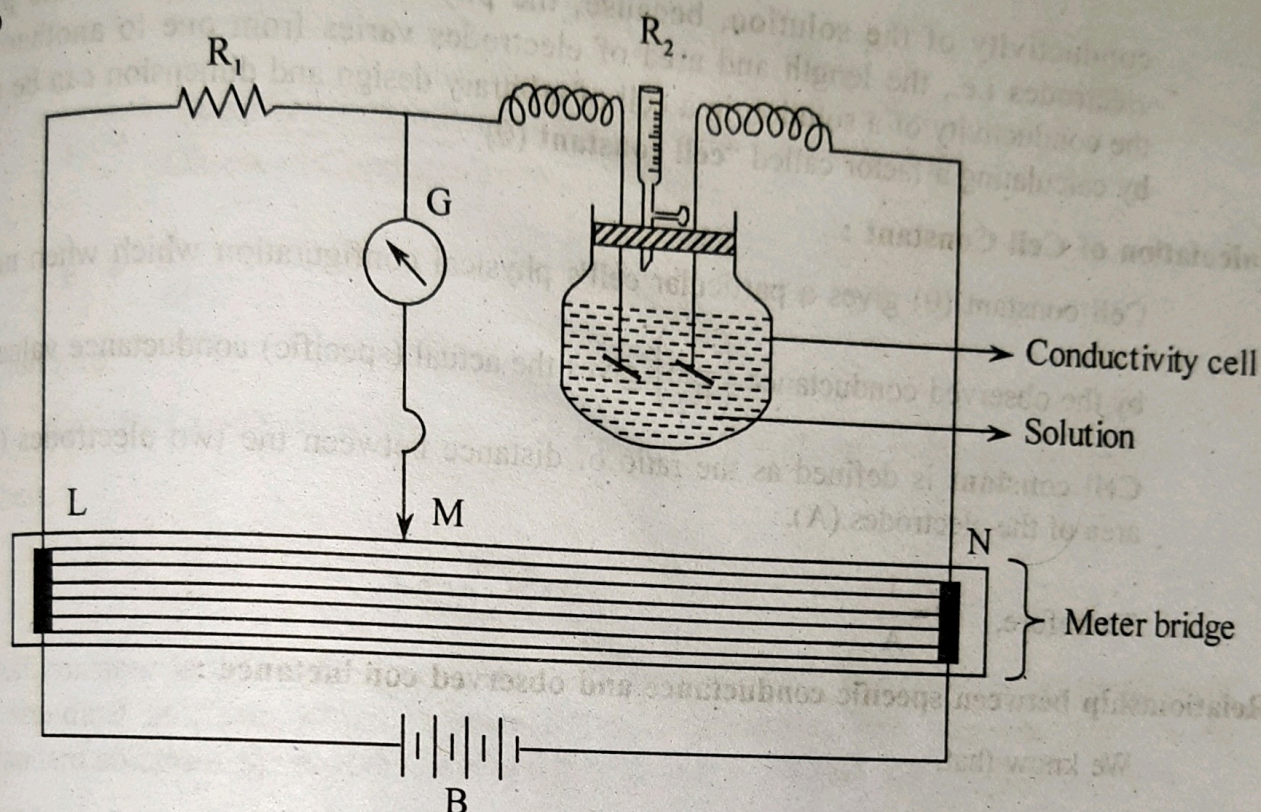
2. **Direct Reading Conductance Bridge :** In this type of conductance bridge, headphone is replaced by magic eye which is an electronic device.



Measurement of Conductance :

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Figure :
Conductivity Measurement
Setup



The set up for measurement of conductance consists of a metre bridge LN attached to a standard resistance R_1 and a conductivity cell containing the solution whose conductivity has to be determined, is also called as unknown resistance R_2 .

The cell is connected to standard resistor R_1 at one side and to the metre bridge LN at the other side. The sliding contact with a galvanometer (G) can be moved on the wire of the metre bridge by means of jockey (M) so that the resistance of the unknown solution is balanced with that of the standard resistance. When galvanometer shows a null deflection, the resistance of the unknown solution is determined by using the following formula :

$$\frac{ML}{NL} = \frac{R_2}{R_1}$$

$$R_2 = \frac{ML}{NL} \times R_1$$

Hence, conductivity of the unknown solution is :

$$\frac{1}{R_2} = \frac{NL}{ML} \times R_1$$

The measured (or observed) conductivity $\left(\frac{1}{R_2}\right)$ is not always equal to the specific conductivity of the solution, because, the physical configuration of the platinum electrodes i.e., the length and area of electrodes varies from one to another. Hence, the conductivity of a solution in a cell of arbitrary design and dimension can be obtained by calculating a factor called "cell constant (θ)".

Calculation of Cell Constant :

Cell constant (θ) gives a particular cell's physical configuration which when multiplied by the observed conductance $\left(\frac{1}{R_2}\right)$ gives the actual (specific) conductance value.

Cell constant is defined as the ratio of distance between the two electrodes (l) to the area of the electrodes (A).

Therefore, $\theta = \frac{l}{A}$

Relationship between specific conductance and observed conductance :

We know that,

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

$$R = k \frac{l}{A}$$

Where,

R - Observed resistance

k - Specific conductivity

l - Length of the electrodes

A - Area of the electrodes

Therefore,

$$R = k\theta \quad \left(\because \theta = \frac{l}{A}\right)$$

$$(\text{Or}) \quad \theta = \frac{R}{k}$$

$$\text{i.e., } \theta = \frac{\text{Observed Resistance}(R)}{\text{Specific Conductivity}(k)}$$

$$\theta = \frac{1}{\frac{\text{Observed Resistance}}{\text{Specific Conductivity}}} = \frac{1}{\frac{G}{k}}$$

$$\theta = \frac{\text{Specific Conductivity}}{\text{Observed Conductivity}}$$

$$\theta = \frac{k}{G}$$

Therefore,

$$\text{Specific Conductivity } (k) = \text{Cell Constant } (\theta) \times \text{Observed Conductivity } (G).$$

Then,

$$k = \theta \times G$$

Cell constant is determined by substituting the value of known specific conductance of a standard solution which is prerecorded in literature. The most commonly used standard solutions for calibration of cell constant are 0.1M KCl or 0.01M KCl solution.

Kohlrausch determined the value of specific conductance of 0.1M KCl as $0.002768 \text{ S.cm}^{-1}$ and for 0.01 M KCl as $0.001412 \text{ S.cm}^{-1}$ at 25°C .

The conductivity of a solution in a cell is then obtained by using the following formula :

$$\text{Cell Constant } (\theta) = \frac{0.002768}{\text{Observed Conductance}}$$

Once, the cell constant has been determined, the specific conductance of any solution can be calculated using the relation.

$$\text{Specific Conductance } (k) = \text{Cell Constant } (\theta) \times \text{Observed Conductance } (G).$$

Theoretical cells have cell constants 1.0. Cells with cell constants of 0.1 or less, have large and closely placed electrodes whereas, cells having cell constant of 1.0 or greater have small and widely spaced electrodes.

6.2.4 Conductometric Titrations

Introduction :

Titration is a process of qualitative chemical analysis in which the concentration of constituents of a sample (analyte) is determined. This is done by adding a reagent (titrant) of known concentration in measured volumes (from a calibrated burette) into the sample (analyte). The analyte reacts with the titrant in definite proportions to give the desired result. The amount of analyte consumed is determined from the end point at which the titration is stopped.

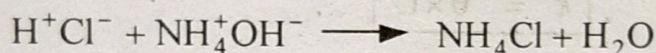
End point is defined as a point at which the number of moles of titrant is equal to the number of moles of analyte i.e., the point at which an exactly equivalent amount of titrant is added to the sample analyte. The end point can be detected by either chemical indicators or by electrical methods.

Theory and Principle of Conductometric Titrations :

One of the most important applications of conductometry is conductometric titrations. In conductometric titrations, the end point is detected by measuring the change in the electrical conductance of the solution which is being titrated. This analytical method is applicable to titrations which show an appreciable change in the conductance at the end point.

Conductometric titrations are based on the principle that the conductance of a solution depends on the concentration and the conductivity (mobility) of the ions. It is also based on the substitutions of ion of one mobility by the ion of another mobility.

Example : Addition of Hydrochloric acid to ammonium hydroxide

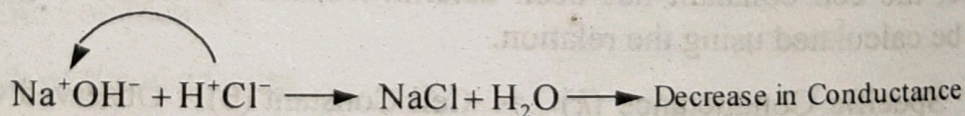


The high conductivity H^+ ions (350) are replaced by low conductivity NH_4^+ ions (73).

At infinite dilutions, each individual ion present in the solution possess independent conductivity and contributes towards the conductance of the solution. When an electrolyte solution is added to another electrolyte solution, the net conductance of the solution will depend on whether.

- (i) Chemical reaction will occur between the electrolytes.

Example : Addition of sodium hydroxide to hydrogen chloride

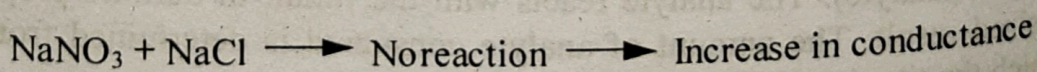


H^+ ions of high conductivity (350) are replaced by Na^+ ions of low conductivity (50). Hence, the overall conductance decreases.

If a chemical reaction occurs between the electrolytes, then either replacement or substitution of ions takes place. Depending upon the ionic conductivities of the replacing and replaced ions, the overall conductance either increases or decreases.

- (ii) Chemical reaction does not occur between the electrolytes.

Example : Addition of sodium nitrate to sodium chloride (NaNO_3 to NaCl)



If a chemical reaction does not occur between the electrolytes, then the total conductance of the solution increases because all the free ions will contribute towards the conductance of the solution.

In conductometric titrations, the titrant is added in small volumes from calibrated microsyringe burettes (5 ml capacity) and the conductivities are measured during the course of titration using a device called conductometer. The values of conductivities are then plotted (on Y-axis) against the volume of titrant added (on X-axis). The graph obtained consists of two straight lines (also referred as curves) intersecting each other at a point called 'end point' or 'equivalent point'. Sometimes, the titration curves show a slight curvature near the end point. This arises due to hydrolysis, dissociation of the product or due to solubilization of the precipitate. In such cases, the end point is obtained by extrapolating the curved portions. More acute the angle of the intersecting lines, more accurate the results will be.

Conductivity of a solution is greatly affected by changes in temperature. For every 1°C rise in temperature, the conductance increases by 2%. Therefore, to obtain accurate results it is necessary to carry out measurements at constant temperature using a thermostat. Also, to obtain straight line graphs, it is essential that the total volume of the solution be kept constant during the titration. In order to keep the volume change small, the concentration of the titrant must be about 10 times to that of the titrate. Whenever necessary, or at each increment of titrant added, a correction for dilution effect is made by multiplying the observed conductivity by a factor called dilution factor.

$$C_c = \frac{V+v}{V} \times C_o$$

where,

C_c – Corrected conductance

C_o – Observed conductance

V – Initial volume of the titrate

v – Volume of the titrant added.

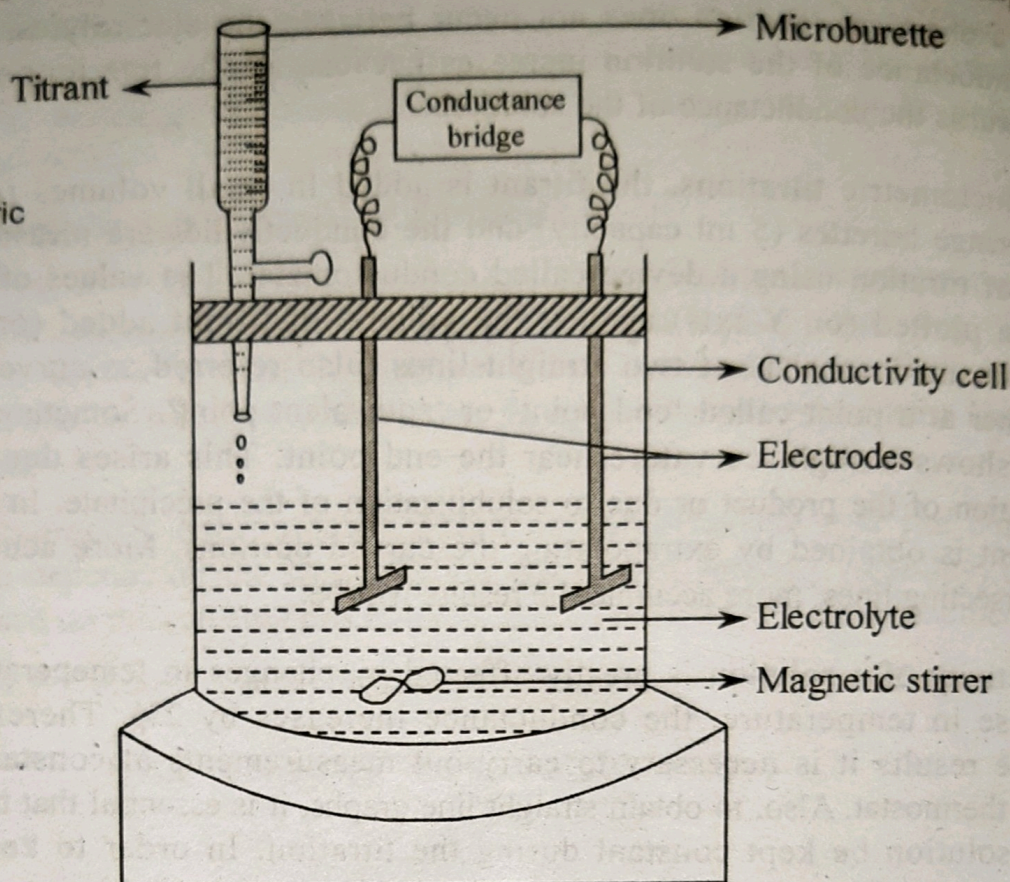
Apparatus and Procedure for Conductometric Titrations

Apparatus :

The apparatus for conductometric titration consists of conductivity cell, automatic or manual burette, conductance bridge, magnetic stirrer.

The conductivity cell is placed within the titration vessel which is thermostatically maintained at laboratory temperature.

Figure :
Apparatus for
Conductometric
Titrations

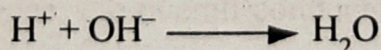


Procedure :

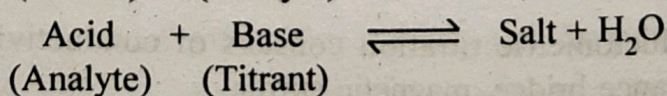
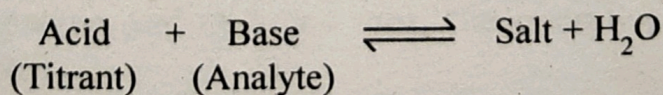
1. Titrant is added in appropriate volumes at a time from the microburette.
2. Each time the titrant is added, the solution is mixed thoroughly by means of a magnetic stirrer and the conductivity readings are recorded.
3. A plot of conductance (on Y-axis) against volume of titrant (on X-axis) is made. The values of observed conductance can be multiplied by the dilution factor in order to correct the volume change. If necessary.
4. The end point is determined from the point of intersection of the linear portions of the graph.

Types of Conductometric Titrations :

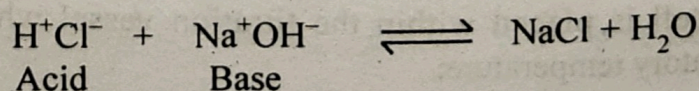
1. **Acid-Base or Neutralization Titrations :** Acid-base titrations (neutralization titrations) are based on neutralization reaction.



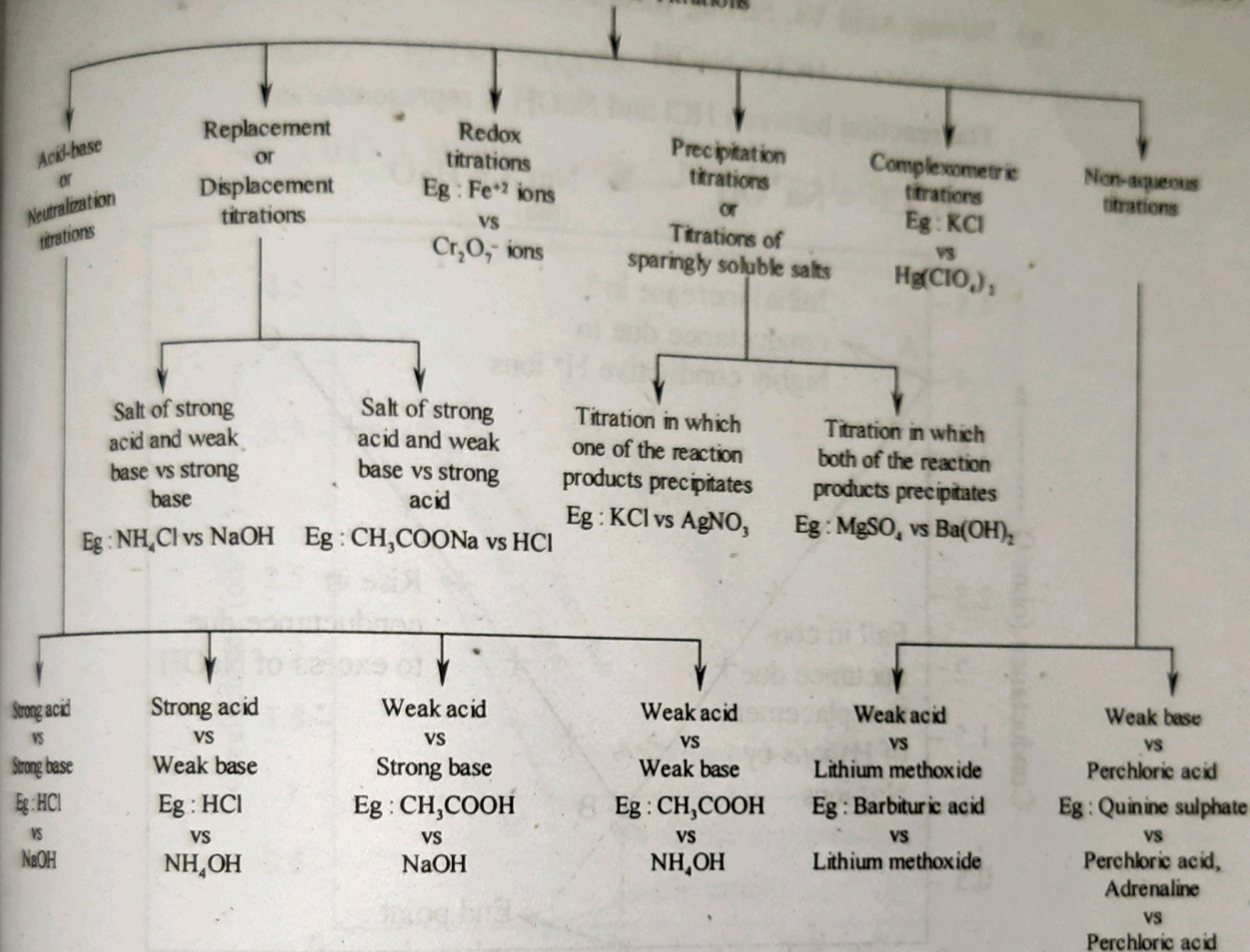
It involves reaction between the analyte and an acid or basic titrant to give a salt along with neutral water.



Example :



Conductometric Titrations



Water is formed by the interaction of H^+ ions of the acid (i.e., HCl) and OH^- ions of the base (i.e., NaOH).

In acid-base titration, standard solution of acid is used for the quantitative estimation of a base and standard solution of base is used for estimation of an acid. In case of strong acid vs strong base titrations, the end point is reached when the pH of the solution is equal to 7. However, for weak acids and bases, the end point need not occur at pH 7.

Types of Acid-Base Titrations :

(a) Strong Acid Vs. Strong Base

Example : HCl Vs. NaOH

(b) Strong acid vs weak base

Example : HCl Vs. NH_4OH

(c) Weak Acid Vs. Strong Base

Example : CH_3COOH Vs. NaOH

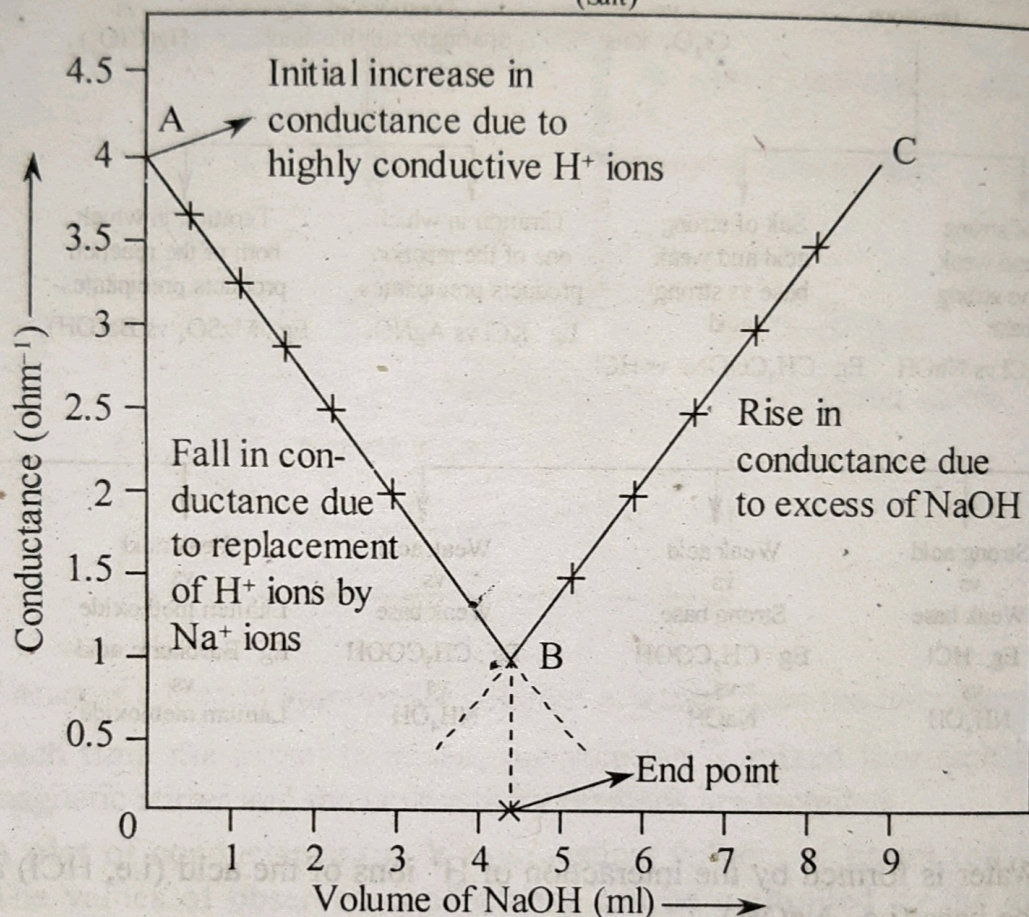
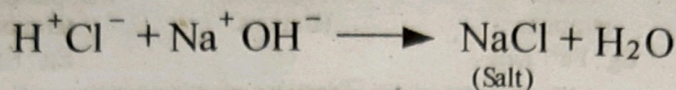
(d) Weak Acid Vs. Weak Base

Example : CH_3COOH Vs. NH_4OH

(a) Strong Acid Vs. Strong Base :

Example : HCl vs NaOH

The reaction between HCl and NaOH is represented as :



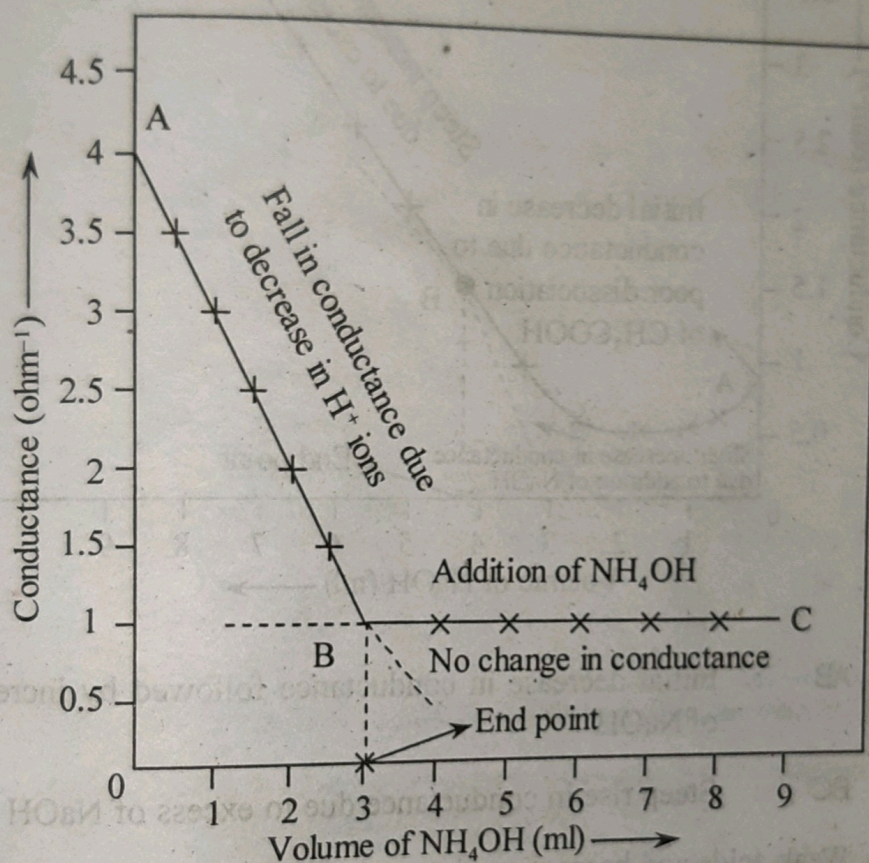
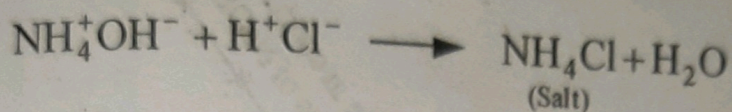
AB : Fall in conductance due to replacement of high conductivity H^+ ions by poor conductivity Na^+ ions.

BC : Steep rise in conductance due to excess concentration of OH^- ions.

The curve shows initial high conductivity at point A, because strong acid (HCl) dissociates completely to give H^+ ions which have high conductivity. When NaOH is added to HCl, the H^+ ions of HCl reacts with OH^- ions of NaOH to produce water. The highly conducting H^+ ions are replaced by poorly conducting Na^+ ions because for each amount of NaOH added, an equivalent amount of H^+ ions are removed. As a result, the number of H^+ ions decreases. This continues until the end point is reached i.e., the mixture contains only NaCl in water. After the end point, when all the H^+ ions have been consumed, further addition of NaOH causes increase in the number of OH^- ions and hence the conductivity increases.

The first part of the curve (AB) shows a steeply descending curve. Thus, the curve obtained is of 'V' shape. The end point of titration occurs at the intersection of the two linear segments.

(b) Strong Acid Vs. Weak Base :

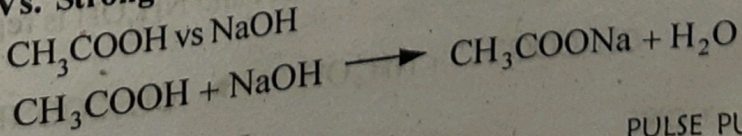
Example : HCl Vs. NH_4OH 

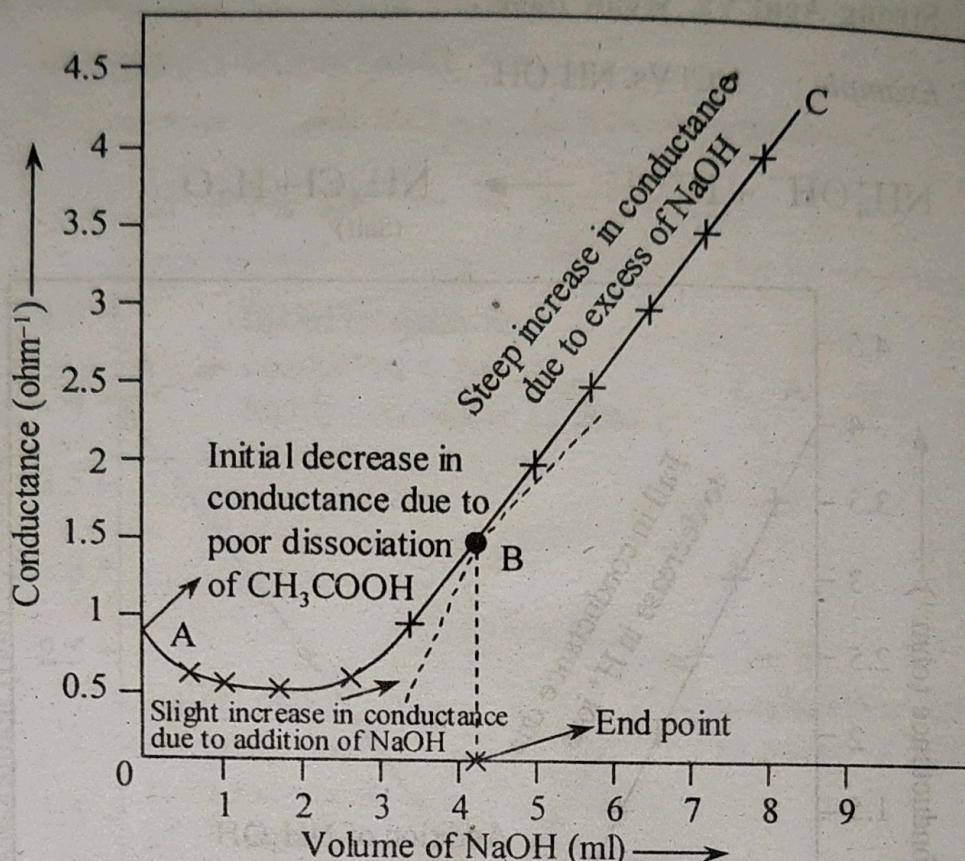
AB : Fall in conductance due to replacement of H^+ ions NH_4^+ ions.

BC : Conductance remains constant due to suppression of the ionization of NH_4OH by NH_4Cl .

At point A, the conductivity is high because strong acid (HCl) dissociates completely into H^+ ions. When NH_4OH is added to HCl , the conductivity decreases because the high conductivity H^+ ions are replaced by the poor conductivity NH_4^+ ions. This continues with each increment of NH_4OH until all the H^+ ions have been utilized and the mixture contains only ammonium chloride (NH_4Cl) in water. This is the end point. Addition of (NH_4OH) after the end point does not show any significant effect on the conductance because NH_4Cl formed during neutralization prevents the ionization of NH_4OH . Therefore, the conductance remains constant.

(c) Weak Acid Vs. Strong Base :

Example : CH_3COOH vs NaOH 



AB : Initial decrease in conductance followed by increase due to addition of NaOH

BC : Steep rise in conductance due to excess of NaOH

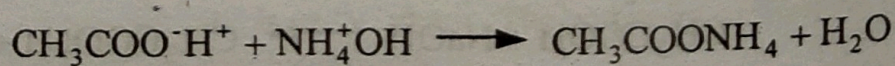
Weak acids and bases dissociate only to a small extent.

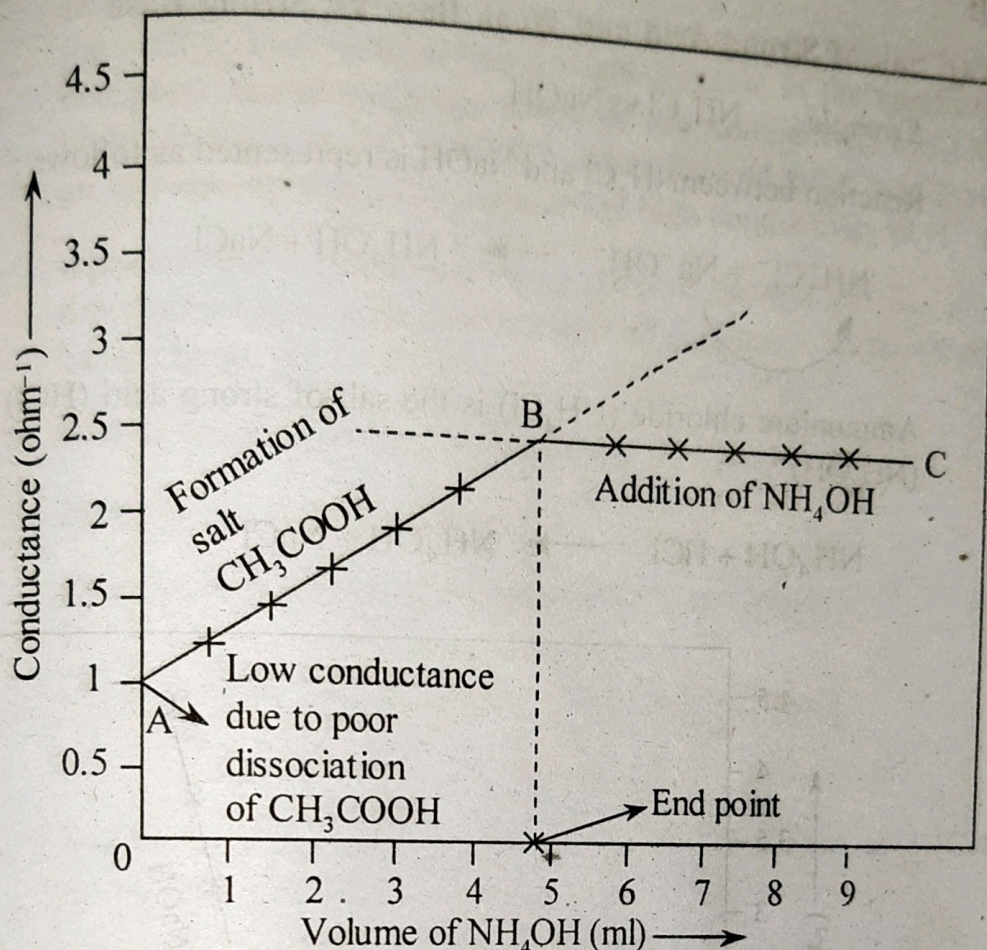
The undissociated molecules of acetic acid (CH_3COOH) are transferred into undissociated molecules of sodium acetate (CH_3COONa). The titration curve shows an initial decrease in conductivity (point A) due to poor dissociation of CH_3COOH into H^+ ions. After addition of a few drops, of NaOH, there is slight increase in conductance as neutralization reaction occurs between the H^+ ions of CH_3COOH and OH^- ions of NaOH thereby forming sodium acetate (CH_3COONa) [Seen in Curve AB]. This continues until the end point is reached. After the end point, addition of excess of NaOH leads to a sharp increase in conductance (BC) due to increased concentration of high conductivity OH^- ions.

(d) Weak Acid Vs. Weak Base :

Example : CH_3COOH Vs. NH_4OH

Reaction between CH_3COOH and NH_4OH is represented as :





AB : Increase in conductance due to conductivity of CH_3COONa salt.

BC : Conductance becomes constant due to suppression of the ionization of NH_4OH by CH_3COONa .

At point A, the conductivity is low because weak acid (CH_3COOH) does not dissociate effectively. When NH_4OH is added, the NH_4^+ ions replace the H^+ ions of CH_3COOH to form a conducting salt ammonium acetate ($\text{CH}_3\text{COONH}_4$). The salt formed has better conductivity than CH_3COOH or NH_4OH . This leads to a gradual increase in the conductivity. The conductance increases with each increment of NH_4OH until all the acetate ions are used up and the salt formation completes. This represents the end point. After the end point, addition of NH_4OH does not affect the conductance because, the ionization of NH_4OH is suppressed by the acetate salt. Hence, the conductivity reaches a plateau.

2. **Replacement or Displacement Titrations** : This type of titrations involve the replacement (or displacement) of one ion by the other ion. Replacement titrations.

Types of Replacement or Displacement Titrations :

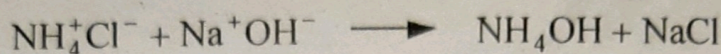
- (a) Salt of strong acid and weak base Vs. strong base.

Example : NH_4Cl vs NaOH

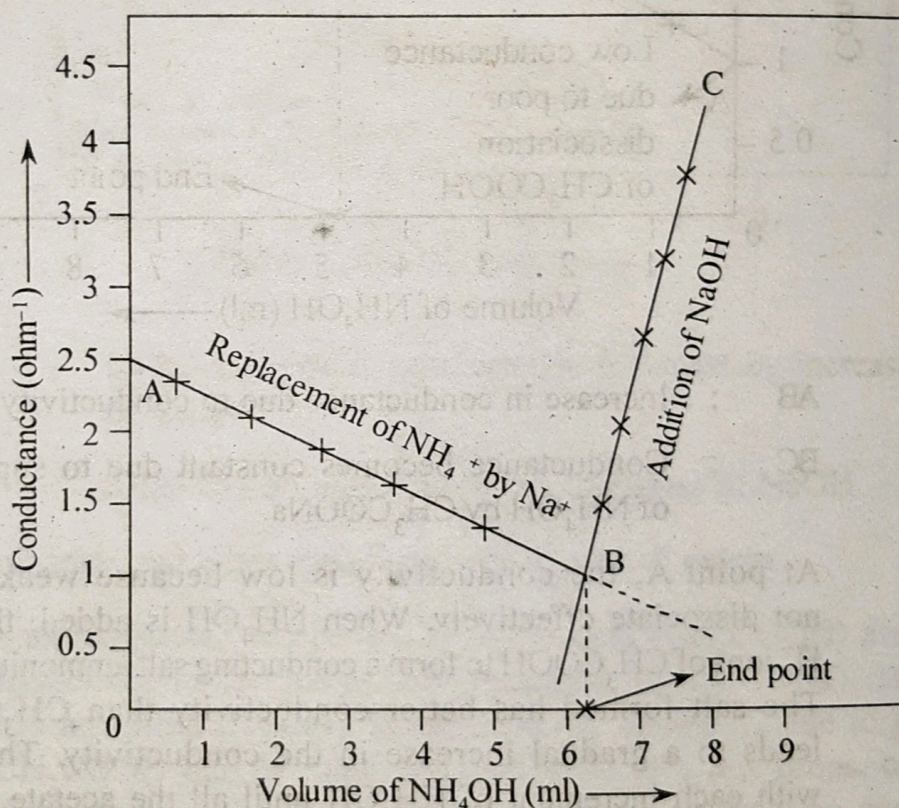
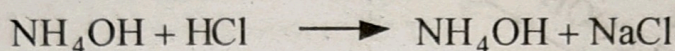
- (b) Salt of weak acid and strong base Vs. strong acid.

Example : CH_3COONa Vs. HCl

(a) Salt of Strong Acid and Weak Base Vs. Strong Base

Example : NH_4Cl vs NaOH Reaction between NH_4Cl and NaOH is represented as follows :

Ammonium chloride (NH_4Cl) is the salt of strong acid (HCl) and a weak base (NH_4OH)



AB : Slight decrease in conductance due to replacement of NH_4^+ ions by Na^+ ions.

BC : Steep rise in conductance due to addition of NaOH

In this titration, there is replacement or displacement of high conductivity NH_4^+ ions (73) by low conductivity Na^+ ions (50).

The initial part of the curve AB shows a slight decrease in conductivity due to replacement of the NH_4^+ ions by the Na^+ ions until the end point is reached. After end point, there is a sharp rise in the conductance due to the addition of high conductivity OH^- ions of NaOH .

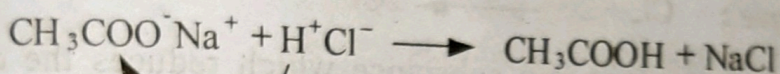
In this titration, there is a replacement of acetate ions (CH_3COO^-) by chloride ions (Cl^-). The curve shows a slight increase in the conductance towards the end point due to the replacement of low conductivity CH_3COO^- ions (41) by high conductivity Cl^- ions (76). After the end point, addition of HCl leads to an increase in conductivity due to the high conductivity of H^+ ions of HCl .

Application : Replacement or displacement titrations are applied in the determination of alkaloids because of their poor water solubility and weakly basic character.

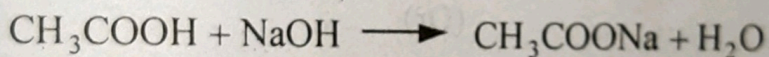
(b) Salt of Weak Acid and Strong Base Vs. Strong Acid :

Example : CH_3COONa vs HCl

Reaction between CH_3COONa and HCl is as follows :

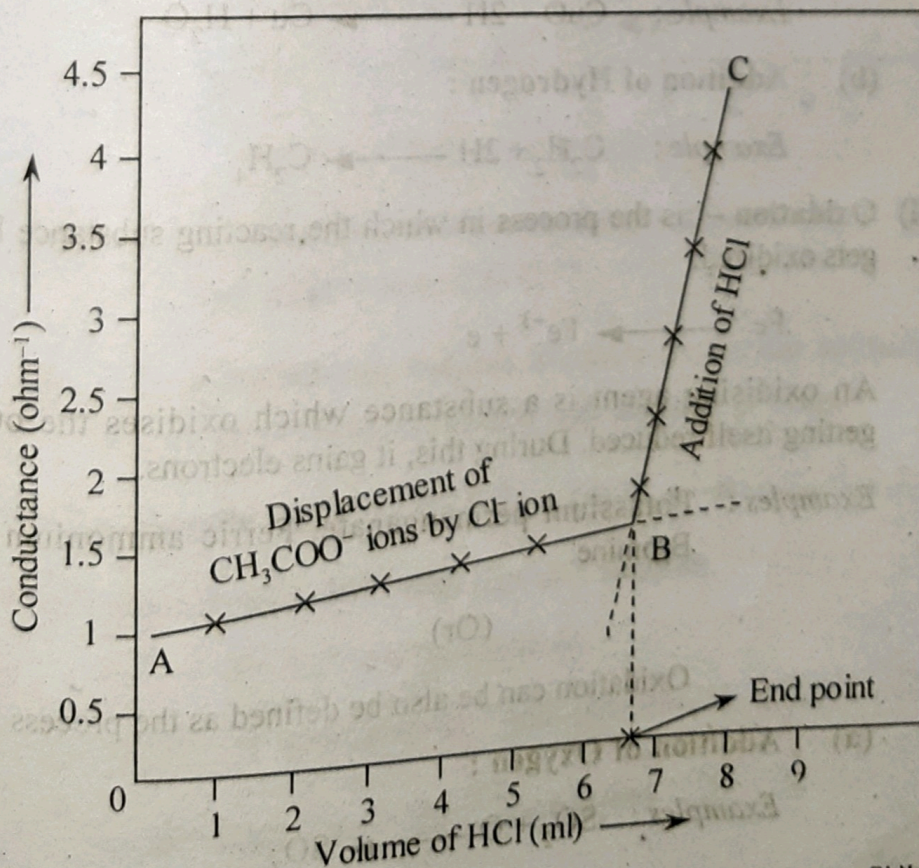


Sodium acetate (CH_3COONa) is the salt of a weak acid (CH_3COOH) and a strong base (NaOH)



AB : Slight increase in conductance towards the end point due to Cl^- ions.

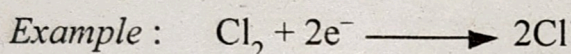
BC : Sharp increase in conductance due to high conductivity H^+ ions.



At point A, the conductivity is low because, sodium acetate (CH_3COONa) is a salt of weak acid and does not dissociate effectively. On addition of a strong acid (HCl), there is a slight increase in the conductance (Curve AB) due to the replacement of low conductivity CH_3COO^- ions (41) by high conductivity Cl^- ions (76). Further addition of HCl causes a sharp increase in conductance (Curve BC) due to high conductivity H^+ ions.

3. **Redox Titrations** : Redox titrations are based on oxidation-reduction reaction between the titrant and the analyte. In these titrations, both oxidation and reduction occur simultaneously. One substance becomes reduced in the process of oxidizing the other.

- (i) **Reduction** – is defined as the process in which the reacting substance gains electrons and get reduced.



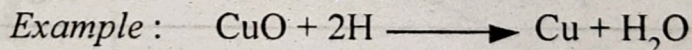
A reducing agent is a substance which reduces the other substance by getting itself oxidized. In doing so, it loses electrons.

Examples of reducing agents are : Oxalic acid, Ferrous ammonium sulphate, Sodium thiosulphate

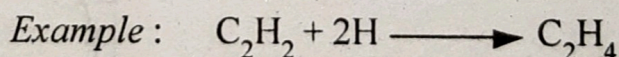
(Or)

Alternately, reduction can be also defined as the process which involves :

- (a) **Removal of Oxygen** :



- (b) **Addition of Hydrogen** :



- (ii) **Oxidation** – is the process in which the reacting substance loses electrons and gets oxidized.



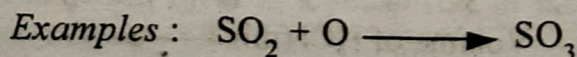
An oxidising agent is a substance which oxidises the other substance by getting itself reduced. During this, it gains electrons.

Examples : Potassium permanganate, Ferric ammonium sulphate, Iodine, Bromine.

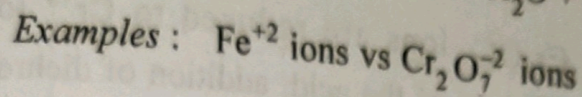
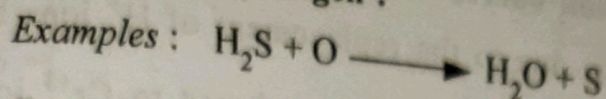
(Or)

Oxidation can be also be defined as the process which involves :

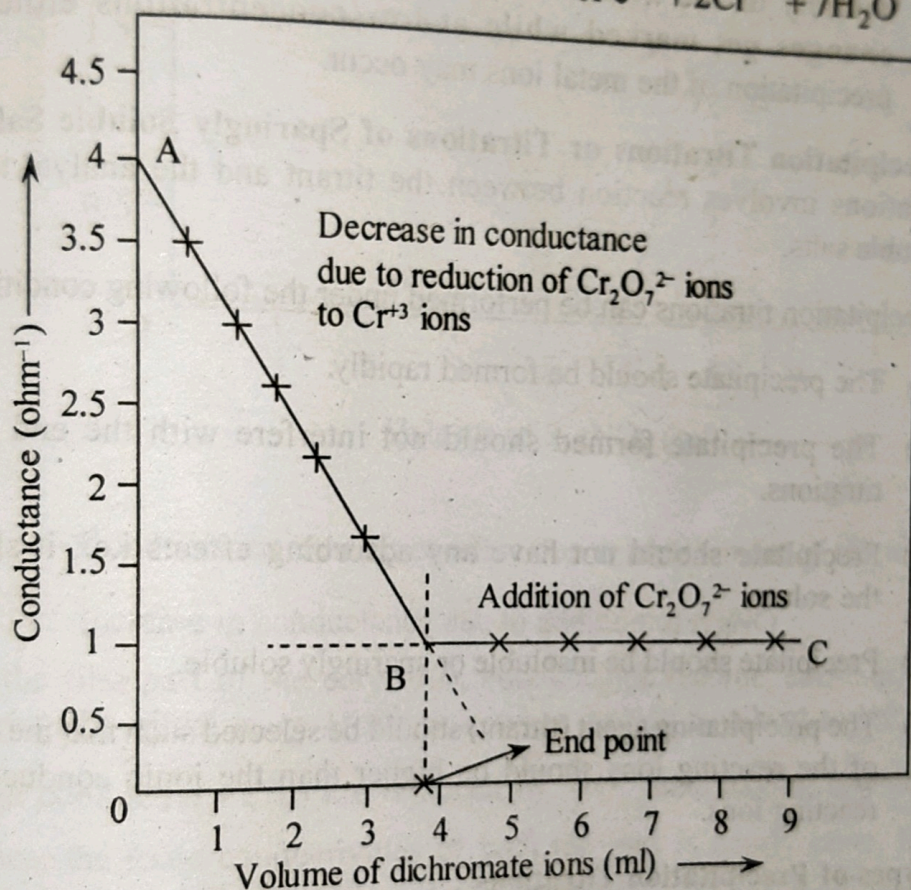
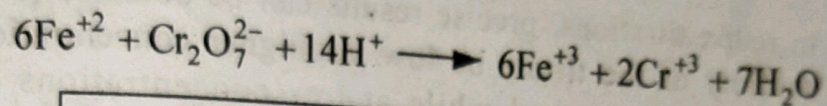
- (a) **Addition of Oxygen** :



(b) Removal of Hydrogen :

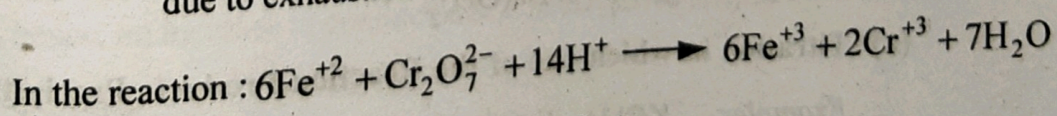


The redox reaction between ferrous (Fe^{+2}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ions in acidic medium is represented as :

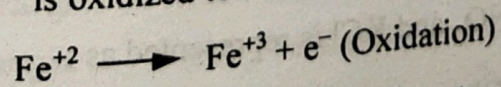


AB : Decrease in conductance due to replacement of H^+ ions by $\text{Cr}_2\text{O}_7^{2-}$ ions to get reduced to Cr^{+3} .

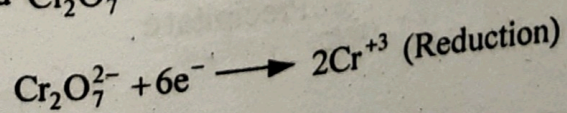
BC : Conductance remains constant on further addition of $\text{Cr}_2\text{O}_7^{2-}$ ions due to exhaustion of the high mobility H^+ ions.



Fe^{+2} is oxidized to Fe^{+3} with loss of 1 electron.



and $\text{Cr}_2\text{O}_7^{2-}$ is reduced to Cr^{+3} with gain of 6 electrons.



In the titration curve, the early portion (AB) shows a sharp decrease in concentration due to the replacement of H^+ ions by $Cr_2O_7^{2-}$ ions. During this process, $Cr_2O_7^{2-}$ ions are reduced to Cr^{+3} ions. After the complete replacement of H^+ ions of the acid, addition of dichromate ions does not show any change in the conductance. Infact, the conductance reaches a constant value (BC) due to exhaustion of all the H^+ ions.

In redox titrations, precise results can be obtained provided that the initial acidity of the titrate be low. At higher concentrations, the conductance changes get marked while at low concentrations either hydrolysis or precipitation of the metal ions may occur.

4. **Precipitation Titrations or Titrations of Sparingly Soluble Salts :** Precipitation titrations involves reaction between the titrant and the analyte to form sparingly soluble salts.

Precipitation titrations can be performed under the following conditions :

- The precipitate should be formed rapidly.
- The precipitate formed should not interfere with the end point during the titrations.
- Precipitate should not have any adsorbing effects i.e., it should not absorb the solute.
- Precipitate should be insoluble or sparingly soluble.
- The precipitating agent (titrant) should be selected such that the ionic conductance of the reacting ions should be higher than the ionic conductance of the non-reacting ions.

Types of Precipitation Titrations :

- Titration in which one of the reaction product precipitates

Example : KCl Vs. $AgNO_3$

- Titrations in which both the reaction products precipitate.

Example : $MgSO_4$ Vs. $Ba(OH)_2$

- Titration in which one of the Reaction Products Precipitates :**

Example : KCl Vs. $AgNO_3$

Reaction between $AgNO_3$ and KCl is represented as :

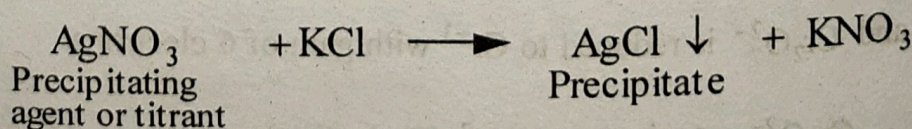
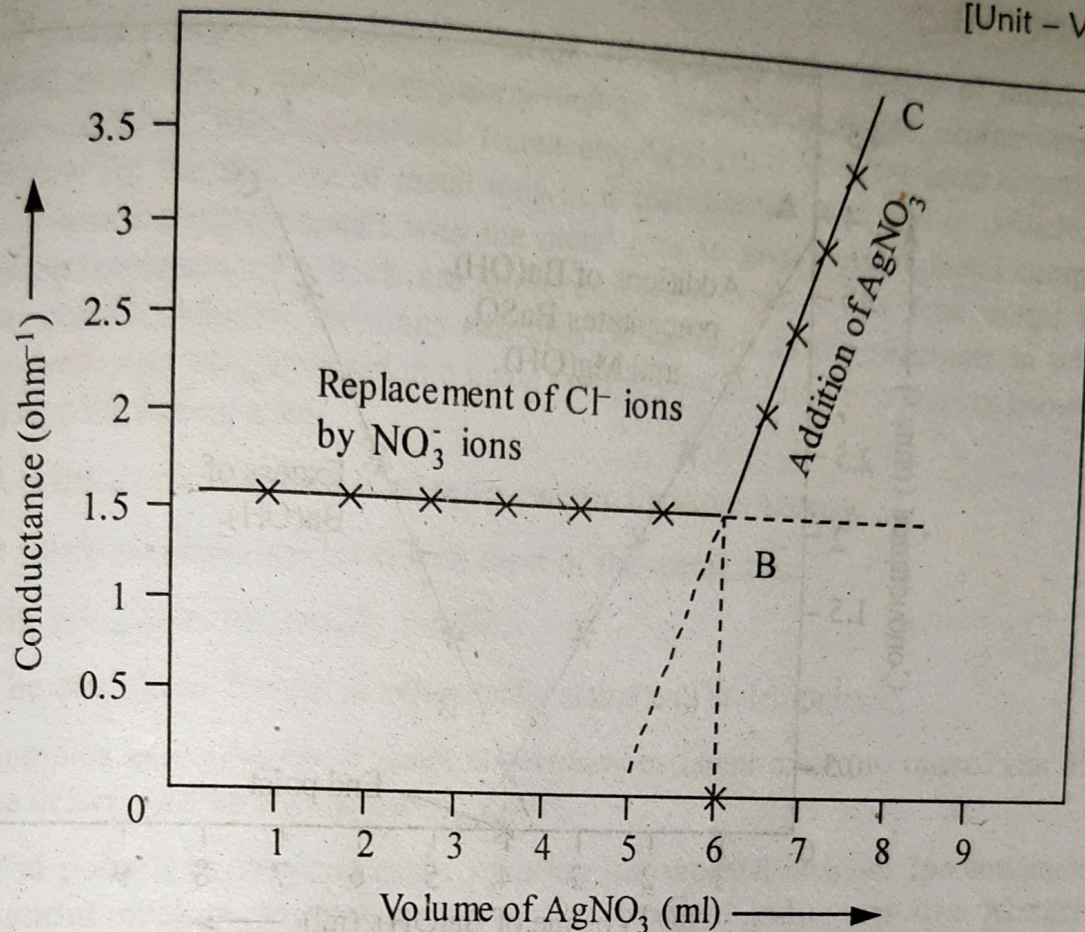


Figure :
Titration
Curve of
KCl Vs. AgNO_3



AB : Conductance remains constant due to replacement of Cl^- ions by NO_3^-

BC : Increase in conductance due to addition of AgNO_3

In the first part of the curve AB, conductance remains constant. This is because, during the initial stage of titration, when AgNO_3 is added to KCl, the Cl^- ions of high conductivity (76) are replaced by NO_3^- ions having low conductivity (71).

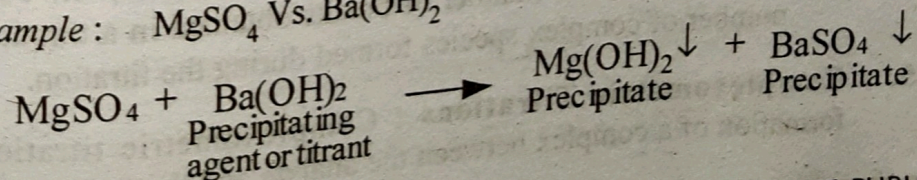
Since, the ionic conductivities of both the ions is nearly same, their contribution towards the conductance is not much apparent. Further addition of AgNO_3 leads to precipitation of Ag^+ and Cl^- ions as AgCl . This is represented as the end point B where all the free Cl^- ions are utilized by the Ag^+ ions to form the precipitate.

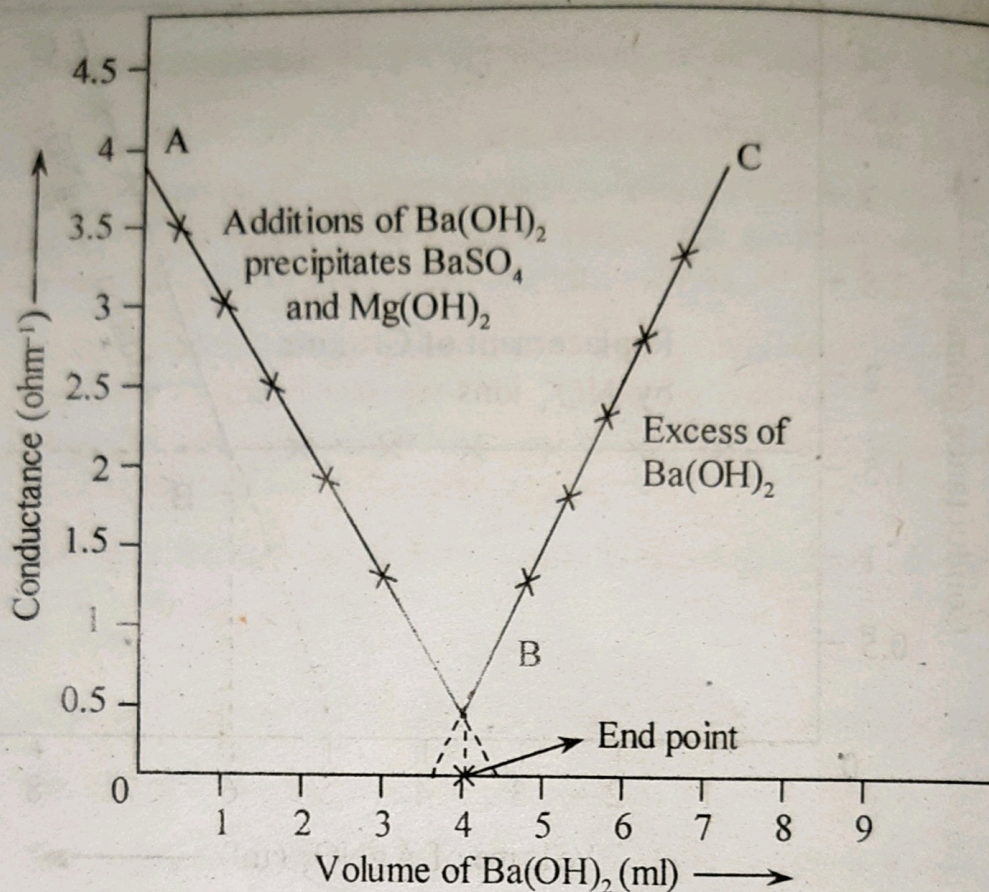
At this point, the solution contains K^+ and NO_3^- ions.

After the end point, addition of further AgNO_3 causes replacement of K^+ ions by Ag^+ ions, hence, an increase in conductance is seen (curve BC) due to excess concentration of NO_3^- ions.

(b) Titrations in which both the Reaction Products Precipitates.

Example : MgSO_4 Vs. Ba(OH)_2





AB: Decrease in conductance due to precipitation of Mg(OH)_2 and BaSO_4

BC: Increase in conductance due to excess of free Ba(OH)_2

The reaction between MgSO_4 and Ba(OH)_2 is represented as follows :

In this type of titration, both the products of reaction i.e., Mg(OH)_2 and BaSO_4 are sparingly soluble precipitates.

Addition of Ba(OH)_2 to MgSO_4 gives a downward sloping curve AB due to the replacement of SO_4^{2-} ion by $(\text{OH})_2^-$ ions and Mg^{+2} ions by Ba^{+2} ions to form BaSO_4 and Mg(OH)_2 simultaneously. This leads to decrease in conductance until all the SO_4^{2-} ions are consumed. After the end point, addition of further amounts of Ba(OH)_2 leads to an increase in conductance (curve BC) due to excess of Ba(OH)_2 .

In a complexometric titration curve, absence of complex species is depicted by the linear portion of the curve, whereas any deviations from the linearity shows the formation of complex species which contribute towards the conductance. The number of breaks obtained in a titration curve gives the total number of complex species formed during the titration.

5. **Complexometric Titrations** : Complexometric titrations are based on the formation of a complex between the analyte and the titrant.

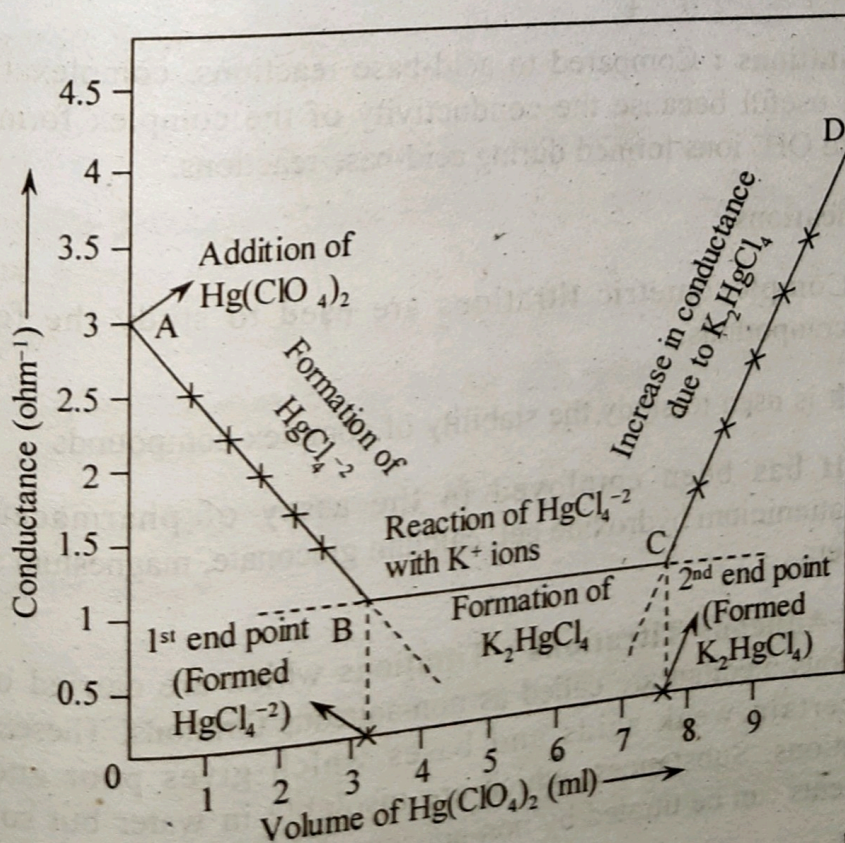
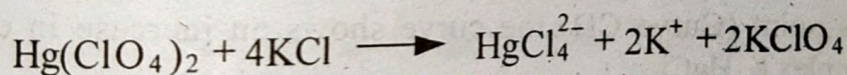
During complexometric titrations, addition of titrant to the solution of metal ions (analyte) produces a metal complex which is chemically stable, stoichiometric and undissociated. Ethylenediamine Tetraacetic Acid (EDTA) is the most commonly used titrant for the titration of metal ions. It is also known as ligand or complexing agent. It forms covalent bonds with the metal ions to give a stable metal complex, the characteristics of which are different from that of the free metal ion. Hence, complexometric titrations can also be defined as the reactions in which simple metal ions are converted into metal complex by addition of a reagent known as ligand or complexing agent.

EDTA is the agent of choice in complexometric titrations because :

- It forms soluble complexes with most of the metal ions.
- The complexes are rapidly formed.
- The complexes formed are chemically stable and stoichiometric.
- Samples present even in small concentrations (semi macro to micro) can also be determined by titrations using EDTA.
- End point is determined easily by using instrumental methods (potentiometry, conductometry, amperometry) or by chemical indicators like Alizarin, Xylenol orange, Erichrome black T, Mordant black II.

Example : KCl Vs. $\text{Hg}(\text{ClO}_4)_2$

Reaction between $\text{Hg}(\text{ClO}_4)_2$ and KCl is represented as follows :

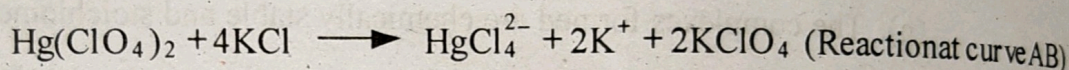


AB : Decrease in conductance due to formation of low conductivity HgCl_4^{2-} ions.

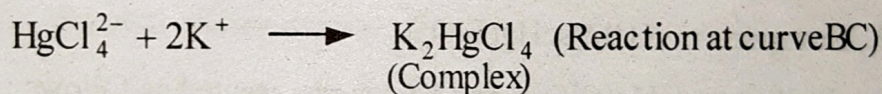
BC : Conductance remains constant due to reaction between K^+ and HgCl_4^{2-} ions to form K_2HgCl_4 .

CD : Increase in conductance due to K_2HgCl_4 complex.

The titration curve of $\text{Hg}(\text{ClO}_4)_2$ and KCl shows two end points (at B and C). Initially at point A, the conductivity of KCl is high due to the high ionic conductance of Cl^- ions (76) and K^+ ions (74). When $\text{Hg}(\text{ClO}_4)_2$ is added to KCl , the conductance decreases as shown by the curve AB due to the formation of HgCl_4^{2-} ions which have low ionic conductivity (53).



When $\text{Hg}(\text{ClO}_4)_2$ is further added, it does not influence the conductance (linear portion BC) until the HgCl_4^{2-} ions react completely with the free K^+ ions to produce a complex K_2HgCl_4 .



At this point (Curve CD) the curve shows an increase in conductance due to the complex K_2HgCl_4 .

Limitations : Compared to acid-base reactions, complexation reactions are not much useful because the conductivity of the complex formed is not that of the H^+ and OH^- ions formed during acid-base reactions.

Applications :

- Complexometric titrations are used to study the formulae of complex compounds.
- It is used to study the stability of complex compounds.
- It has been employed in the assay of pharmaceutical products like aluminium hydroxide gel, calcium gluconate, magnesium sulphate, zinc sulphate etc..

- Non-Aqueous Titrations :** Titrations which are carried out in the absence of aqueous medium are called as non-aqueous titrations. These are used for the assay of certain weak acids and bases which gives poor end points in aqueous solutions. Substances, which are insoluble in water but soluble in non-aqueous solvents can be titrated by non-aqueous titrations.

Examples of Titrants used in Non-aqueous Titrations are :

- (i) **Acidic Titrants** – Perchloric acid, Fluorosulphonic acid, p-toluene sulphonic acid.
- (ii) **Basic Titrants** – Sodium methoxide, Potassium methoxide, Lithium methoxide, Tetra alkyl ammonium hydroxide.

The solvent selected for non-aqueous titrations should fulfill the following conditions :

- (i) It should be readily available and not expensive.
- (ii) It should be pure and nontoxic.
- (iii) It should be miscible with the titrant and the solute.
- (iv) It should have high dielectric constant.
- (v) It should not interfere with the end point of titration.
- (vi) It should not produce any undesirable effects by interacting with the solute or the titrant.

Types of Non-aqueous Solvents :

- (a) **Aprotic Solvents** : These solvents are chemically neutral (unreactive) in nature, i.e., they neither accept nor donate protons. Their dielectric constants are low, they do not produce ionization of the electrolyte and neither reacts with acids nor bases. These solvents are generally used for dilution of the reaction mixtures.

Examples : Carbontetrachloride, Benzene, Toluene.

- (b) **Protogenic Solvents** : These solvents are acidic in nature i.e., they donate protons to enhance the strength of the weak bases.

Examples : Sulphuric acid, Hydrochloric acid.

- (c) **Protophilic Solvents** : These solvents are basic in nature, they enhance the acidity of weak acids.

Examples : Ammonia, Pyridine, Ethylene diamine

- (d) **Amphiprotic Solvents** : They act as both acids and bases, i.e, they accept as well as donate protons.

Examples : Glacial acetic acid, Dioxan.

Types of Nonaqueous Titrations :

- (a) **Weak Acid Vs. Lithium Methoxide**

Example : Barbituric Acid Vs. Lithium Methoxide

- (b) **Weak Base Vs. Perchloric Acid**

Example : Quinine sulphate Vs. perchloric acid, Adrenaline Vs. perchloric acid.

- (a) **Weak Acid Vs. Lithium Methoxide :** Weakly acidic substances are titrated against basic titrants like alkali methoxides (Na, K, Li, Methoxides). Protophilic solvents like pyridine, ethylene diamine, dimethyl formamide etc., are used to dissolve the analyte as well as to enhance the acidity of weak acids.

Example : Titration of barbituric acid with lithium methoxide.

- (b) **Weak Base Vs. Perchloric Acid :** Weakly basic substances are titrated against acidic titrants like perchloric acid in the presence of amphiprotic solvents like glacial acetic acid and dioxan. Solution of perchloric acid in glacial acetic acid is an official titrant indicated by Indian Pharmacopoeia.

Examples : Titration of quinine sulphate with perchloric acid, Adrenaline with perchloric acid.

Applications :

1. Non-aqueous titrations are used for the analysis of weak acids like phenols and weak bases like amines and amino acids.
2. It is applied in phytochemistry for the analysis of alkaloids.
3. A number of drugs belonging to the class of barbiturates, thiazide diuretics and sulpha drugs have been determined by non-aqueous titrations.

Examples of drugs analysed by non-aqueous titrations are adrenaline, caffeine, ephedrine, chlorpromazine, levodopa, mebendazole, etc.

Advantages of Conductometric Titrations :

1. Conductometric titrations does not require indicators for end point detection since change in conductance of the solution is measured by conductometer.
2. This method of analysis is suitable for coloured solutions. If ordinary indicators are used then satisfactory results are not obtained.
3. Since the end point is determined by graphical means, accurate results are obtained with minimum errors.
4. Conductometric titrations can be used for the analysis of weak acids, weak bases, mixture of weak and strong acids as well as turbid suspensions.
5. Titrations of weak acids against weak bases which fail to give reproducible results with chemical indicators can be successfully performed by conductometric methods.
6. In the titrations of dilute solutions, the end point of solutions is not effectively detected by potentiometric or indicator method. Hence, conductometric method is performed.
7. If the same electrodes are being used during the entire course of titrations, then determination of cell constant is not necessary.
8. In aqueous conductometric titrations, use of conductivity water is not compulsory.

9. Determination of specific conductance of the analyte (titrant) is not necessary because the conductance values shown by the conductometer are plotted against the volume of the titrant added.
10. A few measurements before and after the end point are sufficient because the conductivity depends on the concentration and mobility of the ions and the curves obtained are linear.

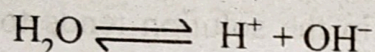
Disadvantages of Conductometric Titrations :

1. Lack of specificity of conductometric methods compared to other electrochemical methods like amperometry, potentiometry, voltametry has limited its applications.
2. Increased levels of salt concentration in the solution masks the conductivity changes. In such cases, this method does not give accurate and satisfactory results.
3. Application of conductometric titrations to redox systems is limited because, the high concentration of the hydronium ions in the solution tends to mask the changes in conductance of the solution.

6.2.5 Applications of Conductometry

1. Conductometric methods are employed to check water pollution in rivers and lakes.
2. It is used to determine the alkalinity of fresh water.
3. Conductometry is employed to determine the salinity of sea water in oceanography.
4. Deuterium oxide (D_2O) content in water - Deuterium mixture is determined by conductivity measurements.
5. Conductometry is applied to study the conformational changes of synthetic polyelectrolytes in aqueous solutions.
6. An important application of conductometry is in the field of food microbiology for the quantitative and qualitative tracing of microorganisms. This is done by measuring the changes in the electrical conductances of the culture media. It deals with the determination and enumeration of enterobacteria particularly Salmonella in food.
7. Conductometry is also employed in tracing antibiotics and testing additives for their antimicrobial effects.
8. Conductometers with special electrodes are being used for the estimation of ash content in sugar juices and in the estimation of moisture content of wood for pulping purposes in paper industry.
9. Conductometry is applied in the study of reaction kinetics before, during and at the end of a chemical reaction.

10. Quantitative analysis of substances like acids, bases and electrolytes can be performed by conductometry upto a concentration of 10% by weight. This is seen due to dependence of conductivity of a solution on the amount of solute present in it.
11. Solubility of sparingly soluble salts like AgCl , BaSO_4 , PbS can be determined by conductometry.
12. The purity of distilled and deionized water (used for practical purposes) can be determined by conductometry. The value of purity of water is found to be $5 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$.
13. Ionic equilibrium during chemical reactions can be determined by conductometry by measuring the changes in ionic conductance of a solution.
14. Ionic product of water (product of the concentrations of H^+ and OH^- ions) can be determined by conductometry.



$$\text{Ionization constant of water } K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

Where,

$$K_w = [\text{H}^+][\text{OH}^-]$$

$$K_w = \text{Ionic Product of Water}$$

$$K_w = 1 \times 10^{-14} \text{ at } 25^\circ \text{C}$$

15. Conductometry is employed in the determination of basicity (Defined as the number of carboxylic acid groups present in an acid) of organic acids. It is calculated by Ostwald's relation :

$$B = \frac{\wedge_{1024} - \wedge_{32}}{10.8}$$

where,

$$B = \text{Basicity of the acid}$$

$$\wedge_{1024} \text{ and } \wedge_{32} = \text{Equivalent conductance of the salt at } 25^\circ \text{C and dilution of } 1024 \text{ lt and } 32 \text{ lt/gm.}$$

16. The degree of dissociation of weak electrolytes is determined by using the formula :

$$\alpha = \frac{\wedge_v}{\wedge_\infty}$$

where,

$\wedge_v$ - Equivalent conductance at given dilution V .

$\wedge_\infty$ - Equivalent conductance at infinite dilution ∞ .

$\wedge_v$ is determined experimentally, while the value of $\wedge_\infty$ is obtained from the literature where they are prerecorded.

17. Degree of hydrolysis of a weak acid or base is calculated by conductometry using the formula

$$K_H = \frac{\alpha^2 C}{1 - \alpha}$$

where,

α - Degree of dissociation

C - Concentration of the acid or base

18. Estimation of nitrogen in organic substances can be carried out by conductometric measurements.
19. Determination of atmospheric SO_2 .
20. Quantitative estimation of Vanillin in Vanilla Essence
21. Conductometric Titrations

Conductometry is applied in the titrations of redox systems, complex compounds, sparingly soluble salts, acids and bases, precipitating agents etc.,