

ELECTROMETRIC METHODS

6.1 POTENTIOMETERS

6.1.1 Introduction

Potentiometry is an electrochemical method of analysis which deals with the measurement of electrical potential of an electrolyte solution (analyte) under the conditions of constant current (zero current). The measured electropotential is used for qualitative and quantitative analysis of the analyte. The quantitative analysis includes the determination of concentration of analyte by measuring the changes in the electromotive force (potential or voltage) which are brought about by the addition of a titrant to the sample. Quantitative aspect also includes measurement of the concentration of H^+ ions i.e., pH. Hence, pH metry is also a form of potentiometry. Qualitative analysis includes the analysis of a given sample to detect the presence of certain ions using ion selective electrodes.

6.1.2 Principle

Potentiometry is concerned with the measurement of electrical potential of an electrolyte solution to determine its concentration. The principle is based on the fact that the potential of the given sample is directly proportional to the concentration of its electroactive ions or more clearly the activity of the electroactive ions i.e., pH.

6.1.3 Theory

The theory of potentiometry is based on Nernst equation. It gives the basic relationship between the potential generated by an electrochemical cell and the concentration of the ions.

Nernst Equation :

The potential E (half cell potential) of any electrode is given by Nernst equation. It is named after the German physical chemist Walter Nernst. The equation is represented as :

$$E = E^0 - \frac{2.303RT}{nF} \ln \frac{[Ox]}{[Red]}$$

where,

E – Electrode potential of the half cell.

E^0 – Standard electrode potential.

- R – Universal gas constant (8.3145 J/K/mole).
 T – Temperature (298 K or 25° C).
 F – Faraday's constant (charge/mole of electrons, 96500 c/mole).
 n – Number of electrons transferred in the half reaction.
 $[Ox]$ – Concentration of the oxidised species (reducing agent).
 $[Red]$ – Concentration of the reduced species (oxidising agent).

By combining the numerical constants (R , T and F) and converting the logarithm of base e ($\ln$) to logarithm of base 10 ($\log$), the Nernst equation for an electrode at standard conditions of temperature can be written as :

$$E = E^0 - \frac{0.0591}{n} \log \frac{[Ox]}{[Red]}$$

Significance of Nernst Equation :

1. It gives the potential of an electrode.
2. It gives the relationship between the electrode potential and concentration of the electroactive ions.

Limitations of Nernst Equation :

1. It is assumed that at lower concentrations activity of the ions (pH) is equal to their concentration whereas at higher concentrations, it is not true.
2. The equation holds good only when no current flows through the electrodes. Application of current across the electrodes causes changes in the ionic activity at the electrode surface and may lead to variations in the measured potential.

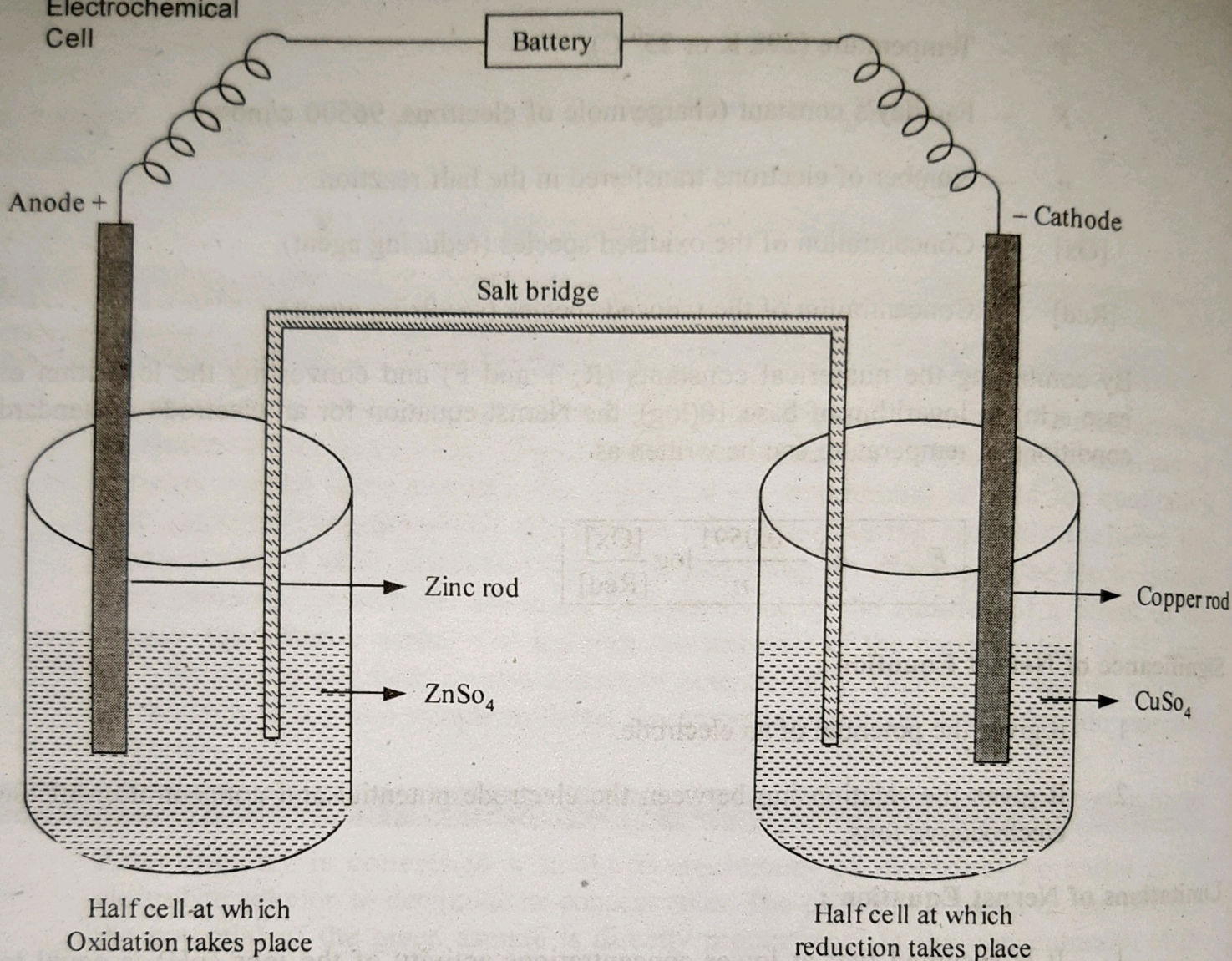
6.14 Electrochemical Cell

Electrochemical cell is a device which converts chemical energy into electrical energy. It is used to generate potential and electric current from chemical reactions.

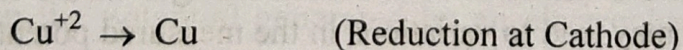
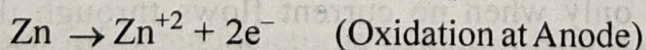
Electrochemical cell consists of two electrodes in contact with an electrolyte solution. The current is generated by the chemical reaction which involves releasing and accepting of electrons at the two electrodes i.e., the basic chemical reaction undergoing in an electrochemical cell is redox reaction.

Example : Consider an electrochemical cell consisting of a copper electrode and zinc electrode dipped into their respective electrolyte solutions i.e., zinc sulphate ($ZnSO_4$) and copper sulphate ($CuSO_4$) respectively.

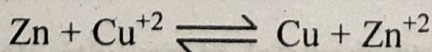
Figure :
Electrochemical
Cell



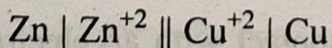
The half reaction contributing to the electrochemical cell are :



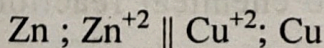
The net reaction is :



The electrochemical cell is represented as :



(Or)



While representing an electrochemical cell, the anode half cell is always written on the left hand side and the cathode half cell on the right hand side while the metal electrodes are always written on the terminal ends.

Half Cell :

Each electrode of an electrochemical cell is referred to as half cell. One half cell lose electrons (oxidation) and the other half cell gain electrons (reduction). The half cell at which oxidation occurs is anode and the half cell at which reduction takes place is cathode.

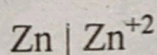
Out of the two electrodes (half cells), one is called the **reference electrode** which has a stable and constant potential and the other is called the **indicator electrode**, the potential of which is to be determined. Electric current is generated by virtue of the potential difference between the indicator and the reference electrodes. The two electrodes are connected to an external circuit to give a complete electrochemical cell. A salt bridge which is a solidified agar bridge or a strip of filter paper saturated with potassium nitrate or potassium chloride or ammonium nitrate serves as a contact between the two electrolyte solutions. It also inhibits the liquid junction potential or diffusion potential arising due to transfer of ions between the two solutions.

Types of Half Cells :

1. **Metal Half Cell :** It consists of a metal electrode dipped into a solution of the same metal ions

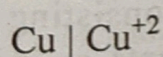
Example : Zinc rod dipped into zinc sulphate (ZnSO_4) solution.

The half cell is represented as :



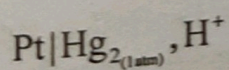
Copper rod dipped into copper sulphate (CuSO_4) solution.

The half cell is represented as :



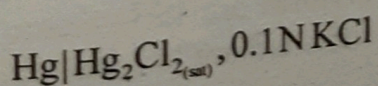
2. **Gas Half Cell :** It consists of a non-reactive metal plate (gold or platinum) or a graphite rod dipped into a solution and gas is bubbled over the metal plate. If the atoms or ions involved in the reaction are non-metallic in such cases, electrodes cannot be designed. To make an electrode suitable for such type of reactions, a non-reactive metal plate is dipped into a solution containing H^+ ions and gas is bubbled over the plate at a standard pressure of 1 atmosphere.

Example : Hydrogen half cell is represented as :



3. Half cells in which a metal is in contact with an insoluble salt or oxide of a solution.

Example : Saturated calomel electrodes are represented as :



Silver-Silver Chloride electrode

 $\text{Ag}/\text{AgCl}_{(\text{sat})}, \text{NaCl}$

Mercury - Mercuric oxide electrode

 $\text{Hg}/\text{HgO}_{(\text{sat})}, \text{NaOH}$ **Standard Electrode Potential (E^0) :**

Electrode potential or reduction potential is defined as the potential difference between the two electrodes (half cells).

Standard electrode potential also known as **standard reduction potential** or **oxidation-reduction potential** is defined as the tendency of a chemical species to gain electrons. The more positive the reduction potential, greater is the tendency of the species to gain electrons.

Standard electrode potential of the ions participating in the chemical reaction is measured in volts or millivolts at standard conditions of temperature (25^0C or 298K), pressure (1 atm) and concentration (1 M). The standard electrode potential of a single electrode cannot be measured independently. Hence, a complete electrochemical cell is built by combining a reference electrode and an indicator electrode. The potential of the indicator electrode is measured against the potential of the reference electrode which has a known standard potential. The potential of the indicator electrode is calculated from the relationship.

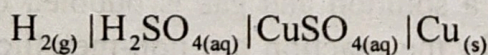
$$E_{(\text{cell})} = E_{(\text{reference})}^0 + E_{(\text{indicator})}^0$$

or

$$E_{(\text{cell})} = E_{(\text{anode})}^0 - E_{(\text{cathode})}^0$$

The Standard Hydrogen Electrode (SHE) has half cell potential exactly 0 V at 25^0C against which all the other standard redox potentials are determined.

For example : Consider an electrochemical cell consisting of SHE as reference electrode and copper - copper sulphate as indicator electrode. The electrochemical cell is represented as :



The emf of the cell was found to be 0.34 V at 25^0C , since, we know that the E^0 of SHE is '0' V at 25^0C .

E^0 of copper electrode can be determined by substituting the standard potential values in the equation.

$$E_{(\text{cell})} = E_{(\text{reference})}^0 - E_{(\text{indicator})}^0$$

$$0.34 = E_{(\text{Cu})}^0 + E_{(\text{H}_2)}^0$$

$$0.34 = E_{(\text{Cu})}^0 + 0$$

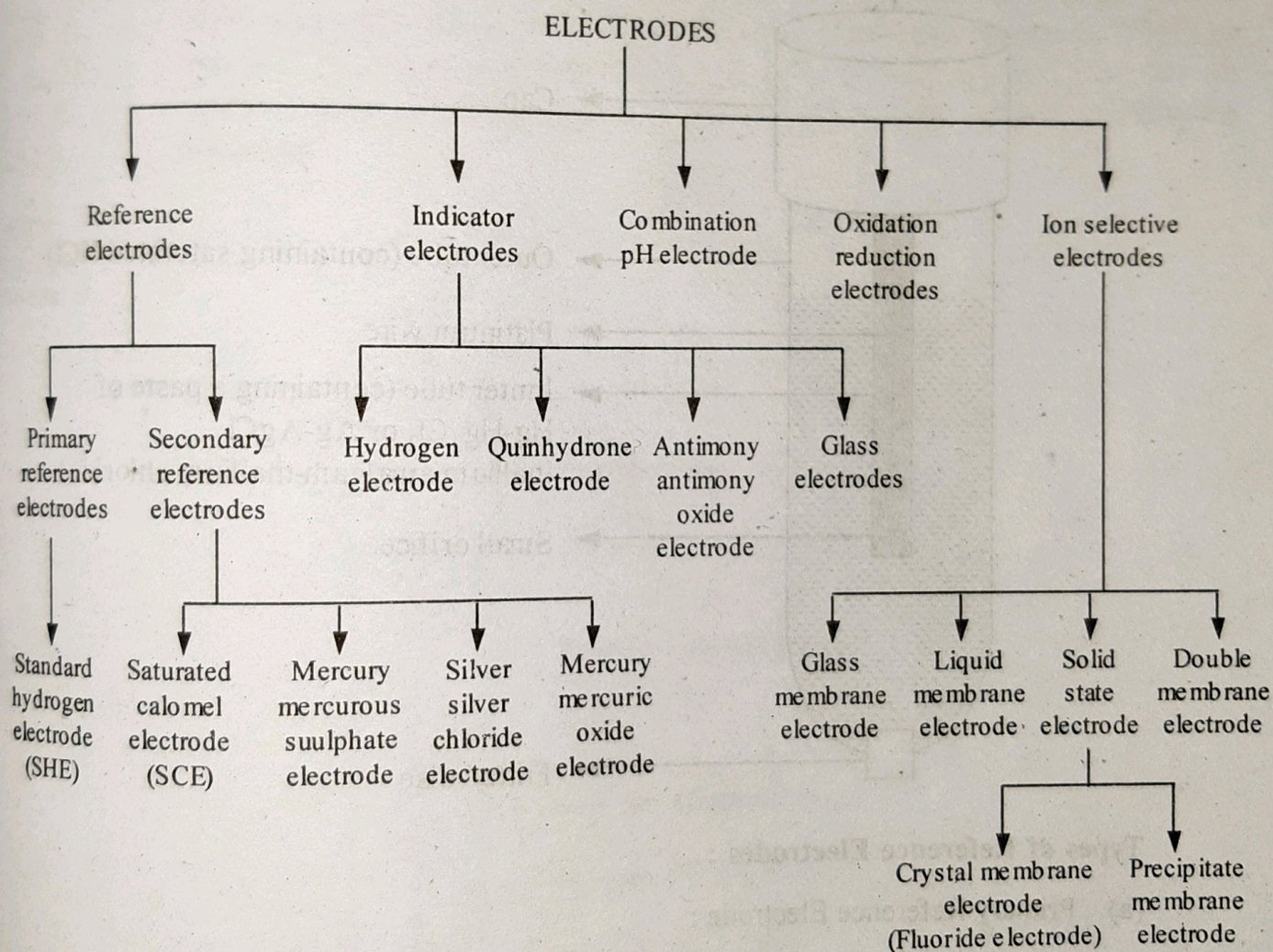
$$\therefore E_{(\text{Cu})}^0 = 0.34\text{V}$$

The standard electrode potential of some of the reference electrodes at 25°C with respect to SHE are as follows :

Reference Electrode	E^0 (Volts)
Saturated Calomel Electrode (SCE)	0.2422
Silver-silver Chloride Electrode (Ag-AgCl)	0.2224
Mercury-Mercuric Oxide (HgHgO)	0.098
Mercury-Mercurous Sulphate (Hg-HgSO ₄)	0.6141

6.1.5 Types of Electrodes

The various electrodes used in potentiometry and pH metry are classified as follows :

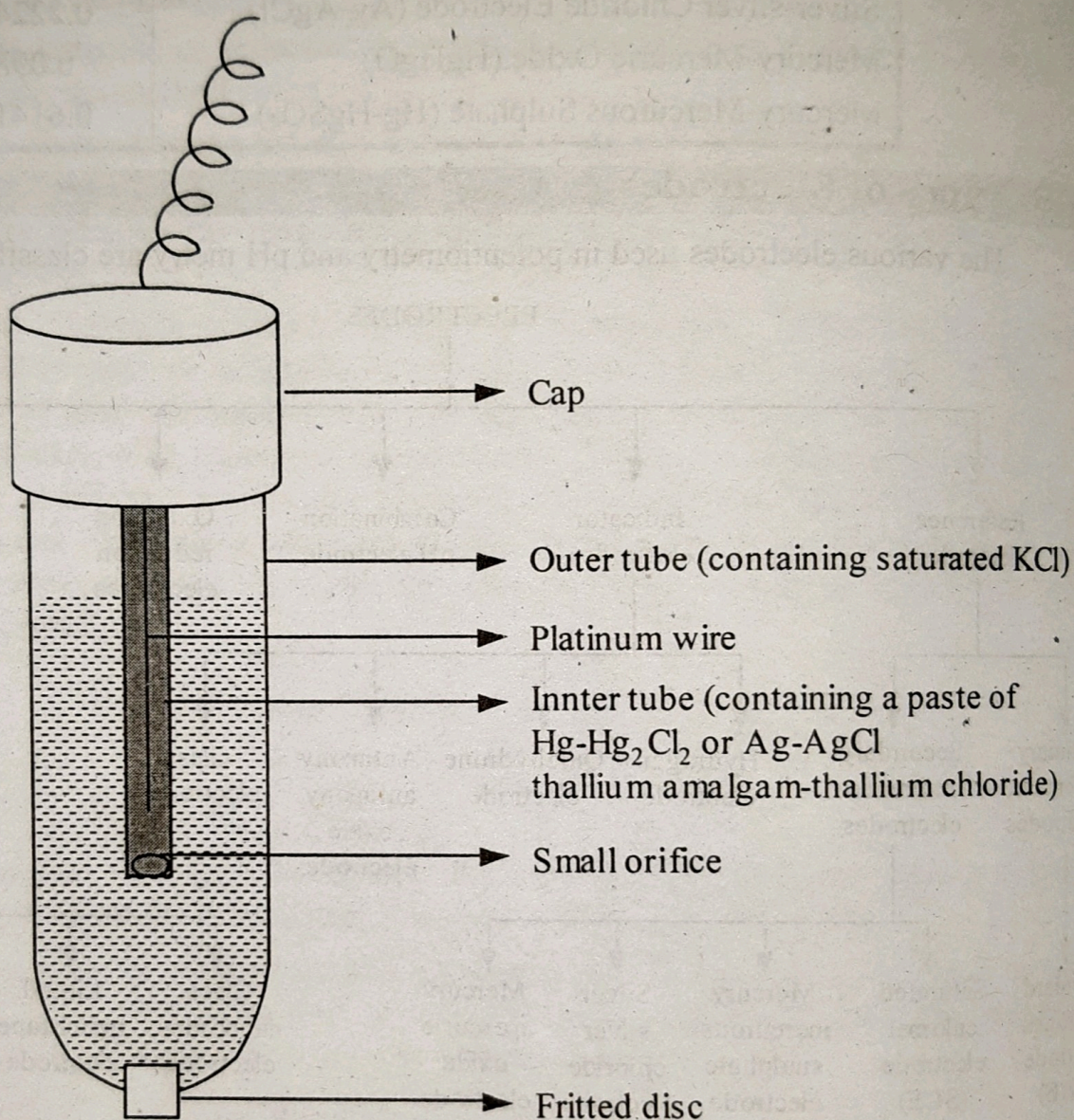


Reference Electrodes :

Reference electrode is defined as an electrode which has a stable and fixed potential i.e., the potential of reference electrode does not change on dipping into any solution. It gives the standard or known potential. Reference electrode is used as one half of the electrochemical cell for determining the potential of the given sample. It is used in combination with an indicator electrode to measure the potential or pH of a given electrolyte. The potential of the reference electrode is taken as the primary standard against which the potential of the indicator electrode is compared.

Reference electrode consists of an inner tube filled with $\text{Hg-Hg}_2\text{Cl}_2$ or Ag-AgCl and thallium amalgam-thallium chloride paste; an outer tube containing a suitable filling solution (saturated KCl) and a device like ground glass sleeve, ceramic plug or fritted disc to form liquid junction with the solution into which it is immersed.

Figure :
Reference
Electrode



Types of Reference Electrodes :

(a) Primary Reference Electrode :

- Standard Hydrogen Electrode (SHE)

(b) Secondary Reference Electrodes :

- (i) Saturated Calomel Electrode (SCE)
- (ii) Mercury-Mercurous Sulphate Electrode
- (iii) Silver-Silver Chloride Electrode
- (iv) Mercury-Mercuric Oxide Electrode

A reference electrode should fulfil three main requirements :

1. Stability

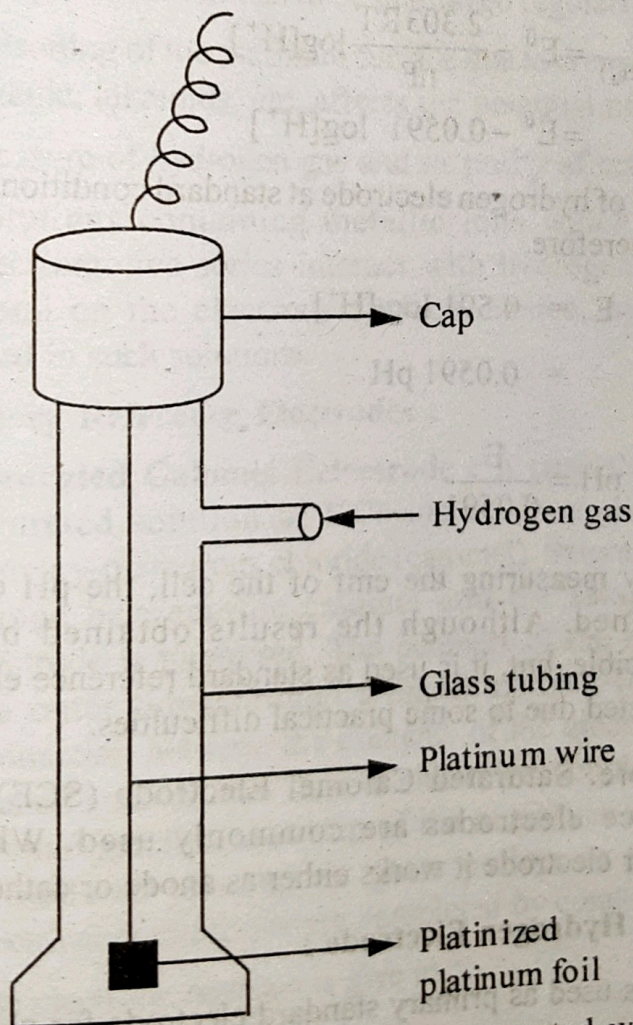
2. Reversibility

3. Reproducibility

1. **Stability** : Reference electrode should be stable over long period of time.
2. **Reversibility** : It should be in equilibrium with its ions and should not show any deviations in its potential when small current is applied.
3. **Reproducibility** : It should obey Nernst equation and should measure the potential within the accepted standard deviation range.

(a) **Primary Reference Electrode** : Standard Hydrogen Electrode (SHE). Hydrogen electrode is also called **Standard Hydrogen Electrode (SHE)** or **Normal Hydrogen Electrode (NHE)**. It is the primary standard electrode for measuring the pH and potential. It acts as both indicator as well as reference electrode.

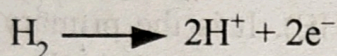
Figure :
Hydrogen
Electrode



It consists of a platinum foil which is coated with a layer of finely divided platinum called platinum black. This coating increases the surface area of the electrode and also helps in rapid establishment of the electrode reaction across the electrode solution interface.

The platinum foil is soldered to a platinum wire and is enclosed in a glass tubing which has an inlet through which pure hydrogen gas (99.8%) is bubbled continuously at a pressure of 1 atmosphere. When the electrode is immersed into a standard acid solution, it serves as a reference electrode and when dipped into an unknown solution containing H^+ ions whose potential or pH is to be determined, it serves as an indicator electrode. The electrode and solution should be completely saturated with the hydrogen gas. Platinum does not take part in the electrochemical reaction. It serves as a site for electron transfer. It absorbs some of the H^+ ions from the solution onto its surface thereby maintaining an equilibrium between the absorbed hydrogen and the H^+ ions in the solution.

The electrode reaction is given as :



The potential of the electrode is given as :

$$\begin{aligned} E_{(H^+, H_2)} &= E^0 - \frac{2.303RT}{nF} \log[H^+] \\ &= E^0 - 0.0591 \log[H^+] \end{aligned}$$

Since, E^0 of hydrogen electrode at standard conditions of temperature and pressure is 0 V, therefore,

$$\begin{aligned} E &= 0.0591 \log [H^+] \\ &= 0.0591 \text{ pH} \end{aligned}$$

$$\text{pH} = \frac{E}{0.0591}$$

Thus, by measuring the emf of the cell, the pH of a sample solution can be determined. Although the results obtained by hydrogen electrode are reproducible, but, it is used as standard reference electrode in pH measurements is restricted due to some practical difficulties.

Therefore, Saturated Calomel Electrode (SCE) and silver-silver chloride reference electrodes are commonly used. When coupled with suitable indicator electrode it works either as anode or cathode.

Uses of Hydrogen Electrode :

- (i) It is used as primary standard electrode for pH measurement.
- (ii) It is used to check the accuracy of other pH electrodes.
- (iii) It is used to determine the sodium error of the glass electrode.
- (iv) It is used to determine the stability and accuracy of the reference buffer solutions.

Advantages :

- (i) It can be used as a reference and indicator electrode. When dipped into standard acid solution, it acts as reference electrode and when dipped into sample solution it acts as an indicator electrode.
- (ii) It is the fundamental reference electrode against which the measurements of pH and potentials of other electrodes are measured.
- (iii) It gives accurate results.
- (iv) Its internal resistance is low.
- (v) It does not show any acid error.
- (vi) It is suitable for measuring the pH over the entire pH range.

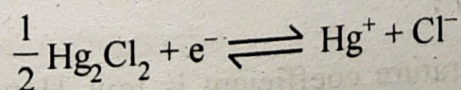
Disadvantages :

- (i) Presence of strong oxidising agents or reducing agents affects the functioning of the electrodes.
- (ii) The platinum foil has to be platinized regularly.
- (iii) Poisoning of the platinum surface due to compounds like sulphides, cyanides, arsenic, alkaloids, etc. affects the potential of the electrode.
- (iv) Pressure of hydrogen gas and its purity affects the electrode potential.
- (v) Solutions containing metallic ions which are below hydrogen in the electromotive series interact with hydrogen and cause deposition of the metal on the electrode surface. Hence, hydrogen electrode cannot be used in such solutions.

(b) Secondary Reference Electrodes :

- (i) **Saturated Calomel Electrode :** It consists of an outer tube containing saturated solution of KCl and an internal tube containing a paste of mercury-mercurous chloride (calomel). Saturated KCl serves as a conductive bridge between the calomel and the sample solution into which the electrode is immersed. The contents of the inner tube are in contact with the outer tube through a small orifice. To maintain stable electrical connection between the contents of the electrode and the sample solution, a small and constant flow of electrolyte solution (KCl) is maintained through a liquid junction at the tip of the outer tube of the electrode. The junction is made of asbestos or glass pellets or sintered carborundum. The electrical connections are completed by connecting it with platinum wire.

The electrode reaction is given as :



The electrode is represented as :

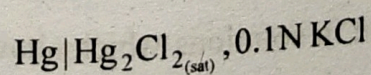
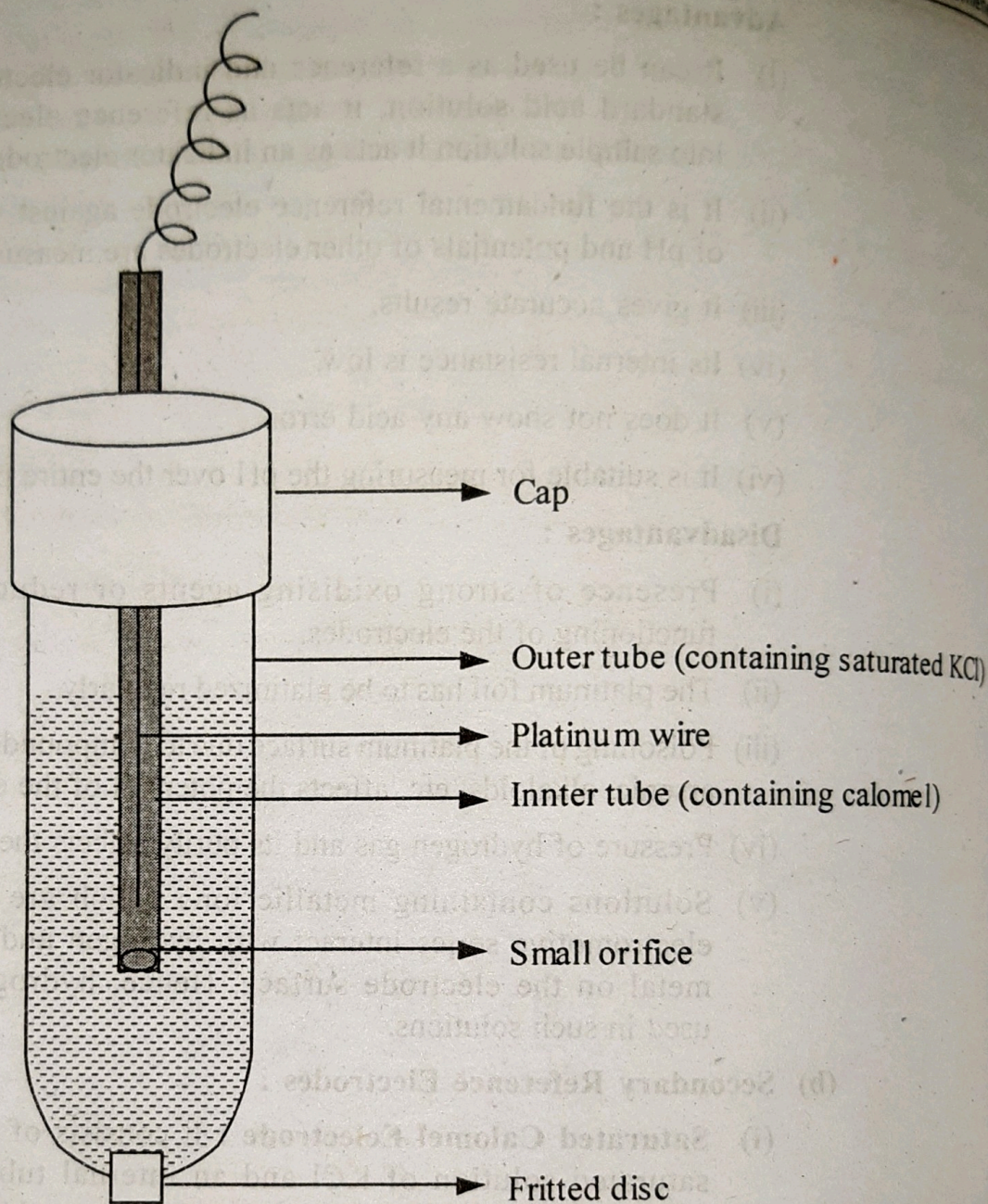


Figure :
Saturated
Calomel
Electrode



Calomel electrode with saturated lithium chloride (LiCl) as salt bridge instead of potassium chloride (KCl) is used for measurement of potential in nonaqueous solutions.

Advantages :

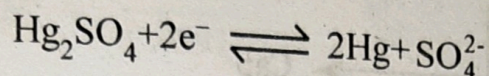
1. Saturated Calomel Electrode (SCE) can be used in various solvents.
2. It can be used over wide pH range.
3. It is strong.

Disadvantages :

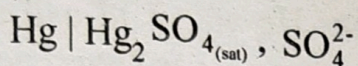
1. Its temperature coefficient is low. Hence, cannot be used at high temperatures.
2. It cannot be used in solutions which shows Cl^- interference.

- (ii) **Mercury-Mercurous Sulphate Electrode** : Its construction is similar to SCE. It contains mercury in a solution containing sulphate ions usually 0.05M H_2SO_4 saturated with mercurous sulphate. It is used in solutions which shows interference due to Cl^- , Ag^+ or Pb^{+2} ions.

The electrode reaction is given as :

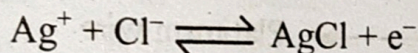


The electrode is represented as :

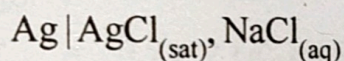


- (iii) **Silver-Silver Chloride Electrode** : It consists of a platinum or copper wire which is electrolytically coated with silver chloride by dipping into a solution containing chloride ion such as KCl, NaCl of definite strengths. It is used with in a range of -10°C to $+110^\circ\text{C}$.

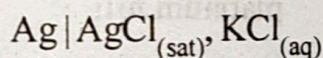
Electrode reaction is given as :



Electrode is represented as :

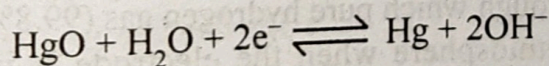


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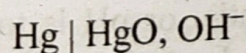


- (iv) **Mercury-Mercuric Oxide Electrode** : It consists of mercury in contact with a solution of sodium hydroxide and potassium hydroxide saturated with mercuric oxide. This electrode is reversible to OH^- ions, hence, useful in alkaline solutions.

Electrode reaction is given as :



Electrode is represented as :



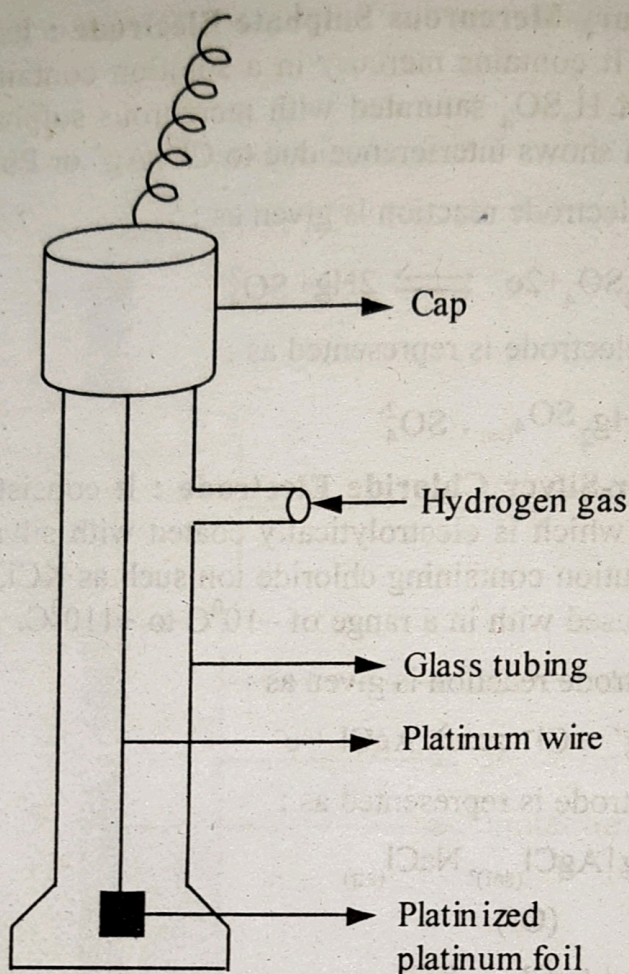
Indicator Electrodes :

Indicator electrode is defined as an electrode which is used to measure the unknown potential or pH of a given solution. It gives the measure of the potential or pH of a solution into which it is dipped in comparison to a reference electrode of known stable potential. Indicator electrodes respond to changes in emf or pH of a solution occurring due to redox reactions taking place at its surface.

Types of Indicator Electrodes :

- (a) **Hydrogen Electrode** : Hydrogen electrode is also called **Standard Hydrogen Electrode (SHE)** or **Normal Hydrogen Electrode (NHE)**. It is the primary standard electrode for measuring the pH and potential. It acts as both indicator as well as reference electrode.

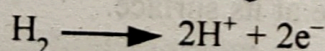
Figure :
Hydrogen
Electrode



It consists of a platinum foil which is coated with a layer of finely divided platinum called platinum black. This coating increases the surface area of the electrode and also helps in rapid establishment of the electrode reaction across the electrode solution interface.

The platinum foil is soldered to a platinum wire and is enclosed in a glass tubing which has an inlet through which pure hydrogen gas (99.8%) is bubbled continuously at a pressure of 1 atmosphere when the electrode is immersed into a standard acid solution it serves as a reference electrode and when dipped into an unknown solution containing H^+ ions whose potential or pH is to be determined, it serves as an indicator electrode. The electrode and solution should be completely saturated with the hydrogen gas. Platinum does not take part in the electrochemical reaction. It serves as a site for electron transfer. It absorbs some of the H^+ ions from the solution onto its surface thereby, maintaining an equilibrium between the absorbed hydrogen and the H^+ ions in the solution.

The electrode reaction is given as :



The potential of the electrode is given as :

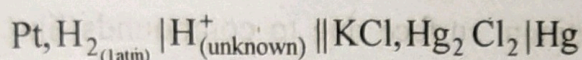
$$\begin{aligned} E_{(H^+, H_2)} &= E^0 - \frac{2.303RT}{nF} \log[H^+] \\ &= E^0 - 0.0591 \log[H^+] \end{aligned}$$

Since E^0 of hydrogen electrode at standard conditions of temperature and pressure is 0 V, therefore,

$$\begin{aligned} E &= -0.0591 \log [H^+] \\ &= 0.0591 \text{ pH} \end{aligned}$$

$$\text{pH} = \frac{E}{0.0591}$$

By combining the hydrogen electrode (indicator electrode) with a reference electrode like SCE, the pH value of the sample solution can be determined. The cell is represented as :



The emf of the electrochemical cell is given as :

$$E_{\text{cell}} = E_{\text{ref}} - E_{\text{indicator}}$$

In this case, E_{ind} is hydrogen electrode

$$\therefore E_{\text{ind}} = 0.0591 \text{ pH}$$

$$E_{\text{ref}} = 0.2422 \text{ (} E^0 \text{ of SCE at } 25^\circ \text{C)}$$

Therefore,

$$E_{\text{cell}} = 0.2422 + 0.0591 \text{ pH}$$

$$0.0591 \text{ pH} = E_{\text{cell}} - 0.2422$$

$$\text{pH} = \frac{E_{\text{cell}} - 0.2422}{0.0591}$$

Uses of Hydrogen Electrode :

- (i) It is used as primary standard electrode for pH measurement.
- (ii) It is used to check accuracy of other pH electrodes.
- (iii) It is used to determine the sodium error of the glass electrode.
- (iv) It is used to determine the stability and accuracy of the reference buffer solutions.

Advantages :

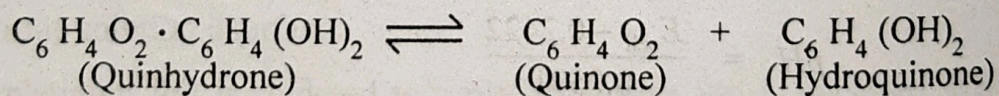
- (i) It can be used as a reference and indicator electrode. When dipped into standard acid solution, it acts as reference electrode and when dipped into sample solution, it acts as indicator electrode.
- (ii) It is the fundamental reference electrode against which the measurements of pH and potentials of other electrodes are measured.

- (iii) It gives accurate results.
- (iv) Its internal resistance is low.
- (v) It does not show any acid error.
- (vi) It is suitable for measuring the pH over the entire pH range.

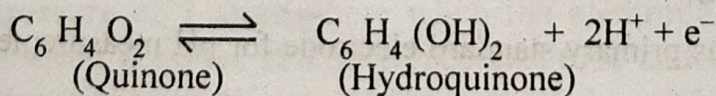
Disadvantages :

- (i) Presence of strong oxidising agents or reducing agents affects the functioning of the electrode.
 - (ii) The platinum foil has to be platinized regularly.
 - (iii) Poisoning of the platinum surface due to compounds like sulphides, cyanides, arsenic, alkaloids etc. affects the potential of the electrode.
 - (iv) Pressure of hydrogen gas and its purity affects the electrode potential.
 - (v) Solutions containing metallic ions which are below hydrogen in the electromotive series interact with hydrogen and cause deposition of the metal on the electrode surface. Hence, hydrogen electrode cannot be used in such solutions.
- (b) **Quinhydrone Electrode :** This is another type of indicator electrode introduced by E. Billman in the year 1921 for measuring pH of solutions. It consists of a platinum wire dipped into a solution which is saturated with quinhydrone.

Quinhydrone is a chemical compound which undergoes reversible decomposition in a solution to give equimolar (1 : 1) quantities of quinone and hydroquinone.



Quinone and hydroquinone gives a reversible redox reaction.



This redox reaction is used for the determination of pH. The potential of this electrode is given by :

$$\begin{aligned} E_{\text{ind}} &= E^0 - \frac{2.303RT}{2F} \log \frac{[\text{QH}_2]}{[\text{Q}][\text{H}^+]^2} \\ &= E^0 - \frac{2.303RT}{2F} \log [(\text{QH}_2) - (\text{Q})(\text{H}^+)^2] \\ &= E^0 - \frac{2.303RT}{2F} \log [(\text{QH}_2)] - \frac{2.303RT}{2F} + \log(\text{Q}) + \frac{2.303RT}{2F} \log [\text{H}^+]^2 \\ &= E^0 - \frac{2.303RT}{2F} \log \left(\frac{[\text{QH}_2]}{\text{Q}} \right) + \frac{2.303RT}{2F} \log [\text{H}^+]^2 \end{aligned}$$

In aqueous solution of quinhydrone, concentration of hydroquinone is equal to the concentration of quinone. i.e.,

$$[\text{QH}_2] = [\text{Q}]$$

Therefore,

$$\begin{aligned} &= E^0 - \frac{2.303RT}{2F} \log 1 + \frac{2.303RT}{2F} \log [\text{H}^+]^2 \\ &= E^0 + \frac{2.303RT}{2F} \log [\text{H}^+]^2 \\ &= E^0 + \frac{2.303RT}{2F} \cdot 2 \log [\text{H}^+] \quad (\because \log 1 = 0) \\ &= E^0 + \frac{2.303RT}{F} \log [\text{H}^+] \\ &= E^0 - \frac{2.303RT}{F} \text{pH} \\ &= E^0 - 0.0591 \text{pH} \quad \left(\because \frac{2.303RT}{F} = 0.0591 \right) \end{aligned}$$

The E^0 of quinhydrone electrode is 0.699 V. Thus, the equation becomes,

$$E_{\text{ind}} = 0.699 - 0.0591 \text{pH}.$$

SCE is used as reference electrode whose $E_0 = 0.2422$ at 25°C .

Hence, emf of the electrochemical cell is determined by the equation.

$$\begin{aligned} E_{\text{cell}} &= E_{\text{ref}} + E_{\text{ind}} \\ E_{\text{cell}} &= 0.2422 + (0.699 - 0.0591 \text{pH}) \\ E_{\text{cell}} &= 0.2422 + 0.699 - 0.0591 \text{pH} \\ E_{\text{cell}} &= 0.9412 - 0.0591 \text{pH} \\ E_{\text{cell}} &= 0.9412 - 0.0591 \text{pH} \\ -(-E_{\text{cell}} + 0.9412) &= -0.0591 \text{pH} \\ (-E_{\text{cell}} + 0.9412) &= 0.0591 \text{pH} \\ \text{i.e.,} \quad \text{pH} &= \frac{0.9412 - E_{\text{cell}}}{0.0591} \end{aligned}$$

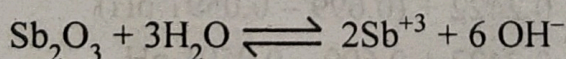
Advantages :

- (i) Internal resistance offered by this electrode is low.
- (ii) Simple and easy to operate.
- (iii) Gives accurate results.
- (iv) Equilibrium of electrode with the sample solution is attained quickly within 1 – 5 minutes.

- (v) Used in wide variety of solutions containing organic substances like unsaturated fatty acids, aromatic acids and solutions of metals where hydrogen electrode is not suitable.
- (vi) It is used for nonaqueous solvents.
- (v) Used in wide variety of solutions containing organic substances like unsaturated fatty acids, aromatic acids and solutions of metals where hydrogen electrode is not suitable.
- (vi) It is used for nonaqueous solvents.
- (vii) It remains unaffected by the presence of dissolved oxygen.

Disadvantages :

- (i) It cannot be used above pH 8, because, hydroquinone gets oxidised in alkaline medium.
 - (ii) It causes contamination of the test solution by altering the equilibrium between quinone and hydroquinone.
 - (iii) Its use is restricted in the presence of oxidising and reducing agents.
 - (iv) It gives salt error.
 - (v) It is unstable above 30⁰ C.
- (c) **Antimony-Antimony Oxide Electrode** : It consists of 2 - 3 cm long antimony rod enclosed in an ebonite tube or glass sleeve and connected to a copper wire. When exposed to air, the antimony rod deposits a thin layer of antimony oxide (Sb₂O₃) which does not dissolve in acid. The electrode is dipped into the sample solution containing H⁺ ions. It is stored in water, when not in use.



The solubility product (K_{sp}) of antimony oxide is given as :

$$K_{sp} = [\text{Sb}^{+3}]^2 [\text{OH}^-]^6 \quad \dots[1]$$

$$\frac{K_{sp}}{[\text{OH}^-]^6} = [\text{Sb}^{+3}]^2$$

$$\sqrt{\frac{K_{sp}}{[\text{OH}^-]^6}} = [\text{Sb}^{+3}]$$

$$\frac{[K_{sp}]^{1/2}}{[\text{OH}^-]^3} = [\text{Sb}^{+3}]$$

$$\text{i.e., } [\text{Sb}^{+3}] = \frac{[K_{sp}]^{1/2}}{[\text{OH}^-]^3} \quad \dots[2]$$

Ionic product of water is :

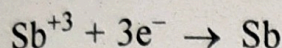
[Unit – VI] 6.19

$$K_w = [\text{OH}^-][\text{H}^+]$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]}$$

Electrode reaction for antimony is written as :

.....[3]



Electrode potential is given as :

$$E_{\text{Sb}^{+3}} = E^0 - \frac{2.303RT}{3F} \log \left(\frac{[\text{Sb}]}{[\text{Sb}^{+3}]} \right)$$

.....[4]

$$= E^0 - \frac{0.0591}{3} \log \left(\frac{1}{[\text{Sb}^{+3}]} \right) (\because [\text{Sb}] = 1)$$

$$= E^0 - \frac{0.0591}{3} (\log 1 - \log [\text{Sb}^{+3}])$$

$$= E^0 - \frac{0.0591}{3} \log 1 + \frac{0.0591}{3} \log [\text{Sb}^{+3}] (\because \log 1 = 0)$$

$$= E^0 + \frac{0.0591}{3} \log [\text{Sb}^{+3}]$$

.....[5]

Substituting the value of $[\text{Sb}^{+3}]$ from equation (2), we get,

$$E_{\text{Sb}^{+3}} = E^0 + \frac{0.0591}{3} \log \left(\frac{[\text{K}_{\text{sp}}]^{1/2}}{[\text{OH}^-]^3} \right)$$

$$= E^0 + \frac{0.0591}{3} (\log [\text{K}_{\text{sp}}]^{1/2} - \log [\text{OH}^-]^3)$$

$$= E^0 + \frac{0.0591}{3} \left(\frac{1}{2} \log [\text{K}_{\text{sp}}] - 3 \log [\text{OH}^-] \right)$$

$$= E^0 + \frac{0.0591}{3} \left(\frac{1}{2} \log [\text{K}_{\text{sp}}] - 3 \log \left[\frac{K_w}{[\text{H}^+]} \right] \right)$$

$$\left([\text{OH}^-] = \frac{K_w}{[\text{H}^+]} \text{ from equation (3)} \right)$$

$$\begin{aligned}
 &= E^0 + \frac{0.0591}{6} \log[K_{sp}] - 0.0591 \log\left(\frac{K_w}{[H^+]}\right) \\
 &= E^0 + \frac{0.0591}{6} \log[K_{sp}] - 0.0591 (\log K_w - \log[H^+]) \\
 &= E^0 + \frac{0.0591}{6} \log[K_{sp}] - 0.0591 \log K_w + 0.0591 \log[H^+] \\
 &= E^0 + \frac{0.0591}{6} \log[K_{sp}] - 0.0591 \log K_w + 0.0591 \text{ pH}
 \end{aligned}$$

Advantages :

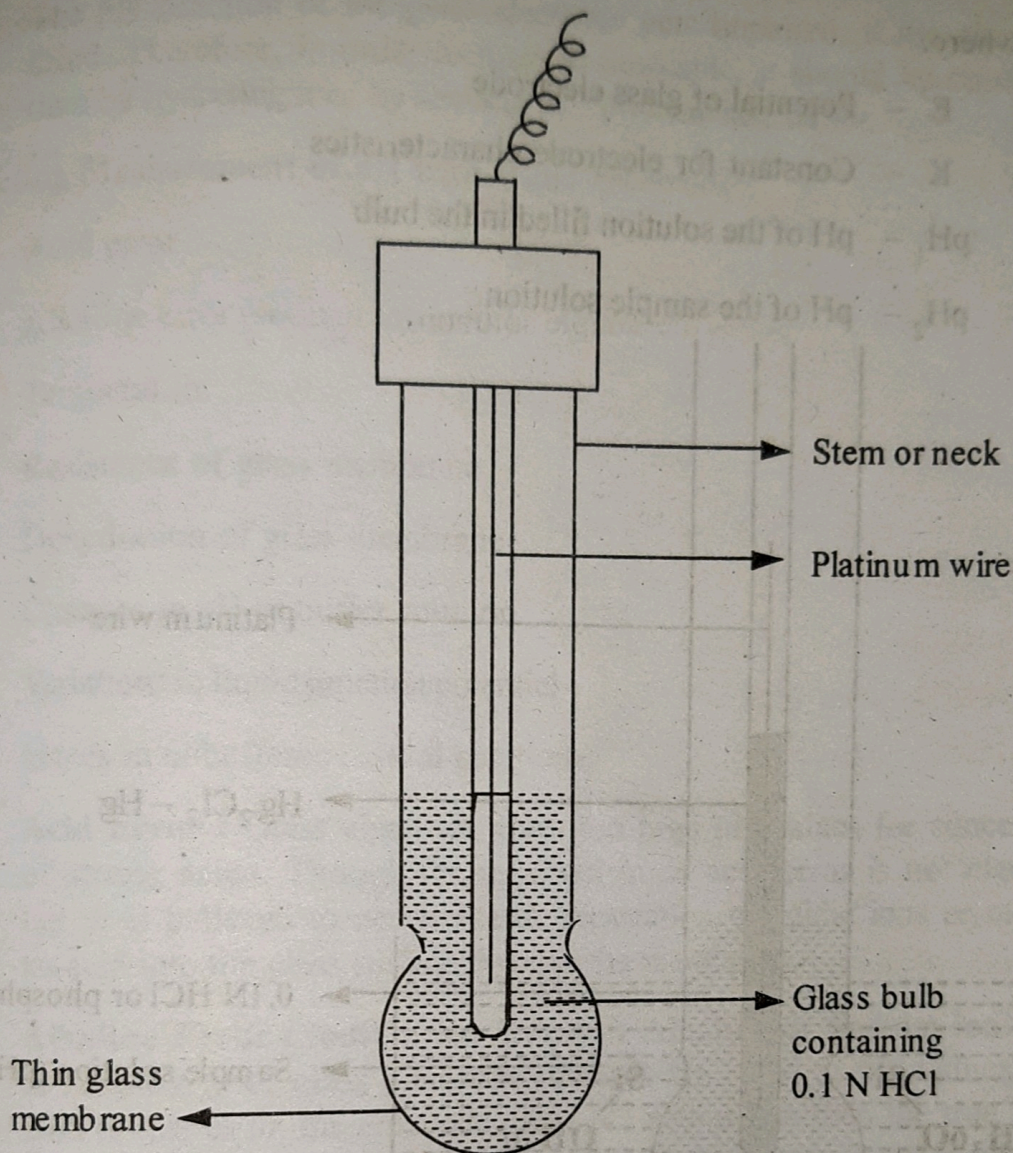
- (i) It is reversible
- (ii) Its resistance is low
- (iii) pH of solutions in the range of 4 - 12 can be determined.
- (iv) It does not cause contamination of the test solution.
- (v) pH of viscous solutions can be measured using this electrode.

Disadvantages :

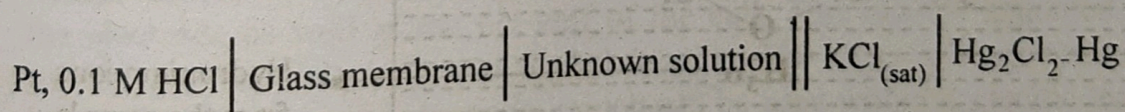
- (i) It is sensitive to changes in temperature of the test solution.
 - (ii) It gives salt errors.
 - (iii) It's use is restricted in the presence of acidic or basic solutions, complexing agents, oxidising agents, dissolved oxygen, heavy metals, hydrogen sulphide.
 - (iv) It cannot be used in the presence of metals like Cu, Ag, Au which are below antimony in electromotive series.
- (d) **Glass Electrode :** Glass electrode is one of the first discovered pH electrode and still the most significant of all the other indicator electrodes. This electrode is sensitive to H^+ ions but is irresponsive towards OH^- ions. Its potential is proportional to pH of the solution. It is composed of a glass membrane which is made up of special type of glass (corning glass) of low melting point comprising of 72% SiO_2 , 22% Na_2O , and 6% CaO .

The electrode consists of a thin glass bulb at one end of the tube and a long neck (stem) at the other end. The bulb is filled with 0.1 N HCl or phosphate buffer containing Cl^- ions. A platinum wire is inserted into the solution in order to complete the electrical contact. The tube is dipped into a beaker containing the solution whose pH is to be determined. At neutral pH, electrode has zero potential. It is usually used in conjugation with a reference electrode for calibrating the pH of the unknown solution.

Figure:
Glass
Electrode



The electrochemical cell is represented as :



Working : The electrode is highly sensitive to H^+ and H_3O^+ ions, which get accumulated at the interface between the glass membrane (SiO_2 surface) and the solution on its either side. Though the glass membrane is responsive to H_3O^+ ions but it is partially permeable to these ions. However, it is permeable to other alkali metal ions like Na^+ , K^+ and Li^+ . The H_3O^+ ions of the sample solution modifies the charge on the silica layer of the membrane. The charge modification of the hydrated silica layer is transmitted across the inner layer by Na^+ , K^+ and Li^+ ions. The H_3O^+ ion activity leads to development of potential difference across the glass membrane that can be measured by using the expression given below.

$$E = K - 0.0591 (\text{pH}_1 - \text{pH}_2)$$

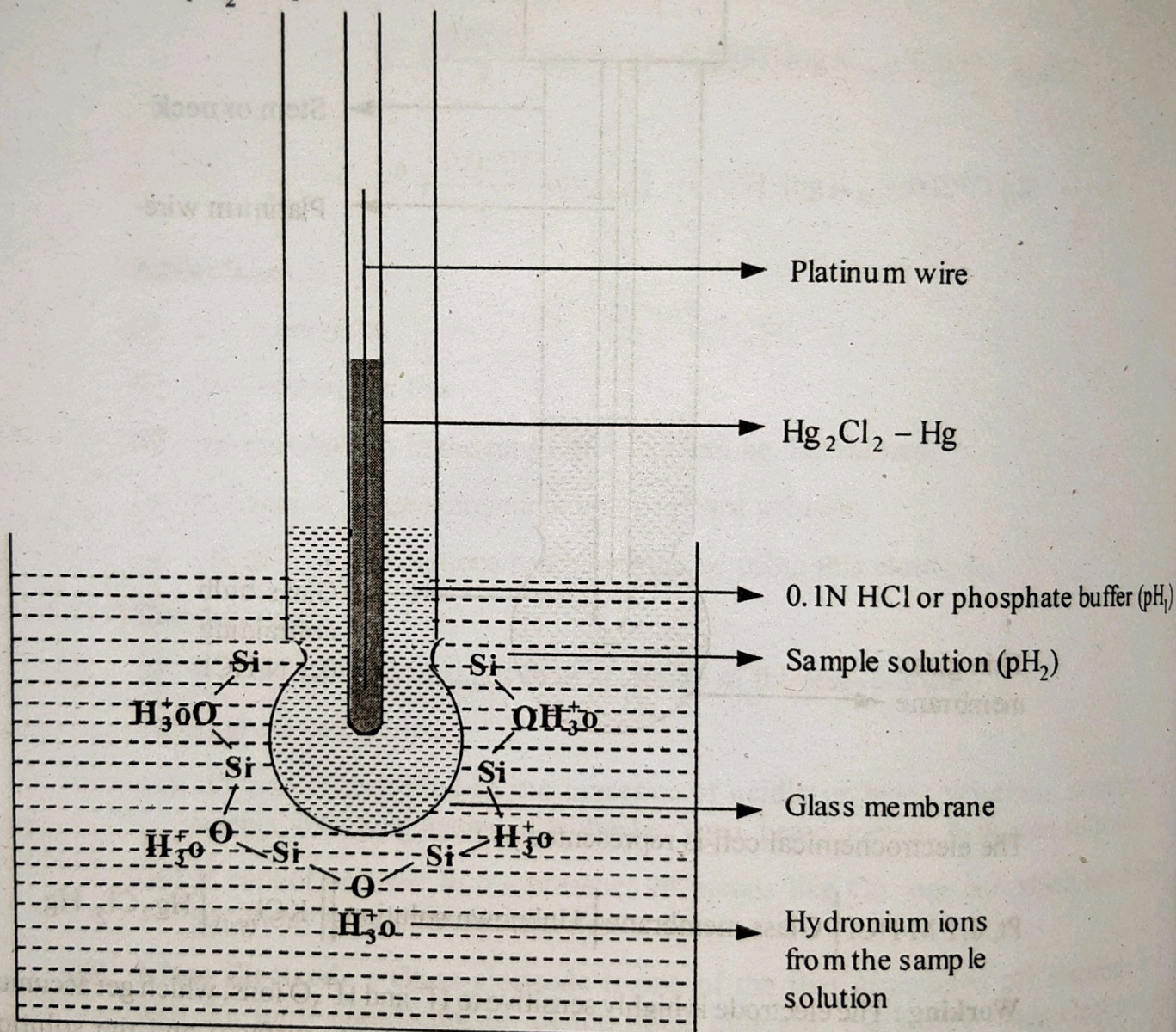
where,

E – Potential of glass electrode

K – Constant for electrode characteristics

pH_1 – pH of the solution filled in the bulb

pH_2 – pH of the sample solution.



Since, pH_1 is known, therefore,

$$E = K - 0.0591 pH_2$$

Electrode Characteristics (K) : Every glass electrode has its own characteristic potential which depends upon various factors like :

1. Size of the glass membrane.
2. Area of the glass membrane.
3. Thickness of the glass bulb.
4. Composition of the glass.

The pH function of the glass electrode gets impaired, if the glass membrane gets dried. Therefore, in order to make it workable, it should be conditioned for some time by hydrating it or by soaking in a dilute acidic buffer.

Factors Affecting Measurement of pH with Glass Electrode :

1. Acid error
2. Alkaline error (sodium ion error)
3. Temperature
4. Resistance of glass membrane
5. Dehydration of glass membrane
6. Changes in pH of buffer solution
7. Variations in liquid junction potential
8. Errors in unbuffered neutral solutions.

1. **Acid Error :** Glass electrode gives too high pH values for concentrated solutions of strong acids. Though the mechanism of acid error is not clearly understood, but, it is believed to occur due to permeation of acidic ions or molecular form of an acid into the glass surface through the membrane.
2. **Alkaline Error (Sodium ion Error) :** Alkaline or Sodium ion error arises due to sensitivity of glass electrode towards Na^+ ions at pH values more than 9.5. Due to this error, the electrode gives pH values less than the true value. This error can be avoided by employing electrodes made of special glass whose composition is changed by substituting Na_2O with Li_2O .
3. **Temperature :** Fluctuations in temperature of the solution affects the potential of the electrode as well as the net emf of the cell. This can be regulated by using suitable reference electrode and shaded solution. The affect of temperature can also be avoided by designing electrodes which can be used within a specific temperature range.
4. **Resistance of Glass Membrane :** The glass electrode shows a very high internal resistance ranging from 10 - 500 mega ohms.
5. **Dehydration of Glass Membrane :** Exposure of the electrode to dehydrating agents like alcohol or acids for long period causes dehydration which gives erroneous results. Therefore, the electrode should be hydrated by placing/immersing it in distilled water when not in use.
6. **Changes in the pH of Buffer Solution :** Storage of buffers for long periods leads to their decomposition due to bacteria. Therefore, buffers should be calibrated regularly to check any bacterial contamination as well as any errors in their preparation.

7. **Variations in Liquid Junction Potential :** Liquid junction potential arises due to the differences in the mobilities of different ions. It develops when an ion moves towards the electrode more rapidly than the other ion. Though it is difficult to completely eliminate this error but it can be overcome by using strong electrolytes in solutions or in the salt bridge.
8. **Errors in Unbuffered Neutral Solutions :** In unbuffered neutral solutions or poorly buffered solutions, electrode attains equilibrium very slowly. To avoid this, the solution should be thoroughly stirred and sufficient time should be allowed for measuring the readings. Also, the electrode must be washed with distilled water several times before measuring pH of the poorly buffered solutions.

Advantages :

- (i) Glass electrode is highly versatile and mostly useful for measuring pH.
- (ii) It remains unaffected by the presence of oxidising or reducing agents.
- (iii) It can be used for the measurement of pH of a wide variety of solutions like viscous, coloured suspensions or colloidal solutions.
- (iv) It gives fast and instantaneous results.
- (v) Simple and easy to operate.

Disadvantages :

- (i) It is extremely fragile. Minute scratches can make the electrode useless. Hence, should be handled with extreme care.
- (ii) It gives unsatisfactory results at very low and very high pH due to acid error and alkaline error.
- (iii) The glass membrane shows a high internal resistance ranging from 10 - 500 mega ohms which makes the measurements of pH electrode potential quite difficult.

6.1.6 Instruments Used For Measuring Potential

The instrument used for measuring the electrode potential of a solution is called potentiometer. There are three types of potentiometers :

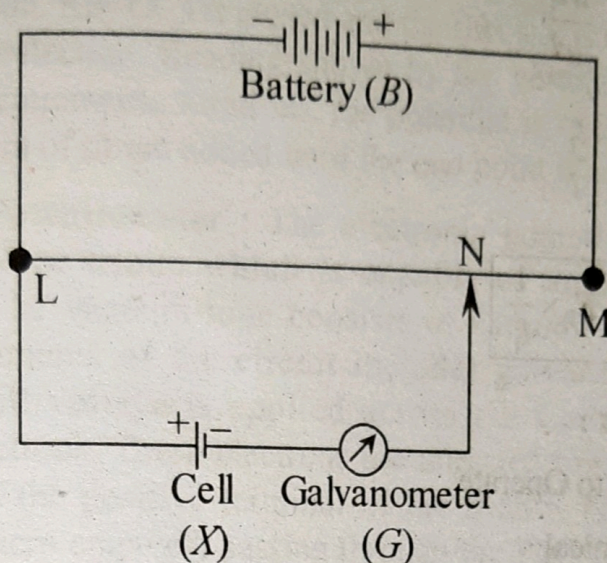
1. Simple potentiometer (Or) Nonelectronic (Or) Null Point Potentiometer.
2. Electronic Potentiometer.
3. Automatic Potentiometer.

1. Simple potentiometer (Or) Nonelectronic (Or) Null Point Potentiometer :

- (a) The principle of simple potentiometer is based on the measurement of potential of a given cell and comparing of a standard cell.

Simple potentiometer consists of a battery (B) which maintains a steady current in the circuit, a sliding wire LM of uniform dimension and known resistance ' r ' provided with a linear scale (in cm) and a galvanometer (G).

Figure :
Second
Derivative
Curve



When a cell of unknown potential is connected in the circuit, current starts to flow which is indicated by a deflection in the galvanometer. The sliding contact N is balanced over the sliding wire LM until the potential of the cell exactly balances the potential of the battery. This is indicated by null deflection (zero reading) in the galvanometer. At this point, the length of the sliding wire (l) is measured. Similarly, the length of the sliding wire is measured for a standard cell denoted as l_1 .

$$E_1 = irl_1 \quad \text{.....[1]}$$

Where,

E_1 - Potential or emf of the standard cell.

i - Current flowing through the sliding wire.

r - Resistance of the sliding wire.

l_1 - Length of the sliding wire at which galvanometer showed null deflection.

Similarly,

$$E = irl \quad \text{.....[2]}$$

Where,

E - Potential or emf of the sample cell.

i - Current flowing through the sliding wire.

r - Resistance of the sliding wire.

l - Length of the sliding wire at which galvanometer showed null deflection.

Combining equations - (1) and (2), we get

$$\frac{E_1}{E} = \frac{irl_1}{irl}$$

$$\frac{E_1}{E} = \frac{l_1}{l}$$

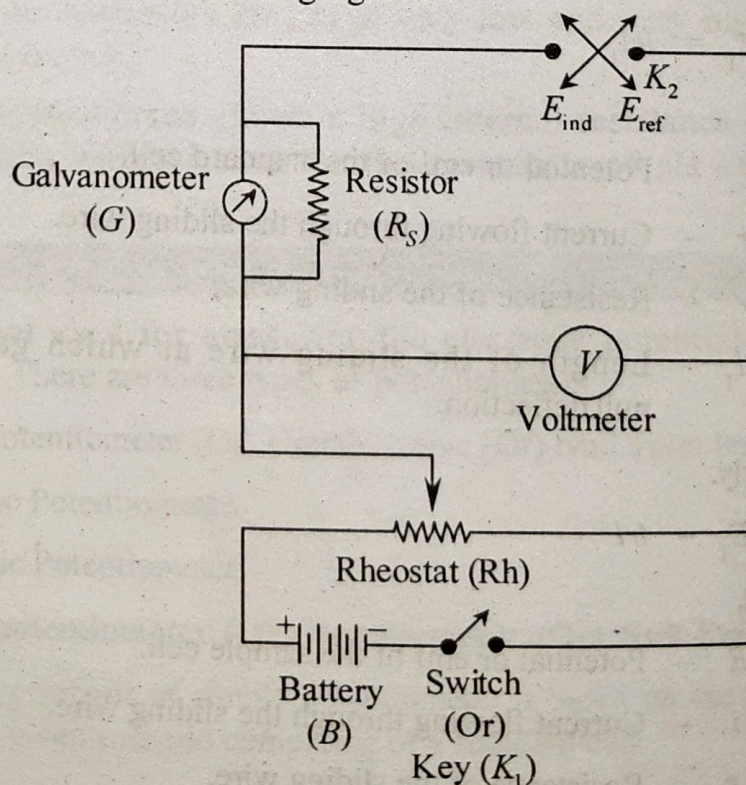
$$E = E_1 \times \frac{l}{l_1}$$

Advantages :

- (i) Simple to Operate
- (ii) Economical
- (iii) Easy to Construct

Disadvantages :

- (i) The instrument needs to be calibrated with a cell of known emf everytime before the potential of sample is to be determined.
 - (ii) It does not have temperature correction knob or slope correction.
- (b) Another type of nonelectronic potentiometer used in potentiometric titrations is shown in the following figure :

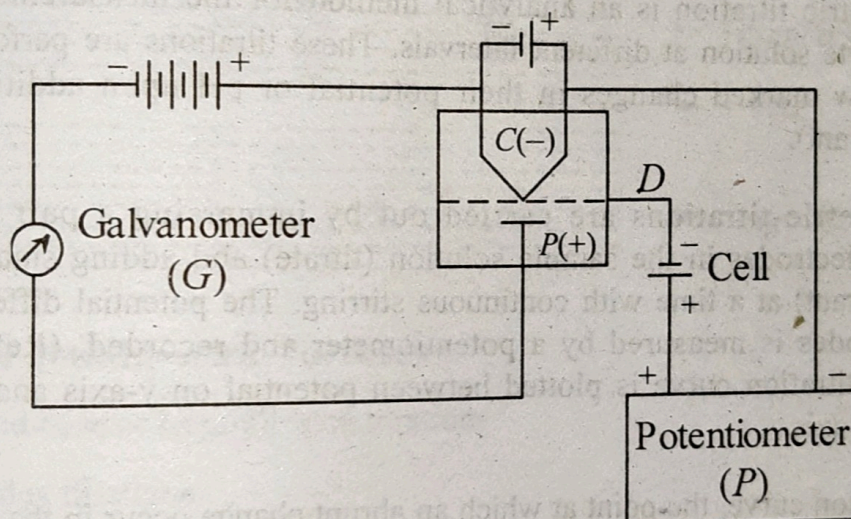


This instrument consists of a power source or battery (B), a variable resistor (Rheostat Rh), voltmeter (V), Galvanometer (G) shunted with resistor (R_s), a switch or Key (K_1) and a reversible key (K_2) which aids in connecting the reference (E_{ref}) and indicator (E_{ind}) electrodes in either polarity.

To operate the instrument, the two electrodes (E_{ind} and E_{ref}) are immersed in the given sample solution. Key (K_1) is closed and the rheostat is adjusted until the galvanometer shows null deflection. Reading shown by the voltmeter at this point gives the emf value. In potentiometric titrations, the potential is recorded in a similar manner with each increment of titrant added until the end point is reached..

2. **Electronic Potentiometer :** The electronic potentiometer consists of electronic vacuum tube or triode which is capable of amplifying the current flowing through it. The vacuum tube consists of cathode (C), Plate (P) and Grid (D). Other components of the circuit includes galvanometer (G) and Battery (B). When a small voltage is applied across the Cathode (C), it gets heated and produces electrons. These electrons are attracted towards the Plate (P). Since it is connected to the positive terminal of the Battery (B). Galvanometer detects the current (in micro amperes) passing through the Plate (P).

Figure :
Electronic
Potentiometer



The magnitude of current passing through the vacuum tube can be amplified or controlled by applying negative potential on the Grid (D). The Grid (D) is connected to the negative terminal of the cell whose potential is to be determined. Any imbalance between the potentiometer and cell produces a deflection in the galvanometer. Balance is restored by adjusting the potentiometer until the galvanometer shows a null deflection. This extent of adjustment gives the potential drop in the cell.

3. **Automatic Potentiometer :** Automatic potentiometric titrators consists of a delivery unit which is controlled by an electrically operated valve. The valve in turn is controlled by a vacuum tube amplifier. This valve is activated by an anticipation control located in the control unit of the titrator. Before starting the titration, the potentiometer is set at a potential at which the end point is anticipated to occur. The electrodes are dipped into the sample solution and the operation switch is turned on. Burette valve allows the reagent to flow from it until the cell potential reaches close to the anticipated value of end point. Flow of reagent is slowed down towards the end point. End point is indicated by a light signal on the display panel.

6.1.7 Potentiometric Titrations

Titration is a process of qualitative chemical analysis in which the concentration of constituents of a sample (analyte) is determined. This is done by adding a reagent (titrant) of known concentration in measured volumes (from a calibrated burette) into the sample (analyte). The analyte reacts with the titrant in definite proportions to give the desired result. The amount of analyte consumed is determined from the end point at which the titration is stopped.

End point is defined as a point at which the number of moles of titrant is equal to the number of moles of analyte i.e., the point at which an exactly equivalent amount of titrant is added to the sample analyte. The end point can be detected by either chemical indicators or by electrical methods.

Potentiometric titration is an analytical method for the measurement of potential of an electrolyte solution at different intervals. These titrations are performed on solutions which show marked changes in their potential or pH upon addition of a chemical reagent (titrant).

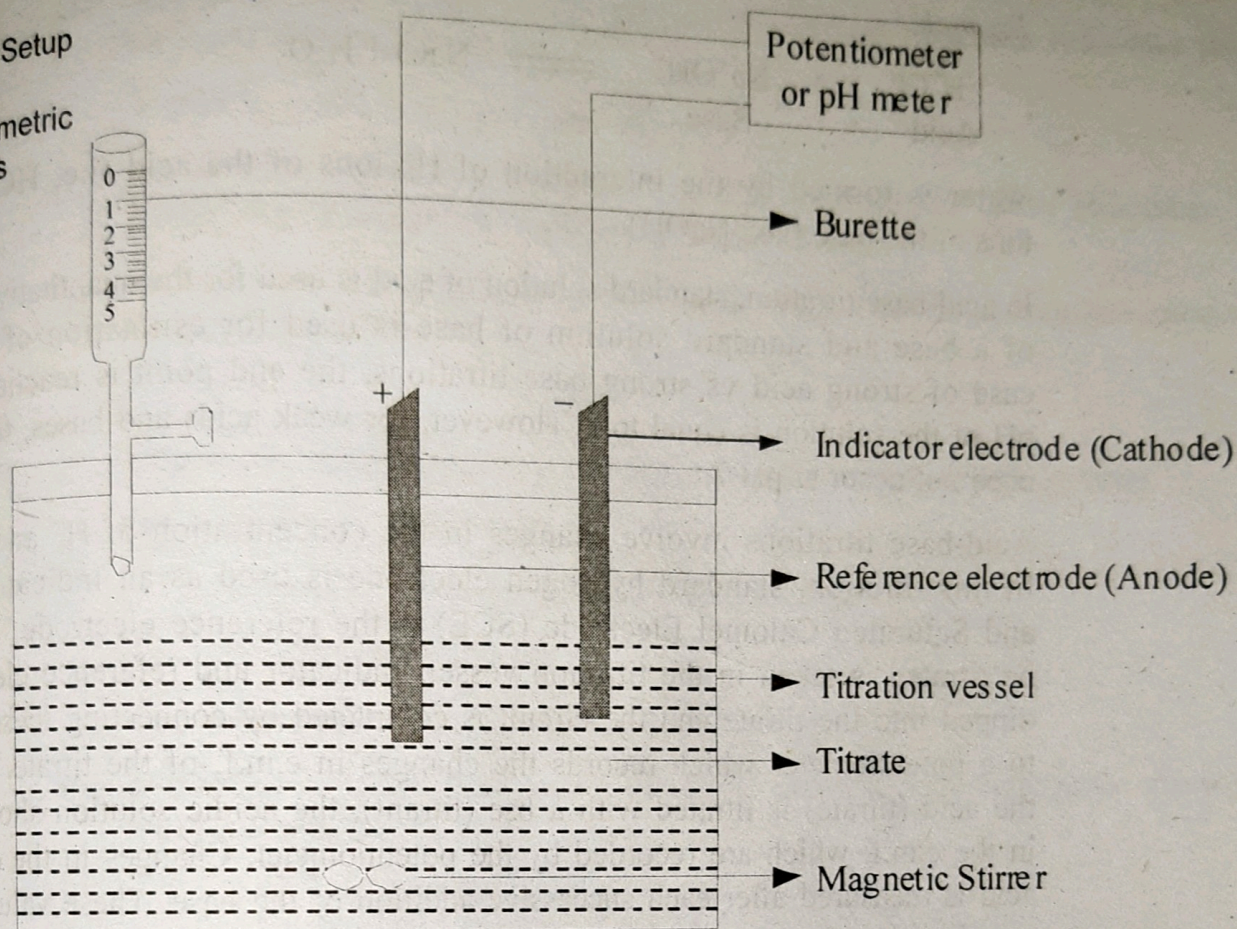
Potentiometric titrations are carried out by immersing a pair of reference and indicator electrodes in the sample solution (titrate) and adding small increments of a reagent (titrant) at a time with continuous stirring. The potential difference between the two electrodes is measured by a potentiometer and recorded. (Refer to the diagram below). A titration curve is plotted between potential on y-axis and volume of titrant added on x-axis.

In the titration curve, the point at which an abrupt change occur in the potential is marked as the end point of titration. The choice of indicator electrode in the potentiometric titrations depends on the type of chemical reaction taking place. In the case of acid base titrations, glass electrode is used and for redox titrations, platinum electrode is found to be more suitable. Reference electrode selected for titration purpose should provide a constant potential throughout the titration. The most commonly employed reference electrode is Saturated Calomel Electrode (SCE).

Apparatus for Potentiometric Titrations : The apparatus for potentiometric titrations consists of the following parts :

1. Titration vessel
2. Automatic or manual burette
3. A pair of indicator and reference electrode
4. Magnetic stirrer
5. Potentiometer or pH Meter.

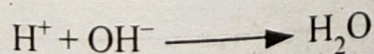
Figure :
General Setup
for
Potentiometric
Titrations



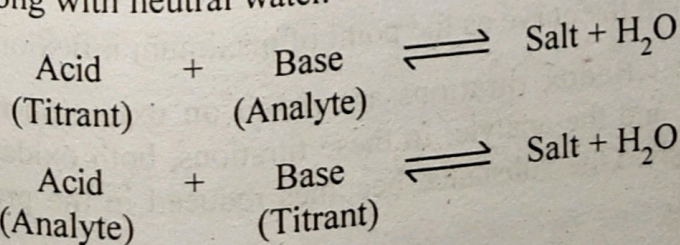
Types of Potentiometric Titrations :

1. Acid-base or Neutralization titrations
2. Redox titrations
3. Complexometric titrations
4. Precipitation titrations or Titrations of sparingly soluble salts.
5. Diazotisation titrations
6. Non-aqueous titrations

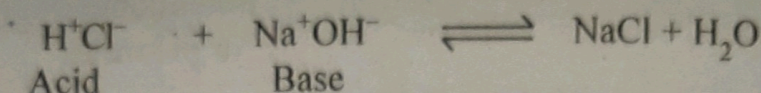
1. **Acid-Base or Neutralization Titrations :** Acid-base titrations (neutralization titrations) are based on neutralization reaction.



It involves reaction between the analyte and an acidic or basic titrant to give a salt along with neutral water.



Example :

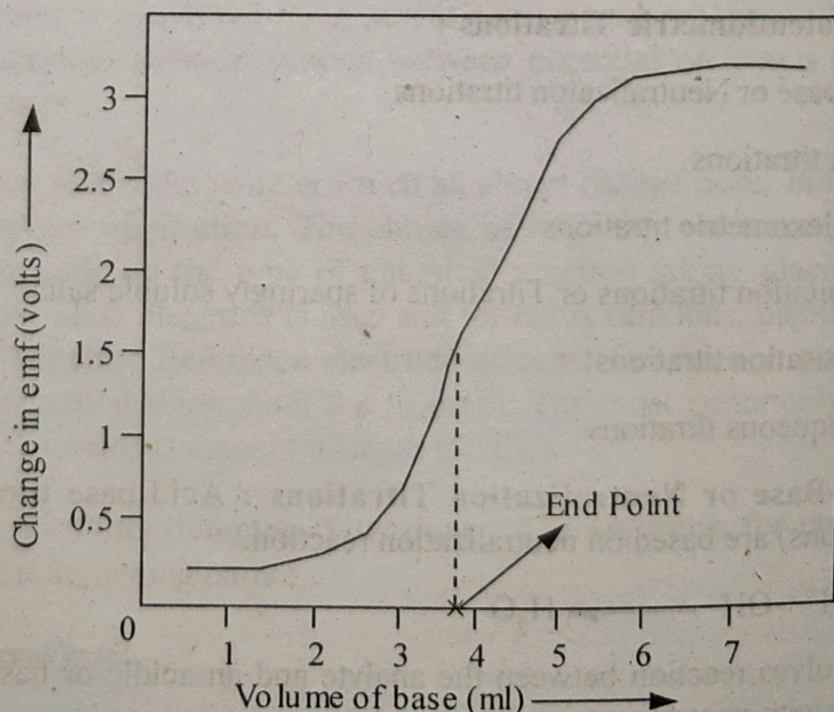


Water is formed by the interaction of H^+ ions of the acid (i.e., HCl) and OH^- ions of the base (i.e., NaOH).

In acid-base titration, standard solution of acid is used for the quantitative estimation of a base and standard solution of base is used for estimation of an acid. In case of strong acid vs strong base titrations, the end point is reached when the pH of the solution is equal to 7. However, for weak acids and bases, the end point need not occur at pH 7.

Acid-base titrations involve changes in the concentration of H^+ and OH^- ions. In this titration, standard hydrogen electrode is used as an indicator electrode and Saturated Calomel Electrode (SCE) is the reference electrode. The acid to be titrated is taken in the titration vessel. Indicator and reference electrodes are dipped into the titrate and the circuit is completed by connecting these electrodes to a potentiometer which records the changes in e.m.f. of the titrate. As soon as the acid (titrate) is titrated with a base (titrant), the acidic solution shows changes in the e.m.f. which are recorded by the potentiometer. Changes in the e.m.f. of an acid is measured after each successive addition of the base. These values of e.m.f. are plotted against volume of base to give a titration curve as follows :

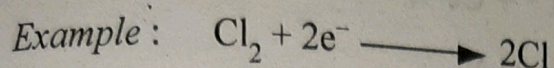
Figure :
Potentiometric
Acid-base
Titration Curve



End point is shown in the curve as the point of maximum inflexion.

2. **Redox Titrations :** Redox titrations are based on oxidation-reduction reaction between the titrant and the analyte. In these titrations, both oxidation and reduction occur simultaneously. One substance becomes reduced in the process of oxidizing the other.

- (i) **Reduction** – is defined as the process in which the reacting substance gains electrons and get reduced.



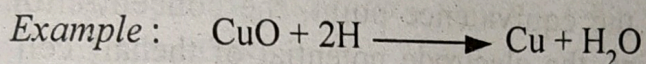
A reducing agent is a substance which reduces the other substance by getting itself oxidized. In doing so, it loses electrons.

Examples of reducing agents are : Oxalic acid, Ferrous ammonium sulphate, Sodium thiosulphate

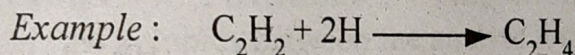
(Or)

Alternately, reduction can be also defined as the process which involves :

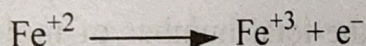
- (a) **Removal of Oxygen :**



- (b) **Addition of Hydrogen :**



- (ii) **Oxidation** – is the process in which the reacting substance loses electrons and gets oxidized.



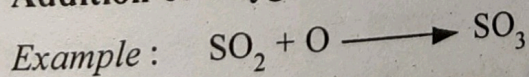
An oxidising agent is a substance which oxidises the other substance by getting itself reduced. During this, it gains electrons.

Examples : Potassium permanganate, Ferric ammonium sulphate, Iodine, Bromine

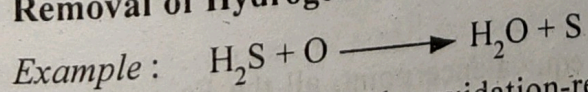
(Or)

Oxidation can be also be defined as the process which involves :

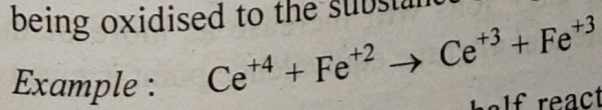
- (a) **Addition of Oxygen :**



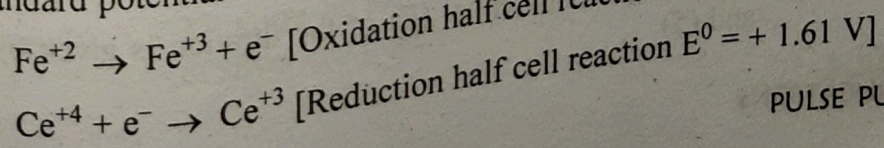
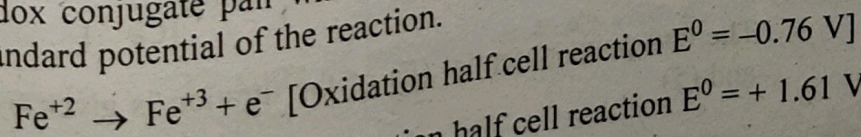
- (b) **Removal of Hydrogen :**



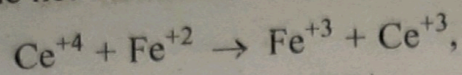
Redox titrations is based on the oxidation-reduction reaction between the analyte and the titrant. It involves the transfer of electrons from the substance being oxidised to the substance being reduced.



Redox titrations involve two half reactions. Each half reaction involves a redox conjugate pair whose standard potentials are used to calculate the net standard potential of the reaction.



The net standard potential of the reaction is given as :



$$E^0 = +0.85 \text{ V}$$

At the beginning of the titration, when Ce^{+4} ions are added to Fe^{+2} ions, Ce^{+4} ions are converted to Ce^{+3} ions (reduction), while Fe^{+2} ions are converted to Fe^{+3} ions (oxidation). The number of Fe^{+3} ions created during the reaction will remain equal to the number of Ce^{+3} ions because, for each mole of Fe^{+3} created, a mole of Ce^{+3} is created. Therefore, throughout the titration,

$$[\text{Fe}^{+3}] = [\text{Ce}^{+3}] \quad \dots[1]$$

Before the equivalence point, the concentration of Fe^{+2} ions is more. At this point, the electrode potential of the half cell at which oxidation occurs is given as :

$$E = E_{\text{Fe}^{+2}/\text{Fe}^{+3}}^0 - \frac{0.0591}{1} \log \frac{[\text{Fe}^{+2}]}{[\text{Fe}^{+3}]} \quad \dots[2]$$

At the equivalence point, the total number of moles of Fe ions equals to the total number of moles of Ce ions.

$$\text{i.e., } [\text{Fe}^{+2}] + [\text{Fe}^{+3}] = [\text{Ce}^{+3}] + [\text{Ce}^{+4}] \quad \dots[3]$$

Subtracting equation – (1) from equation – (3), we get,

$$[\text{Fe}^{+2}] = [\text{Ce}^{+4}]$$

Therefore, at equivalence point :

$$[\text{Fe}^{+2}] = [\text{Ce}^{+4}] \quad \dots[4]$$

After the equivalence point, all the Fe^{+2} ions are converted to Fe^{+3} ions and no more of Ce^{+3} ions can be created. However, the number of moles of Ce^{+3} ions present will be equal to the original amount of Fe^{+2} ions. The concentration of Ce^{+4} ions will increase as more of them are added to the solution. The potential after the equivalence point is given as :

$$E = E_{\text{Ce}^{+4}/\text{Ce}^{+3}}^0 + \frac{0.0591}{1} \log \frac{[\text{Ce}^{+3}]}{[\text{Ce}^{+4}]} \quad \dots[5]$$

The end point potential (E) of the titration is given by adding equations – (2) and (5)

$$2E = E_{Fe^{+2}/Fe^{+3}}^0 - \frac{0.0591}{1} \log \frac{[Fe^{+2}]}{[Fe^{+3}]} + E_{Ce^{+4}/Ce^{+3}}^0 + \frac{0.0591}{1} \log \frac{[Ce^{+3}]}{[Ce^{+4}]}$$

(Or)

$$2E = E_{Fe^{+2}/Fe^{+3}}^0 + E_{Ce^{+4}/Ce^{+3}}^0$$

$$E = \frac{E_{Fe^{+2}/Fe^{+3}}^0 + E_{Ce^{+4}/Ce^{+3}}^0}{2}$$

Potentiometric redox titrations are applied in agricultural and biochemical studies, monitoring water pollution, sewage treatment, cyanide wastes from metal plating industries, chlorine compounds in bleaching agents and paper manufacturing.

3. Complexometric Titrations : Complexometric titrations are based on the formation of a complex between the analyte and the titrant.

During complexometric titrations, addition of titrant to the solution of metal ions (analyte) produces a metal complex which is chemically stable, stoichiometric and undissociated. Ethylenediamine Tetraacetic Acid (EDTA) is the most commonly used titrant for the titration of metal ions. It is also known as ligand or complexing agent. It forms covalent bonds with the metal ions to give a stable metal complex, the characteristics of which are different from that of the free metal ion. Hence, complexometric titrations can also be defined as the reactions in which simple metal ions are converted into metal complex by addition of a reagent known as ligand or complexing agent.

EDTA is the agent of choice in complexometric titrations because :

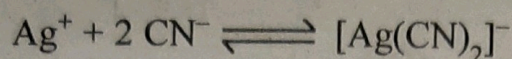
- (a) It forms soluble complexes with most of the metal ions.
- (b) The complexes are rapidly formed.
- (c) The complexes formed are chemically stable and stoichiometric.
- (d) Samples present even in small concentrations (semi macro to micro) can also be determined by titrations using EDTA.
- (e) End point is determined easily by using instrumental methods (potentiometry, conductometry, amperometry) or by chemical indicators like Alizarin, Xylenol orange, Erichrome black T, Mordant black II.

Complexometric titrations are carried out potentiometrically using an indicator electrode made up of the same metal, the ion of which is involved in the complex formation.

Example :

Titration of mercuric cyanide with silver chloride in the presence of silver electrode.

Titration of cyanide ions with silver ions results in the formation of silver cyanide complex which is seen as follows :



Equilibrium constant for the above reaction is given as :

$$K = \frac{[\text{Ag}^+][\text{CN}^-]^2}{[\text{Ag}(\text{CN})_2]^-}$$

$$K[\text{Ag}(\text{CN})_2]^- = [\text{Ag}^+][\text{CN}^-]^2$$

At equivalence point,

$$2[\text{Ag}^+] = [\text{CN}^-]^2$$

Therefore,

$$K[\text{Ag}(\text{CN})_2]^- = [\text{Ag}^+] (2[\text{Ag}^+])^2$$

$$K[\text{Ag}(\text{CN})_2]^- = [\text{Ag}^+] (4[\text{Ag}^+]^2)$$

$$K[\text{Ag}(\text{CN})_2]^- = 4[\text{Ag}^+]^3$$

$$\frac{K}{4}[\text{Ag}(\text{CN})_2]^- = [\text{Ag}^+]^3$$

$$\therefore [\text{Ag}^+] = \sqrt[3]{\frac{K}{4}[\text{Ag}(\text{CN})_2]^-}$$

After the equivalence point, $[\text{Ag}(\text{CN})_2]^-$ gets precipitated. Further, addition of Ag^+ ions does not bring about any change in the concentration of complex or Ag^+ ions.

4. **Precipitation Titrations or Titrations of Sparingly Soluble Salts :** Precipitation titrations involves reaction between the titrant and the analyte to form sparingly soluble salts.

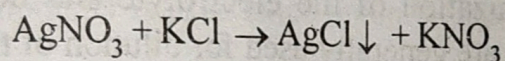
Precipitation titrations can be performed under the following conditions :

- The precipitate should be formed rapidly.
- The precipitate formed should not interfere with the end point during the titrations.
- Precipitate should not have any adsorbing effects i.e., it should not absorb the solute.
- Precipitate should be insoluble or sparingly soluble.

Precipitation titrations are carried out for metallic ions like Ag, Au, Cu, Hg, Pb which form sparingly soluble salts with the titrants. The titrants used in such type of titrations are called as precipitating agents or precipitants as they lead to precipitation of the salt by reacting with the analyte. The end point of potentiometric precipitation titration depends on the solubility of the precipitate and also on the concentration of the analyte. The indicator electrode used in this type of titration should be reversible with one of the participating ions i.e., it should be in equilibrium with one of the ions. Example : Silver electrode is used in the titration of silver nitrate with potassium chloride.

Reference electrode can be any electrode of stable potential which may be a saturated calomel electrode or standard hydrogen electrode.

In the titration of AgNO_3 with KCl , KCl is added in small volumes to the titrate. As the titration proceeds, Ag^+ ions get precipitated as AgCl .



With each increment of KCl , concentration of Ag^+ ions decreases and potential of the electrode increases. Near the end point, the electrode shows a sharp change in the potential due to precipitation of all the Ag^+ ions as AgCl . The values of electrodes potential are plotted against the volume of KCl added. End point is depicted as the point of maximum inflexion in the titration curve.

5. **Diazotisation Titrations** : Analytes (drugs or substances) containing primary aromatic amino groups are titrated against sodium nitrite in acidic medium to give diazonium salts. The end point of titration is determined by potentiometry.

Examples of drugs containing primary amino groups which are potentiometrically titrated are dapsone, sulphacetamide, procainamide, amino alkaloids etc.,

The indicator electrode used in glass electrode and the reference electrode used in saturated calomel electrode.

6. **Non-Aqueous Titrations** : Titrations which are carried out in the absence of aqueous medium are called as non-aqueous titrations. These are used for the assay of certain weak acids and bases which gives poor end points in aqueous solutions. Substances, which are insoluble in water but soluble in non-aqueous solvents can be titrated by non-aqueous titrations.

Examples of Titrants used in Non-aqueous Titrations are :

- (i) **Acidic Titrants** : Perchloric acid, Fluorosulphonic acid, p-toluene sulphonic acid.
- (ii) **Basic Titrants** : Sodium methoxide, Potassium methoxide, Lithium methoxide, Tetra alkyl ammonium hydroxide.

The solvent selected for non-aqueous titrations should fulfill the following conditions :

- (i) It should be readily available and not expensive.
- (ii) It should be pure and nontoxic.
- (iii) It should be miscible with the titrant and the solute.
- (iv) It should have high dielectric constant.
- (v) It should not interfere with the end point of titration.
- (vi) It should not produce any undesirable effects by interacting with the solute or the titrant.

Types of Non-aqueous Solvents :

- (a) **Aprotic Solvents** : These solvents are chemically neutral (unreactive) in nature, i.e., they neither accept nor donate protons. Their dielectric constants are low, they do not produce ionization of the electrolyte and neither reacts with acids nor bases. These solvents are generally used for dilution of the reaction mixtures.

Examples : Carbontetrachloride, Benzene, Toluene.

- (b) **Protogenic Solvents** : These solvents are acidic in nature i.e., they donate protons to enhance the strength of the weak bases.

Examples : Sulphuric acid, Hydrochloric acid.

- (c) **Protophilic Solvents** : These solvents are basic in nature, they enhance the acidity of weak acids.

Examples : Ammonia, Pyridine, Ethylene diamine

- (d) **Amphiprotic Solvents** : They act as both acids and bases, i.e., they accept as well as donate protons.

Examples : Glacial acetic acid, Dioxan.

Types of Nonaqueous Titrations :

- (a) Weak acid vs Lithium methoxide

Examples : Barbituric acid vs lithium methoxide

- (b) Weak base vs perchloric acid

Examples : Quinine sulphate vs perchloric acid, Adrenaline vs perchloric acid.

- (a) **Weak Acid Vs. Lithium Methoxide** : Weakly acidic substances are titrated against basic titrants like alkali methoxides (Na, K, Li, Methoxides). Protophilic solvents like pyridine, ethylene diamine, dimethyl formamide etc., are used to dissolve the analyte as well as to enhance the acidity of weak acids.

Examples : Titration of barbituric acid with lithium methoxide.

- (b) **Weak Base Vs. Perchloric Acid** : Weakly basic substances are titrated against acidic titrants like perchloric acid in the presence of amphiprotic solvents like glacial acetic acid and dioxan. Solution of perchloric acid in glacial acetic acid is an official titrant indicated by Indian Pharmacopoeia.

Examples : Titration of quinine sulphate with perchloric acid, Adrenaline with perchloric acid.

In potentiometry, titrations of weak acids like barbituric acid and weak bases like ephedrine HCl, quinine SO_4^{2-} can be carried out in non-aqueous solvents like lithium or potassium methoxide and perchloric acid respectively. Glass electrode and saturated calomel electrode are used as indicator and reference electrode respectively.

In non-aqueous titrations instead of employing the pH scale, the millivolt scale of potentiometer is used since potential has a tendency to exceed the pH scale.

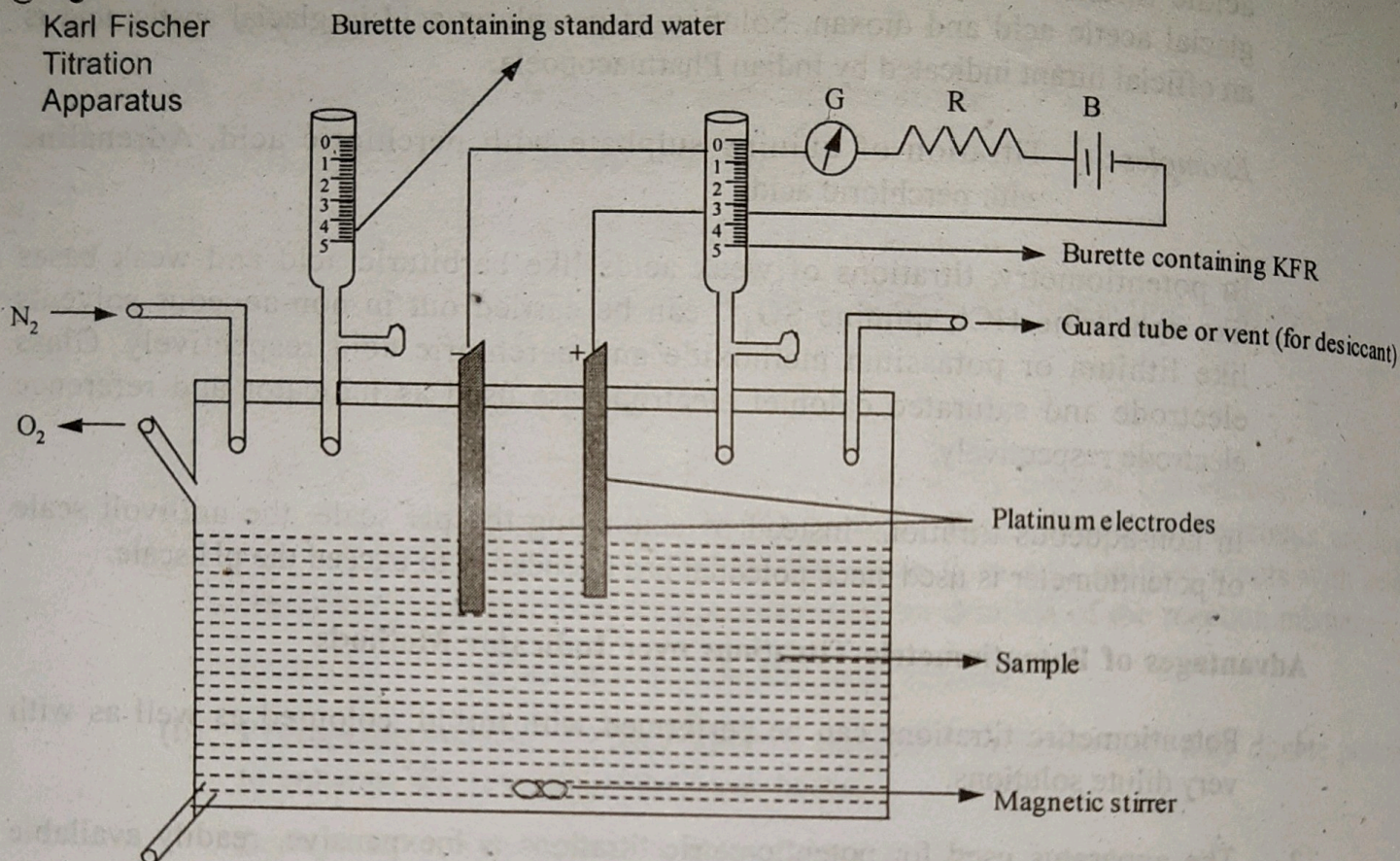
Advantages of Potentiometric Titrations over Indicator Methods

1. Potentiometric titrations can be performed with turbid, coloured as well as with very dilute solutions.
2. The apparatus used for potentiometric titrations is inexpensive, readily available and can give accurate results.
3. Detection of end point is easy because of automated apparatus.
4. Titrations of weak acids against weak bases can be easily carried out potentiometrically.
5. Interpretation of the titration curves is easy.
6. Titration of mixtures of acids, bases or halides can be performed by potentiometric titrations.

Karl Fischer Titration or Dead Stop End Point Technique :

Titrimetric analysis by Karl Fischer Method is one of the most important methods for determination of moisture (water) content in a sample. This method was proposed by Karl Fischer in the year 1935. It is a sensitive and specific method in which water content of a sample which is present either in absorbed form or as water of hydration is determined.

Titration is carried out by employing Karl Fischer Reagent (KFR) which is a mixture of iodine, sulphur dioxide, anhydrous methanol and pyridine in the molar ratio $\text{I}_2 : \text{SO}_2 : 1\text{CH}_3\text{OH} : 3\text{C}_5\text{H}_5\text{N}$. It is essentially a solution of iodine and sulphur dioxide in pyridine and anhydrous methanol.

Apparatus :**Figure :**Karl Fischer
Titration
Apparatus

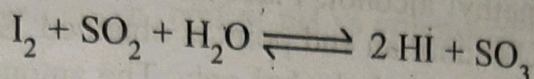
The apparatus consists of a closed titration vessel of 60 ml capacity fitted with a pair of platinum electrodes (each of 0.05 cm^2 in area) placed 2 cm apart, a nitrogen inlet tube, two automatic burettes, a magnetic stirrer, a guard tube or vent for suitable desiccant like silica gel, phosphorous pentoxide or anhydrous granular calcium to keep the air dry, and 1.5 V battery which provides constant current across the two electrodes. A full scale deflection galvanometer ($10 - 100 \mu\text{A}$) reads the amount of current generated. The galvanometer is shunted with a variable resistor R so that upon addition of KFR, the needle of galvanometer shows deflection which immediately returns to its starting point.

Preparation of KFR :

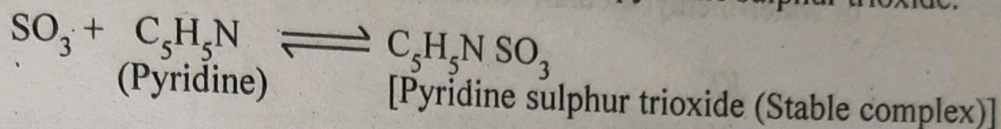
In a glass stoppered flask, about 400 ml of anhydrous methanol is taken. To this, 80 gm of anhydrous pyridine is added and the flask is placed in a freezing mixture. A stream of dried sulphur dioxide is passed through the mixture until its weight shows an increase by 20 gm. To it, 45 gm of iodine is added and dissolved by shaking. This mixture is allowed to stand for about 24 hours before use. Freshly prepared KFR has a deep brown colour and strength of about 80%. However, on storage, the strength falls to 50% in 1 month and 40% in 3 months. KFR used for microscale titrations has a strength of 3-6 mg of water per ml of reagent. KFR is unstable and undergoes self oxidation. Hence, stored in well sealed glass stoppered containers which is protected from light and atmospheric moisture.

Reaction between KFR and water involves the following steps :

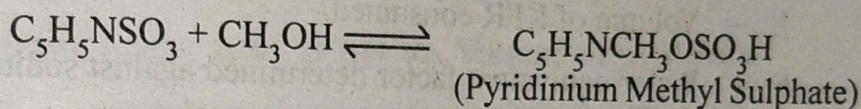
Step - 1 : Sulphur dioxide is oxidised by iodine to sulphur trioxide.



Step - 2 : Pyridine reacts with sulphur trioxide to yield pyridine sulphur trioxide.



Step - 3 : In this step, pyridine sulphur trioxide reacts with methyl alcohol to yield a complex called pyridinium methylsulphate.



Pyridine Plays an important role in KFR, because :

1. Its alkaline nature prevents the reverse reaction which occurs due to the concentration of acidic reagents like HI and H_2SO_4 .
2. It is miscible with methanol.
3. It prevents oxidation of HI to I_2 by neutralising HI.
4. It forms a stable complex with sulphur trioxide.

Standardisation of KFR :

KFR is standardized against sodium tartrate or water-methyl alcohol reagent.

1. **Standardization against Sodium Tartrate :** Place about 30 ml of methyl alcohol in the titration vessel and add sufficient quantity of KFR dropwise to obtain an end point. At the end point, a slight excess of KFR leads to increased flow of current and a fall in the potential (due to reduction of I_2 to HI). This current produces a deflection in the galvanometer which remains for 30 seconds or longer. Upon reaching the endpoint, add quickly about 150 - 300 mg of sodium tartrate dihydrate ($C_4H_4Na_2O_6 \cdot 2H_2O$) and again titrate to the end point. The difference between the two titrations gives the volume of KFR consumed by the titrate. The factor equivalent to the amount of water present per ml of reagent is given by the formula :

$$F = \frac{0.156 \times W}{V}$$

Where,

W - Weight of Sodium Titrate (mg).

V - Volume of Reagent Consumed (ml).

2. **Standardization against Water-Methyl Alcohol :** For standardization against water-methyl alcohol, 0.2% v/v solution is prepared by adding 2 ml of water to 1000ml of anhydrous methyl alcohol. Place 25 ml of this solution in the titration vessel and titrate with KFR until an end point is obtained. Similarly, a blank titration is performed using 25ml of methyl alcohol only. The amount of water in mg per ml of water-methyl alcohol solution is determined by using the formula :

$$\frac{VF}{25}$$

Where,

V – Volume of KFR consumed.

F – Water equivalent factor determined against sodium tartarate.

Determination of Water Content in Sample :

Take about 25 ml of methyl alcohol in a titration flask and titrate with KFR until the end point. Weigh sufficient amount of sample such that it contains 10 - 50 ml water. Transfer it to the titration vessel and adjust the potential so that a current equivalent to 10 μ A passes between the platinum electrodes. Stir vigorously and again titrate with KFR until an end point is obtained which is indicated by a steep fall in the potential due to excess of iodine. The difference between the two titration readings give the amount of KFR consumed. Water content of a sample is given by the formula NF.

Where,

N – Volume of KFR consumed

F – Water equivalent factor determined against sodium tartarate.

The optimal pH range to carry out titration is 4 – 7.

Advantages :

1. Karl Fischer method is a simple and rapid method of analysis.
2. This method is specific for determination of water or moisture content in a sample.
3. This method requires small amount of sample.
4. Samples containing water in microquantities (0.1 – 10 mg) can be detected by this method.
5. Since, the reaction between KFR and water is stoichiometric, calibration is not needed.

Limitation : Oxidising agents like peroxides, chromates, dichromates, reducing agents like sulphides, sulphites and other agents which form water with KFR interferes with the titration process.

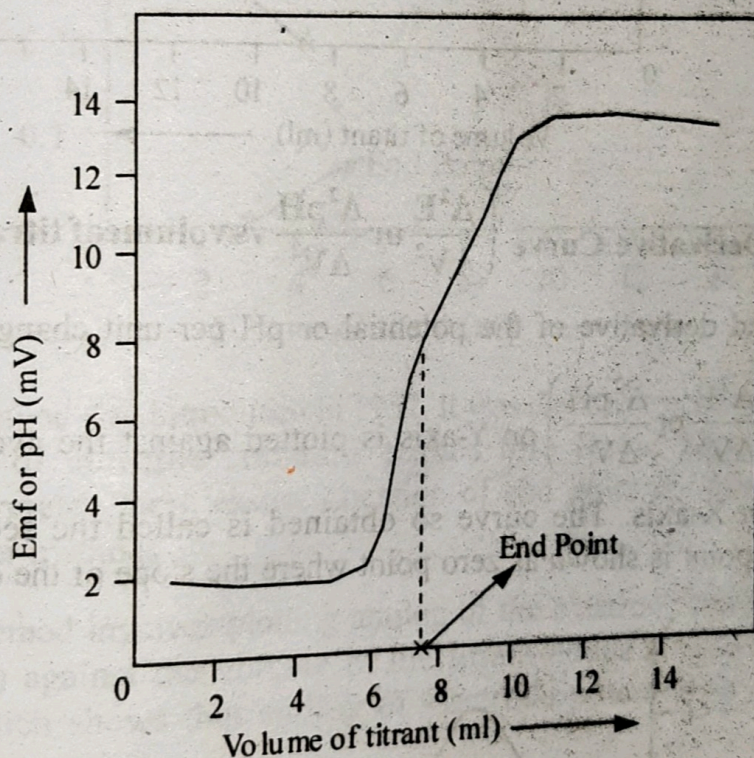
Application : Karl Fischer titration has been applied to determine the water content in drugs like rifamycin, prednisolone and sodium methyl hydroxy benzoate.

6.1.8 Methods of Detecting End Point

The various methods for determination of end point in potentiometric titrations are :

1. Normal titration curve (emf or pH vs volume of titrant).
 2. First derivative curve $\left(\frac{\Delta E}{\Delta V} \text{ or } \frac{\Delta \text{pH}}{\Delta V} \text{ vs volume of titrant} \right)$.
 3. Second derivative curve $\left(\frac{\Delta^2 E}{\Delta V^2} \text{ or } \frac{\Delta^2 \text{pH}}{\Delta V^2} \text{ vs volume of titrant} \right)$.
 4. Gran's method (Antilog E vs volume of titrant).
1. **Normal Titration Curve (emf or pH Vs. Volume of Titrant) :**

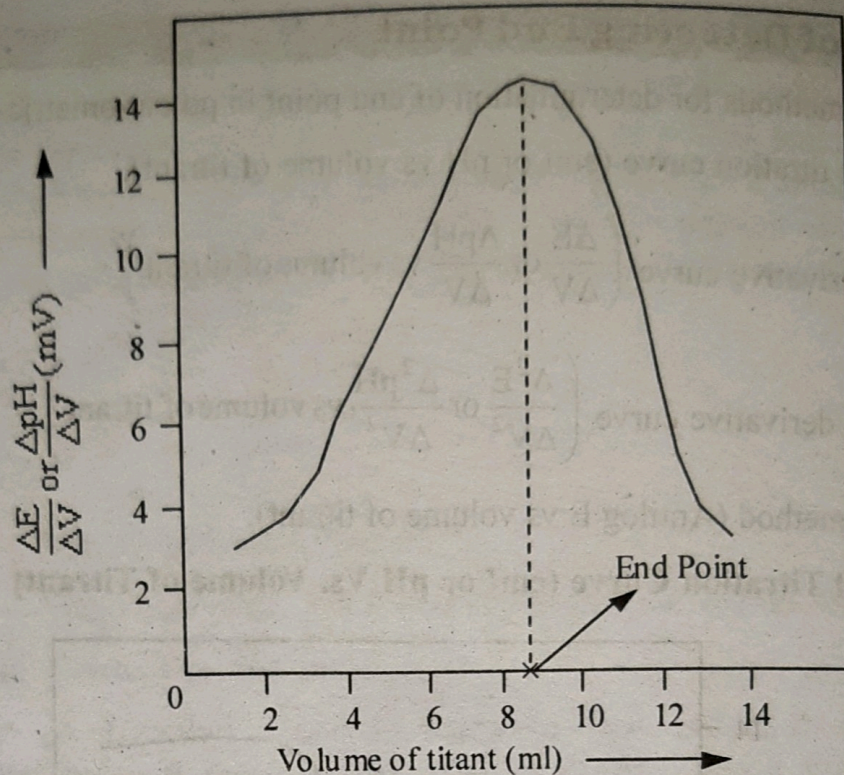
Figure :
Normal
Curve



In this method, the volume of titrant added (X-axis) is plotted against the values of emf or pH (Y-axis) which results in sigmoid curve. The end point is the point on the curve at which there is maximum inflexion (rise) in the potential.

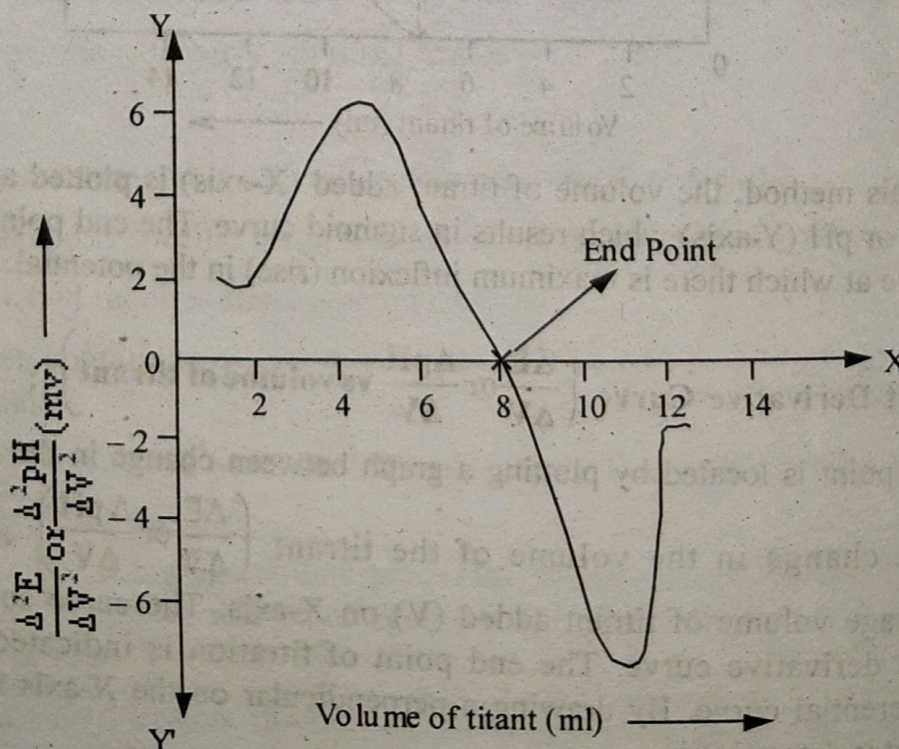
2. **First Derivative Curve $\left(\frac{\Delta E}{\Delta V} \text{ or } \frac{\Delta \text{pH}}{\Delta V} \text{ vs volume of titrant} \right)$:** In this method, the end point is located by plotting a graph between change in the potential or pH per unit change in the volume of the titrant $\left(\frac{\Delta E}{\Delta V} \text{ or } \frac{\Delta \text{pH}}{\Delta V} \right)$ on Y-axis and the average volume of titrant added (V) on X-axis. The curve so obtained is called first derivative curve. The end point of titration is indicated by a peak in the differential curve. By drawing a perpendicular on the X-axis from the peak, end point is determined.

Figure :
First Derivative
Curve

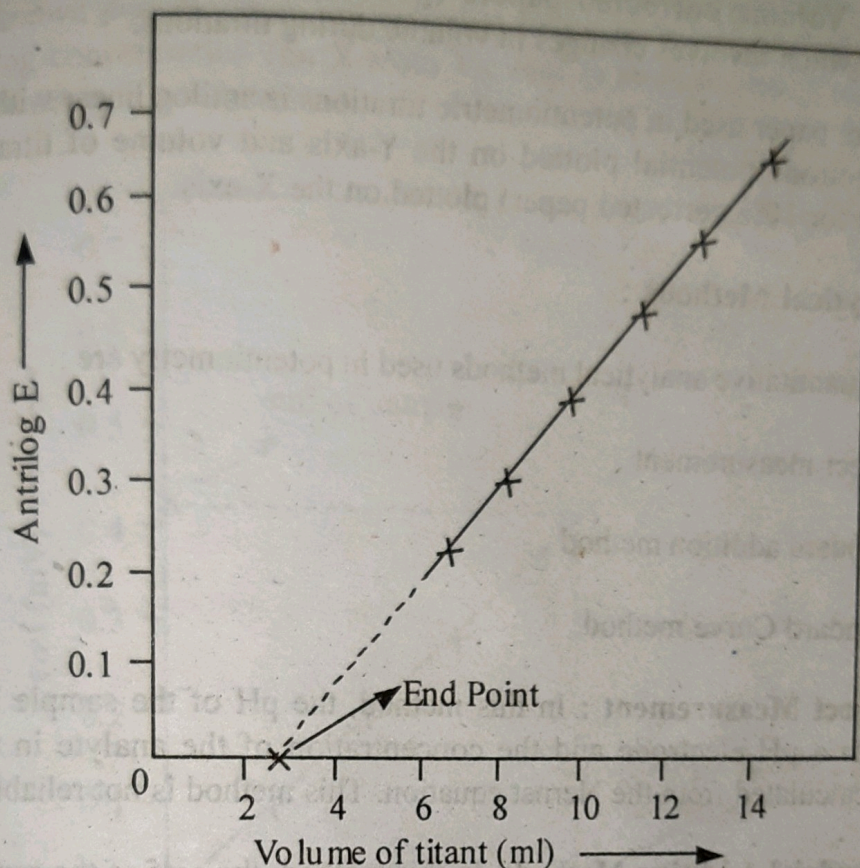


3. **Second Derivative Curve** $\left(\frac{\Delta^2 E}{\Delta V^2} \text{ or } \frac{\Delta^2 \text{pH}}{\Delta V^2} \text{ vs volume of titrant} \right)$: In this method, the second derivative of the potential or pH per unit change in the volume of the titrant $\left(\frac{\Delta^2 E}{\Delta V^2} \text{ or } \frac{\Delta^2 \text{pH}}{\Delta V^2} \right)$ on Y-axis is plotted against the average volume of titrant added on X-axis. The curve so obtained is called the second derivative curve. The end point is shown as zero point where the slope of the curve is maximum.

Figure :
Second
Derivative
Curve



4. Gran's Method (Antilog E Vs. Volume of Titrant) :

Figure :
Gran's Plot

This method was introduced in 1952. It was devised to convert sigmoid potentiometric curves or multiple standard curves into linear form such that results can be interpreted more easily. Location of end point by this method is simpler than the other methods.

This method involves plotting antilog of the electrode potential (E or emf) readings (Y-axis) against the volume of the titrant added (X-axis). This gives a straight line which shows that antilog of electrode potential is directly proportional to the concentration.

The straight line so obtained is extrapolated to the X-axis until it cuts the axis at a point referred as the end point of titration.

Advantages of Gran's Method :

1. It is not necessary to continue the titration till the end point since, few observations before the end point are sufficient to obtain a straight line.
2. Reliable results will be obtained if the potential readings are accurately measured near the equivalence point.

Disadvantage of Gran's Method : The Calculations involved in this method are cumbersome. This drawback can be overcome by using semi-antilog Gran's plot paper. This paper is available in two forms : volume uncorrected and volume corrected.

Volume uncorrected papers are used in titrations which does not involve any volume changes. Volume corrected papers (generally 10% volume corrected) are used in titrations which involves changes in volume during titrations.

Gran's plot paper used in potentiometric titrations is antilog linear with electrode potential. It has electrode potential plotted on the Y-axis and volume of titrant added (10 ml of the titrate for 10% corrected paper) plotted on the X-axis.

Quantitative Analytical Methods :

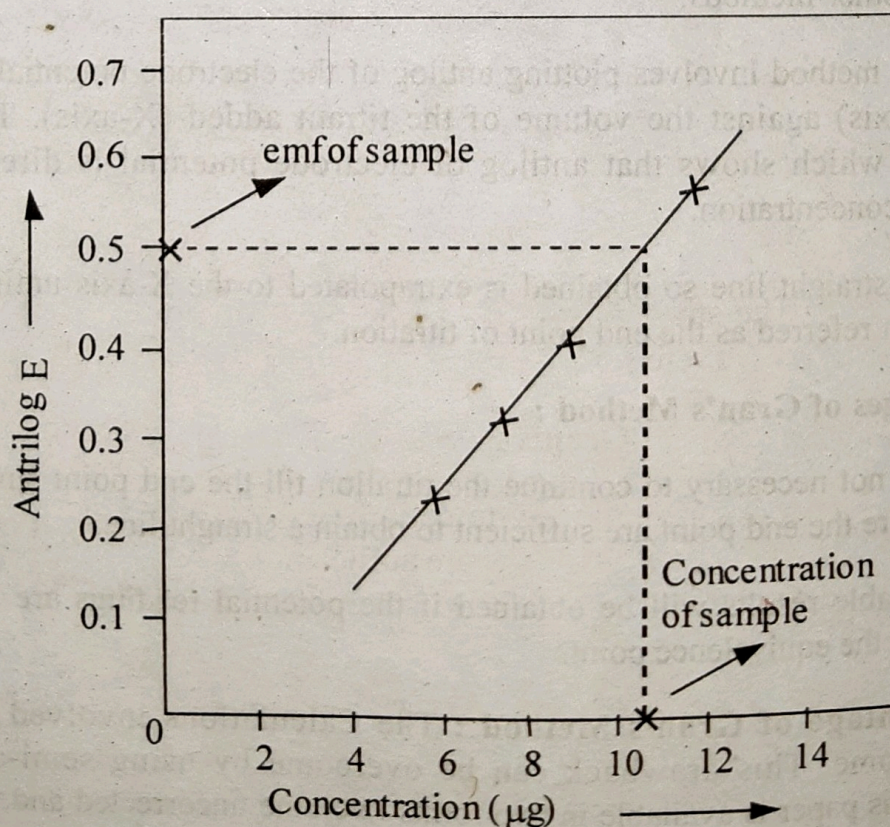
Various quantitative analytical methods used in potentiometry are :

1. Direct measurement
2. Standard addition method
3. Standard Curve method

1. **Direct Measurement :** In this method, the pH of the sample is measured directly with a pH electrode and the concentration of the analyte in the sample solution is calculated from the Nernst equation. This method is not reliable and seldom used.

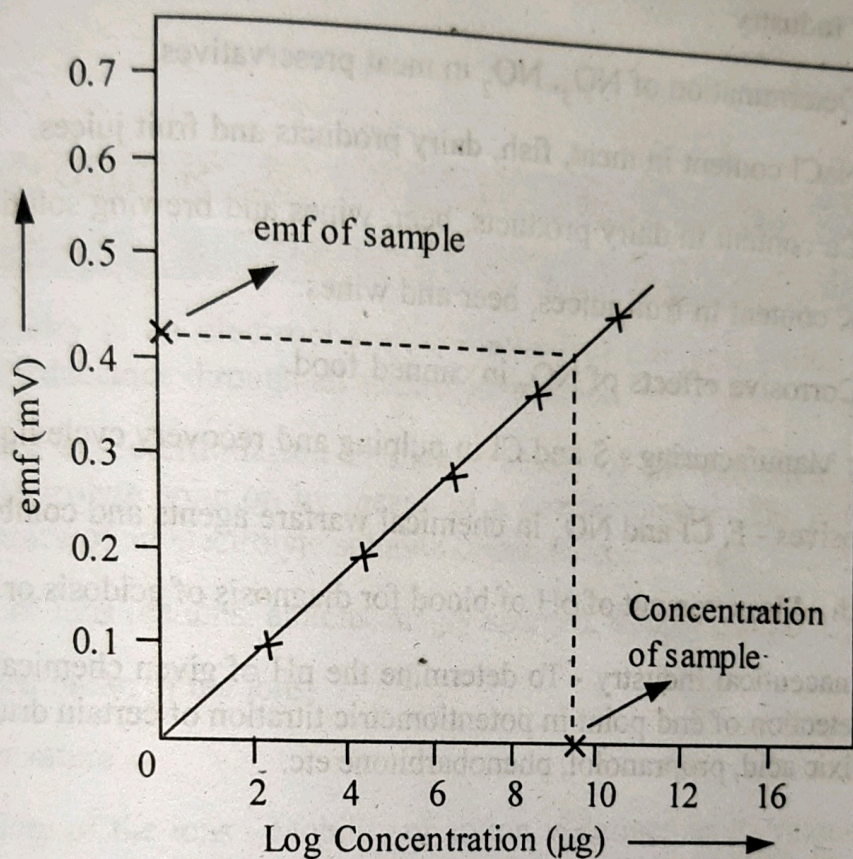
2. **Standard Addition Method :** In this method, the emf of the sample is recorded first followed by addition of known volumes of standard to the sample and again recording the emf. A plot of standard concentration vs antilog of emf (E) is plotted from which the concentration of the sample is determined.

Figure :
Standard
Addition Curve



3. **Standard Curve Method :** In this method, the emf of a series of standard solutions of known concentration are recorded followed by the emf of the sample. A graph of log concentration (on X-axis) Vs. emf is plotted from which the concentration of the sample is determined.

Figure :
Standard
Curve



6.1.9 Applications of Potentiometry

The various applications of potentiometry are :

1. Determination of equilibrium constants.
2. Determination of ionic product of water.
3. Determination of dissociation constant of acids.
4. To study the solubility and solubility product of sparingly soluble electrolytes.
5. To know the activity coefficients.
6. To study the composition of complex compounds and instability constants of complex ions in complexometry.
7. To know about the valency of metal ions.
8. In biochemistry, potentiometry is applied in the analysis of Ca, K, Cl in body fluids like blood, plasma, sweat and serum.
9. Pollution monitoring - Estimation of CN, F, S, Cl, NO_3 in industrial water and F in drinking water.

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Potentiometers

10. Agriculture - Estimation of K, Ca, I, Cl, CN, NO_3 , NH_4 in soil, fertilizers, feed stuffs and plant materials.
11. Detergent Manufacturing - To study the effects of Ca, Ba, F on water quality.
12. Food Industry
 - (a) Determination of NO_3 , NO_2 in meat preservatives.
 - (b) NaCl content in meat, fish, dairy products and fruit juices.
 - (c) Ca content in dairy products, beer, wines and brewing solutions.
 - (d) K content in fruit juices, beer and wines.
 - (e) Corrosive effects of NO_3 in canned food.
13. Paper Manufacturing - S and Cl in pulping and recovery cycle liquors.
14. Explosives - F, Cl and NO_3 in chemical warfare agents and combustion products.
15. Health - Measurement of pH of blood for diagnosis of acidosis or alkalosis.
16. Pharmaceutical Industry - To determine the pH of given chemical agents and also in the detection of end point in potentiometric titration of certain drugs like amoxycillin, nalidixic acid, propranolol, phenobarbitone etc.