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Unit - V

Conductometry :-

Conductometry can analysis is based on the measurement of electrical Conductivity of the solution due to the mobility of cations and Anions towards respective Electrodes.

* The electrical Conductivity is affected by following factors :-
  (i) No. of Ions
  (ii) Charge of Ions
  (iii) Size of Ions
  (iv) Temperature

Principle of Conductometry :-

* The main principle involve in this method that the movement of the Ions creates the electrical Conductivity.
* The movement of the Ions mainly depends on Conc. of Ions.

$$\underset{\text{(Strong electrolyte) (Analyte)}}{A^+B^-} + \underset{\text{(Reagent) (Titrant)}}{C^+D^-} \longrightarrow AD + BC$$

* In Conductometry the Ionic Conc. of A^+ is determined by reacting the electrolyte solution with the reagent solution so, that A^+ Ion is replaced by C^+ Ion.

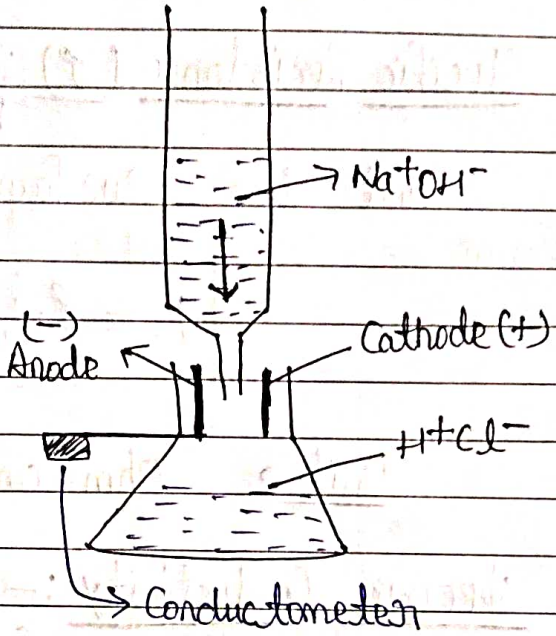
* This replacement of Ion with other Ions shows the Conductance either Increased or decreased.

* This is done mainly by replacement of Hydrogen Ion with other Cation.

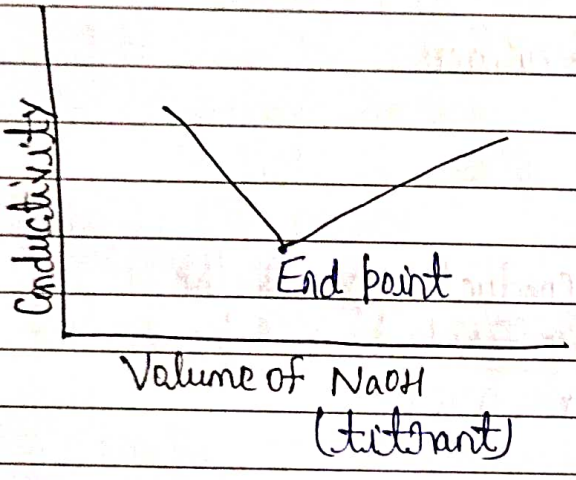
Ex:-

$H^+Cl^- + Na^+OH^- \longrightarrow NaCl + H_2O$

Electrolyte (Analyte) Reagent (Titrant)



Graph:-



Ohm's law:-

According to this law, the strength of current (I) flowing through a conductor is directly proportional to potential difference (V) applied across the conductor. and Inversely proportional to resistance of the conductor.

$$I \propto V$$

$$I \propto \frac{1}{R}$$

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

$$\boxed{V = IR}$$

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Conductance :- The Conductance is reciprocal to resistance.

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

Specific Resistance (ρ) :- Specific resistance flow is by a substance of 1cm length and $1 cm^2$ surface area.

$$R = \rho \frac{l}{a}$$ → area of surface

Unit → Ohm-cm.

Specific Conductivity :- Specific conductivity is the Conductivity offered by a substance of 1cm length & $1 cm^2$ surface area.

Unit → $Ohm^{-1} cm^{-1}$
or $mho\ cm^{-1}$

Equivalent Conductivity (χ_v) :-

Equivalent Conductivity is the Conductivity of a solution containing equivalent weight of the solute between electrodes 1cm Apart and $1 cm^2$ surface area.

Unit → $Ohm^{-1} cm^{-1}$
or
$mho\ cm^{-1}$

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Relation between Specific Conductance & Equivalent Conductance

$$\lambda_v = K_v \times V$$

Where, λ_v = Equivalent Conductance.
K_v = Specific Conductance.
V = Volume of solution in cm^3.

Conductometer :-

The instrument used for measurement of Conductance is called Conductometer.
It Consist of 3 main parts :-

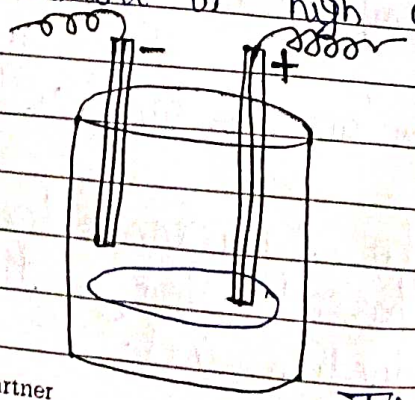
1. Current source
2. Conductivity Cells
3. Electrodes

Conductivity Cells :- Conductivity cells is made of Pyres or Quartz and are fitted with to platinum electrodes. that are placed in vessel containing water to maintain constant temperature.

These are of 3 types :-

(i) Type-A
(ii) Type-B
(iii) Type-C.

(i) Type-A :- This Consists of the electrodes placed at a large distance and is used for the measurement of high conductance.



Type-A

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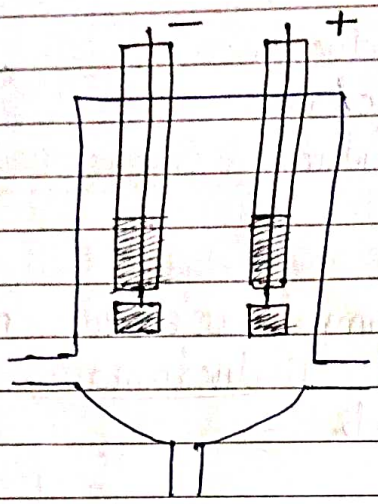
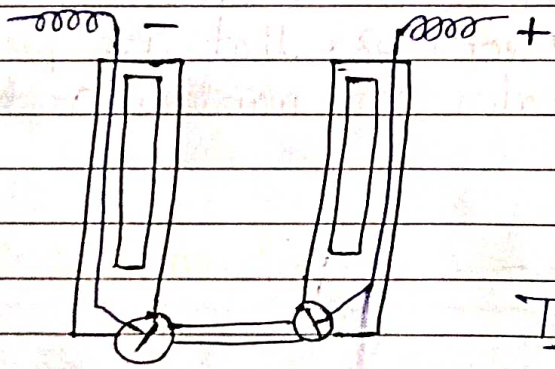
(ii) Type-B :- In this type the cell is dipped in the sample solution to measure the conductance during titration.



Type-B

(iii) Type-C :- In this type large electrodes are placed at small distance this type of cell is mainly used for the measurement of low conductance.



Type-C

Method of Measurement of Conductivity :-

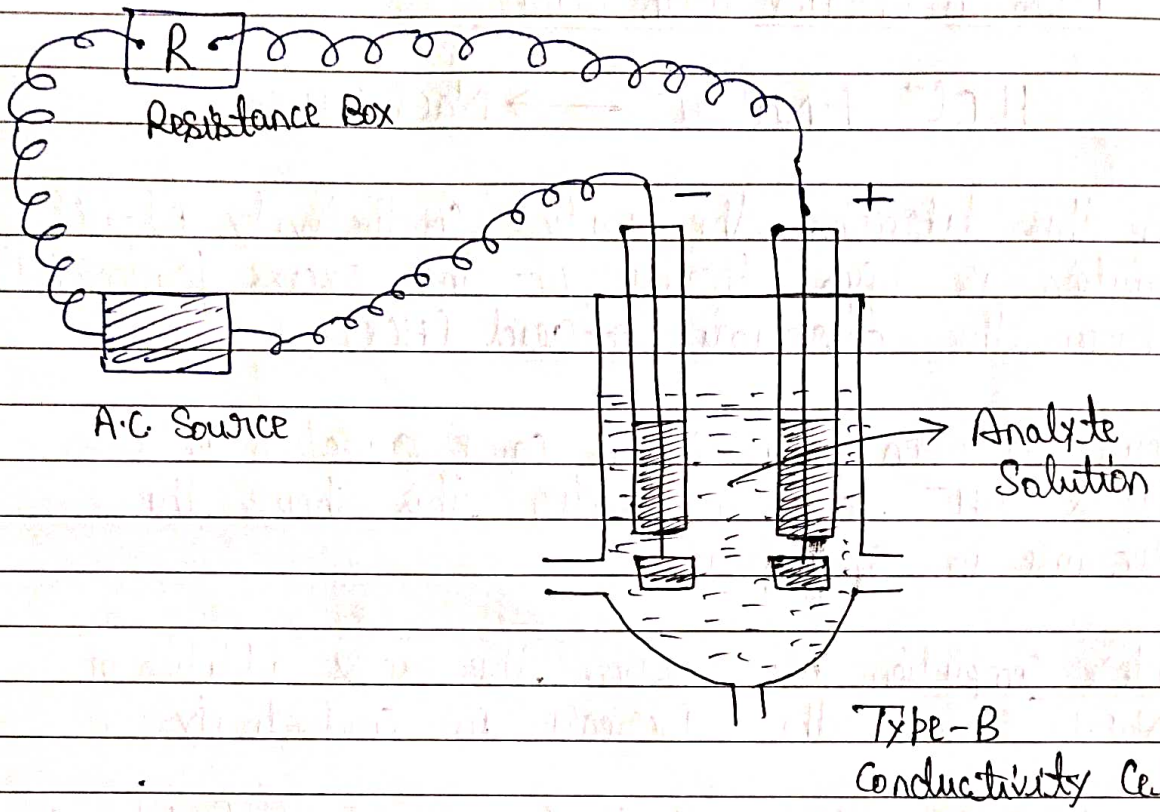
(i) The sample solution is ~~taken~~ placed in the conductivity cell at constant temperature.

(ii) The temperature is maintain constant with the help of thermostat.

(iii) The cell is connected to resistance box and the alternating current is passed through the cell with the help of Induction coil.

(iv.) The conductivity of ~~solute~~ cell is measured by following equation:-

$$\text{Conductivity of solution} = \frac{1}{\text{resistance of solution}}$$



Type-B Conductivity Cell

Types of Conductometry Titration :-

1. Acid - Base Titration :-

Titration of
(i) Strong Acid with Strong Base
(ii) Strong Acid with Weak Base
(iii) Weak Acid with Strong Base
(iv) Weak Acid with Weak Base.

2. Precipitation Titration.

3. Complexometric Titration

4. Redox Titration.

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1. Acid - Base Titration :-

In this method, the Conductan of Hydrogen ion & Hydroxyl ion are compared with the Conductivity of Sample Solution (Analyte).

E.g.:-

Titration of HCl with NaOH

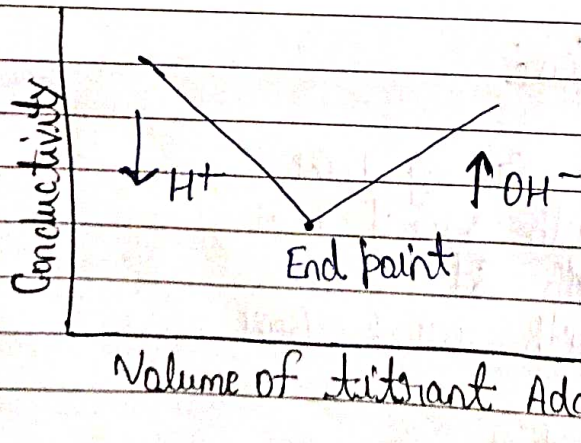
$$H^+Cl^- + Na^+OH^- \longrightarrow NaCl + H_2O$$

* In this titration, the initial Conductivity of HCl Solution is high because of the excess protons (H^+) from the dissociation of acid (HCl).

* Now titration with NaOH cause reaction between H^+ & OH^- to form water this shows the decrease in Conductivity.

* After completion of reaction the excess addition of NaOH shows the increase in Conductivity.

* The plot b/w the Conductivity & Volume of titrant shows V-shaped Curve.



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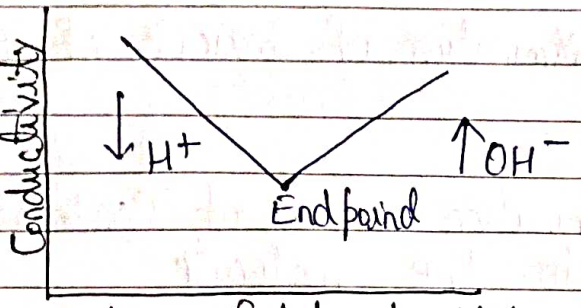
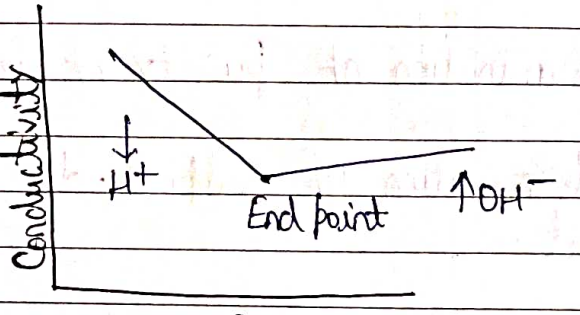
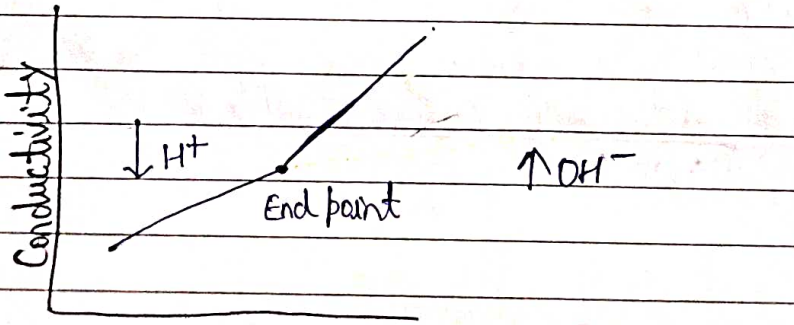
(i) Strong Acid with Strong Base



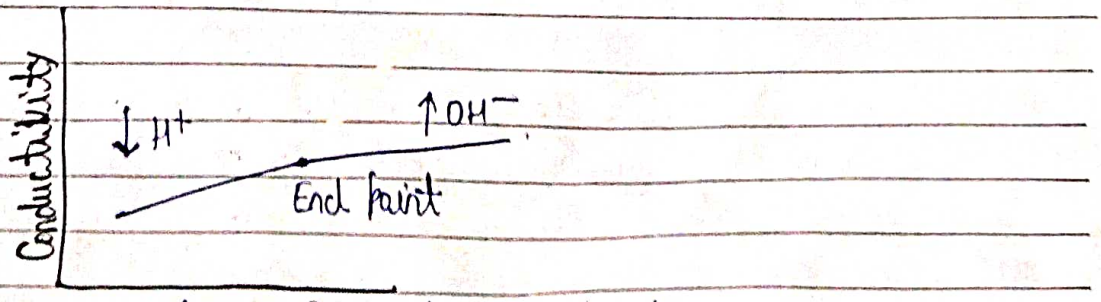
(ii) Strong Acid with Weak Base



(iii) Weak acid with Strong Base



(iv) Weak Acid with Weak Base



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Application of Conductometry :-

* Used for the determination of basicity of Acid or Acidity of Base.

* Used for the determination of no. of Carboxalic acid groups attached to the molecule

* Used for the estimation of Sparingly Soluble salt such as Barium Sulphate and Lead Sulphate.

* Used for the determination of purity of water.

* Used for the determination of Sulphur-di-oxide in air as pollutant.

* Used for the determination of Salinity of Sea water.

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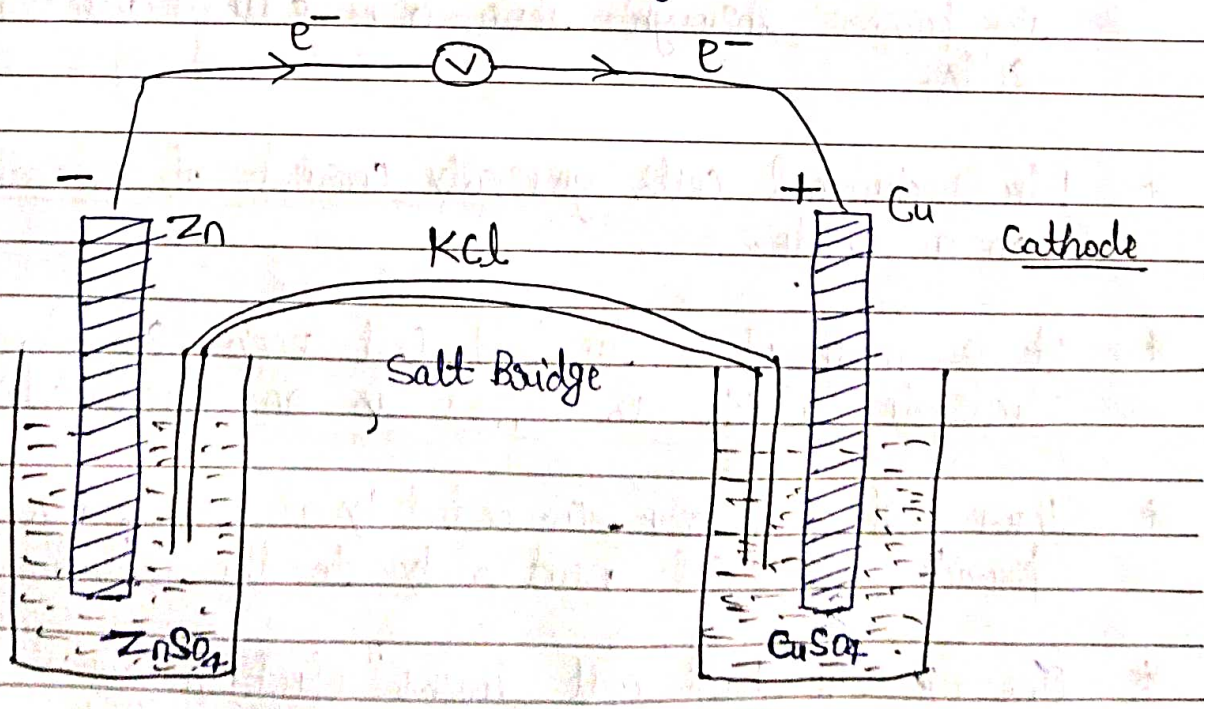
Potentiometry

* Potentiometric titration is on measuring the potential difference or EMF of solution by using and indicator electrode and a reference electrode.

* It is a method of analysis in which we determine the concentration substance by measuring the potential develop when an indicator electrode and a reference electrode each inursed (dipped in solution in solution to be analysed.

* Potential determination of indicator electrode serves as an indicator during titration.

* Potentiometric titration is based on the fact that when the potential and appropiate indicator electrode is measured against a reference electrode, it relates to the concentration change in the solution being titrated.



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Electrochemical Cell

$Zn(s) / ZnSO_4(aq) // CuSO_4(aq) / Cu(s)$

Oxidation half Cell Rea^n Reduction half Cell Reaction

$$Zn \longrightarrow Zn^{2+} + 2e^- \quad \text{(oxidation)}$$

$$Zn^{2+} + 2e^- \longrightarrow Zn \quad \text{(Reduction)}$$

Electrochemical Cell :-

An electrochemical cell is a device that generate electrical energy (current) from the chemical reaction occuring with in it.

* This is capable of Converting chemical energy into electrical energy.

* Alternatively the cells which cause chemical reactions to occurs in them when an electric current is passed through them are called electrolity cells.

* Electrochemical cells generally consist of a cathode an a anode.

* It is made up of to half cell each consisting of electrode which is dipped in an electrolyte.

* These half cell are connected by a salt bridge which provide electrical neutrality to the solution.

* One of the half cell looses electron due to oxidation and other half cell gains electron due to Reduction.

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* The tendency of an electrode to loose or gain electron is described by its electrode potential that is used to predict to overall cell potential.

* The electrode potential is measured with the help of reference electrode.

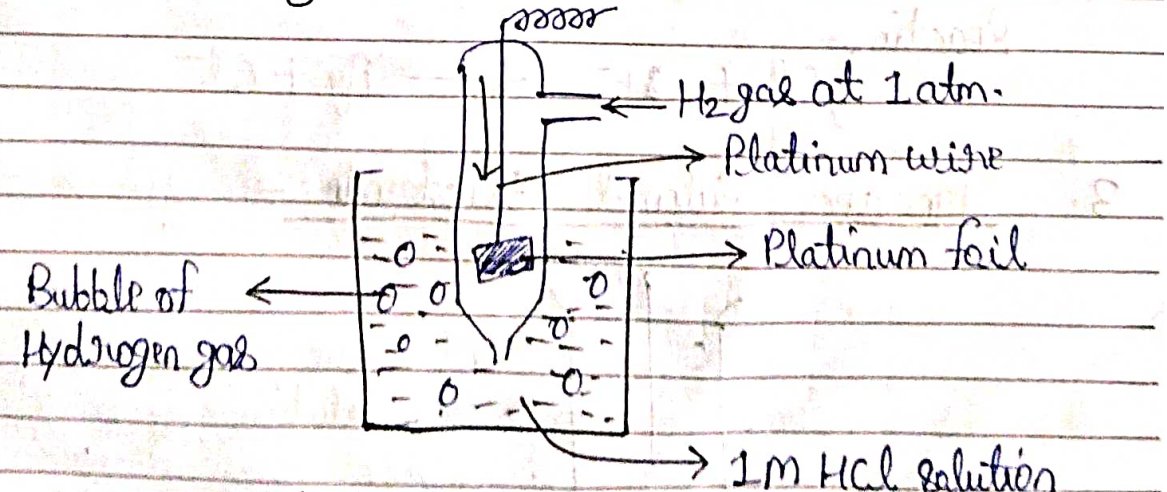
Construction and Working of Reference Electrode

An electrode whose electrode potential is well known and stable is called reference electrode.

Example of reference electrode :-

1. Standard Hydrogen Electrode (SHE)
   (E = 0.00 V)
2. Silver / Silver Chloride Electrode
   (E = 0.197 V)
3. Standard Calomel Electrode
   (E = 0.242 V)

1. Standard Hydrogen Electrode :-



Standard Hydrogen Electrode (SHE)

The following reaction occurs in this Half cell :-

Reaction:-

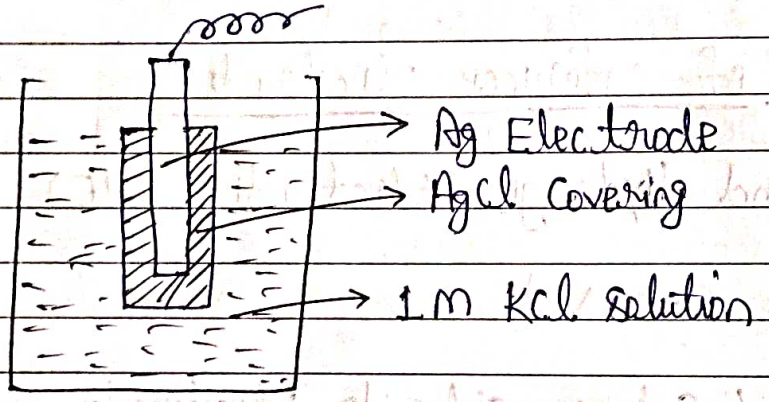
$H_2(g) \longrightarrow H^+ + 2e^-$

(If SHE acts as Anode)

$2H^+ + 2e^- \longrightarrow H_2(g)$

(If SHE acts as Cathode)

2. Silver / Silver Chloride Electrode :-

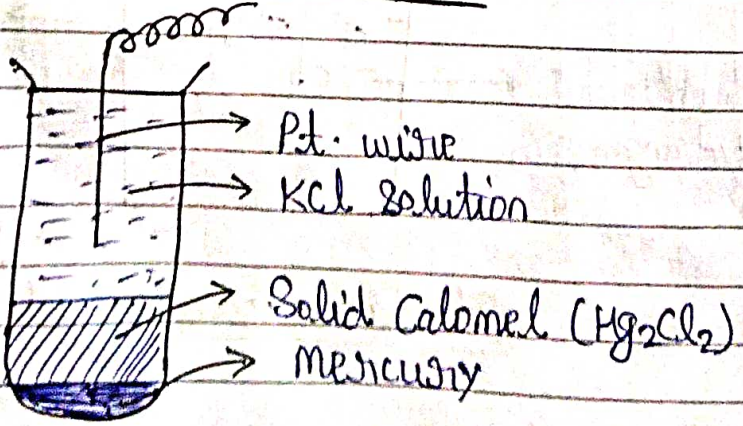


* The Silver / Silver Chloride electrode is represented as Ag, AgCl / Cl^- (1M) and the reaction of half cell is :-

Reaction:-

$AgCl + 1e^- \longrightarrow Ag + Cl^-$

3. Standard Calomel Electrode :-



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* The Standard Calomel electrode is represented as Cl^- (1M) / Hg_2Cl_2, Hg.

Reaction:-

$$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$$

Construction and working of Indicator Electrode

Potentiometric titration involves and electrode which is dipped in Analyte. This electrode acts as an indicator and thats why called as Indicator electrode.

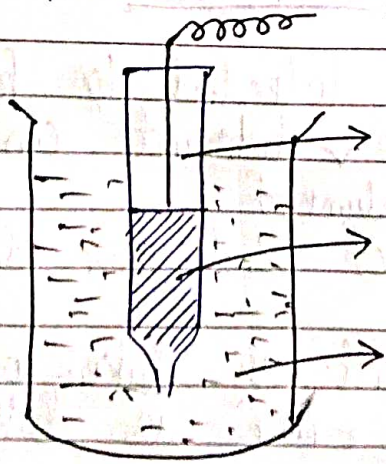
Example of Indicator Electrode:-

1. Metal electrode
2. Glass electrode

1. Metal electrode:-

* Metal electrode generate a potential as a result of redox reaction on the surface of metal.

* The metal used in metal electrode may be either ~~as~~ ~~a~~ platinum and gold.



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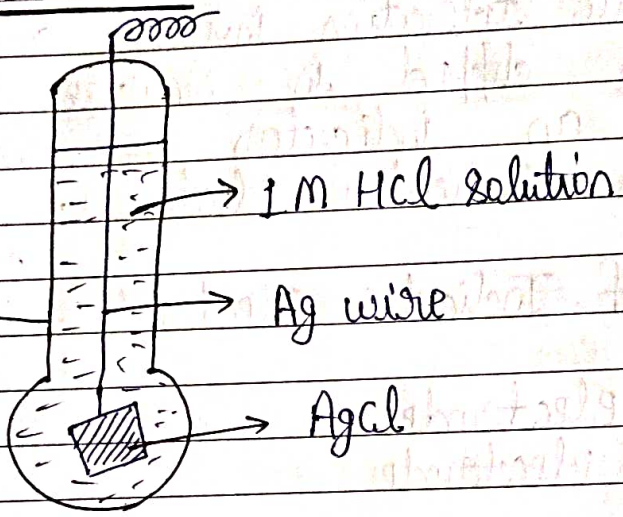
(i) * It is represented as $Ag/AgCl$, Hg/Hg_2Cl_2

Reaction:-

$$Ag \longrightarrow Ag^+ + e^-$$

$$Hg \longrightarrow Hg^{2+} + 2e^-$$

2. Glass Electrode:-



(ii) * Ag, AgCl / 1M HCl

Reaction:- $Ag \longrightarrow Ag^+ + 1e^-$

Methods to determine end point of potentiometric titration:-

(i) * The end point is detected by plotting a graph between the volume of titrant consume and E.M.F or Voltage of Indicator electrode.

(ii)

(iii) * The volume of titrant is taken on X-axis and the value of E.M.F. is taken on Y-axis

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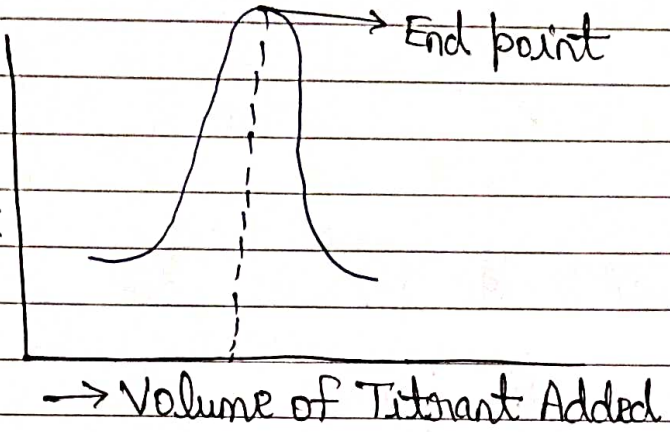
* Now the graph is plotted by addition of titrant in analyte solution.



~~Applicati~~

⇒ Types of Potentiometric Titration :-

(i) Acid- Base Titration
(ii) Complexometric Titration
(iii) Oxidation - Reduction Titration (Redox Titration)
(iv) Precipitation Titration
(v) Argentometric Titration

Application of Potentiometric Titration :-

(i) Assay of Diazepam and Nitrazepam.
(ii) Assay of Allopurinol.
(iii) Assay of Clonidine.