# Instrumental Methods of Analysis

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## * Introduction:

It is a method that is used to determine the concentration of a chemical compound or chemical element. There are a wide variety of techniques used for analysis.

1.Gravimetric analysis (simple weighing),

2. Volumetric analysis (titrations),

3. Electroanalytical

**Methods** :   pH metry, Conductometry , Spectroscopy

E**lectrochemical cell**  :  A device capable of either deriving   electrical energy from chemical reactions, or facilitating chemical reactions through the introduction of

**Voltaic (galvanic) cells** :  Spontaneous reaction generates electrical energy.
                                        C. E. --E. E.
**Electrolytic cells** : Absorbs  free energy from an electrical source to drive  nonspontaneous reaction
                              E. E. -------C. E.
**Galvanic Cell**:
Cell setup:        Zn (s) | Zn2+(1 M) || Cu2+(1 M) | Cu (s)
**Reduction potential /Standard Cell Potentials**

   **Ecell= E$_{red}$ (cathode) − E$_{red}$ (anode)**

**Nearst equation of Reduction potential at 298k**

   $E = E^{0} - 0.0591/n \log [ M^{+n} ]$

## *Types of Reference electrodes

**Definition of  Reference electrodes** :
Reference electrode is defined as the **electrode which has stable and reproducible potential and completes the cell ,acting as half cell.**
**-Purpose of reference electrode**
 1. To complete the cell
 2. provide stable potential
 3.Reference electrode helps in measuring potential of any other electrode connected to it.
Following electrodes are commonly used as Reference electrode.
There are two types of reference electrode
**1)Primary reference electrode :** e.g Standard hydrogen electrode Calomel Electrode
**2)Secondary reference electrode** :e.g Calomel electrode, Glass electrode, Ag-AgCl electrode , Quinhydrone electrode

# 1)Calomel Electrode

**Construction:**

1.Calomel electrode consist of a narrow glass tube at the **bottom of which is liquid mercury.**

2)**Above it is a paste of Hg-Hg₂Cl₂**and remaining portion of **glass tube is filled with1N or 0.1 N solution or saturated solution of KCl.**

3)A **platinum wire** dipping into the mercury layer is used to make **electrical contact.**•

4)There is side tube filled with gel for acting as **salt bridge** and making the electrical contact
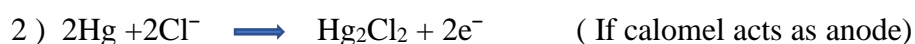
**Diagram:**
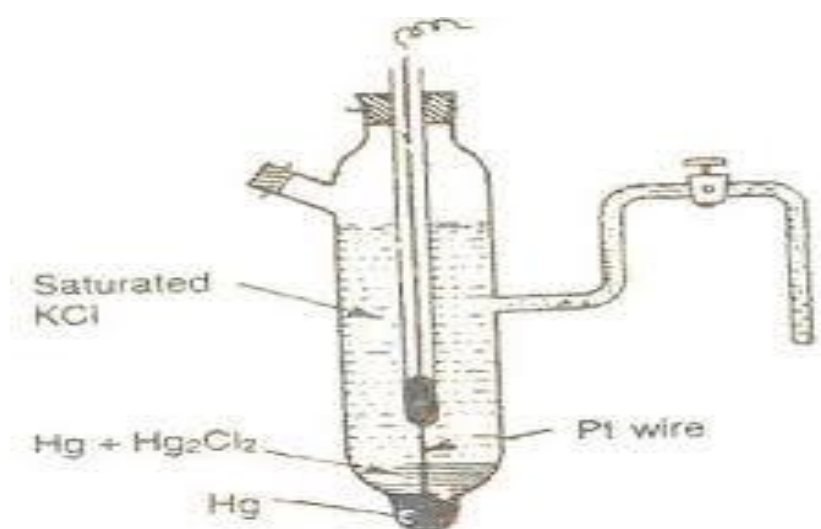


**Demerits of Calomel Electrode:**
1) This electrode **Cannot be use above 50°C**as Hg2Cl2starts decomposing .
2) It involves handling of **poisonous Hg and Hg2Cl2**

**Representation**:  Pt, Hg (l)/ Hg₂Cl₂ / KCl sat.
**OR**                Hg (l)/ Hg₂Cl₂/Cl⁻  sat.
**Reactions**:
1 )  $Hg_2Cl_2 + 2e^-$  $\longrightarrow$        $2Hg +2Cl^-$ (If calomel acts as cathode)

2 )  $2Hg +2Cl^-$  $\longrightarrow$  $Hg_2Cl_2 + 2e^-$       ( If calomel acts as anode)

**Potential**:

   $E_{cal} = E° + 0.0591 \log [ Cl^- ]$

• Thus Potential of the calomel electrode being dependent on [ Cl⁻ ] .

| KCl conc. | 0.1N | 1N | Sat. |
|-----------|------|------|------|
| E° calomel | 0.3334 volts | 0.2810 volts | 0.2422 volts |

## 2) **Indicator electrode- Glass Electrode:**

When glass surface is in contact with a solution it acquires a potential which depends upon H+ ion concentration. Glass electrode was developed for determining pH of solution.

**Principle:** When two solutions of different $[H^+]$ are separated by a thin glass membrane , a potential difference is develop at the two surfaces of membrane . The potential difference developed is proportional to the difference $[H^+]$ of the two solutions.

**Construction:** A Glass electrode is made of a **long glass tube** with a **thin walled glass membrane bulb** at the bottom . A pt. wire is dipped in the **0.1 M HCl** solution in the bulb
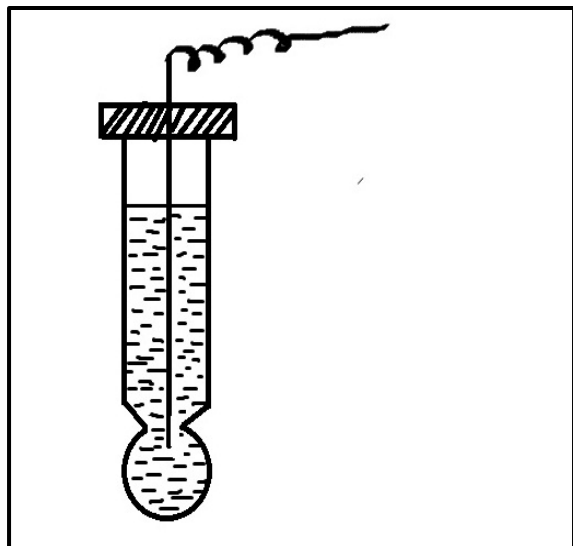
**Cell  Representation** :  Pt , 0.1 M HCl / glass bulb

**Potential**   :   $EG = EG^0 + 0.0591\ P^H$

(Where $E°_G =$ Potential of glass electrode in known pH solution)

**Diagram:**
**(Note : See the diagram of book and label it)**



**Determination of pH of solution**

**A glass electrode is coupled with calomel electrode** to determine the $P^H$ of solution. The electrodes are dipped into the solution of unknown $P^H$ of solution.
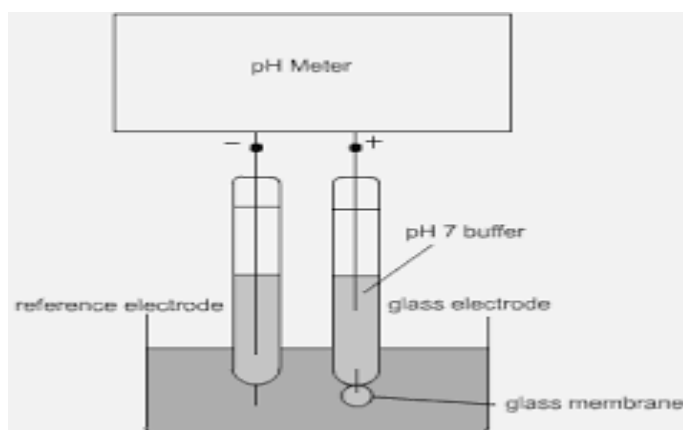
**Cell representation** :

   Glass electrode / solution of unknown pH // Sat. calomel

**EMF of cell is measured (E cell) :**

E cell = Ecal - EG

$\qquad$ = 0.2422  -( $EG^0$ + 0.0591 pH )

pH = 0.2422 – Ecell -  $E^0G$ / 0.0591



**Advantages of Glass Electrode**

❖ It is  It is **stable electrode** and can be used in     presence of strong    **oxidizing and strong**   reducing agent

❖ **Compact and Portable**.

❖ Can be used in presence of biological fluids/ proteins.

❖  It attained **equilibrium** quickly.,

❖  It can detect and **estimate $H^+$ ion** in presence of other ions.

**\*Ion-Selective Electrode (ISE):**

• **Definition(ISE): " A membrane of a half cell is sensitive to particular ion in solution and ion exchange takes place between the membrane and the solution containing specific ions and develops potential** which depends upon the concentration of that ion."

• The potential develop at the ion sensitive sensor is a measure of concentration of the ions of interest.

e.g. $H^+$ sensor  ( glass electrode)  , $Ca^{++}$ ( sensor Calcium ISE )

It is also called as **chemical sensors**.

$\qquad$ **Types of ion selective electrodes:**

I)Glass membrane electrode- Sensitive to $H^+$

II)Solid state membrane electrode- Consist crystal of inorganic compound doped with rare earth metals.

III)Enzyme based membrane electrode- Enzymes to convert the substance in the solutions to ionic products, which are measured using ISE.

IV)Gas sensing electrodes-Convert the gas into ions which are then quantified.

# I ] Glass – Membrane electrode

**Construction:**

- These electrodes are formed by doping molten SiO2 with various chemicals. Most common such electrode is H+ sensitive electrode or pH electrode

$$Li + Gl^- + H^+ \longrightarrow H + Gl^- + Li^+$$

- Different glass compositions can be made to be made to measure $Na^+$, $Ag^+$, $K^+$, $NH4^+$
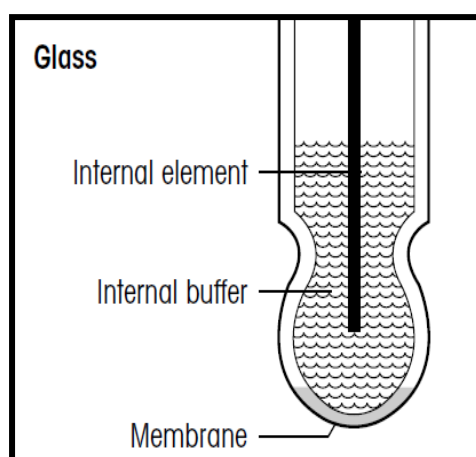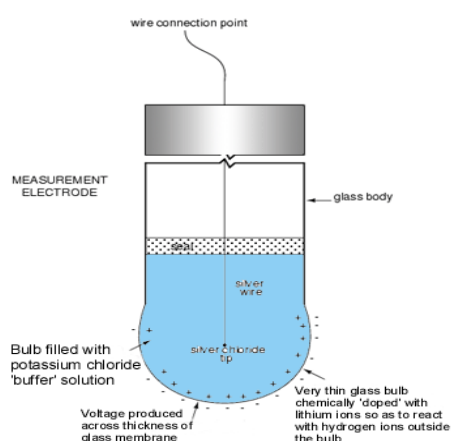
On immersing glass electrode in a solution , a hydrated gel layer formed causes swelling membrane .The ion exchange takes place in the gel layer of glass membrane ,generate a phase boundary potential.

$$Egl = E^0gl + 0.0591 \log [ M^{+n} ]$$

- $E^0gl$ = Standard Electrode Potential

[ $M^{+n}$ ] = Concentrations of the ions of interest in solution

**OR**



**II)Solid state membrane electrode-**

These membrane are made from ionic compound single crystal or homogeneous mixture of ionic compounds (polycrystalline).

**Fluoride ion determination-**(Fluoride in water),

**Chloride ion determination-**Ag2S ,AgCl pellet attached using epoxy resin

**Construction-**

Membrane is made from lanthanum trifluoride (**Laf3**) crystal doped with europium fluoride(**EuF2**).Crystal is sealed at the bottom of polymeric container containing internal reference solution (**Naf +NaCl** ) or (**KF+KCl**)and consisting of reference electrode.



**Solid State Electrodes Fluoride Ion-Selective Electrod**
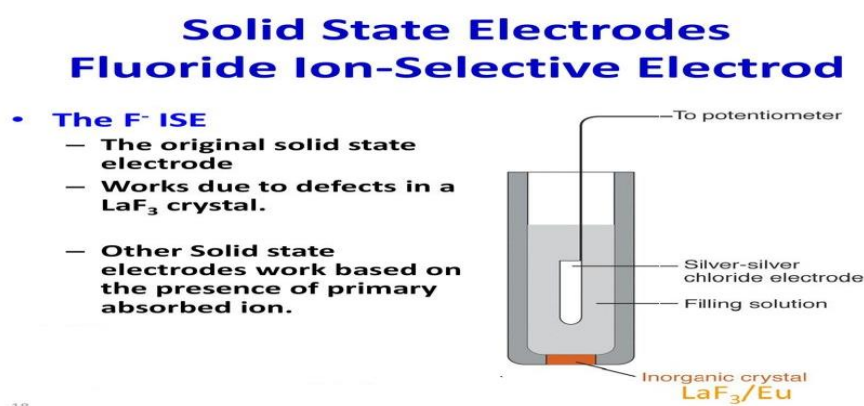
**III)Enzyme based membrane electrode :**

It is used to convert substance in the solution into ionic products, which are measured ISE.Enzyme is immobilized at the surface of the electrodes. e .g EBME used for determination of urea (membrane of electrode sensitive towards NH4+ions.)

**-Urea in the solution is converted intoNH4+ions using urase enzyme as follows.**



$2NH3 +2H2O \rightarrow 2NH4+ + 2OH^-$
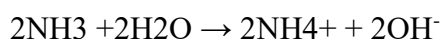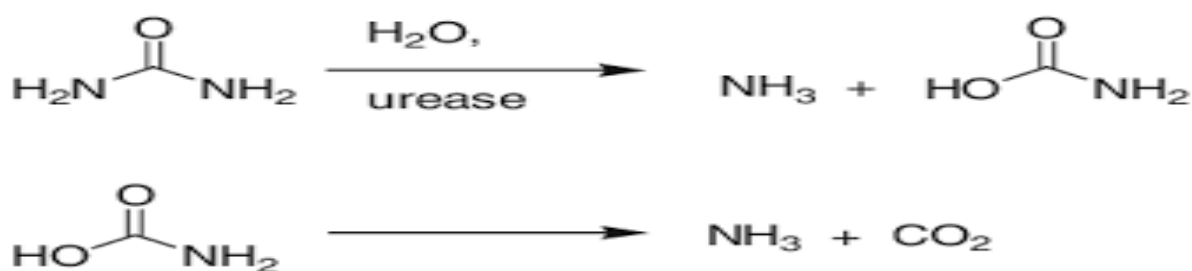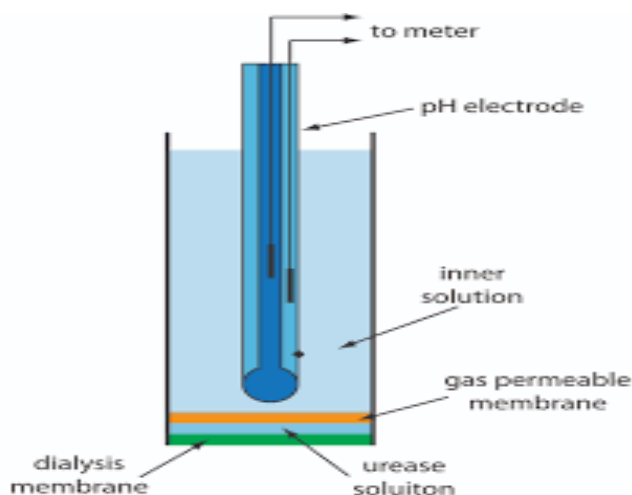
These produced NH4+ions can be measured by using NH4+ion selective glass membrane electrode.

**Working-**

Urease enzyme is mixed with polymer –polyacryloamide gel and is coated on the membrane of NH4+ions selective electrode. When electrode is dipped in the solution containing unknown amount of urea. Urea is converted into equivalent quantity of NH4+ions (1 molecule of urea produces 2 NH4+ions) NH4+ion selective membrane electrode has known Conc. of NH4Cl in it. Thus across the membrane electrode potential is developed, due to difference in Conc. of NH4+ions of 2 solutions & which is measured.

**IV)Gas sensing membrane electrode:**

These electrodes are used for measurement of NH3, CO2, H2S and nitrous oxide. These electrodes detects the ion into which the gas is Converted after it passes through the outer membrane.The gas permeable membrane is made of a hydrophobic Porous polymer. The gas is in the test solution diffuses through the membrane and react with internal filling Solution to form the ions . These ions are detected using ion selective electrode.

**Ex. Gas sensing membrane for determination of ammonia**

These electrodes are capable of monitoring gas molecules dissolved in the solution.The electrode does not detect the presence of molecular gas but rather than an ion into which the gas is converted after it passes through the membrane.Gas in test solution diffuses through the membrane and react with the internal filling solution to form the ions .These ions are detected using a gas sensing electrode.Membrane used as gas sensing electrode is gas permeable porous polymer membrane(silicon rubber/teflon) which allow the passage to dissolved gases but prevents solution to pass through it.
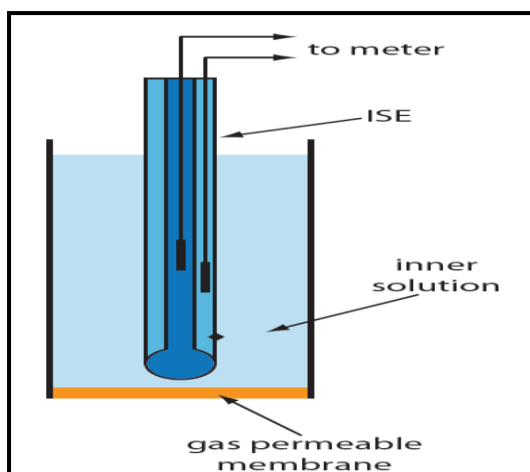
# pH -Metry

The term pH was introduce by Sorensen in 1909.

$$pH = - \log [H^+]$$

## Buffer Solution :

**Definition:** Buffer solution is the solution which resists change in ph even small amount of an acid or a base is added in it.

The pH metric titration requires a solution of known pH, for calibration of pH meter. Usually ,a buffer solution of pH 4, 7, 9.20 is prepared

## Types of buffer solution:

**1. Acidic buffer :** Weak acid with a salt of weak acid.

**e.g. CH3COOH + CH3COONa**
**NaH2PO4 + Na2HPO4**

**2. Basic Buffer:** Weak base with a salt of weak base .

• **e.g. NH4OH + NH4Cl**

From Henderson equation buffer solution can be prepared

$$pH\, of\; acidic\; buffer \; = pKa + \log \frac{[salt]}{[WA]}$$

$$pOH\; of\; basic\; buffer = pKb + \log \frac{[salt]}{[WB]}$$

pKa = -log 10 of dissociation constant of Weak acid
pKb = - log 10 of dissociation constant of Weak base

## *Applications of buffer solutions

1. Used in quantitative inorganic analysis.
2. Useful in electro-deposition of metals.
3. In colorimetric determination of pKa of indicator.
4. Many life forms thrive only in a relatively small pH range so they utilize a buffer solution to maintain a constant pH e.g a buffer solution found in nature is blood.

5. Industrially, buffer solutions are used in fermentation processes and in setting the correct conditions for dyes used in colouring fabrics.
6. They are also used in chemical analysis and calibration of pH meters.
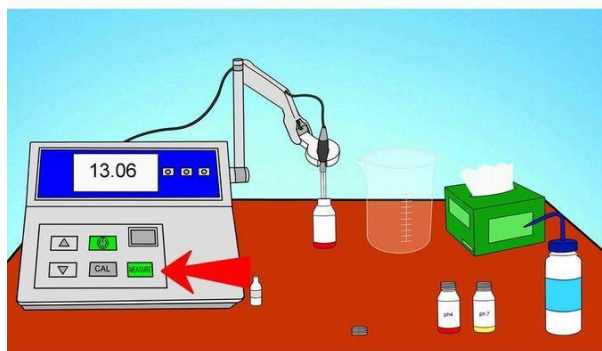
# pH metric titration:

**Principle** : In an acid- base titration ,pH of titration mixture changes abruptly/suddenly near the equivalence point.

1)Titration in which equivalence point of titration is found by use of pH meter(without use of indicator).
2)It s used for acid -base ,redox titrations by using suitable electrodes e.g pH glass electrode and reference electrode , or combined electrode .

## * Standardisation  of pH meter
**Procedure:**
1.Make the connections pH meter to electricity and electrodes to pH meter

2.Clean the combined electrode

3.Immerse the electrode in the solution of known pH

4.Adjust temperature knob on instrument on 20 0C and mode on pH

5.Adjust the pH reading on display with the standardize knob equal to pH of the solution
**(Note : See the diagram of book and label it)**



## *Strong Acid Vs Strong Base pH metric titration
**Theory:**
1.A strong acid & a strong base are completely dissociated into ions.

2.pH of titration mixture changes abruptly near the equivalence point

**e.g NaOHvs HCl titration**
$$Na^+ + OH^- + H^+ + Cl^- \longrightarrow Na^+ + Cl^- + H_2O$$

**Procedure :**
**1.Strong base : In Burette NaOH,Strong Acid :  HClin Beaker**

2.Cleaned combined electrode is dipped in beaker

3.The addition of burette solution and noting of pH is continued till appreciable change in pH noticed and titration continued to record 4 to 5 readings after the abrupt change in pH.

**Titration Curve /Graph :** Graph of pH Vs ml. of base added plotted
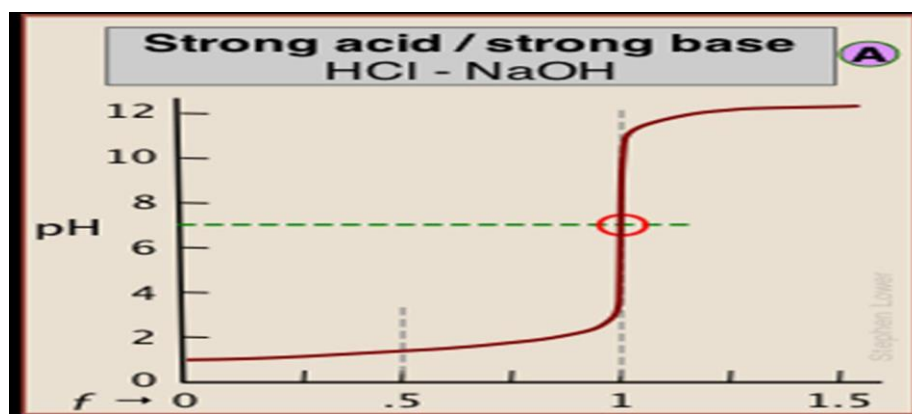


1) **Up- to Equivalence point** : Gradual change in pH in the beginning
2) **At Equivalence point :** pH is 7, there is suddenly change in pH near equivalence point from **about 4 to 10**

3)**After Equivalence point : pH is slow** after equivalence point.

Graph can be plotted as **ΔPH vs ΔV**
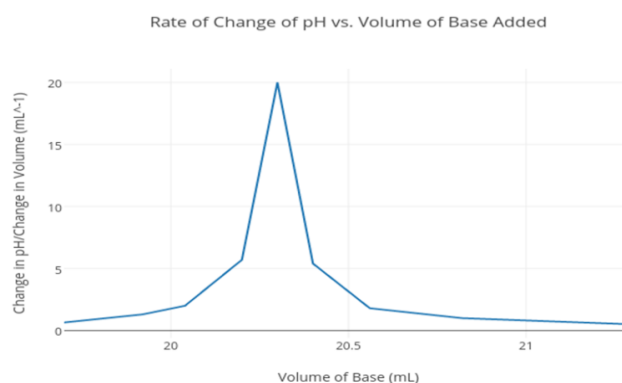


The volume corresponds to peak of the curve gives the equivalence point of titration .
**Calculation :**
**NaOH vs HCl titration**
Acid **vs** Base
N1V1 = N2V2
N1 = Normality of acid
N2 = Normality of base ( known )
V1 = Volume of acid
V2 = Volume of base ( burette reading )

The grams per litre of the solution can be calculated by
**Strength = Normality x Equivalent weight**


# Conductometry
## *Conductance by Electrolyte solutions:
•When potential difference is applied between two electrodes, then cations of electrolyte will move towards cathode and anions will move towards anode. It results in conduction of electricity through solution ( electrolyte )

•Mobility of ions and degree of ionization increases with increase in temperature ,which results in increase in current

**1)Electrolytic Conductance** : Conductance is ease with which current flow through solution/Conductor . **OR** Reciprocal of resistance .
**Formula**: C= 1/R
**Unit :** Ohm-1 or mho
**2) Equivalent conductance**(^) : Conductivity of the solution by all the ions produced from 1 gm equivalent is called **Equivalent Conductance.**
**Formula**: (^) = kV= k x 1000 / C
**Unit :**Ohm-1 Cm2/ equivalent
**3) Specific resistance (p):**
Resistance of conductor is directly proportional to length and inversely proportional to cross sectional area
$$R \propto l/A$$
4) **Specific conductance (**k )**:** Conductance of 1 cm3 of solution
**OR** Reciprocal of specific resistance (p) is conductance
R= p l/A , p = Specific resistance , l= length , A = area
1/p = k(kappa) i.e. specific conductance
k= 1/p = 1 / A*R I .e. k = l/ A * 1/R
Reciprocal of resistance is conductance ,
But, l/A = Cell constant
**Specific conductance is the product of cell constant and conductance.**
**Unit:** Ohm-1Cm-1or Mhos per cm Sm-1 Sm= Siemen
**5) Cell constant (**l/A) : If electrodes are l centimetre apart having area A in conductivity cell then l/A is constant and called as cell constant
**6) Molar conductance (u) :** The conductance shown by 1 molar electrolyte solution
Formula : u= kV= 1000 k / M
Unit: Ohm-1 Cm2/ mole
        Measurement of conductance is done by wheatstone bridge.
## *Effect of Dilution on Specific Conductance and equivalent conductance:

**Effect of Dilution on Specific Conductance :**
•The specific conductance depends on the number of ions present per unit volume of the solution. Since on dilution the degree of dissociation increases but the number of ions per unit volume decreases, therefore it is expected that the specific conductance also.
.
**Effect of Dilution on equivalent conductance:**

•The value of equivalent conductance increases on dilution. Equivalent conductance is the product of specific conductance (k) and the volume (V) of the solution containing 1 gm of the

electrolyte. As the decreasing value of specific conductance is more than compensated by the increasing value of 'V', thus the value of equivalent conductance ($\lambda m$) will increase with dilution

•The maximum value of the equivalent conductivity is termed as the equivalent conductivity at zero concentration (or infinite dilution) and is termed $\lambda \infty m$ .

**\*Conductimetric Titration** :
**Definition:** The titrations in which end point of titration is noted by measurement of conductance of titration mixture, known as conductimetric titration.
-Conductometry deals with measurement of electric conductance of solution containing electrolytes such as acids, bases. These solutions conduct current due to movement of ions towards oppositely charged electrodes.
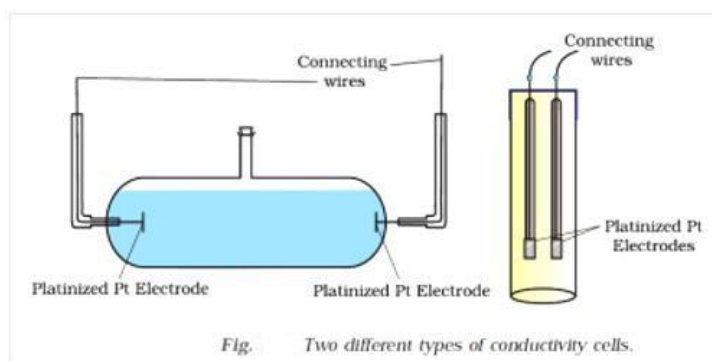**Principle :**
"The ability of any ion to transport charge depends on the mobility of ion. Mobility of ion is affected by size, charge on ion, mass of ion & extent of solvation".



# *Conductivity cell :

**Definition:** The solution whose conductance is to be determined is placed in a special type of cell known as the conductivity cell.



Fig.    Two different types of conductivity cells.

**(Note : Refer In-sem model answer paper solution diagram)**

A simple type of conductivity cell used in the laboratory is as shown in above figure. The electrodes fitted in the cell are made up of platinum plates coated with platinum black. These plates are welded to platinum wires fused in two thin glass tubes. The contact with copper wires

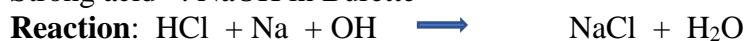of the circuit is made by dipping them in mercury contained in the tubes.

**1) Conductometric titration of Strong Acid with Strong Base titration**



cm³ of NaOH
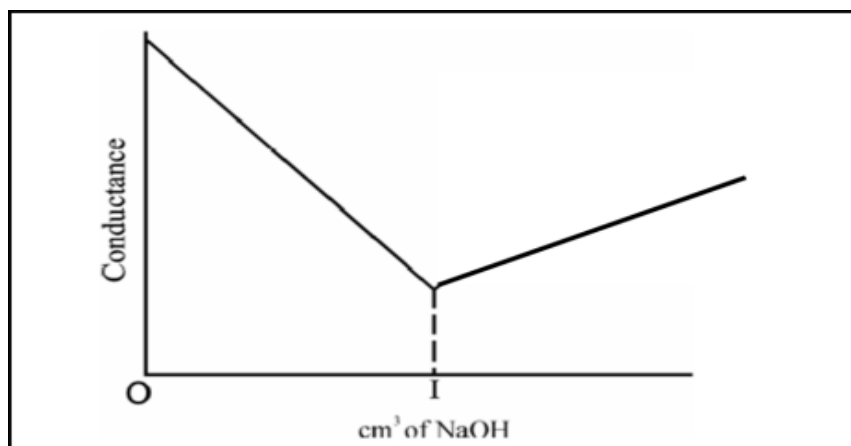
e. g Strong acid   HCl Vs Strong acid NaOH
Strong acid   :  HCl in beaker
Strong acid   : NaOH in Burette
**Reaction**: HCl  + Na  + OH  ⟶          NaCl  +  H₂O
1)Initially and up-to equivalence point:  conductance is high due to  presence of highly mobile H+ions Conductivity goes on decreasing as H+ions of  higher mobility will be replaced by slower moving  Na+ ..When the base is added, the conductance falls due  to the replacement of H+ ions by added H+ ions react with OH- ions to form water.This decreases in the conductance continues till equivalence point.
2)At the equivalence point: The solution contains only NaCl.
3) After equivalence point: conductance increase due to large conductivity of OH- ions.

> **1 ml 1 N NaOH = 36.5 mg of HCl**
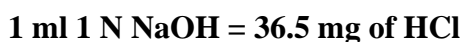
**2) Conductometric titration of Weak  Acid with Strong Base**
e.g Weak  Acid CH3COOH  with Strong Base NaOH
Weak acid   :  CH3COOH  in beaker
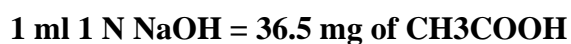Strong base: NaOH in Burette
**Reaction**:  CH3COOH + NaOH  ⟶     CH3COONa  +  H2O
1)Initially and up-to equivalence point:  Conductance of acetic acid is low due to the low ionization of acetic acid .On the addition of base ,there is decrease in conductance due to replacement of H+ by Na+ . The conductance increases slowly due to formation of completely dissociated salt Na -acetate which is strong electrolyte. This increase in conductance continues up to the equivalence point.
2)At the equivalence point: Graph at equivalence point is curved due the hydrolysis of salt CH3COONa  .
3)After equivalence point: Conductance increases more rapidly with addition of NaOH
    due to the highly conducting OH- ions.

> **1 ml 1 N NaOH = 36.5 mg of CH3COOH**
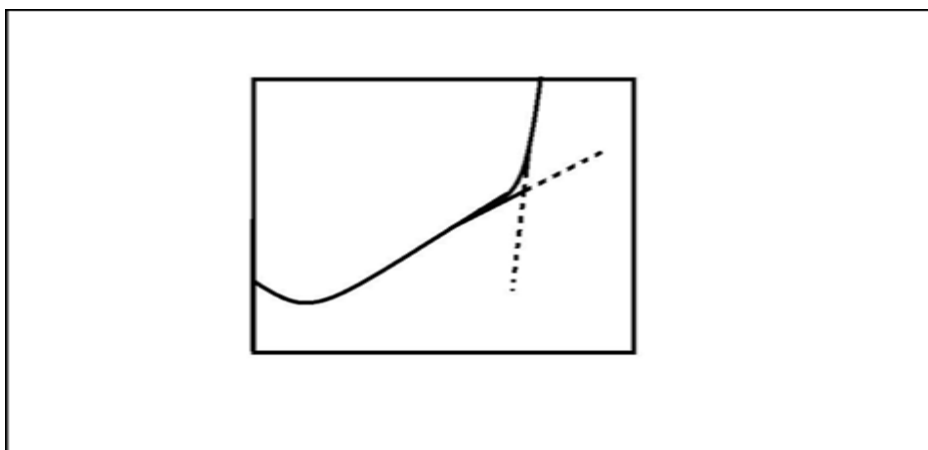
**(Note : See the graph/ curve in book and label it)**
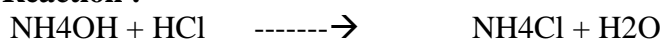
 **3) Conductometric titration :Weak base  Vs Strong acid**

e.g Weak base NH4OH  Vs strong acid HCl
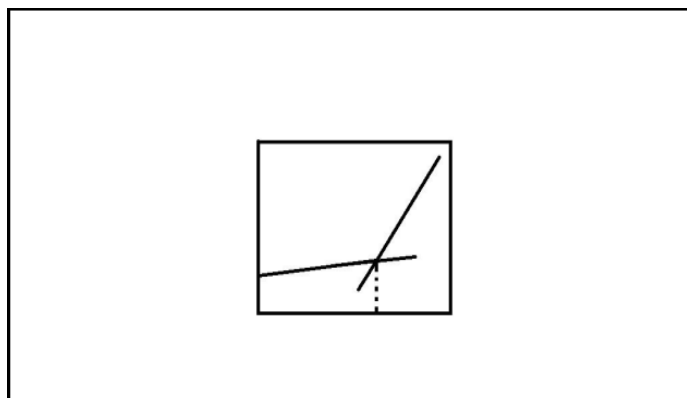Weak base :    NH4OH in beaker
 Strong acid:    HCl  in Burette
**Reaction :**
 NH4OH + HCl      -------→           NH4Cl + H2O
 1)Initially and up-to equivalence point:   At the beginning  conductance of NH4OH  is low as a weak electrolyte and then it upto the equivalence point, this increase in conductance due to the addition of H+ ion.
2)At the equivalence point: Conductance increases slowly due to formation of completely dissociated salt NH4chloride .  Formation up to equivalence point
3)After equivalence point: t conductance increases because of H$^+$& Cl$^-$from burette .



**(Note : See the graph/ curve in book and label it)**

4) **Conductometric titration of Weak acid Vs Weak  base**
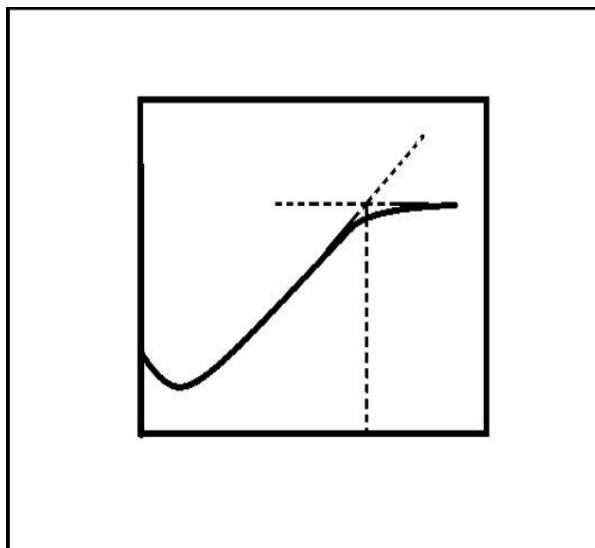e.g Weak acid CH3COOH Vs Weak  base NH4OH
Weak  acid  : CH3COOH  in  beaker
Weak  base  : NH4OH in Burette
 R**eaction**
CH3COOH  + NH4OH    ⟶        CH3COO-+ NH4++ H2O

1)Initially and up-to equivalence point: conductance of CH3COOH is low increases slowly due to formation of completely dissociated salt NH4-acetate.

2)At the equivalence point: Complete formation of NH4-acetate.

3)After equivalence point: after that conductance increases negligibly because of NH4+& OH -from burette .



**(Note : See the graph/ curve in book and label it)**

-------------------------------------------x--------------------------x-------------------------------------