Unit-V

★ Electrochemical method of analysis:-

① Conductometry:-

Conductometric titration is an electro-analytical method of analysis which is very useful when no suitable colour indicator are ~~aa~~ available for the detection of end point or when the indicator methods are not suitable for analysis.

→ Conductometric titration is based on measurment of Conductance of ions in a solution.

→ The Conductance is due to the migration of ions.

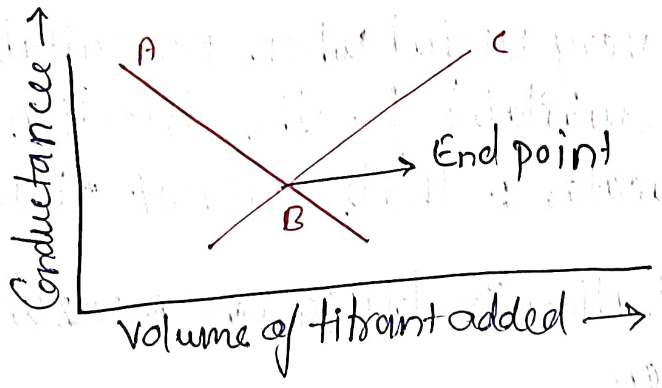
→ Conduction involves migration of positively charged ions (H^+, Na^+, K^+, NH_4^+ etc) towards cathode and negatively charged ion (OH^-; Cl^-, I^-, Br^-, CO_3^-, SO_4^- etc) towards anode.

Concept of Conductometric titrations:-

- Each cation and anion has different degree of ionic mobility (conductance).
- When a solution of one electrolyte is added (titrant) to a solution of another electrolyte the overall Conductance will depend upone whether a reaction occur between them or not
- If no chemical reaction occurs then overall Conductance of a solution will increase and each ion contribute to conductance of solution.

- When a chemical reaction occurs replacement or Substitution of ions takes place which decides that Conductance will either Increase or decrease.
- Conductometric titration is based on the principle of Substitutio of one ion of particular Conductance by the ions of different Conductance.

$$A^+B^- + C^+D^- \longrightarrow A^+D^- + C^+B^-$$



★ Instrumentation :-

There are two main Components for measurment of Conductance of an electrolyte Solution. These are.

1| Conductivity Cell
2| Conductometer

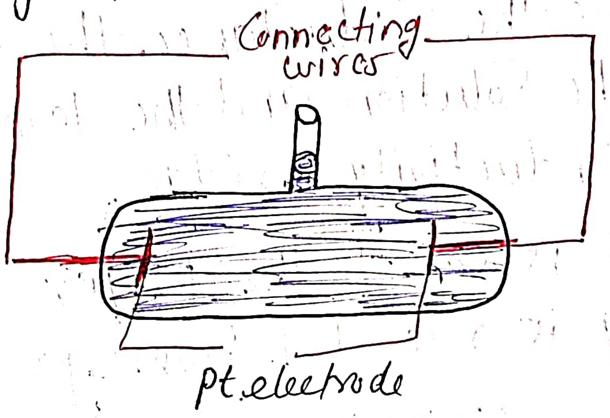
① Conductivity Cell :-

The Solution whose Conductance is to be measured is taken in a Cell known as Conductivity Cell.

#Composition of Conductivity Cell :-

① made up of glass Such as pyrex or of quartz glass.
② platinum electrodes Coated with the finely divided platinum black.
③ mercury for Connection.
④ Thermostats for regulating temperature

- The Cell basically Consists of a glass Container, in which two electrodes are fixed.



- Determination of cell Constant by Using 0.02 kcl at 25°c.

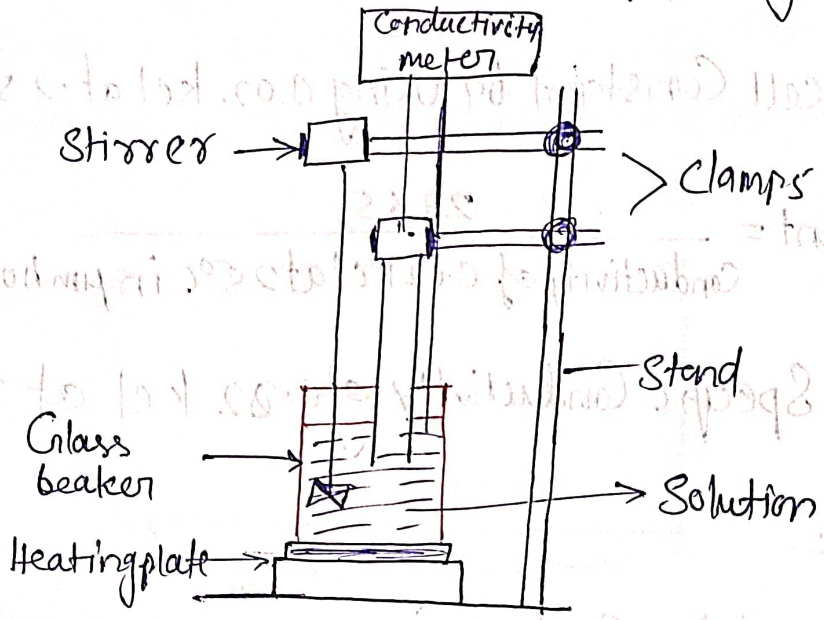
$$\text{Cell Constant} = \frac{2765}{\text{Conductivity of } 0.02\ \text{kcl at } 25^\circ c \text{ in } \mu\text{mhos}}$$

∴ 2765 is the Specific Conductivity of 0.02 kcl at 25°c

② Conductometer :-

- The apparatus used for Conductance measurment is a form of wheat stone bridge also known as Conductivity Bridge.
- It is made by ~~st~~ using wheat stone bridge circuit having four arms. Cell is placed in one arm and resistance Constitutes the Second arm.
- The other two arms are in the form of Calibrated Slide wire resistor.
- The detecter used may be a galvanometer, or Calibrate ~~Switch is there to~~ digital display.

- An alternating Current of frequency 50-60 Hz is used in the Circuit.
- A Calibrate Switch is there to Calibrate the desired value of Conductance.
- In order to determine the Conductance, the Conductivity Cell is dipped into the Solution and the terminals are Connected to the Conductivity bridge.
- The Selector Switch is set to the proper Conductance range and reading is recorded from galvano meter.



★ Conductometric titration:-

- Various types of titration Can be performed using Conductometry. Major titration which Can be performed with Conductometry Can be Classified as under.

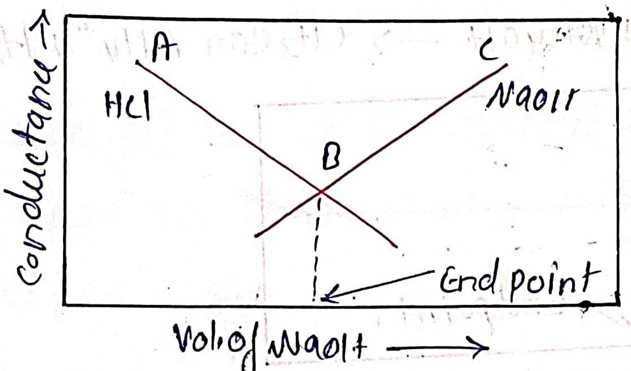
(A) Acid base titrations:-

It Can be Classified into following types:-

(i) Titration of strong acid with Strong base:-

HCl is a Strong acid and NaOH is a Strong base. The Strength of HCl Can be determined by titrating it directly with Standard NaOH Solution.

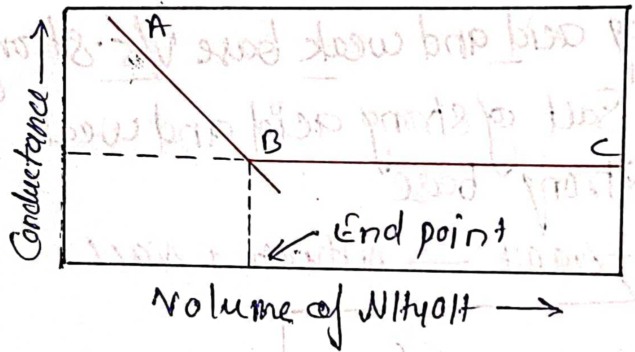
$(H^+ + Cl^-) + (Na^+ + OH^-) \longrightarrow (Na^+ + Cl^-) + H_2O$



(2) Titration of strong acid with weak base :-

- HCl is a Strong acid and NH_4OH is a weak base. Initially Conductivity ~~with~~ of Solution is high due to HCl:

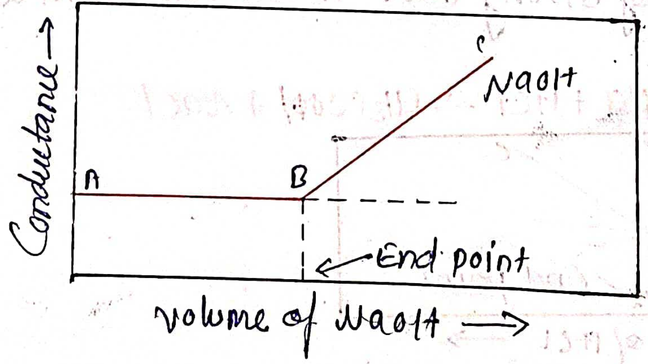
$HCl + NH_4^+OH^- \longrightarrow NH_4^+Cl^- + H_2O$



(3) Titration of weak ~~acid~~ acid with Strong base :-

- Acetic acid is a weak acid and NaOH is a Strong base. Initially the Conductivity of Solution is Low because acetic acid doesn't dissociate into H^+ ions.

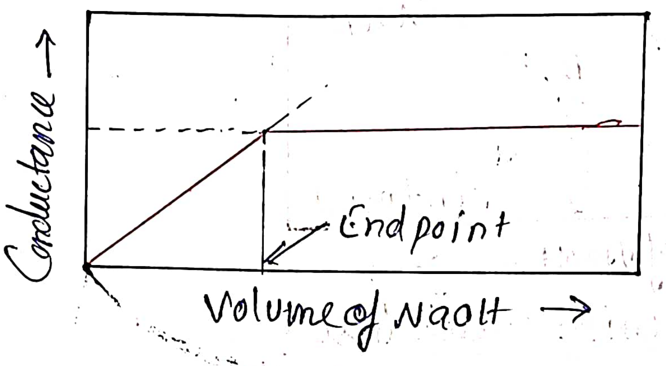
$CH_3COOH + Na^+OH^- \longrightarrow CH_3COO^-Na^+ + H_2O$



(4) Weak acid with weak base:-

- Acetic acid is a weak acid and NH_4OH is a weak base. Initially Conductivity is low because acetic acid doesint dissociate into H^+ ions.

$$CH_3COOH + NH_4OH \rightarrow CH_3COO^-NH_4^+ + H_2O$$



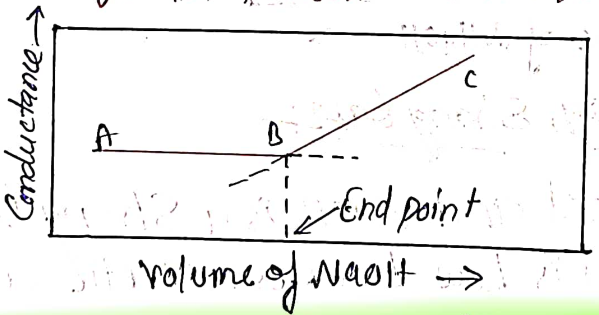
(B) Displacement titration:-

Displacement titrations involves displacement of one ion by another. Displacement titrations are of following types.

(i) Titration of Salt of Strong acid and weak base v/s Strong base:-

Ammonium chloride is a Salt of strong acid and weak base while Sodium hydroxide is a Strong base.

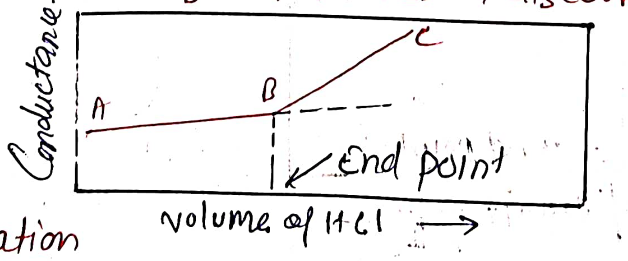
$$NH_4Cl + NaOH \rightarrow NH_4OH + NaCl$$



(ii) Titration of Salt of strong base and weak acid v/s Strong acid:-

- Sodium acetate is a salt of strong base and weak acid while hydrochloric acid is a strong acid.

$$CH_3COONa + HCl \rightarrow CH_3COOH + NaCl$$



(C) Redox titration
(D) precipitation "
(E) Non-aqueous "

☆ Application of Conductometry:-

→ ~~Solubility~~

— It can be used for the determination of :-

- Solubility of Sparingly Soluble Salts
- Ionic product of water
- Basicity of organic acids
- Salinity of sea water
- Chemical equilibrium in ionic reaction.
- Conductometric titration.

—

☆ Potentiometry:-

- potentiometric titration is an electrochemical analytical method of analysis which is based upons the measurment of change in the electrode potential of a solution using two electrodes i.e. Reference electrode and Indicator electrode.

→ Reference electrode has its own Standard potential and remains unchanged when dipped in the solution while indicator electrode responds to the change is EMF (electromotive force) of a solution

→ EMF of an electrolyte Cell can be Calculated as follows:-

$$E_{cell} = E_{reference} + E_{indicator} + E_{junction}.$$

$E_{junction}$ - remains Constant
$E_{reference}$ - is the potential on ~~indico~~ reference electrode.

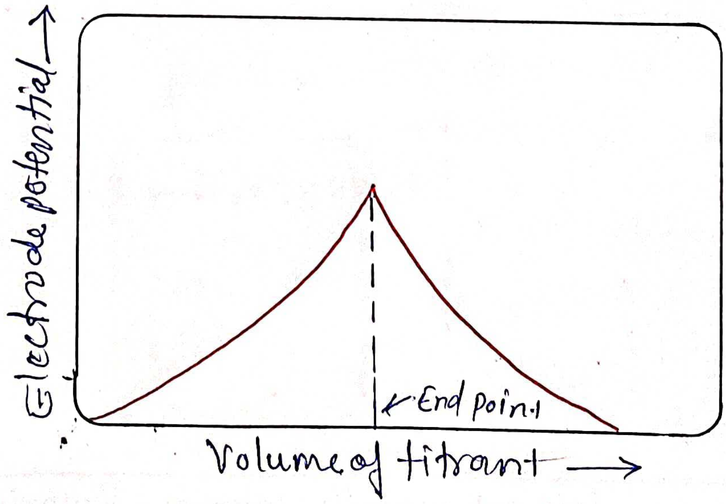
- There is linear relationship exist between the potential and pH of a solution at given temp.. therefore Sometimes pH instead of potential is determined.

$$E = K - 0.0591\,pH$$

or

$$\Delta E / \Delta pH = -0.0591$$

where - E - electrode potential
k - Constant potential



✱ Electrochemical Cell :-

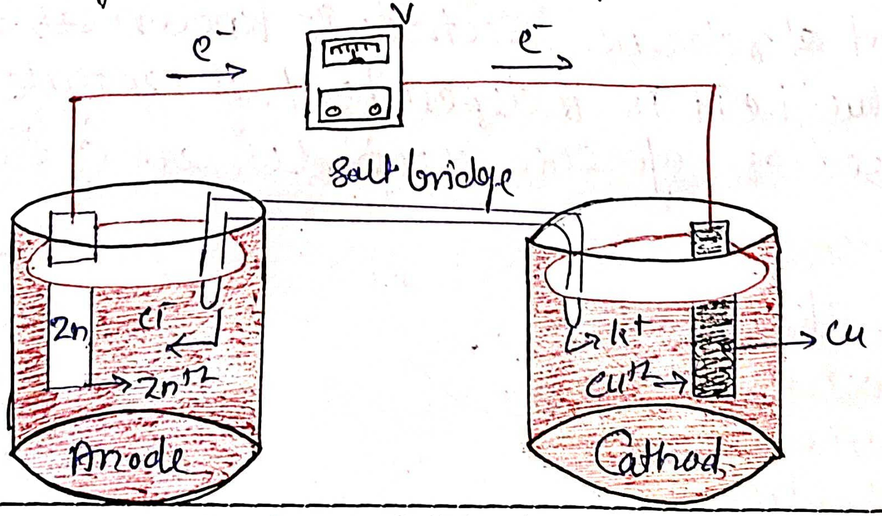
- A electrochemical Cell is consist two electrolyte Solutions which are Connected to each other by electrodes ~~as~~ and a Salt bridge.

→ Each Solution with electrode acts as a half Cell therefore we Can Say that an electrochemical Cell is consists of two half cells are Connected to each other to form an electrical circuit.

- Example :-
An electrochemical Cell Consists of two half Cells Consists of two metallic electrodes zinc and Copper electrode immersed in zinc Sulphate ($ZnSO_4$) and Copper Sulphate ($CuSO_4$) Solution.

- These two half Cells are Connected to each other throug a voltmeter and a salt bridge which is Consist of a tube filled with Saturated Salt Solution like kcl, Nacl etc.

- Through the salt bridge movement of ions b/w the Solutions takes place. End of the Salt bridge tube are fitted with porous frits ~~which~~ prevent mixing of solution but uniform movement of ions is allowed throug them.



- In $CuSO_4$ Solution, Copper electrode acts as a Cathode and Positivelly Charged Copper ions move toward it and negatively Charged Sulphate ions away from it, while in $ZnSO_4$ Solution, Zinc electrode acts as a anode and positivelly Charged Zinc ions move away from it and negatively Charged Sulphate ions move towards it.
- Through the Salt bridge positive ions move to the left Side and negative ions toright Side. On electrodes following reactions take place.

on Zinc electrode,

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

on Copper electrode,

$$Cu^{+2} + 2e^- \longrightarrow Cu\downarrow$$

✶ Electrodes used in potentiometry :-

For determination of potential of a given Solution, two electrodes are used.

① Reference electrodes
② Indicator electrode

① Reference electrodes :-

The potential of reference electrode is known ~~as~~ and has Constant value i.e it is independent of analyte Composition.

- Electrodes used as reference electrodes are of two types.

① Primary electrode :-
 ① Hydrogen electrode
② Secondry electrode
 ① Silver chloride electrode
 ② Calomel electrode.

① primary electrode :-

(a) Hydrogen electrode :-

→ It Can be used as both reference electrode as indicator electrode.

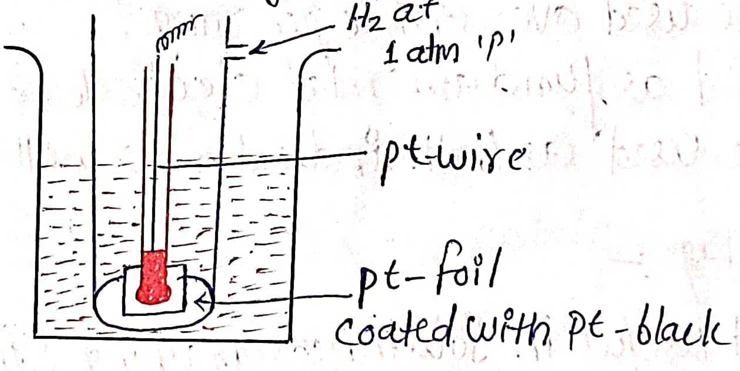
→ It is used as a primary Standard for the measurment of potential of other electrodes therefore also Called primary reference electrode.

→ Hydrogen electrode when dipped in the Standard acid Solution Can be used as reference electrode while when dipped in analyte or test Solution Can be used as indicator electrode.

Apparatus :-

→ It Consists of a glass tube having having holes at bottom.

→ This tube consists of one more tube having platinum or Copper wire with a platinum foil.



Working :-

- The potential of this electrode is taken as zero at all temperature.
- when hydrogen electrode is Connected to other electrode (indicat through the Salt bridge, the potential of indicator electrode Can be measured easily.
- For e.g Zn electrode is Connected to hydrogen electrode through kcl Salt bridge.

$$Pt, H_2/H^+ // Zn^{+2}/Zn$$

The Cell reaction is

$$H_2 + Zn^{+2} \longrightarrow 2H^+ + Zn$$

Half Cell reaction is

$$Zn^{+2} + 2e^- \rightarrow Zn$$

In this way we can determine potential of any electrode

- If hydrogen electrode is connected to another hydrogen electrode by kcl salt bridge, EMF of the cell can be measured as.

$$Pt, H_2/H^+ // H^+/H_2, Pt$$

$$E = E^0 - 0.0591/n + \log [1/H^+]$$

E^0 = zero as it is standard potential and $n=1$

Advantage:-

1) It gives reproducible results.
2) It has no salt error.
3) It can be used over entire pH range.
4) It is used as fundamental electrode.
5) It can be used as both indicator as well as reference electrode.

Disadvantage:-

1) It is not useful in solutions containing strong oxidizing or reducing agent.
2. It is not useful in solution having metal ions that are below hydrogen in potential series.

② Secondry electrode:

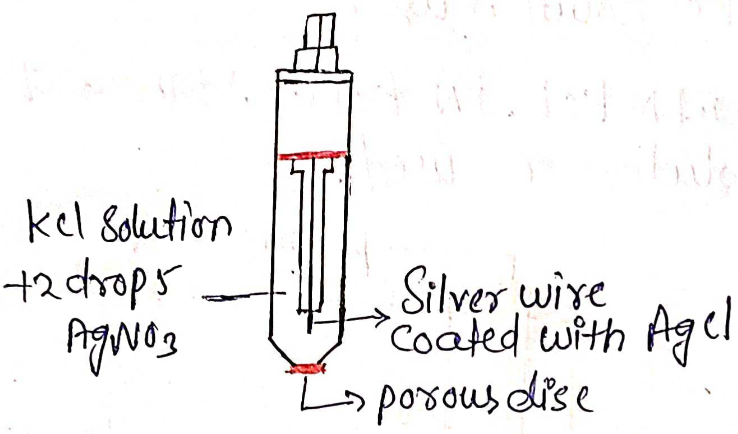
ⓐ Silver-chloride electrode:-

Apparatus:-

→ It Consists of a Silver Chloride and is dipped in a Solution of kcl of known Concentration.

→ Generally 0.1 M kcl or Saturated kcl Solution is used.

→ potential of this half depends upone the Concentration of potassium chloride as well as temperature.



Working:-

- The Standard potential of this electrode is obtained by Combing it with hydrogen electrode..
- The EMF of the Cell ~~be~~ Can be Calculated i.e.

$$Ag / AgCl \text{ Saturated } KCl // H_2 / H^+ Pt$$

- This electrode is used Similarly as Calomel electrode.
- It Can't be used where Chloride ions interfere.

(b) Calomel electrode:-

- It is also known as mercury-mercurous chloride electrode.

Apparatus:-

- It Consists of glass-tube having a side arm tube.

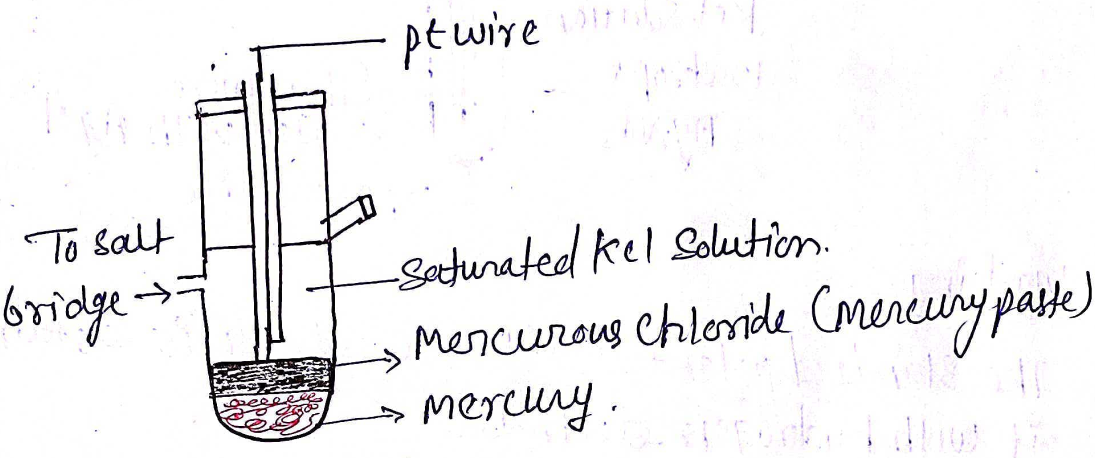
→ pure mercury is placed at the bottom of glass tube and is Covered with a paste of Calomel (mercury chloride) and kcl.

→ The tube is filled with kcl solution through the Side arm tube.

→ A platinum wire is also placed at the centre of the glass tube wit which makes electrical Connection with mercury.

→ The potential of the Calomel electrode depends upone the Concentration of kcl Solution used.

→ most Commonly 0.1 N kcl, 1 N kcl or Standard kcl and Saturated kcl solution are used.



Calomel electrode.

working:-

when Calomel electrode is Connected with another electrode (indicator), Emf of the Indicator electrode Can be Calculated. Half cell of Calmel Calomel Can be written as.

$$Hg / Hg_2Cl_2 \text{ (saturated) } kcl //$$

Calomel electrode Can be Connected to hydrogen Electrode for measuring pH of a Solution i.e.

$$Hg / Hg_2Cl_2 . kcl // H^+ / H_2 . pt$$

$$pH = E_{observed} - E_{calomel} / 0.0591$$

Advantage :-

1. It can be used over wide pH range.
2. It Can be used in various Solvent.

Disadvantage :-

1. It is unstable at temperature above 80°c
2. It is not Suitable When Chloride ions Show incompatibility.

② Indicator Electrodes :-

- In order to determine the EMF of a given Solution proper indicator electrode is required.
- Various types of indicator electrode are-

① Glass electrode :-

- The electrode is useful in determining pH of a Solution.
- It Selectively responds to the change in Concentration of hydrogen ions.

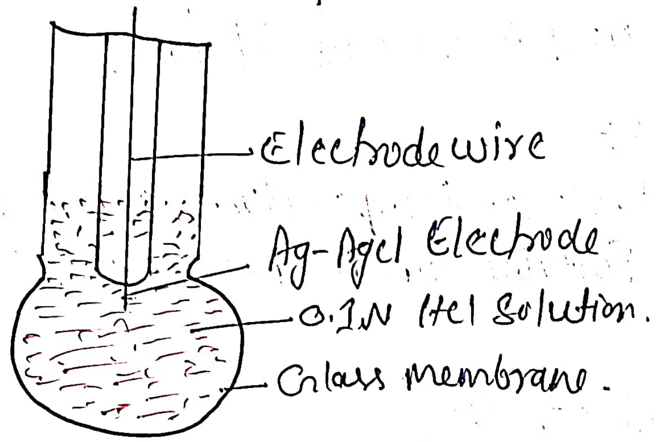
→ It Consists of a very thin Walled glass bulb made from glass membrane of high electrical Conductivity.

- The bulb Contains HCl of a particular Concentration and Ag / Agcl wire to Make electrical Contact.

- The measurment of pH of solution is based on the fact that when a glass surface is placed in a solution then a potential is established b/w the glass and the solution.
- The value of potential depends upon hydrogen ion conc. of the solution.
- From the above basis pH of the solution can be calculated as.

$$E_G = E_{0G} - 0.0591\,pH$$

E_{0G} is constant and depends upon the nature and composition.



#Advantage :-

→ It is not affected by oxidizing and reducing agent, colloids and salts, dissolved gases etc in the solution.

→ It can be used over entire pH range.

→ It is simple to operate.

→ It can be used in viscous; colored solution ~~to withstand~~.

→ It has no salt error.

#Disadvantage :-

→ It is fragile, so should be handled carefully.

→ minute scratches make glass electrodes useless.

→ It must be hydrated all the time.

② Metal ion electrode:-

→ The develop electric potential in response to redox reaction on the Metal Surface.

→ platinum or Au are used as metal indicator electrode.

→ These are mainly classified into three types of electrodes used in the potentiometry.

→ They are as follows.

○ First kind electrodes:-

- They are composed of the metal rod immersed in its Metal Solution.
- These electrodes respond to the ionic activity of the electrode

Ex. Silver electrode dipped in the Silver nitrate Solution.
Copper electrode dipped in the Copper Sulphate Solution.

○ Second kind electrode:-

- These are Composed of the metal wires Coated with the Salt precipitates.
- These electrode respond to the Changes in the ionic activity through the formation of the complex.

Ex. $Ag/AgCl/KCl$
$Hg/Hg_2Cl_2/KCl$

○ Third kind electrode:-

- These electrode are also known as inert electrodes and redox electrodes.
- They are Composed of inert metal electrode immersed in the redox Solution.

Ex. $Pt-H_2$ electrode.

★ Methods for determination of end point of potentiometric titration :-

There are various Methods to Locate the end point. The main purpose is to know the end point at which the quantities of reacting species are present in equal amount.

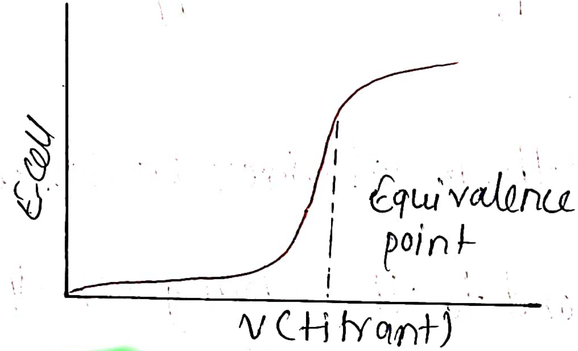
- There are following methods for calculating end point.

① Normal titration Curve :-

→ Values of EMF (E) or pH are recorded after addition of each volume of titrant.

→ Then a graph is plotted between volume of titrant added & v/s values of pH or EMF. At equivalence point there is sharp increase in potential or there is maximum slop of curve.

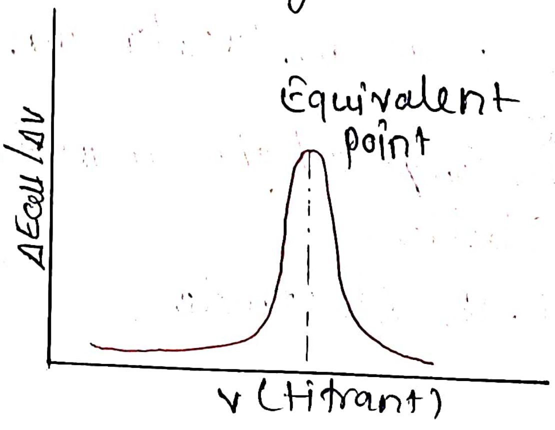
- Generally S-shaped Curve is obtained.



② First derivative Curve :-

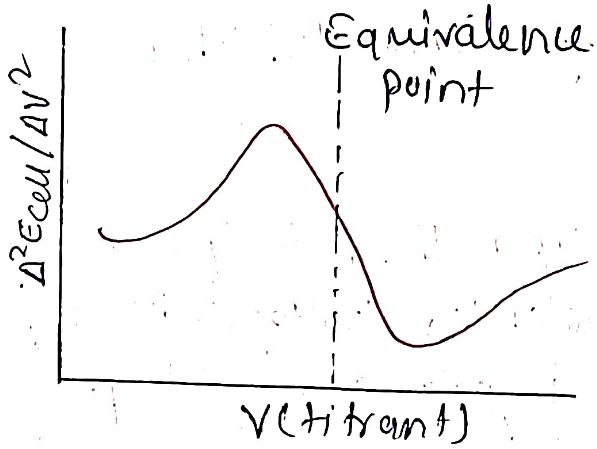
Differente of EMF or pH for the volume of titrant added ($\Delta E/\Delta V$) is plotted against titrant (V) added. A bell shaped graph is obtained and at end point there is maximum change in EMF or pH.

- The end point can be recorded by drawing perpendicular form peak of graph on volume excess.



③ Second derivative Curve :-

$\Delta^2 E/\Delta V^2$ against the volume of titrant added is plotted. The end point can be obtained as zero point where the slope curve of $\Delta^2 E/\Delta V^2$ is maximum.



Application of potentiometry:-

- With the use of potentiometry various type of titrations can be performed. Different titrations performed by using potentiometry with examples are describe here under.

① Acid - based titration
② Redox titration
③ precipitation titration
④ Complexometric titrations
⑤ Aassy of drugs.

- various drugs are assayed by potentiometry and their detailed procedure are available in various official compendia.
- Some of the drugs which are assayed by potentiometry are.

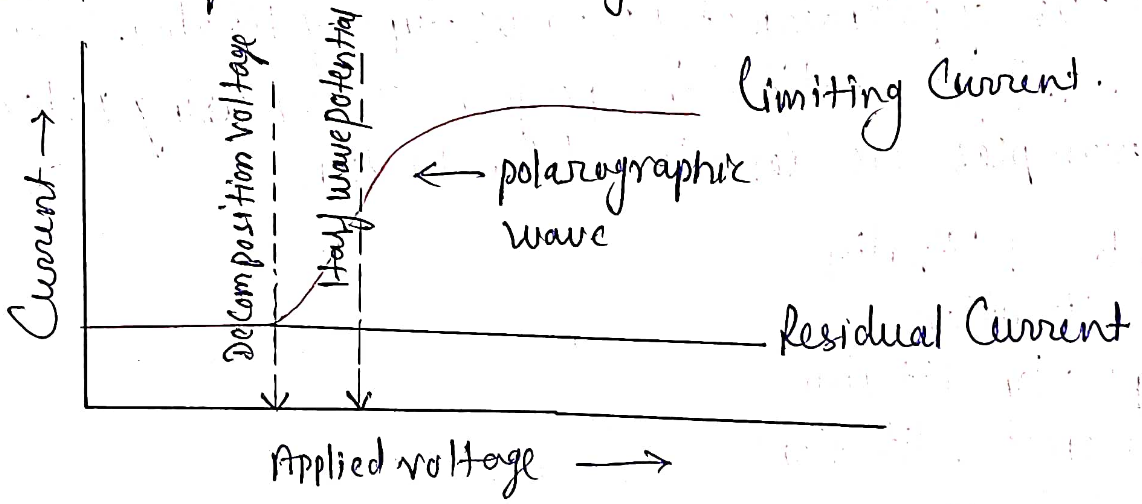
① Carbidopa
② Clonidine hydrochloride
③ climetidine.
④ Flunitrazepam

✩ Polarography :-

- Polarography is an electrochemical method of analysis and is a branch of voltametry in which varying negative potential (voltage) is applied across the non-polarisable and polarisable electrode.
i.e droping mercury electrode and Current is recorded.
The graph is plotted b/w the Current and applied voltage to get Current-Voltage Curve which is Called polarogram.

principle :-

- Polarography is based upon the principle that gradually increasing negative potential (voltage) is applied b/w two electrod one of which is polarisable (dropping mercury electrode) and other is non-polarisable and Current produced is recorded.
- A Sigmoid Shape Current-Voltage Curve is obtained.



- For example :-
when voltage is applied to a Solution Containing lead ion in 1mkcl (supporting electrolyte) the positively charged Lead ions will be attracted to DME by an electrical force and a diffusion force due to Concentration gradient formed at the surface of the electrode.
→ Current started flowing through the Cell. The applied voltage

is allowed to increase with time and the current produced is recorded. A graph is plotted between applied voltage and current produce.

Ilkovic Equation:-

The diffusion current produced by dropping mercury electrode can be designated by ilkovic equation which is as follows.

$$i_d = 607\, n\, D^{1/2}\, C m^{2/3}\, t^{1/6}$$

where.

i_d = diffusion current in microamperes.
n = no. of electrons transferred
C = concentration in mmol / liters
D = diffusion coefficient in $cm^2\ sec^{-1}$
m = mass of mercury drop flowing per sec in mg
t = drop time in sec.

★ Dropping mercury electrode:-

Dropping mercury electrode (DME) is a polarisable and most widely used electrode too.

Construction:-

→ Dropping mercury electrode is consist of a fine capillary having a bore size ranged from 20 to 50 μ and 10 to 15 cm long which connected to a mercury reservior by a rubber tubing.

→ The height of reservoir is adjusted to set the drop~~of mercury from Capilary~~ time as required i.e 1 to 5 second.

→ Drop time is the time required to form every fresh drop ~~time as~~ of mercury from Capillary.

→ Inside the tubing wire contact is made where mercury flow.

Working:-

- DME is a polarizable electrode and can act as both anode and cathode.
- The pool of mercury acts as counter electrode (in some cases). which is non-polarizable in nature.
- To the analyte solution, electrolyte like kcl is added i.e 50-100 times of the sample concentration
- Then, gradually increasing voltage is applied to the polarographic cell and current is recorded.
- Graph is plotted between voltage and current.

Advantage:-

- Surface area is reproducible with a given capillary.
- Constant renewal of electrode surface eliminate poisoning effect.
- mercury forms amalgum with most of the metals.
- Surface area of a drop can be calculate from the weight of drop.

Pharmaceutical analysis-I

#Limitation:-

- Surface area of each drop of mercury is never constant.
- Mercury is very poisonous, so careful handling is required.

☆ Rotating platinum electrode:

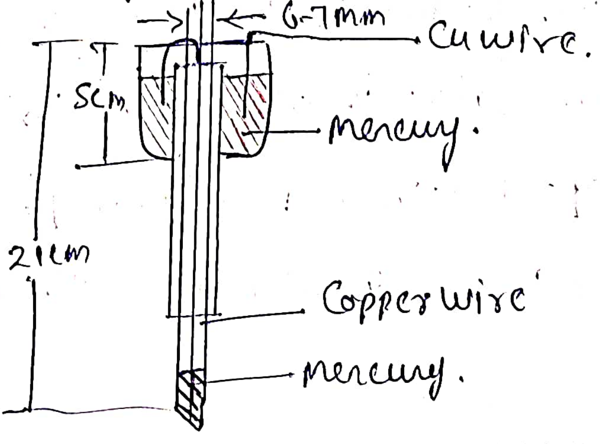
- Dropping mercury electrode has a disadvantage that it can't be used at higher positive potentials due to oxidation of mercury.
- Therefore, platinum electrode is used to extend the range of polarography towards the positive potential.

#Construction:-

- Rotating platinum electrode consist of a about 5mm platinum wire having 0.5mm diameter below standard mercury seal.

→ The copper wire is passed through the 6mm glass tubing ranging from platinum mercury seal to the upper mercury seal by passing through the small hole blown in the stem of the stirrer.

→ A wire from mercury seal is connected to the source that apply voltage. Tubing is rotated at a constant speed of 600 RPM.



#Working :-

- Rotating platinum electrode is mainly used as an indicator electrode with reference electrode which is non polarisable electrode i.e Saturated Calomel electrode in amperometry.

→ To the analyte Solution Supporting electrolyte like kcl is added i.e 50 to 100 times of the Sample Concentration.

→ pure nitrogen gas is bubbled through the Solution to expel out the dissolved oxygen.

→ potential Corresponding to the limiting Current required for Substance to be analysed is applied and titration is started.

- A graph is plotted b/w the volume of Solution added ~~to~~ v/s diffusion Current and end point is detected.

#Application of polarography :-

1. polarography is used for determination of oxygen Content of fluid including whole body fluids.
2. Several mercury Containing antiseptics and insecticides were determined polarographically.
3. Hormones like thyroxine, Insulin, adrenalline, and several Sex hormone are estimated by polarography.
4. It also use for determination of antibiotic Such as penicillin, Streptomycin and chloramphenical.
5. Several alkaloids can ~~b~~ also be estimated by polarography.

Thank you