

Conductometry

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Conductometry

Conductometry is an **electroanalytical technique** which deals with the **measurement of electrical conductance of solutions** containing electrolytes (acids, bases and salts in water). These solutions conduct electric current due to the movement of ions towards oppositely charged electrodes. Solutions of electrolytes also obey **Ohm's Law** like metallic conductors ($R=E/I$).

Conductance: It is the reciprocal of resistance. *It is the ease of the flow of current through a solution of electrolyte*

Unit: Ohm^{-1} or Mho or Seimen

Conductometry

Conductivity is a parameter used to measure the ionic concentration and activity of a solution.

The more salt, acid or alkali in a solution, the greater its conductivity

The unit of conductivity is **S/m or S/cm**.

The scale for aqueous solutions begins with pure water at a conductivity of $0.05 \mu\text{S/cm}$ (25 °C) and naturally occurring waters such as drinking water or surface water have a conductivity in the range 100 - 1000 $\mu\text{S/cm}$.

Conductivity cells are specially used for the measurements of the conductance

Basic Definitions of Conductometry

Conductance: It is the reciprocal of resistance. **Unit: Ohm^{-1} or Mho or Siemen**

Specific Conductance: Specific conductance of a solution can be defined as the conductance of solution between two parallel electrodes which have cross sectional area 1 cm^2 and which are kept 1 cm apart. **Unit: Mho-cm^{-1}**

Equivalent Conductance: It is defined as the conductance of a solution containing one gram equivalent of an electrolyte at any particular concentration, when placed between two electrodes 1 cm apart. **Unit: $\text{Mho-cm}^2\text{-gm-equiv.}^{-1}$**

Molar Conductance: It is defined as the conductance of a solution containing one mole of an electrolyte at any particular concentration, when placed between two electrodes 1 cm apart.

Unit: $\text{Mho-cm}^2 \text{-gmole}^{-1}$

Cell Constant = $\frac{\text{Specific Conductance}}{\text{Observed Conductance}}$

Basic Definitions of Conductometry

Conductance: It is the reciprocal of resistance. **Unit: Ohm⁻¹ or Mho or Siemen**

Specific Conductance: Specific conductance of a solution can be defined as the conductance of solution between two parallel electrodes which have cross sectional area 1 cm² and which are kept 1 cm apart. **Unit: Mho-cm⁻¹**

Equivalent Conductance: It is defined as the conductance of a solution containing **one gram equivalent of an electrolyte** at any particular concentration, when placed between two electrodes 1 cm apart. **Unit: Mho-cm²-gm-equiv.⁻¹**

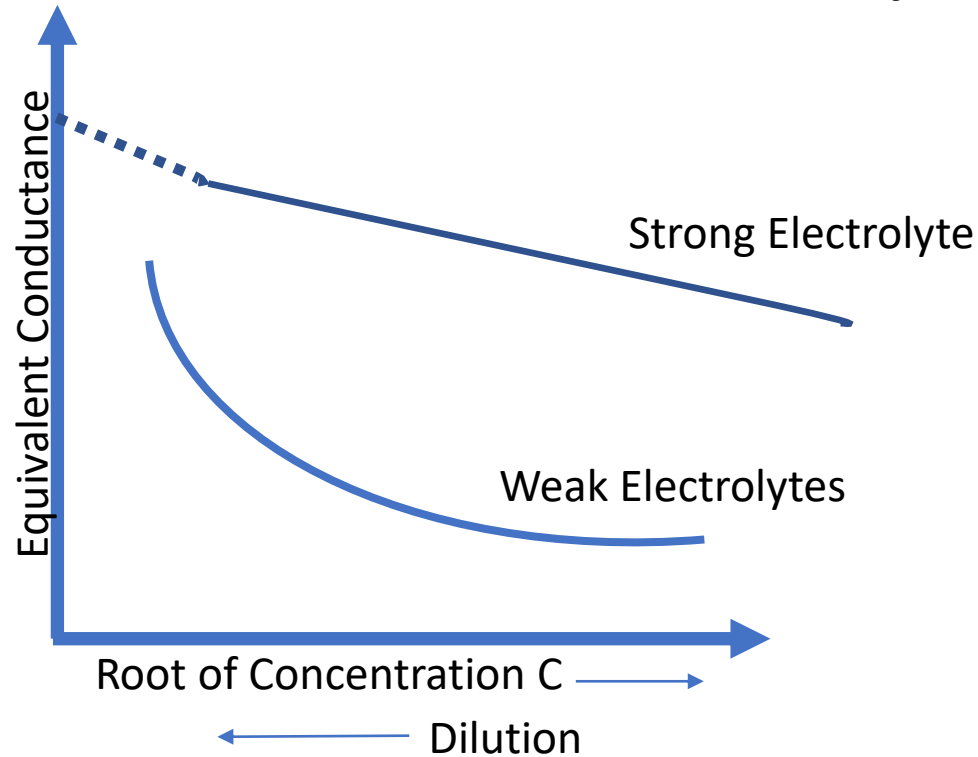
Molar Conductance: It is defined as the conductance of a solution containing **one mole** of an electrolyte at any particular concentration, when placed between two electrodes 1 cm apart.

Unit: Mho-cm² -gmole⁻¹

Cell Constant= $\frac{\text{Specific Conductance}}{\text{Observed Conductance}}$

Basic Definitions of Conductometry

Effect of dilution on Conductivity:



- Equivalent or Molar Conductance increases with increase in dilution.
- Increased Dissociation of the electrolyte on dilution while for strong electrolyte increase is due to the increased mobility of ions.
- Specific conductance of the solution decreases on dilution (due to decrease in the concentration of ions per unit volume)

Basic Definitions of Conductometry

Effect of Temperature:

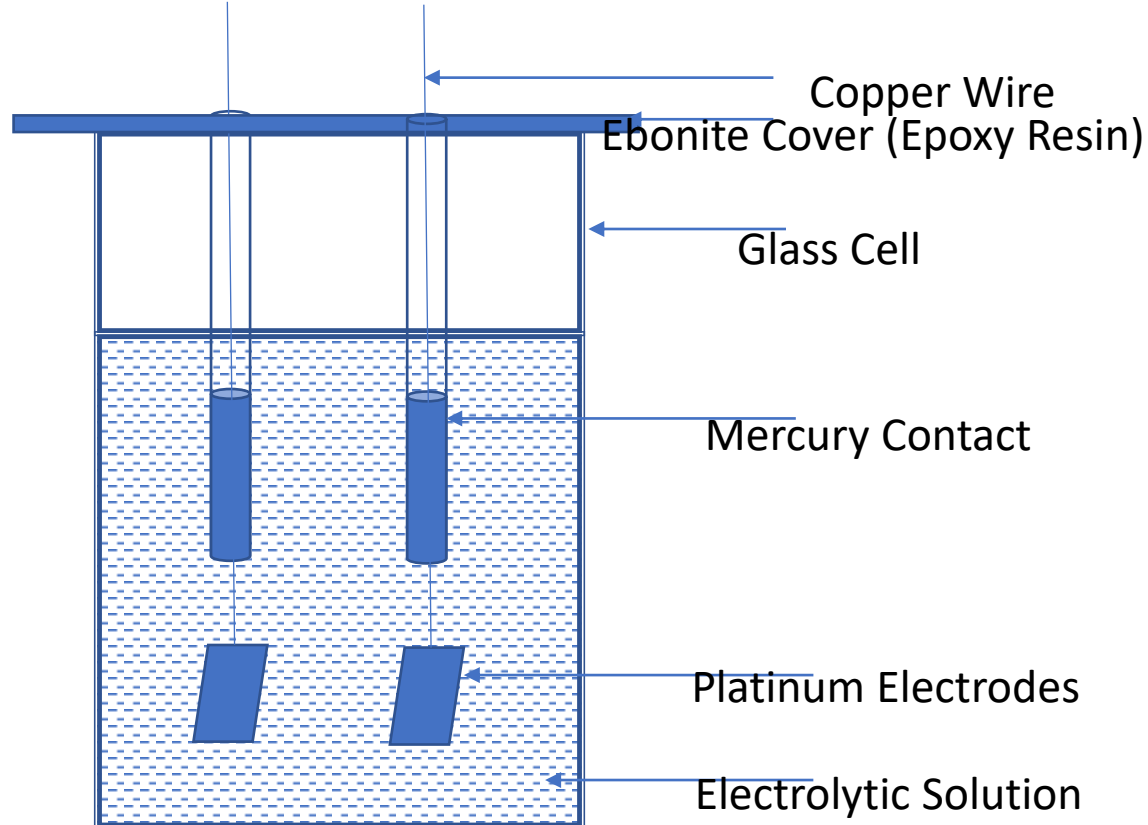
- **Conductance increases** with increase in temperature due to increase in velocity of ions, decrease in viscosity of the medium and decrease in the interaction between the ions

Factors influencing Conductance:

- **Number of free ions:** More the no of free ions, greater is the conductance
- **Charge on the free ions:** Greater the charge, greater is the conductance
- **Mobility of ions:** Greater the mobility, greater is the conductance

Conductivity Cell

- Conductivity Cells are of various shapes and sizes
- The simplest kind of measuring cell used consists of two similar electrodes.
- They are made up of pyrex glass (or some other resistant glass) which is fitted with a pair of Platinum electrodes. These electrodes are platinum plates fused into the glass tubes. The tubes are firmly supported by an ebonite cover.



Conductivity Cell

- The cover along with the platinum electrodes is fitted into the pyrex glass vessel so that the distance between the electrodes may not change.
- An alternating voltage applied to one of the conductivity electrodes causes the ions in the solution to migrate towards the electrodes.
- The more ions in the solution, the greater the current which flows between the conductivity electrodes.

Conductivity Cell

Conductivity cell measurements: Conductivity is measured by using a conductivity cell to make a measurement of the electrical resistance.

- The conductivity meter measures the current produced by the conductivity cell and uses Ohm's law to calculate first the conductance of the solution and then - by taking the cell data into account - the conductivity.

Conductometric Titrations

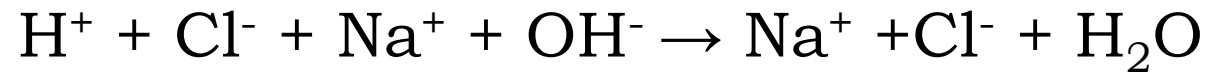
- It is a standard technique used in conductometry which has notable application in **analytical chemistry**.
- In this method we determine the point where reaction is completed (equivalence point) with the help of a conductometer that measures the changes in conductance of solution produced by the ions in the solution.
- At equivalence point we measure the volume of base used to neutralize the acid ions completely in the solution. Putting these values in formula we can get the strength of acid

Conductometric Titrations

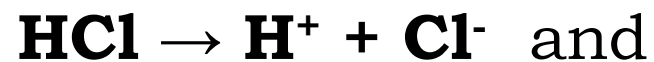
- The principle of conductometric titration is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that conductivity of the solution varies during the course of titration.
- The equivalence point may be located graphically by plotting the change in conductance as a function of the volume of titrant added.

Strong Acid with a Strong Base Conductometric Titration

Consider titration of **HCl against NaOH** wherein Strong base is filled in burette and acid is taken in a beaker

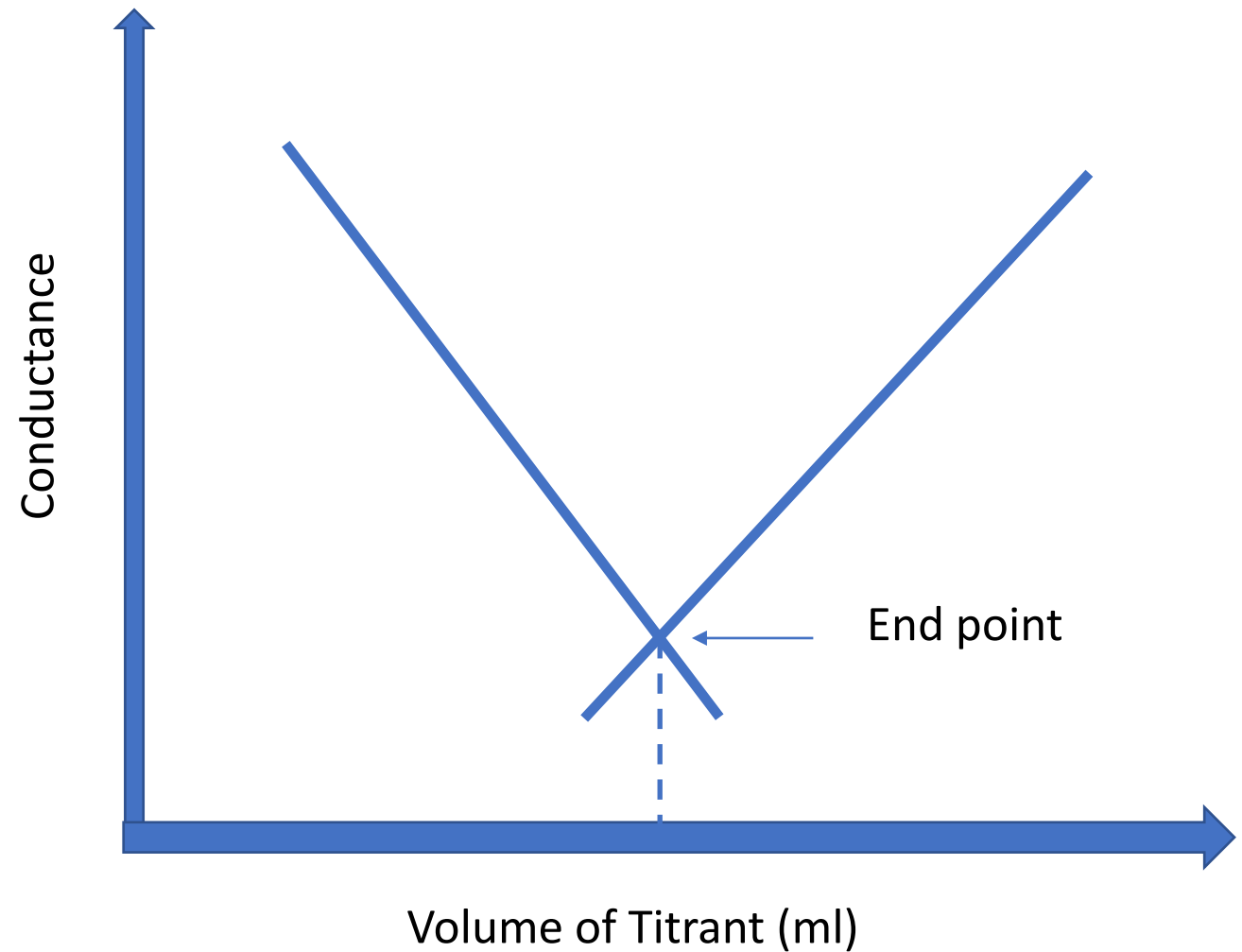


1. Initially, before titration the conductance is high which is due to



mobility of **H⁺** is 350 and that of **Cl⁻** ion is 73.

Conductometric Titration of Strong Acid vs. a Strong Base



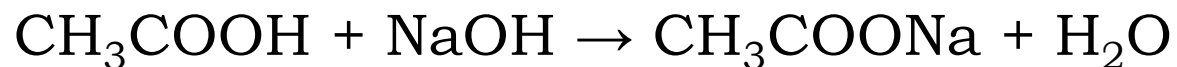
Strong Acid with a Strong Base Conductometric Titration

- 2. Before Equivalence Point:** Upon addition of **NaOH**, the **H** ion reacts with **OH** ion to form the very weakly ionized water molecule. This means that the **H⁺** ion is removed from the medium and replaced by **Na⁺** ion which has a mobility of 43; thus, a continuous abrupt decrease in conductance occurs during the titration till the end point.
- 3. After Equivalence Point:** Beyond the end point there is **excess Na⁺** and **OH⁻** ions with 43 and 198 mobility due to continuous addition of **NaOH**. So there is continuous increase in conductance and the curve will have a V shape.
- 4.** The equivalence point (end point) is the intersection of these two lines which is a minimum of the curve.

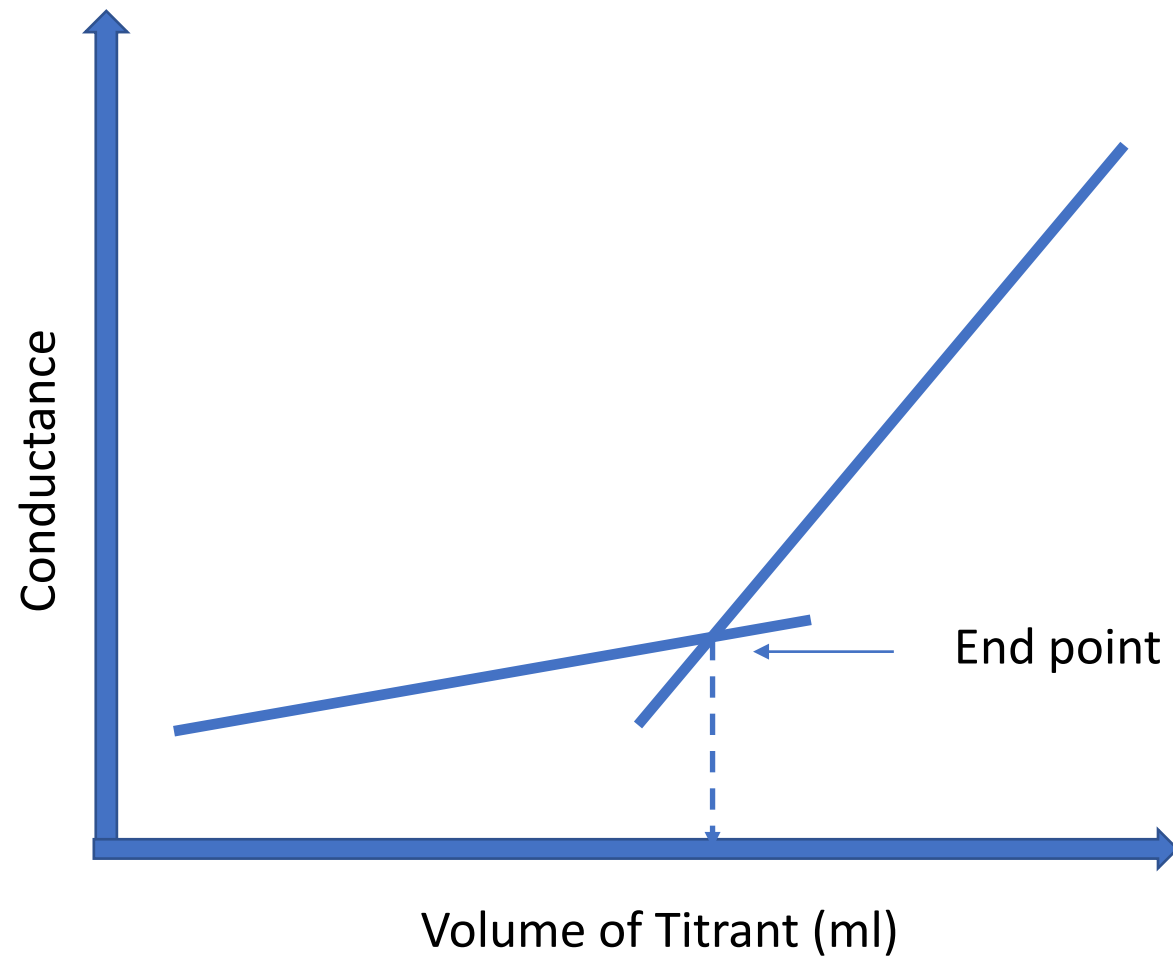
Weak Acid with a Strong Base Conductometric Titration

Consider titration of **CH₃COOH** against **NaOH** wherein Strong base is filled in burette and weak acid is taken in a beaker

Chemical reaction:



1. Initially, before titration the conductance is low which is due to weak acid.



Conductometric Titration of Weak Acid vs. a Strong Base

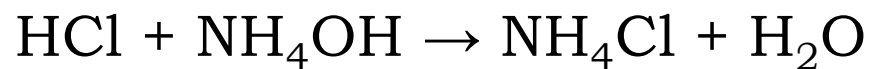
Weak Acid with a Strong Base Conductometric Titration

- 2. Before Equivalence Point:** First conductance decreases on addition of strong base owing to the formation of the salt which suppresses the ionization of weak acid. Mostly this decrease is not observed unless one adds very small volumes of NaOH. As more of NaOH is added, highly ionized salt, sodium acetate is formed thereby increasing the conductance. Conductance increase occurs during the titration till the end point.
- 3. After Equivalence Point:** Beyond the end point there is **excess Na⁺** and **OH⁻** ions with 43 and 198 mobility due to continuous addition of **NaOH**, So there is continuous increase in conductance.
- 4. Equivalence point** (end point) is the intersection of this two lines.

Strong Acid with a Weak Base Conductometric Titration

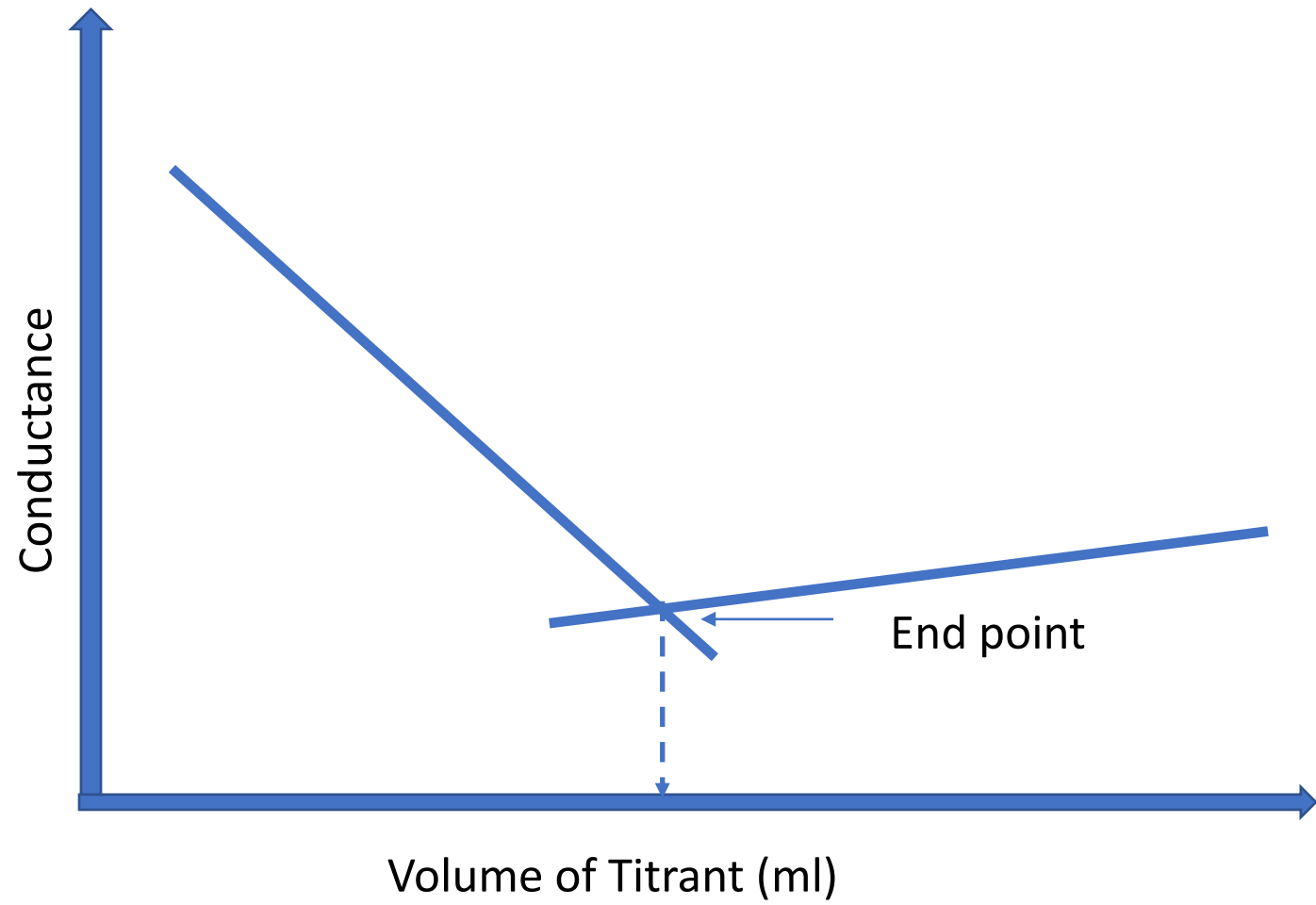
Consider titration of **HCl** against **NH₄OH** wherein weak base is filled in burette and acid is taken in a beaker

Chemical reaction:



1. Initially, before titration the conductance is high which is due to **HCl** \rightarrow **H⁺** + **Cl⁻** and high mobility of **H⁺**.

Conductometric Titration of Strong Acid vs. a Weak Base



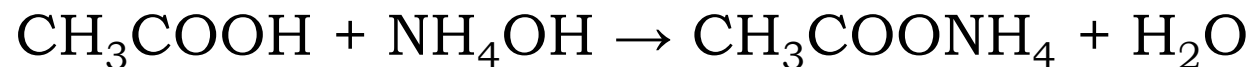
Strong Acid with a Weak Base Conductometric Titration

- 2. Before Equivalence Point:** Upon addition of NH_4OH , the conductance first decreases due to the replacement of H^+ ions. It keeps on decreasing upto the equivalence point.
- 3. After Equivalence Point:** Beyond the end point i.e. after the whole of acid is neutralised, the conductance remains almost constant because the weakly ionised excess base do not produce appreciable change in conductance.
- 4.** The equivalence point (end point) is the intersection of this two lines.

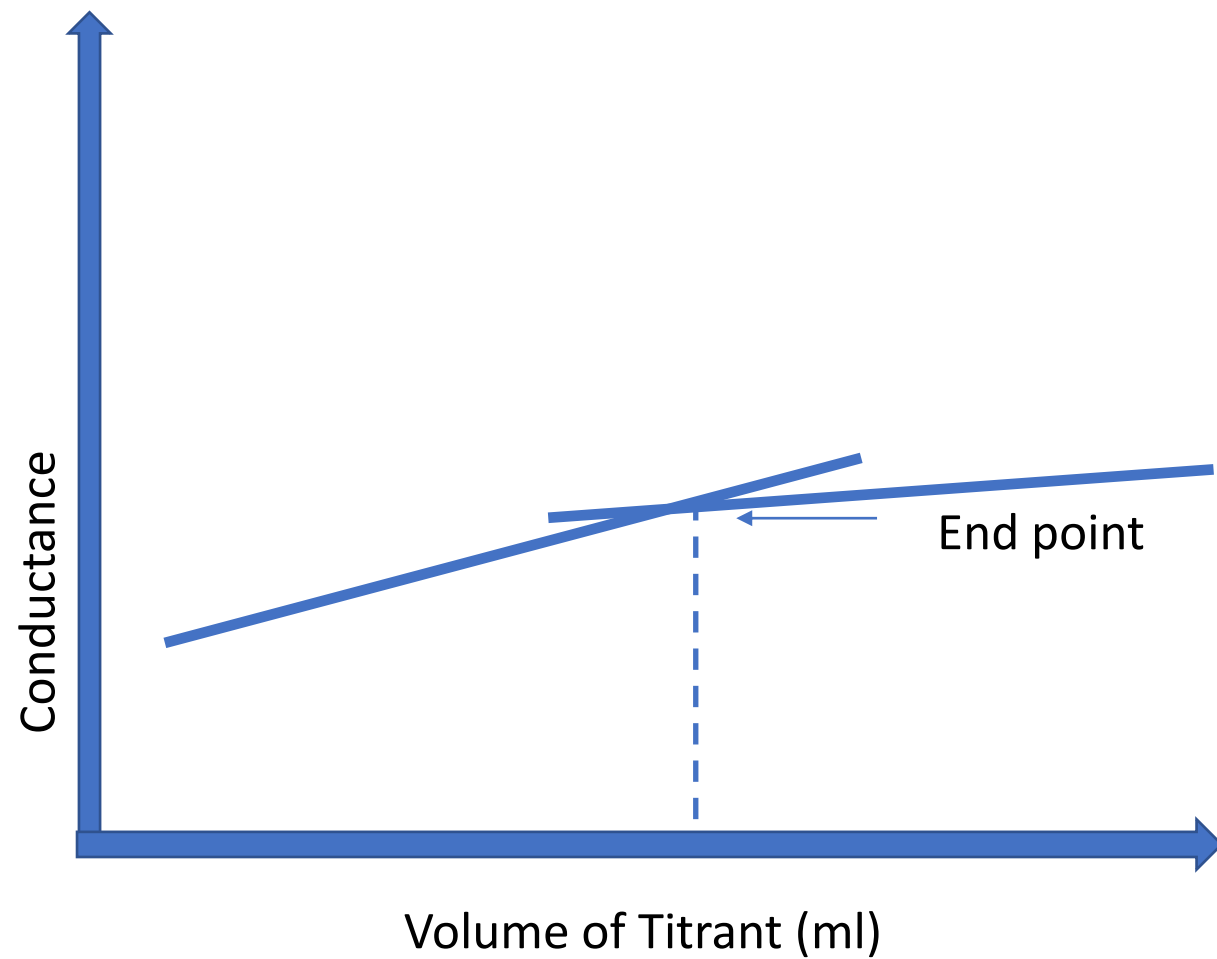
Weak Acid with a Weak Base Conductometric Titration

Consider titration of CH_3COOH and NH_4OH , wherein weak base is filled in burette and weak acid is taken in a beaker

Chemical reaction:



1. Initially, before titration the conductance is low which is due to weak acid.



Conductometric Titration of Weak Acid vs. a Weak Base

Weak Acid with a Weak Base Conductometric Titration

2. **Before Equivalence Point:** First conductance decreases on addition of weak base due to the replacement of H^+ ions. But it soon begins to increase due to the salt formation. Conductance increase occurs during the titration till the end point.
3. **After Equivalence Point:** After the whole of acid is neutralised, the conductance remains almost constant because the weakly ionised excess base do not produce appreciable change in conductance.
4. The **equivalence point** (end point) is the intersection of this two lines

Advantages of Conductometric Titrations

- Employed to very dilute solutions (upto the order of 10^{-4} M solutions).
- Very accurate end points (with an error of $\pm 0.5\%$).
- Very useful for coloured solutions (colour change of indicator is not clear)
- Useful for WAWB titration, which otherwise do not give sharp end point
- Keen observation is not necessary near the end point as it is obtained graphically

Ion Selective Electrode

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Ion Selective Electrode (Membrane)

- Transducer or electroanalytical sensor that converts the **activity of a specific ion** dissolved in a solution into an **electrical potential**
- Used in conjunction with the reference electrode
- Consists of a thin membrane (selective, not specific always) which is separated by two solutions containing same type of ions of different concentrations and indented ion can only be transported
- Difference in concentration of ions results in **Boundary potential**, from which **unknown concentration** can be determined by using the known concentration of ions in the internal solution

Ion Selective Electrodes

Advantages:

- Portable
- Do not affect the test solution
- Short response time
- Wide range of concentration
- Unaffected by colour/turbidity
- Non contaminating
- Non-destructive

Limitations:

- Fouled by other solutes
- Interference by other ions
- Fragile and limited shelf life
- Electrodes respond to complexed ion activity
hence ligands must be absent/masked

Ion Selective Electrodes

Types of Ion Selective Electrodes:

Based on membranes used Ion Selective Electrodes (ISE) can be classified as:

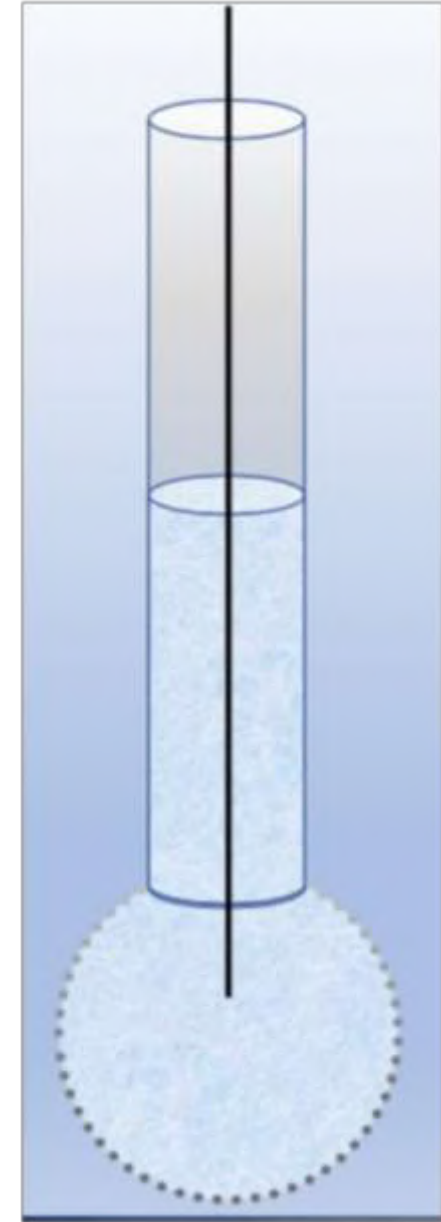
- Glass Electrode (glass membrane specifically for H^+ Ions)
- Solid State Electrode (crystalline membrane for F^- or Cl^- ions)
- Enzyme Electrode (urease on polyacrylamide gel for NH_4^+ ions)
- Gas Sensing Electrode

Indicator Electrode

- Responds rapidly to the changes in the concentration of solution under study
- Used in conjunction with the reference electrode

E.g.: **Glass electrode** (pH electrode), Quinhydrone electrode

Construction:



Glass Electrode

Construction:

Glass used in glass membrane is porous in structure and may be of silicate type or calcinogenide glass. Silicate glass is generally used for monovalent cations while calcinogenide for divalent cations detection

Silicate or Special glass composition: 72% SiO_2 , 22% Na_2O , 6% CaO

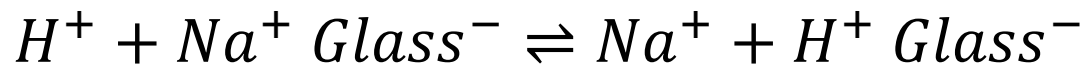
Representation of Glass Electrode: (Half Cell)

$\text{Ag, AgCl} \mid \text{HCl (0.1 M)} \mid \text{Glass membrane} \mid \text{H}^+ \text{ (Test)}$

Glass Electrode

Working of Glass Electrode:

- Glass bulb acts as a semipermeable for H^+ ions
- On immersing glass electrode in a solution, glass membrane gets hydrated
- Exchange of H^+ ions with Na^+ ions takes place on both sides of hydrated glass membrane
- Results into Boundary Potential
- An equilibrium gets established on both sides:



Glass Electrode

Working of Glass Electrode:

- Boundary Potential develops across the glass membrane as a result of a concentration difference of H^+ ions on two sides of the membrane (H^+ ions can pass through the membrane being small in size while Cl^- cannot being bigger, thus only H^+ ions concentration is measured)

pH of Solution:

- Glass electrode coupled with calomel electrode can be used to determine pH of a solution.
- Electrodes are dipped into the solution of unknown pH

Representation of cell:

$\text{Pt.} \mid \text{Hg, Hg}_2\text{Cl}_2 \mid \text{Cl}^- \text{ aq.} \parallel \text{Test Solution} \mid \text{Glass electrode}$

Glass Electrode

Advantages of Glass Electrode:

- Portable and compact
- Attains equilibrium easily
- Stable electrode, used in strong oxidizing and reducing agents
- Accurate and quick results
- Detect H^+ ions in the presence of other type of ions as well

Uses:

- Pure research,
- Control of industrial processes
- Analysis of foods and cosmetics
- Measurement of environmental indicators
- Microelectrode measurements such as cell membrane electrical potential
- Soil acidity.

Glass Electrode

pH of Solution:



EMF of cell (E_{Cell}):

$$\begin{aligned} E_{\text{Cell}} &= E_{\text{Calomel}} - E_{\text{Glass}} \\ &= 0.2422 - (E_G^0 + 0.0591\text{pH}) \end{aligned}$$

$$\text{pH} = \frac{E_{\text{Cell}} + E_G^0 - 0.2422}{0.0591}$$

where, E_G^0 - potential of glass electrode when electrode is in contact with known pH

Solid State Electrode

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Indicator Electrode

Types of Indicator Selective Electrode:

Based on membranes used Ionselective electrode (ISE) can be classified as:

- Glass Electrode
- **Solid State Electrode**
- Enzyme Electrode
- Gas Sensing Electrode

Solid State Membrane Electrodes

- Specifically for the non glass solid state sensors, conducting solid membranes used
- Specific solid membranes used for the detection of concentration of specific ions like F^- , Cl^- etc. present in the test solution
- Membranes used: Homogeneous or Heterogeneous

1) Homogeneous Solid-State Membrane Electrodes:

Membrane used consists of a single crystal or pellet

2) Heterogeneous Solid-State Membrane Electrodes:

Membrane used consists of a sparingly soluble salt in inert binding material like epoxy resin, rubber etc.

Fluoride Selective Electrode

Composition of Fluoride Selective Electrode:

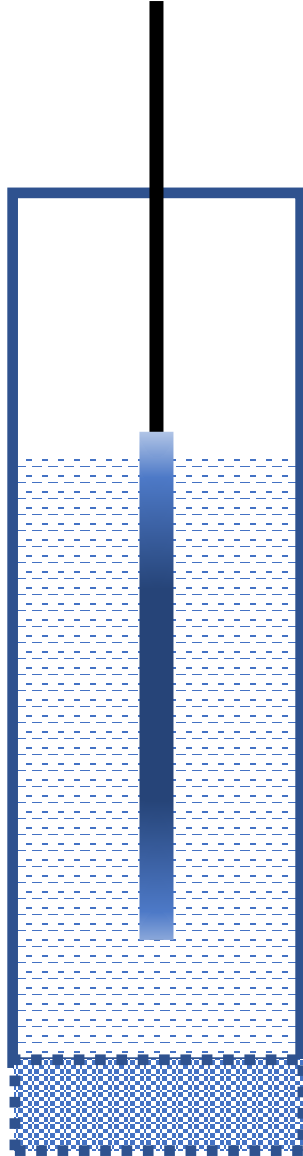
Consists of single crystal of Lanthanum trifluoride (LaF_3) doped with Europium fluoride (EuF_2) in contact with internal reference electrolyte of $\text{NaCl}+\text{NaF}$ or $\text{KCl}+\text{KF}$ with internal reference electrode made up of AgCl coated Ag wire

Representation of of Fluoride Selective Electrode: (Half Cell)



Fluoride Selective Electrode

- **Diagram:**



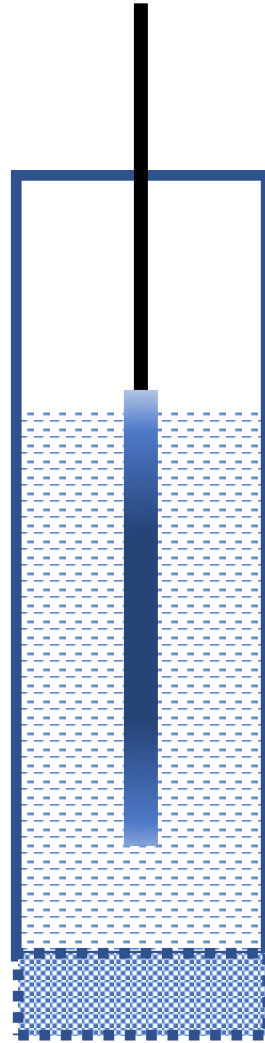
Fluoride Selective Electrode

Working of Fluoride Selective Electrode:

- Pellet or single crystal of LaF_3 doped with EuF_2 acts as a semipermeable membrane for F^- ions
- LaF_3 is 100% selective for F^- ions (except OH^- as interfaced with OH^- to produce $\text{La}(\text{OH})_3$) with the release of F^- can be eliminated by adding buffer to keep pH range 4 to 8)
- EuF_2 doped produces holes in LaF_3 crystal and F^- ions being small move through crystal, results into the conductivity of F^- ions
- Results into Boundary Potential across the membrane which depends on the difference in F^- ions concentration on either side of membrane
- Since Concentration of F^- ions in the internal reference electrolyte (solution) is fixed/known, Unknown F^- ion concentration of the test solution can be calculated from the potential developed across the membrane

Chloride Selective Electrode

Diagram

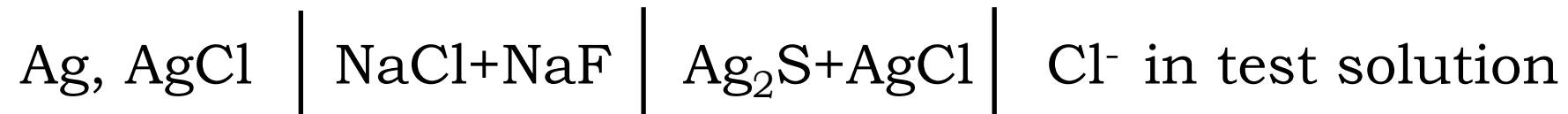


Chloride Selective Electrode

Composition of Chloride Selective Electrode:

Consists of a pellet of $\text{Ag}_2\text{S}+\text{AgCl}$ held in position with epoxy resin in contact with internal reference electrolyte of $\text{NaCl}+\text{NaF}$ with internal reference electrode made up of AgCl coated Ag wire

Representation of of Chloride Selective Electrode: (Half Cell)



Chloride Selective Electrode

Working of Chloride Selective Electrode:

- Pellet of $\text{Ag}_2\text{S} + \text{AgCl}$ acts as a semipermeable membrane for Cl^- ions
- Pellet is selective for Cl^- ions
- Boundary Potential gets developed across the membrane which depends on the difference in Cl^- ions concentration on either side of membrane
- Since Concentration of Cl^- ions in the internal reference electrolyte (solution) is fixed/known, Unknown Cl^- ion concentration of the test solution can be calculated from the potential developed across the membrane

Enzyme Based Electrode

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Indicator Electrode

Types of Indicator Selective Electrode:

Based on membranes used Indicator selective electrode

(ISE) can be classified as:

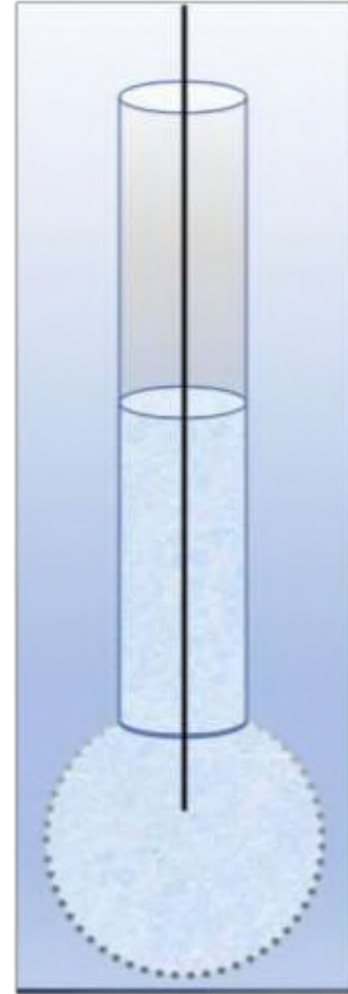
- Glass Electrode
- Solid State Electrode
- **Enzyme Based Electrode**
- Gas Sensing Electrode

Enzyme Based Membrane Electrodes

- Also called as **biochemical or bio-membrane** electrodes
- Membranes uses **enzyme** to convert **substances** in the solution into **ionic products** which are measured using ion selective electrodes
- Electrode coated with an **enzyme incorporated into a polyacrylamide gel**
- Enzyme **immobilised** at the surface of the electrode

Construction:

- Enzyme urease is incorporated into a polyacrylamide gel which is set over the bulb of a glass electrode and supported by nylon gauze for its position



Enzyme Based Membrane Electrode

Working of Ammonium Selective Electrode: For determination of Urea

- Ammonium selective electrode uses urease enzyme
- Electrode immersed into a solution containing urea ammonium ions (NH_4) are produced, gets diffused through the gel
- Boundary potential gets developed due to the difference in concentration of NH_4 on either side of the membrane
- Boundary potential formed measured with the help of reference electrode

Gas Sensing Electrode

Dr. Bhavana Vyas

Indicator Electrode

Types of Indicator Selective Electrode:

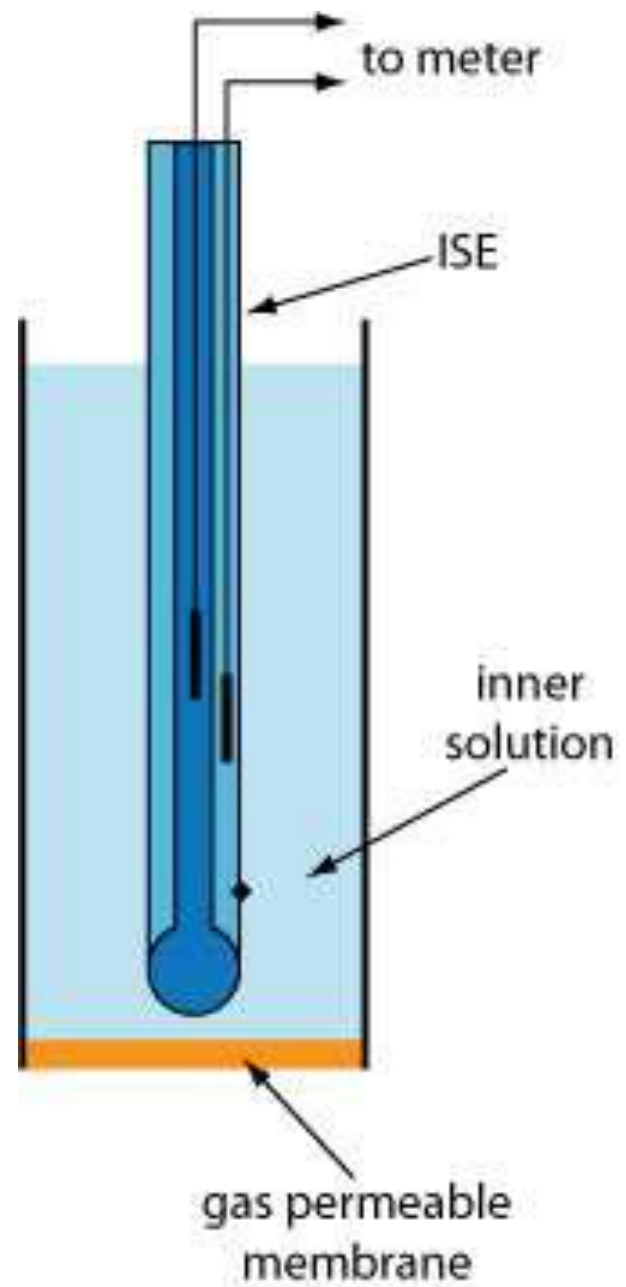
Based on membranes used Indicator selective electrode

(ISE) can be classified as:

- Glass Electrode
- Solid State Electrode
- Enzyme Electrode
- **Gas Sensing Electrode**

Gas Sensing Electrodes

- Specifically used to monitor the gaseous molecules dissolved in solution
- Does not detect the presence of gas rather an ion into which the gas is converted after it passes through the outer membrane
- Used to analyze the solutions of gases such as NH_3 , CO_2 , SO_2 , NO_2 and H_2S (For H_2S , a sulphide ion responsive electrode and for NO_2 nitrate ion responsive electrode is used while for all other gases, glass-pH electrode is used)
- Gas in the test solution diffuses through the membrane and reacts with the internal feeling solution to form the ions. These ions are detected by a gas sensing electrode
- Membranes used are hydrophobic,
gas permeable, porous polymer (silicone rubber
/Teflon/polypropylene/fluorinated ethylene)



Gas Sensing Electrode

Construction and Working :

- Consists of thin hydrophobic gas permeable membrane to separate the sample solution from the internal filling solution of ammonium chloride (NH_4Cl) containing Ion Selective Electrode (ISE)
- Membrane is permeable to the gaseous analyte, but impermeable to non-volatile components if present in the sample
- The gaseous analyte passes through the outer membrane where it reacts with the inner solution, producing a species whose concentration is monitored by the ISE
- Eg. In a CO_2 electrode, CO_2 diffuses across the outer membrane first where it reacts in the inner solution to produce H_3O^+ .

The change in the activity of H_3O^+ in the inner solution is monitored with the pH electrode and is proportional to the concentration of CO_2 in the sample.

Gas Sensing Electrode: For Determination of NH_3

Construction and Working :

For determination of **Ammonia**:

- Ammonia diffuses through external membrane
- When the electrode is dipped in sample solution containing dissolved NH_3 (ammonium ions) from the sample solution diffuses through the membrane until the partial pressure of ammonium ions becomes equal on both sides of the membrane the ammonia which diffuses through membrane dissolves internal filling solution and react reversibly with water
- Partial pressure of ammonium ions is directly proportional to its concentration
- Boundary potential gets developed between the ions formed inside and outside of ion selective electrode (ammonium selective electrode) due to the difference in the concentration of ammonium ions