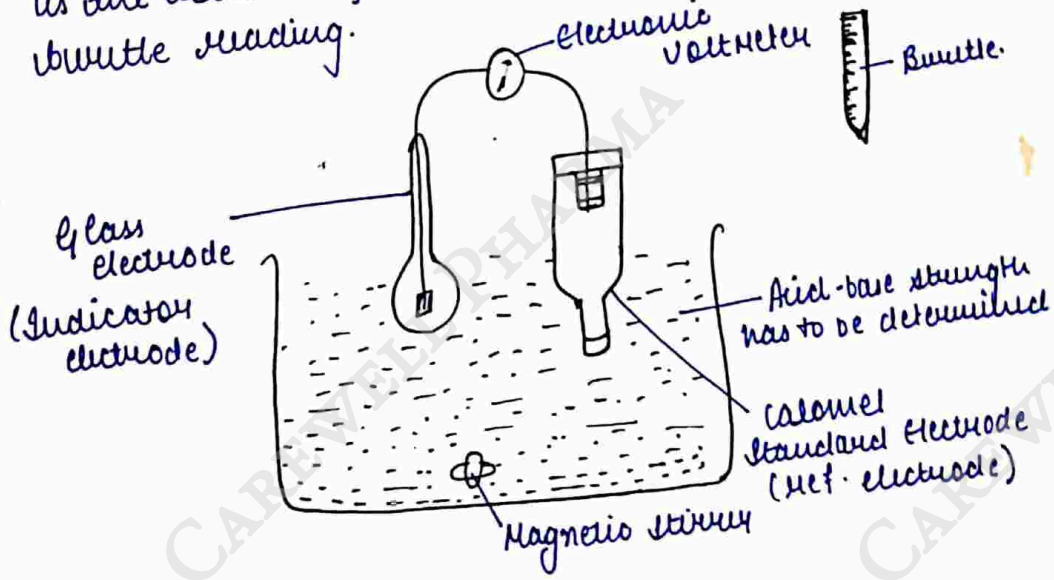
Unit - V

Electrochemical Methods of Analysis:

* Potentiometry:

Principle: In potentiometry, a suitable electrode is immersed in the soln to be titrated. Thus an electrode acts as the indicator. The indicator electrode is paired with the reference electrode and the two electrode are connected to electronic voltmeter. The emf of the indicator electrode changes gradually with the change of conc. of ion caused by addition of titrant from the burette. The end point is indicated with a sharp change in electrode potential. The end point can be found by plotting the graph b/w the cell emf and the vol. of titrant added from the burette. A sharp rise of the curve shows the equivalance point and the corresponding volume on the graph is the volume of the soln used for titration burette reading.

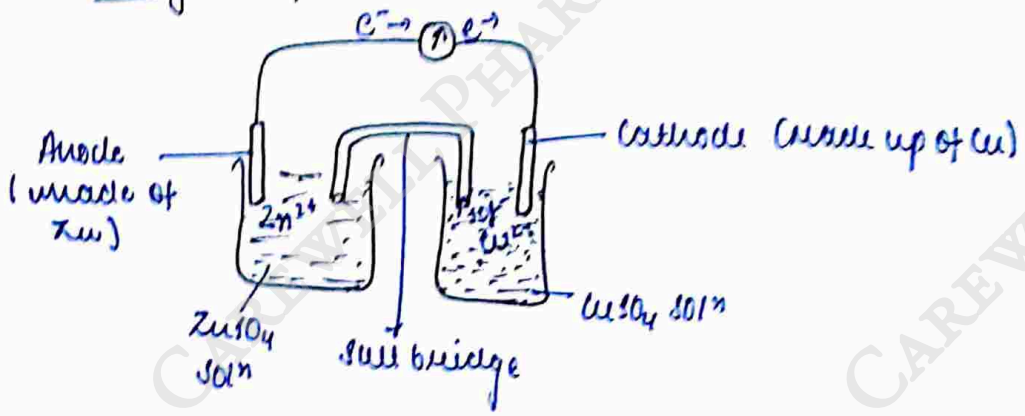


Apparatus for Potentiometer for acid-base titration

Electrochemical cell:

→ A device used for producing an electrical current from a chemical reactⁿ (Redox Reaⁿ) is c/o an electrochemical cell.
Example Volta's cell (Galvanic Cell)

Diagram for volta's cell:



→ Oxidation half reactⁿ at anode-
Zn converted into Zn^{2+}

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

→ Reduction half reactⁿ at cathode -

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

→ Overall Reactⁿ:

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

→ In a voltic cell, there is a flow of electrons from anode to cathode. Oxidation occur at anode and reduction at cathode.

→ A salt bridge is present with which act as passage for movement of ions from one half of the cell to other half.

* Electrode Potential:

In a voltic cell, in which the electrodes are not connected externally, the anode develops a negative charge and cathode a (+)ve charge. The amt. of charge produce on individual electrode is c/a its electrode potential.

* Standard Electrode Potential:

Electrode potential of electron with respect to Standard Hydrogen electrode is c/a std. electrode potential.

* Salt Bridge:

It is U-tube filled with an electrolyte such as NaCl. KCl or K_2CO_4. It provides passage to ions from 1 compartment to other compartment without mixing the two solution.

* NERST Equation:

It is a mathematical relations used to calculate electrode potential of an electrode by using the value of standard electrode potential or the temp. of cell.

$$E = E^\circ - \frac{2.303\,RT}{nF} \log K$$

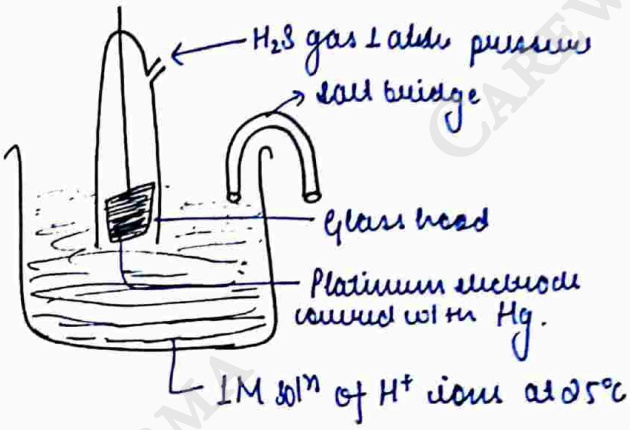
E = Electrode Potential
E° = Standard Electrode Potential
R = gas const.
T = Temp.

n = no. of e- transferred in bay cell rxn
f = faraday of electricity
* = equilibrium const.

* Reference Electrode:
Electrode which are used as standard to determine electrode potential of an electrode are c/a reference electrode.
Example: 1) Std. Hydrogen Electrode
2) Calomel Electrode
3) Std. silver / silver chloride electrode

→ Standard Hydrogen Electrode:

1. Construction:



2. Working:
The H_2 gas is continuously passed over the platinum electrode surface to ensure that the soln at the interphase b/w the electrode & soln is representative of the bulk of the soln. Since the potential of an electrode is quite sensitive to traces of O_2, the air must be excluded from the electrode compartment.
The bay cell reaction is-

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

→ platinum doesn't participate in electrochemical reaction it acts only as an acid for the electron transfer.

→ The potential at 25°c is given by the titration:

$$E_{cell} = 0.0591 \log \frac{[H^+ Std]}{[H^+ unknown]}$$

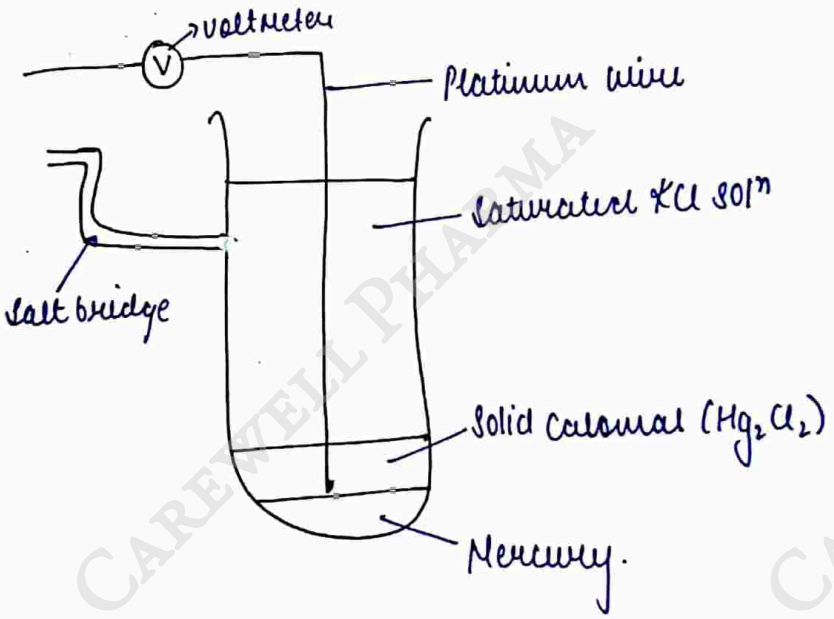
→ The electrode potential of standard Hydrogen electrode is assigned the value of 0 volt.

→ The only cell whose potential is assumed is combined with H^+ electrode and the emf complete cell is determined with the voltmeter

→ For eg. The emf of cell is

$$E^\circ_{cell} = E^\circ \text{Std. } H_2 \text{ electrode} - E^\circ \text{ sample electrode}$$

2) Calomel electrode:



$Cl^-(1M)[Hg_2Cl_2, Hg]$

Calomel electrode is represented as

→ Half-life cell reactⁿ is - $Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$

The emf of the cell -

When we join calomel electrode with Zn electrode at 25°C is +0.280 volt.

→ Calomel electrode can be used both as an anode and as a cathode for determination of electrode pot for a sample electrode.

→ When it act as an anode Hg and Cl react to produce 2e (-ve)

→ When it act as cathode Hg_2Cl_2 consume 2e⁻ to form Hg & Cl^-

→ Electrode pot of calomel electrode is -

$$E = E^\circ - 0.059 \log [Cl^-]$$

→ for 0.1N KCl,

$$E_{calomel} = 0.334V$$

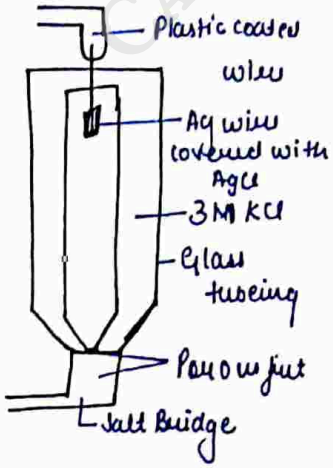
→ for 1N KCl,

$$E_{calomel} = 0.28V$$

→ for Std. KCl -

$$E_{calomel} = 0.242\ V$$

* Silver-Silver Chloride Electrode :



* Working : AgCl electrode can act as both cathode and anode to determine electrode pot of a sample electrode.

→ When it act as anode, a half-cell reaction is-

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

→ When it as cathode, a half cell reaction is-

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

→ Electrode pot of AgCl electrode is - $E_{Ag/AgCl} = E^\circ - 0.0591 \log [Cl^-]$

→ For 1M KCl - $E_{Ag/AgCl} = 0.223V$

→ For saturated KCl - $E_{Ag/AgCl} = 0.199V$

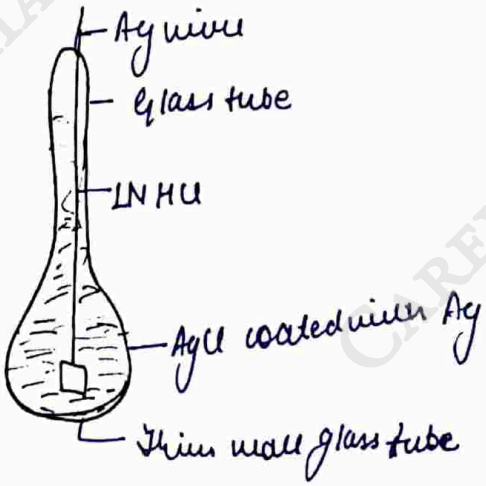
* Indicator Electrode :

The electrode whose potential depends upon the conc. of ion to determine is c/a Indicator Electrode.

Example. Glass electrode, Metal electrode, Std. H^+ electrode.

1) Glass Electrode

Construction:



* Working: The glass electrode may be represented as Ag, AgCl / 1N HCl H^+ (Test soln).

→ When placed in a soln, the potential of glass electrode depends on H^+ ions conc. of the soln.

The potential develops across the glass membrane as a result of a conc.-difference of H^+ ions on the two sides of the glass membrane (inside & outside thin walled glass tube). If H^+ ions conc. changes the magnitude of potential difference also changes and can be calculated using the following eq. at 25°C.

→ $$E_{Glass} = E^\circ_{Glass} + 0.0591 \log [H^+]$$
$$= E^\circ_{glass} - 0.0591\, pH$$

→ Glass rod is used as a secondary std. electrode. The glass electrode is used for determining pH when calomel electrode is coupled with it.

2.) Metal Electrode :

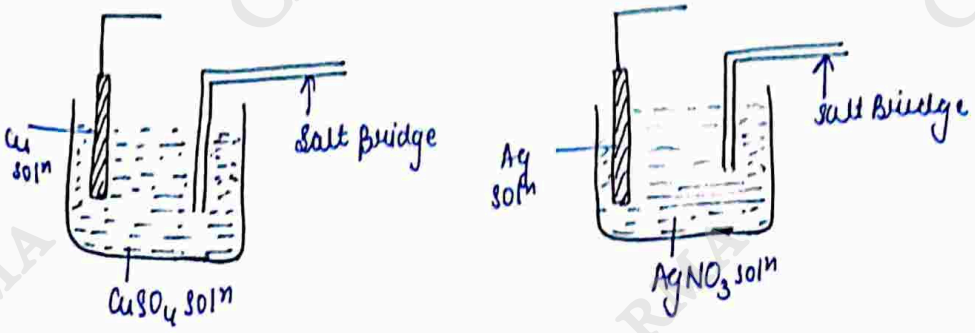
Metal electrode generate electrode potential as a result of redox reactn on the surface of metal. Platinum or Gold metals are generally used as indicator electrodes.

In potentiometry, 3 types of metal electrodes are used -

1.) First Kind Electrode :

These electrodes consist of an metal rod immersed in its soln and are responsible for Ionic activity of electrode

Eg. ① Cu electrode dipped in $CuSO_4$ soln
② Ag electrode dipped in $AgNO_3$ soln.



→ For Cu electrode, reactn involved is -

$$Cu^{2+} + 2e^- \longrightarrow Cu(s)$$

→ Eqn for electrode potential is

$$E_{indicator} = E^\circ_{Cu} + \frac{0.0592}{2} \log [Cu^{2+}]$$

→ for Ag electrode, the reactn involved is -

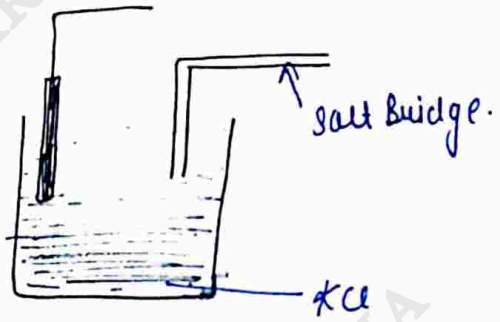
$$AgCl + e^- \longrightarrow Ag(s) + Cl^-$$

→ Eqn for electrode potential is -

$$E_{ind.} = E^\circ_{AgCl} + \frac{0.0592}{1} \log \frac{1}{[Cl^-]}$$

2.) Second Kind electrodes: These electrodes consist of an metal wire coated with the ppt. salt. They respond to the change in the ionic activity by complex formation.

eg: 1) Ag/AgCl/KCl electrodes
2) Hg/Hg_2Cl_2/KCl electrodes



3.) Third Kind Electrodes: These electrodes are also named as Redox or Inert Electrodes as they consist of inert metal electrodes dipped in redox ~~reactn~~. soln.

Eg:- Pt-Hg.

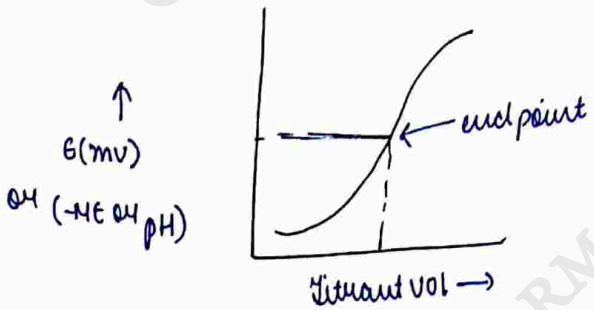
* Methods to Determine end point of Potentiometric Titration:

In potiometriy, three graphically methods are generally used for end point detectation,

1.) In this, graph is plotted b/w the titrant vol. and EMF or pH its values.

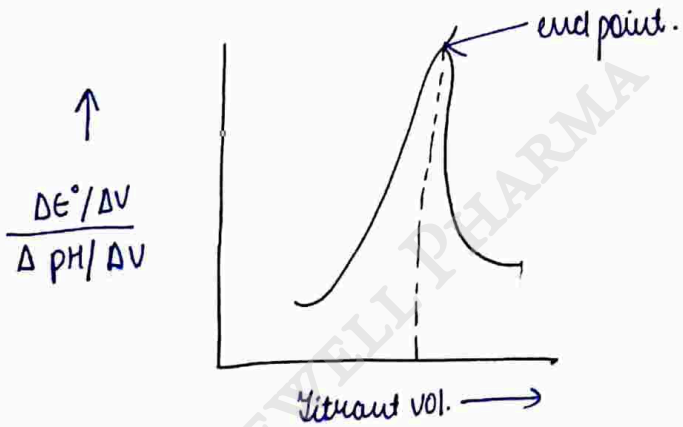
2.) The vol. of titrant is marked on x-axis while the value of EMF or pH is marked on y-axis.

3.) A smooth curve is drawn joining all the points and a point having highest magnitude for gradient (highest slope) is marked from the point, & is are drawn on x and y-axis.



→ **End Method:**

- This method involves plotting of difference emf or pH of each vol. of titrant added.
- On x-axis vol. of titrant is taken and on y-axis ΔE or ΔpH is taken. The graph obt. indicates that at end point the change in pH or emf is maximum.
→ From the highest point of graph for a peak a ⊥ is drawn x-axis which represent the end point.



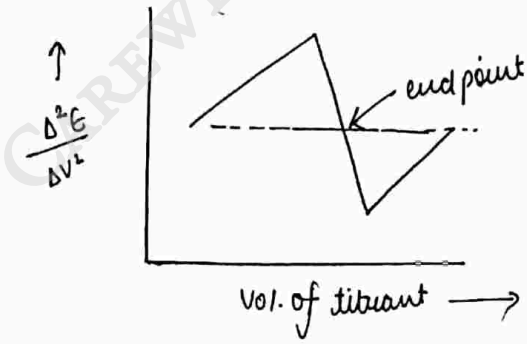
3rd Method:

The second derivatives used in this method is -

$$\frac{\Delta^2 E}{\Delta V^2}$$

→ The difference in pH or potential (emf) of volume added is calculated, squared and then potted.

End point is marked when magnitudes is maximum for the slope of $\frac{\Delta^2 E}{\Delta V^2}$ curve.



* Application of Potentiometry:

1.) **Assay of Nitrazepam:-** Nitrazepam is a basic compound, therefore it can be titrated by non-aqueous titration and the end point can be determined potentiometrically.

Method: Weigh accurately 0.25gm of Nitrazepam and dissolve in it in 20ml of acetic anhydride titrate the resulting soln with previously standardised 0.1 M percloric acid. Determine end point potentiometrically.

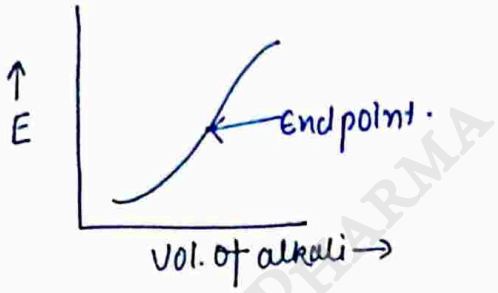
Formula:

$$\text{Percentage purity of Nitrazepam in given sample} = \frac{\text{Burette Reading} \times 0.0281 \times \text{Actual Molarity of } HClO_4 \text{ soln}}{\frac{\text{wt. of sample}}{(0.25)} \times 0.1} \times 100$$

2.) **Assay of Allopurinol:** Weigh accurately 0.25g of allopurinol and dissolve it in 50ml of DMF titrate the resulting soln with previously standarisation 0.1M tetra butyl ammonium hydroxide. Determine the end point potentiometrically:

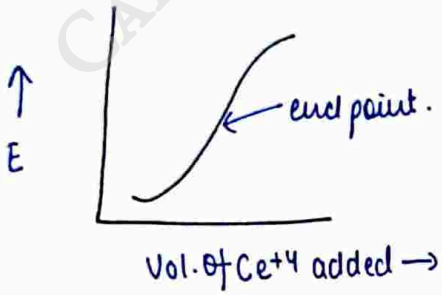
$$\text{Percentage purity of Allopurinal in the given sample} = \frac{\text{Burette Reading} \times 0.0122 \times \text{Actal Molarity of tetra butyl } NH_4OH}{0.25 \times 0.1} \times 100$$

3.) Assay of Determination of Staungth of an acid-

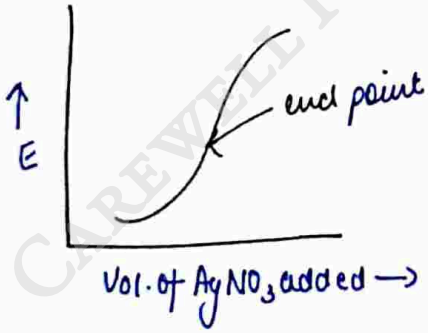


4.) Determination of oxidising and reducing Agent:

Example: Determination of Fe^{+2} by using Ce^{+4}.



5.) Determination of chloride ion:



Determination of NaCl by using $AgNO_3$

6.) Determination of pH.

7.) Determination of amines, amino acids, salts of acids by using non-aqueous titrations.

8.) Determination of phenols and sulphonamide by using non-aqueous titrations.

9.) Determination of fluorides.

* Conductometry -

also f/a - conductometric titration

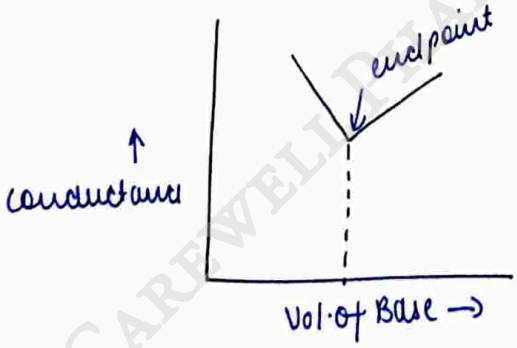
→ Conductometric Titration : Titration in which conductance measurement are used for determining the end point of acid alkali reactn and some displacement reactn are f/a conductometric titration.

In these titration, advantage is taken out of fact that the conductance of soln at const. temp. depends upon the no. of ions present in it and their mobility. For this purpose, the titrant is added from a burette into measured vol of soln to be titrated which is taken in the conductance cell and the conductance reading corresponding to various addition are plotted against the vol. of titrant.

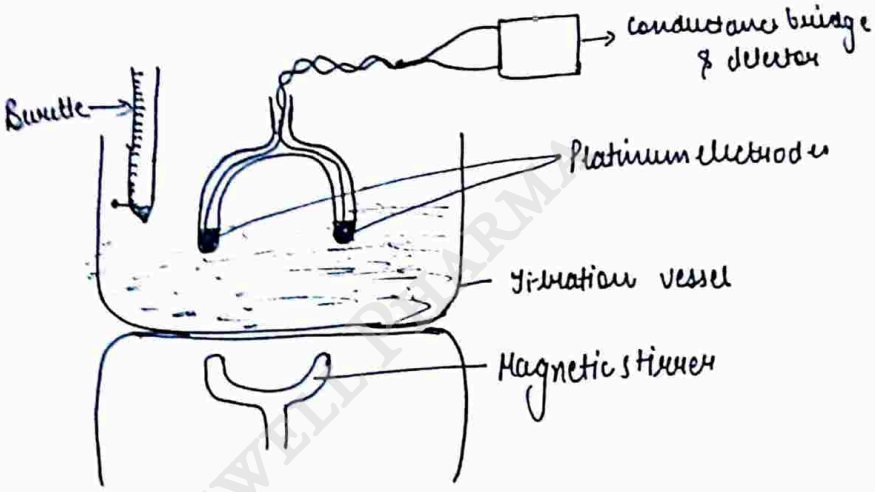
In this way, two linear curves are obt. the point of intersection of which is the end point.

For example:

During the titration with a base we get following conductometric titration curve.

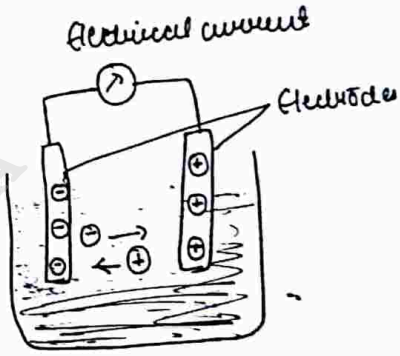


→ The apparatus used for conductometric titration is called conductometer.



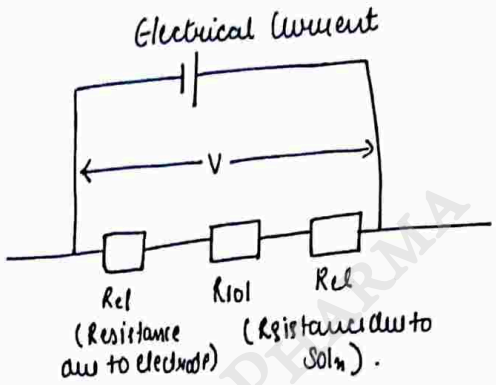
→ A conductometer can be divided into 3 parts:
1.) Current Source
2.) Conductivity cell
3.) Electrodes

Conductivity Cell:



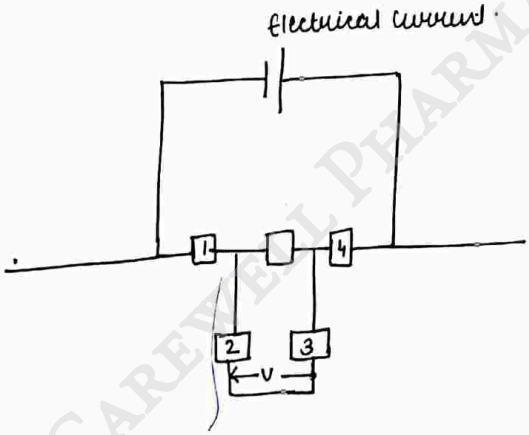
→ In conductometric Techniques, different types of conductivity cells are used.

1.) 2-pole cell -
In this cell, the resulting voltage is measured when an AC current is applied b/w the two poles.



2.) 3-pole cell - In this cell, a third pole is linked to the first pole. This limits the measurement dispersion.

3.) 4-pole cell - In this cell, a const. potential difference needs to be maintained b/w the inner rings (2 and 3) by applying current to the outer rings (1 and 4). As the voltage measurement takes place with a negligible current, these two electrodes (2 and 3) are not polarised.



4.) Platenised Cell:

In this cell, electrodes are coated with platinum black, Black coating inc. the pole surface, inc. the current density and thus minimum polarization effect.

5.) Flow-through Cell:

This cell is used for measuring the flow of small sample volumes.

* Types of Conductometric Titration:

Conductometric Titration are of following types:

1.) Acid-Base Titration
2.) Displacement Titration
3.) Precipitation Titration
4.) Redox Titration
5.) Complexometric Titration

1.) Acid-Base Titration:

In this type of titration, conductometry easily occr of very high conductance of OH^- and H^+ ions.

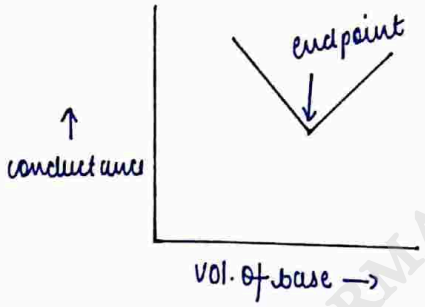
Acid-Base Titration can be of four types:

1.) Titration of a Strong Acid with strong base:

This type of titration, Eg:- HCl with NaOH

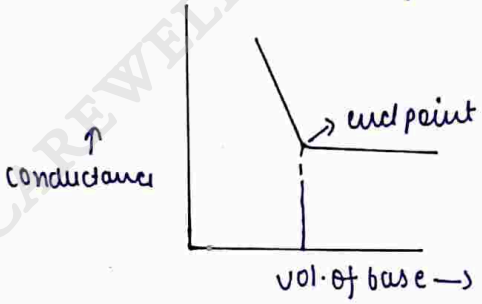
→ when a graph is plotted b/w vol. of base added & conductance two straight lines are obt.

Then point of integration marks the end point.



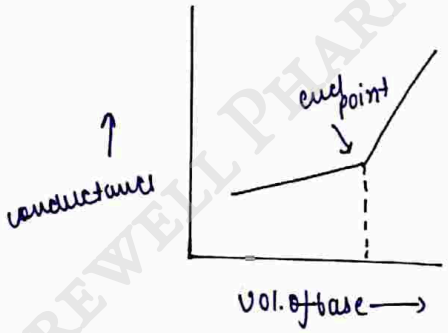
2.) Titration of strong acid with weak base.

Titration of HCl with NH_4OH is example of this type of titration



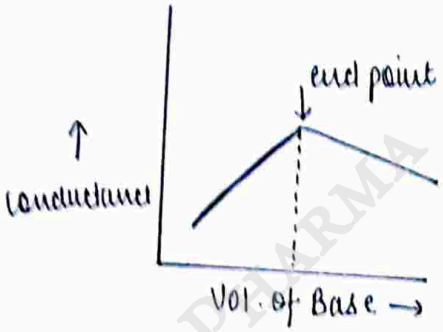
3.) Titration of weak acid with strong base:

Titration of acetic acid with NaOH is example of this type of titration:



4) Titration of weak acid with weak base:

Titration with acetic acid with ammonium hydroxide is example of this type of titration.



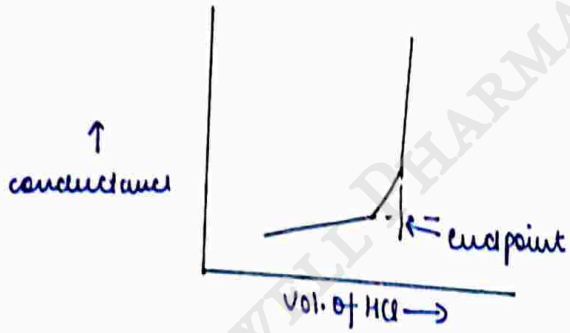
2) DISPLACEMENT TITRATION:

On titrating a salt of weak acid with a strong acid, the anion of strong acid replaces the anion of weak acid and weak acid is liberated in undissociated form.

Eg:- Titration of Sodium Acetate with HCl.

$CH_3COONa + HCl \longrightarrow Na^+Cl + CH_3COOH$

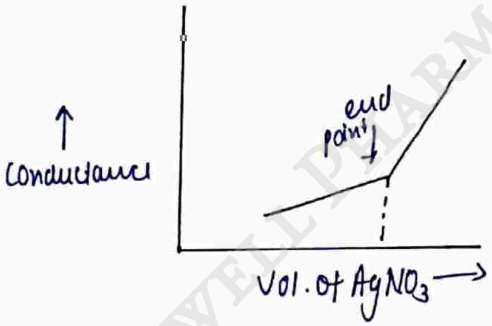
(salt of weak acid) (strong acid) (weak acid)



3) Precipiation Titration:

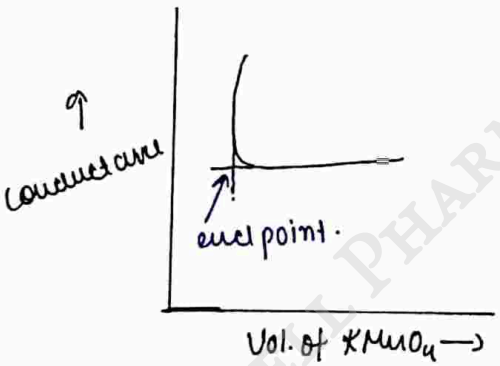
Titration of NaCl with $AgNO_3$ is an example of this type of titration.

$$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$$



4) Redox Titration:

Examples of this type of titration is titration of $FeSO_4$ with $KMnO_4$



* Application of Conductometric Titration :

1) Determination of Basicity of acids :

Basicity of acids can be determined on basis of following formula which includes conductance of sodium salt with no. of acids.

$$\lambda_{1024} - \lambda_{32} = 10.86$$

where, b = basicity of acids

λ_{1024} = Eq. conductance of Na salt of acid dilution of 1024 ltr/eq.

λ_{32} = Eq. conductance of Na salt of acid by dilution of 32 ltr/equ.

2) Determination of Degree of Hydrolysis :

Hydrolysis on dissolving the salt of a weak acid with weak base in water.

Degree of hydrolysis can be determined by following formula:

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

α = degree of hydrolysis
K_f = hydrolysis const.
C = conc.

3) Determination of Ionic Product of Water: (K_w)

This can be obt. from the pure waters, specific conductance and equivalent conductance

The equivalent conductance of infinite dilution is obt. by following equation.

$$\lambda_\infty = 100 \times \frac{k_\infty}{C}$$

λ_∞ = Equivalent conductance at ∞ dilution

k_∞ = Specific conductance at ∞ dilution

C = Conc. of $[H^+]$ or $[OH^-]$ ions, in gm equi/lit.

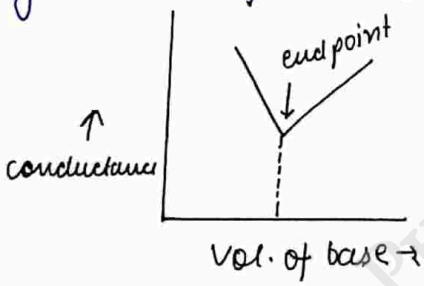
→ From this equation, by substituting the value of k_∞ and λ_∞ value of 'C' can be calculated.

$$C = 100 \times \frac{k_\infty}{\lambda_\infty}$$

$$C = 1.01 \times 10^{-7}$$

$$k_w = C^2 = 1.02 \times 10^{-14}$$

4.) Determination of Strength of an acid or base - Strength of an acid can be determined titrating it with a base and by determining the end point conductometrically.

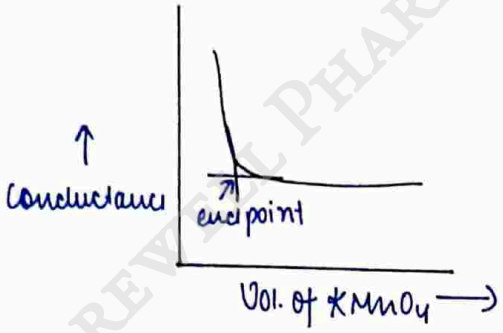


→ Titration curve for titration of strong acid with strong base.

→ Similarly, a strength of base can be determined by titrating it with an acid and determining end point by using Conductometry.

5. Determination of Strength of an oxidising agent or reducing agent.

Strength of oxidising agent can be determined by titration it with a reducing agent and determination of end point using conductivity.



Titration curve for titration of $KMnO_4$ with $FeSO_4$. Similarly Strength of an reducing agent can be determine by using conductometric titration.

* **POLAROGRAPHY:** In this technique, the dropping mercury electrode is used as an indicator electrode. This technique involved electroanalytical method which deals with the electrode potential after of current flowing through an electrolysis cell.

Introduction: The current flows through the sol^{n} is measured in the form of an applied voltage using polarography. In this technique, the working electrode used is generally dropping mercury electrode (DME).

Depending on characteristics of working electrode and the manner in which the voltage is applied, the actual polarographic wave and pattern is obt.

The experimental procedure and polarography includes two methods for voltage application. one is the differential pulse while others in the linear sweep. The working electrode gives a better and sensitive current measurement as compared to the traditional DME.

The working electrode used here is the static Mercury Dropping electrode (SMDE).

In this experiment it is used to get differential pulse and polograms of different Metal ion in sol^{n}.

Polarography is used for both Quantative and Qualitative analysis.

Principle: The simple principle of polarography is the study of sol^{n} by means of electrolysis with two electrodes, one polarisible and one unpolarisable.

The polarisedable electrode is generally dropping Mercury electrode or Static Mercury drop electrode.

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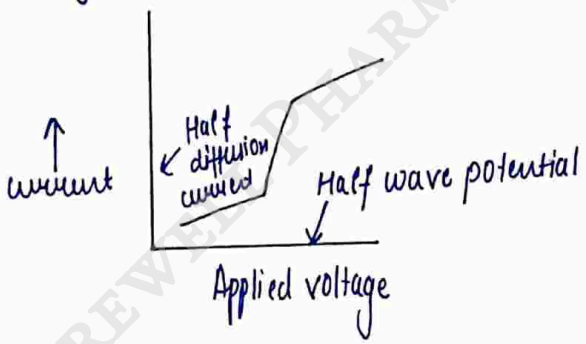
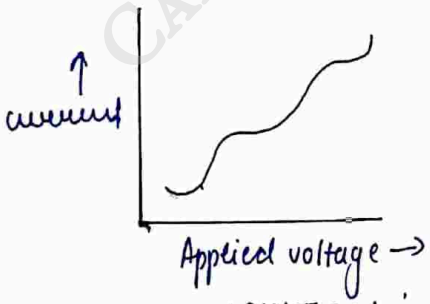
→ In this technique, electrode potential is altered in a linear fashion from an initial potential to final potential.

→ A curve is plotted between voltage and current. The curve had typical sigmoidal shape on the base of curve det. conc. and type of typical species is determined.





→ ILKOVIC EQUATION:

This eqn is used in polarography. This eq. measures the diffusion current (i_j) and conc. of depolarizes (c) which is the sub. reduced or oxidised at the dropping mercury electrode/DME.

The eqn is $i_j = 607 \times N \times D^{1/2} \times C \times M^{2/3} \times t^{1/6}$.

diffusion current

N = no. of faradays of electricity required per mole of electrode reactn

D = Diffusion co-efficient of ions

C = Conc. of depolarizer

M = Rate of flow of Mercury from the dropping electrode capillary.

t = Drop time in sec.

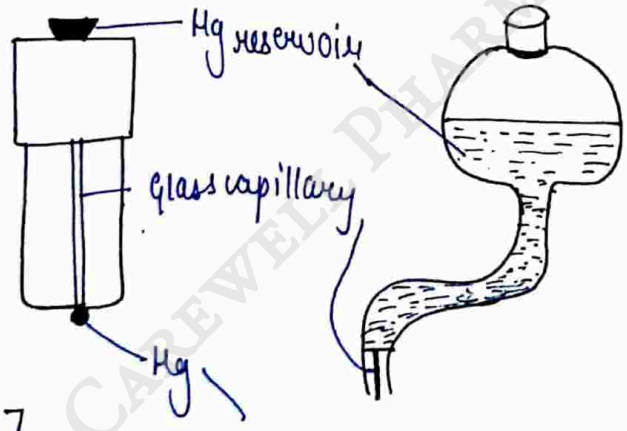
→ The eqn concluded following facts:

1.) The observed diffusion current is directly proportional to the conc. of the electroactive (sample) material. This point from the principle of quantitative analysis (by polarography).

2.) Diffusion current depends upon temp. viscosity of medium, dimension of capillary, pressure on DME and composition of electrolyte.

3.) i_d is proportional to M & droptime (t).

Construction and Working of DME:

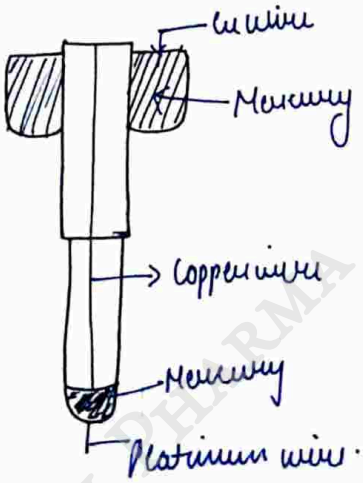


[HMDE] [DME]

→ A flow of Hg gases through an insulating capillary producing a droplet which grows from the end of capillary in a reproducible way. Each droplet grows until it reaches a diameter of about 1mm and releases. The released droplet is no longer in contact with the working electrode as the electrode is used. Hg collect in bottom of cell. In some cell designs this Hg pool is connected to a lead and used as the cells oxylary electrode. Each released drop is immediately followed by the formation of another drop.

The drops are generally produced at a rate of about 0.82 H_2 Hg will be dropped in a stable flow rate of 5-30 drops per min, working at 50-200 milivolt per min.

* **Rotating Platinum Electrode:**



→ In this electrode, a ~~pt~~ Pt wire is sealed in a soft glass tube and rotated by a const. speed motor.

→ Rotating Pt electrode is used in polarography and the electric current is not made, when it is operating with a high speed.
The glass tube and the glass wall are the two parts of rotating Pt electrode.

* Working:
This electrode operates at high speed and possesses mass transfer and inc. the steepness of end point. It shows greatly residual ~~and~~ current due to lack of concense effect.
The thickness of diffusion layer is reduced, thus increasing the sensitivity and also rate of attaining equilibrium.

* Application of Polarography:

The quantative and qualative application are:

1.) Determination of Trace Metals and Metal containing Drugs:

→ Polarography is widely used for determining trace metals and drugs having metallic constituents.
→ The metals that are estimated are Fe, Mg, Zn, Pb and Cu.

2.) Determination of Vitamins:-

Estimation of both fat soln and water soluble vitamins can be done by using DME.

3) Determination of Hormones: Insulin, adrenaline, thiouracil, etc can be determined by using polarography

4) Determination of Antiseptic and Insecticide: Various type of mercury containing antiseptic and insecticides like paramercurian can be determined by using polarography

5) Determination of Antibiotics: Penicillin, streptomycin, chloramphenicol can be determined by using polarography.

6) Determination of Alkaloids: such as quinine, quicine, Isoquinolone, quinoline can be determined by polarography.

7) Determination of dissolved O_2 and peroxides: Polarography can be used to determine dissolved O_2 in a sample.

8) Hydrolysis, complex dimation formation, kinetics of chemicals reactⁿ, Mechanism of electrode reactⁿ can be studied by using polarography.