

UNIT-5

Electrochemical Methods of Analysis

Definition:

Electrochemical methods of analysis involve the measurement of an **electrical quantity (such as potential, current, or charge)** that is related to the **chemical composition** of a solution. These techniques are essential for both qualitative and quantitative analysis of ions and molecules in solution.

Classification of Electrochemical Methods:

1. **Potentiometry** – Measurement of electrical potential (voltage) of an electrochemical cell without drawing appreciable current.
2. **Conductometry** – Measurement of electrical conductance (or conductivity) of a solution.
3. **Polarography (Voltammetry)** – Measurement of current as a function of applied voltage.
4. **Coulometry** – Measurement of total charge passed during an electrochemical reaction.
5. **Amperometry** – Measurement of current under a controlled potential.
6. **Electrogravimetry** – Measurement of mass of a substance deposited on an electrode.

Conductometry

Introduction to Conductometry:

Conductometry is an electrochemical method of analysis based on the measurement of the **electrical conductivity** of a solution. This conductivity arises from the movement of ions present in the solution. As the **concentration of ions changes**, especially during a chemical reaction or titration, the conductivity of the solution also changes.

Basic Concept:

The **conductance (G)** is the reciprocal of **resistance (R)**:

$$G = \frac{1}{R} \quad \text{or} \quad R = \frac{1}{G}$$

The conductance of a solution depends on:

- The **number of ions**
- Their **mobility**
- The **nature of solvent and temperature**

Types of Conductivity:

1. **Specific Conductivity (κ):**
Conductance of 1 cm³ of solution between two electrodes 1 cm apart. Unit: S cm⁻¹.
2. **Equivalent Conductivity (Λ_{eq}):**
Conductivity of all ions produced by 1 gram equivalent of an electrolyte in solution.
3. **Molar Conductivity (Λ_m):**
Conductivity of all ions produced by 1 mole of an electrolyte.

Conductivity Cell:

A **conductivity cell** is the device used to measure the electrical conductance of a solution. It consists of **two electrodes** usually made of **platinum**, coated with **platinized platinum black** to minimize polarization.

Construction:

- Two platinum electrodes are mounted parallel to each other.
- The distance between electrodes (l) and their area (A) determines the **cell constant (K)**.

$$\text{Cell constant (K)} = \frac{l}{A}$$

The measured conductance (G) is converted to **specific conductivity (κ)** using:

$$\kappa = G \times K$$

Cell Constant Determination:

Since the exact dimensions (l and A) are difficult to measure accurately, the cell constant is usually determined by calibrating the cell using a standard solution like **0.01 N KCl**, whose conductivity is known.

Important Features of a Conductivity Cell:

- Must be properly cleaned and calibrated.
- Should be thermostated, as conductivity is temperature-sensitive.
- Electrodes should be coated with platinized platinum for uniform current distribution.

Applications of Conductometry:

1. **Conductometric Titrations:**
 - **Acid–base titrations** (e.g., HCl vs. NaOH)
 - **Precipitation titrations** (e.g., AgNO₃ vs. NaCl)
 - **Redox titrations**

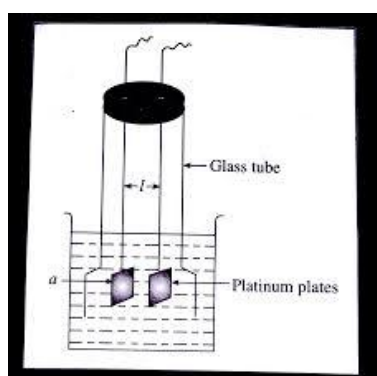
2. **Determination of ion concentration**
3. **Monitoring of water purity**
4. **Detection of end point in weak acid–strong base titrations** (where indicators are ineffective)

Advantages:

- Suitable for **colored or turbid solutions** where visual indicators fail.
- **Highly sensitive** to ionic changes.
- **Applicable to weak electrolytes.**
- **Automatable** and fast.

Disadvantages:

- Temperature-sensitive (requires thermostating).
- Not selective (measures total ionic conductance).



Conductivity cell

Conductometric Titrations

Definition:

Conductometric titrations are a type of volumetric analysis in which the **conductance** of a solution is continuously measured as a titrant is added. The **end point** is determined from the change in conductivity that occurs due to the chemical reaction between the analyte and titrant.

Unlike traditional titrations that rely on visual indicators, conductometric titrations are based on changes in **ionic concentration**, making them highly effective even in **colored, turbid, or dilute solutions**.

Principle:

- The conductance of a solution depends on the number and mobility of ions present.
- As the titration progresses, **ionic species** are either consumed or replaced by **ions with different conductance**.
- A **conductometric curve** (conductance vs. volume of titrant) is plotted.
- The **point of intersection** of two linear segments of the curve gives the **end point**.

Types of Conductometric Titrations:

1. Strong Acid vs. Strong Base (e.g., HCl vs. NaOH)

- H^+ (high conductance) is replaced by Na^+ (lower conductance).
- Conductance decreases until equivalence point, then increases due to excess OH^- .

2. Weak Acid vs. Strong Base (e.g., Acetic acid vs. NaOH)

- Initial conductance is low due to weak dissociation.
- Gradual increase until equivalence point due to salt formation.
- Sharp increase after end point due to excess OH^- .

3. Strong Acid vs. Weak Base (e.g., HCl vs. NH_4OH)

- Conductance decreases slightly due to neutralization.
- Post-equivalence, conductance remains nearly constant or changes gradually.

4. Precipitation Titration (e.g., NaCl vs. AgNO_3)

- Cl^- (highly conductive) is replaced by AgCl (a precipitate).
- Decrease in conductance until all Cl^- is precipitated.
- Then, increase due to excess Ag^+ ions.

5. Redox Titration (e.g., KMnO_4 vs. H_2O_2)

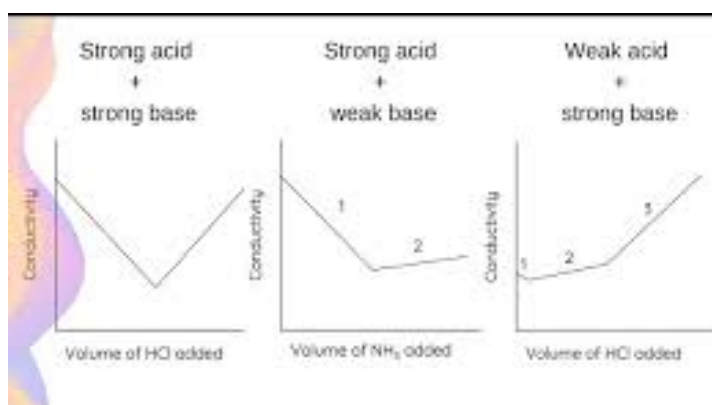
- Changes in ionic species due to oxidation-reduction affect conductance.

Advantages of Conductometric Titrations:

- **No need for indicators** (suitable for colored or turbid solutions).
- Useful for **very dilute solutions**.
- Applicable to **weak acid–weak base titrations** where indicators fail.
- Can be used for **non-aqueous systems**.
- **Automation-friendly** and suitable for precise analysis.

Applications in Pharmaceutical and Chemical Analysis:

1. **Assay of pharmaceuticals:**
 - Sodium benzoate, sodium chloride, and weak acids.
2. **Determination of water hardness.**
3. **Precipitation titrations** involving halides.
4. **Redox titrations** without visual indicators.
5. **Quality control** in the pharmaceutical industry.
6. **Environmental testing** (e.g., analysis of wastewater or effluents).



Potentiometry:

Potentiometry is an electroanalytical method that involves the **measurement of the electromotive force (EMF)** of an electrochemical cell without drawing appreciable current. It is primarily used to determine the **concentration of an analyte** by measuring the potential difference between two electrodes – a **reference electrode** (with known and stable potential) and an **indicator electrode** (whose potential depends on the analyte).

Electrochemical Cell:

An **electrochemical cell** used in potentiometry consists of **two half-cells**:

1. **Reference Electrode** – Maintains a constant potential.
2. **Indicator Electrode** – Develops potential depending on the concentration of the analyte.

The EMF of the cell is given by:

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

This potential is related to the concentration of the analyte through the **Nernst Equation**:

$$E = E^\circ + \frac{0.0591}{n} \log[\text{ion}]$$

Where:

- E° : standard electrode potential
- n : number of electrons involved in the electrode reaction
- $[\text{ion}]$: concentration of the ion being measured

Types of Electrodes Used:

1. Reference Electrodes:

These provide a stable and known potential.

- **Saturated Calomel Electrode (SCE):**
Mercury/mercurous chloride in KCl solution
Potential: +0.241 V vs. SHE
- **Silver/Silver Chloride Electrode (Ag/AgCl):**
Ag wire coated with AgCl in KCl solution
Potential: +0.197 V vs. SHE

2. Indicator Electrodes:

These respond to the activity of the specific ion in solution.

- **Hydrogen Electrode:** For measuring H^+ concentration.
- **Glass Electrode:** For pH determination.
- **Quinhydrone Electrode:** Used in pH measurements for strong acids and bases.
- **Metal Electrodes:** Used for redox systems (e.g., Pt electrode in $\text{Fe}^{2+}/\text{Fe}^{3+}$ systems).

Applications of Electrochemical Cells in Potentiometry:

1. pH Measurement:

- Using a **glass electrode** as the indicator and **SCE** as the reference.
- $\text{pH} = \frac{\text{measured EMF}}{0.0591}$

2. Potentiometric Titrations:

- **Acid-base titrations** (e.g., HCl vs. NaOH)
- **Redox titrations** (e.g., KMnO_4 vs. FeSO_4)
- **Precipitation titrations** (e.g., AgNO_3 vs. Cl^-)
- **Complexometric titrations** (e.g., EDTA titration)

3. Assay of Pharmaceutical Substances:

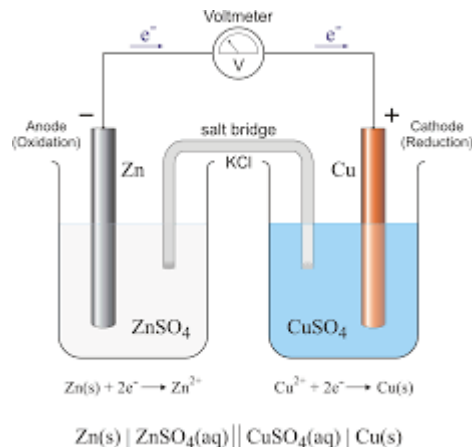
- Assay of halide salts, vitamin C, and many organic drugs.
4. **Determination of endpoint** in titrations where visual indicators are not suitable.

Advantages:

- **High precision and accuracy** in endpoint detection.
- **Useful in colored or turbid solutions.**
- Requires **very small sample volume.**
- **Non-destructive** technique.

Disadvantages:

- Requires **calibration** and maintenance of electrodes.
- Affected by **temperature and ionic strength.**
- Not suitable for **very dilute solutions.**



construction and working of reference

1. Standard Hydrogen Electrode (SHE)

Construction:

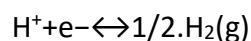
- It consists of a **platinum electrode** (in the form of a thin foil or platinum black coated wire) placed in a solution containing **1 M hydrogen ion concentration (usually HCl)**.
- Pure **hydrogen gas is bubbled** over the platinum surface at a constant pressure of **1 atmosphere**.
- The entire setup is maintained at **25°C**.
- The platinum acts as an inert surface for **redox exchange** between H⁺ ions and H₂ gas.

Cell Representation:

Pt | H₂(g, 1 atm) | H⁺(1 M)

Working:

- It functions on the reversible half-cell reaction:



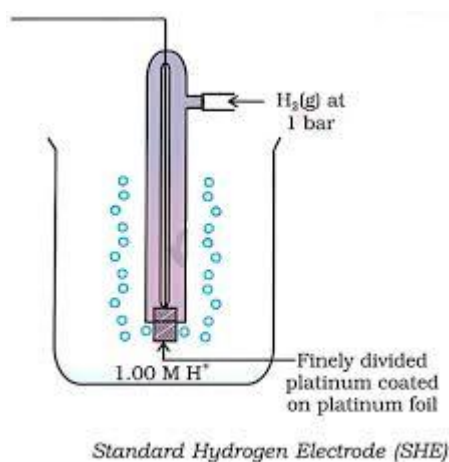
- This electrode is assigned a standard electrode potential of **0.000 V** at all temperatures by convention.
- It can act as either an anode or cathode, depending on the cell it is connected with.

Advantages:

- Serves as the **universal reference electrode**.
- Gives accurate standard potential values.

Disadvantages:

- Difficult to **maintain pure hydrogen gas** and constant pressure.
- Setup is **complex**, fragile, and unsuitable for routine lab use.



2. Silver/Silver Chloride Electrode (Ag/AgCl)

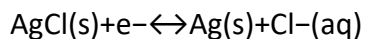
Construction:

- A **silver wire** is coated with a thin layer of **silver chloride (AgCl)**.
- The wire is then immersed in a **solution of potassium chloride (KCl)** saturated with **AgCl**.
- The electrode is usually sealed in a glass tube with a **porous salt bridge** or **ceramic frit** to allow ionic contact with the test solution.

Cell Representation:

$\text{Ag} \mid \text{AgCl(s)} \mid \text{KCl (satd.)}$

The electrode undergoes a reversible reaction:



- The electrode potential depends on the **activity of Cl^- ions** in the solution.
- Commonly used with saturated KCl, where the **potential is +0.197 V** vs SHE at 25°C.

Advantages:

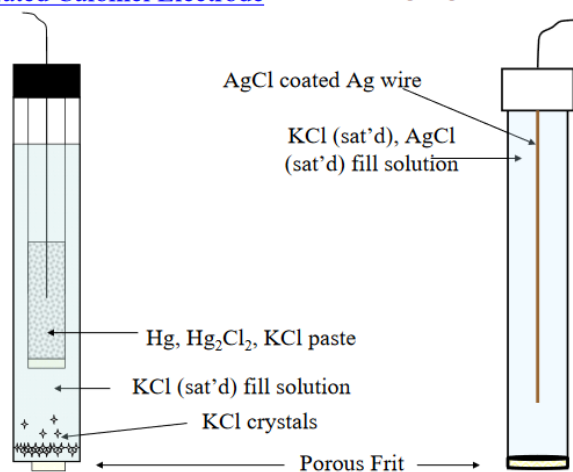
- **Easy to construct**, stable and reliable.
- **Compact and inexpensive.**
- **Non-toxic** and widely used in pH meters.

Disadvantages:

- Sensitive to **chloride ion contamination** in the test solution.
- Not suitable in **non-aqueous** media.

Saturated Calomel Electrode

Ag/AgCl Electrode



3. Saturated Calomel Electrode (SCE)

Construction:

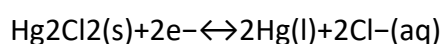
- Made up of **mercury (Hg)** at the bottom of a glass tube, over which a **paste of mercurous chloride (calomel, Hg_2Cl_2)** is placed.
- The upper part of the tube contains **saturated KCl solution**.
- A **platinum wire** is immersed in the mercury to establish electrical contact.
- The tube is equipped with a **porous frit or salt bridge** to maintain ionic connection with the analyte solution.

Cell Representation:

$\text{Hg} \mid \text{Hg}_2\text{Cl}_2(\text{s}) \mid \text{KCl (satd)}$

Working:

- The redox reaction is:



- The **electrode potential is +0.241 V** vs SHE when saturated KCl is used.
- The potential remains **constant and reproducible** under given conditions.

Advantages:

- **Highly stable and reproducible** potential.
- **Widely used** in potentiometric and pH measurements.
- Easy to handle and **less expensive** than SHE.

Disadvantages:

- Contains **toxic mercury**, posing environmental and health hazards.
- **Not suitable in non-aqueous systems** or with strong complexing agents for Cl^- .

Indicator Electrodes

Indicator electrodes are electrochemical sensors whose electrode potential varies in response to the activity (concentration) of a specific ion in solution. These are used in potentiometric measurements to determine the end point in titrations or the concentration of ions like H^+ , Cl^- , etc.

They are classified broadly into **Metal electrodes** and **Membrane electrodes (like glass electrode)**.

1. Metal Electrodes

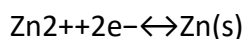
These are of two types based on their function:

A. Electrodes of the First Kind

- These are pure metal electrodes in contact with a solution containing their own ions.
- They obey the Nernst equation.
- The electrode potential varies directly with the activity of the metal ion.

Example:

- Zinc electrode in Zn^{2+} solution:



Metals commonly used: Cu, Ag, Zn, Hg

Applications:

- Determination of metal ion concentration in solution.
- Cu electrode for Cu^{2+} estimation.

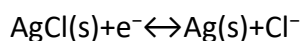
B. Electrodes of the Second Kind

- These consist of a metal coated with its **sparingly soluble salt**, immersed in a solution of the **anion of the salt**.
- They provide potential based on the anion (not the metal ion).

Example:

- Silver/silver chloride electrode ($\text{Ag}|\text{AgCl}|\text{Cl}^-$)
- Calomel electrode ($\text{Hg}|\text{Hg}_2\text{Cl}_2|\text{Cl}^-$)

Reaction for Ag/AgCl:



Applications:

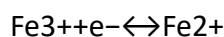
- Used as both reference and indicator electrodes, especially in halide titrations.

C. Inert Metal Electrodes (Redox Electrodes)

- These are **chemically inert metals** like **platinum** or **gold** that do not participate in the electrode reaction.
- They act as a **surface for electron exchange** in redox systems.

Example:

- Pt electrode in $\text{Fe}^{2+}/\text{Fe}^{3+}$ system:



Applications:

- Redox titrations like KMnO_4 vs. FeSO_4 .
- Systems with no suitable metal for direct contact.

2. Glass Electrode

Introduction:

The glass electrode is a type of **membrane electrode**, widely used as an indicator electrode for **pH measurement**. It is highly sensitive to **hydrogen ion activity** and provides a rapid and accurate response.

Construction:

- Consists of a **thin glass membrane** (pH-sensitive glass) blown into a bulb.
- Inside the bulb is a solution of **constant pH (usually 0.1 M HCl)** and a **reference electrode** (commonly Ag/AgCl or calomel).
- The bulb is immersed in the **test solution**, forming a potential difference across the glass membrane due to H^+ exchange.

Working Principle:

- H^+ ions from the test solution interact with the hydrated outer layer of the glass membrane.
- This creates a **boundary potential**, which is measured with respect to the internal reference electrode.
- The measured potential is directly related to the pH of the external solution.

Electrode Reaction:



Ag/AgCl | HCl (internal) || glass membrane || test solution | reference electrode

Advantages:

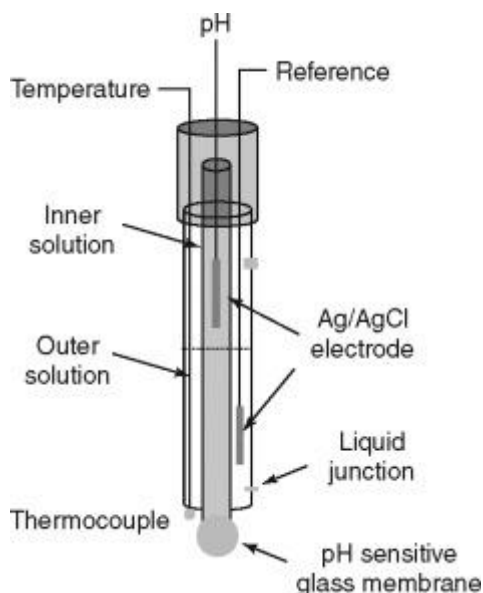
- Highly sensitive to small changes in pH.
- Can be used in **colored or turbid solutions**.
- **Fast response** and **reproducible results**.

Limitations:

- Fragile and requires careful handling.
- Not suitable for **non-aqueous** or **very basic solutions (pH > 10)** due to sodium error.
- Requires **calibration** with buffer solutions.

Applications:

- **Measurement of pH** in various pharmaceutical preparations.
- **pH-metric titrations** of weak acids and weak bases.
- Useful in **biological and environmental analysis**.



Methods to Determine End Point of Potentiometric Titration

Potentiometric titration is a type of volumetric analysis in which the **potential (voltage)** of an electrochemical cell is measured during the addition of titrant to detect the **end point** of the titration, without using any chemical indicator. The change in potential is sharp at the equivalence point due to the sudden change in ionic concentration.

Basic Principle:

In potentiometric titrations, the **potential of the indicator electrode** (which responds to the analyte or titrant) is monitored with respect to a **stable reference electrode**. As titrant is added, the cell potential changes, and a sharp change is observed near the equivalence point.

1. Graphical Method (Titration Curve Method):

- The **measured potential (E)** is plotted against the **volume of titrant added (V)**.
- The plot gives an S-shaped or curve depending on the nature of the titration.
- The point of **maximum slope** or the inflection point is taken as the **equivalence point**.

Example:

- Acid-base titrations show a sharp increase or decrease in potential near the equivalence point.

2. First Derivative Plot ($\Delta E/\Delta V$ vs V):

- The **first derivative** of potential with respect to volume ($\Delta E/\Delta V$) is plotted against the volume of titrant.
- The **peak of this curve** corresponds to the **equivalence point**.
- This method gives a **clear and sharp peak** at the end point.

3. Second Derivative Plot ($\Delta^2 E/\Delta V^2$ vs V):

- The **second derivative** of potential with respect to volume is plotted.
- The **equivalence point corresponds to zero crossing** of the second derivative plot.
- This is more precise when detecting **closely spaced or weak end points**.

4. Differential Titration Method:

- Two electrodes are used, and the difference in their potential is directly measured.
- This difference is plotted against volume to locate the equivalence point.

5. Gran's Plot Method:

- In this method, a mathematical transformation is applied to the potential data before plotting.
- Useful in **weak acid-strong base titrations** where the curve is not steep.

Selection of Method Based on Titration Type:

Titration Type	Suitable Method
Strong acid vs strong base	Graphical or first derivative
Weak acid vs strong base	Second derivative or Gran's plot
Redox titrations	Graphical or differential method
Precipitation titrations	Graphical or first derivative

Advantages of Potentiometric Endpoint Detection:

- **No indicator required**, useful in colored or turbid solutions.
- **Applicable to weak acid/base titrations** where indicator color change is not sharp.
- Can be **automated** for high-throughput analysis.
- **More accurate and reproducible**.

Polarography

Polarography is an electroanalytical technique in which the **current flowing through a solution** is measured as a function of an applied voltage. It is particularly used for the **quantitative and qualitative analysis** of electroactive substances, especially metal ions and organic compounds capable of reduction.

Basic Principle of Polarography:

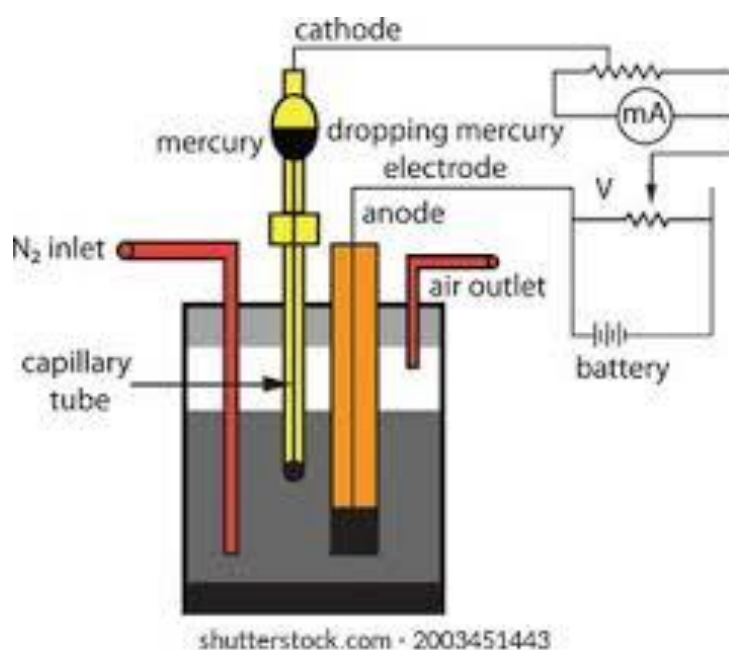
Polarography is based on the measurement of current resulting from the **electrochemical reduction or oxidation** of analyte species at a **dropping mercury electrode (DME)** or **static mercury drop electrode (SMDE)** as a function of the **applied potential**.

When a potential is applied between a **working electrode** (usually DME) and a **reference electrode** (like calomel electrode), the analyte undergoes **reduction (gain of electrons)** or **oxidation (loss of electrons)** depending on its nature. As the potential increases, a stage is reached where the analyte starts to undergo a redox reaction, producing a current called the **faradaic current**.

This current increases with the applied potential until it reaches a **limiting value**, called the **diffusion current (i_d)**, which is proportional to the concentration of the analyte in solution.

Polarogram:

- A plot of current (i) vs. applied potential (E).
- Shows a **sigmoidal curve** with a flat baseline, a rising portion, and a plateau.
- The midpoint of the rising portion gives the **half-wave potential ($E_{1/2}$)** which is characteristic of the analyte and helps in **qualitative analysis**.



Construction and Working of Dropping Mercury Electrode (DME)

Introduction:

The **Dropping Mercury Electrode (DME)** is a unique working electrode used in polarographic analysis. It consists of mercury drops that continuously fall from a fine capillary, providing a **renewable and reproducible surface** for electrochemical reactions, particularly **reduction reactions**.

Construction of DME:

A DME typically consists of the following components:

1. **Mercury Reservoir:**

A glass bulb or container holds **pure mercury**. Mercury used must be chemically pure and free from oxidizing agents.

2. **Fine Capillary Tube:**

A narrow capillary (usually made of glass) is attached to the reservoir.

- Internal diameter: 0.03–0.08 mm
- The length and bore of the capillary determine the **drop size and drop time**.

3. **Capillary Outlet:**

The capillary outlet is immersed in the **electrolyte solution** (analyte). Drops of mercury fall one by one at regular intervals due to **gravity** and **mercury pressure**.

4. **Electrodes Arrangement:**

The DME acts as the **working electrode**, while a **reference electrode** (like SCE or Ag/AgCl) completes the electrochemical cell.

Working of DME:

1. **Mercury Flow:**

Mercury from the reservoir flows through the capillary and forms a **drop** at the outlet. When the drop becomes heavy enough, it detaches and falls into the electrolyte solution.

2. Electrode Reaction:

Each drop serves as a fresh and reproducible **electrode surface**. When a **controlled potential** is applied between the DME and reference electrode:

- **Reduction or oxidation** of electroactive species occurs at the mercury drop.
- The **current generated** is measured and plotted against the applied potential.

3. Drop Time and Rate:

- Drop time is usually **2–5 seconds**.
- The **Ilkovic equation** relates the diffusion current to the drop time, mercury flow rate, and analyte concentration.

4. Renewal of Surface:

After each drop detaches, a **new mercury surface** is formed, minimizing surface contamination and making it ideal for accurate electrochemical measurements.

Advantages of DME:

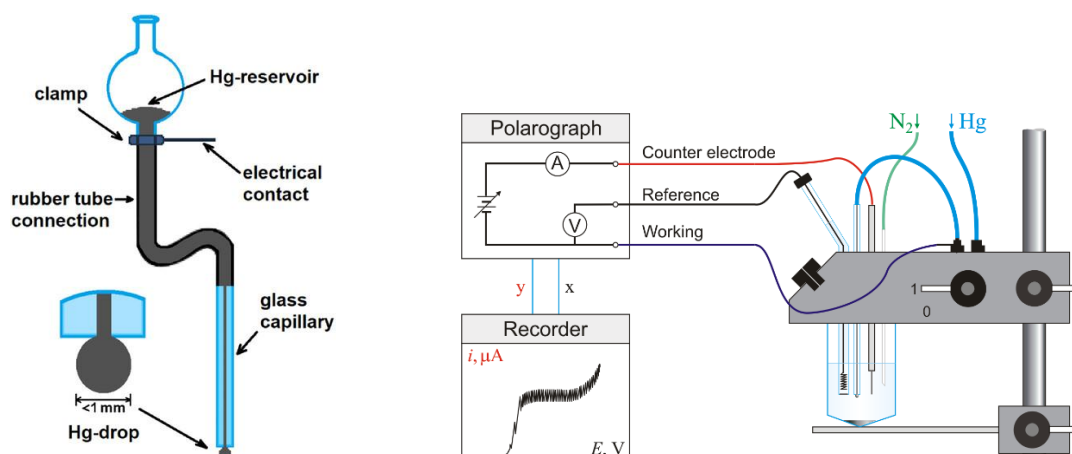
- **Fresh surface** with each drop → high reproducibility.
- **High hydrogen overvoltage** on mercury → allows detection of reducible species without hydrogen evolution.
- **Inert and smooth surface** → minimizes adsorption effects.

Limitations:

- Mercury is **toxic** and requires safe handling and disposal.
- Not suitable for **oxidation reactions**, as mercury itself can oxidize.
- Fragile construction and **manual calibration** of drop rate needed.

Applications:

- **Quantitative and qualitative analysis** of metal ions (e.g., Zn^{2+} , Cd^{2+} , Pb^{2+}).
- Determination of **organic compounds** like nitro groups and carbonyl compounds.
- Analysis in **biochemistry**, **pharmaceuticals**, and **environmental chemistry**.



Dropping Mercuric Chloride diagram

Rotating Platinum Electrode (RPE)

Introduction:

The **Rotating Platinum Electrode (RPE)** is a type of working electrode used in **voltammetry** and **polarographic techniques** to improve mass transport of analyte to the electrode surface. It is particularly useful in systems where **mercury electrodes** are not suitable, such as for oxidation reactions or when mercury is incompatible with the analyte.

Construction:

The RPE consists of the following key parts:

1. **Platinum Electrode Disk:**
A small **platinum disk** is sealed into an inert insulating material (like glass or Teflon), exposing only the circular surface of the metal.
2. **Shaft and Motor Assembly:**
The platinum electrode is attached to a **rotating shaft** connected to a **motor**. The motor allows precise control over the rotation speed of the electrode.
3. **Electrical Contact:**
The rotating shaft is connected to the **potentiostat** via a **slip ring assembly**, which allows electrical connection without restricting rotation.
4. **Electrochemical Cell Setup:**
 - The RPE acts as the **working electrode**.
 - A **reference electrode** (e.g., SCE or Ag/AgCl) and a **counter electrode** (e.g., platinum wire) complete the three-electrode system.

Working Principle:

- When the electrode rotates, it causes the **electrolyte solution to move** around it, reducing the thickness of the diffusion layer.

- This **enhances the mass transfer** of the analyte from the bulk solution to the electrode surface.
- A potential is applied between the working and reference electrode, and the resulting **current is measured** as a function of the potential.
- The rapid renewal of the solution near the electrode surface ensures a **steady-state current** and reproducible results.

Advantages of RPE:

- **Enhanced mass transport** → higher sensitivity and faster response.
- Suitable for both **oxidation and reduction** reactions.
- Can be used with **aqueous and non-aqueous** systems.
- Provides a **clean, inert, and stable surface** (platinum is chemically inert).

Applications:

1. **Voltammetry:**
Used in rotating disk voltammetry (RDV) to study the kinetics of redox reactions.
2. **Electrochemical Analysis:**
Useful in the determination of **trace metals** and **organic compounds**.
3. **Kinetic Studies:**
Helps in understanding **electrode reaction mechanisms** and **diffusion-controlled processes**.
4. **Pharmaceutical Applications:**
Applied in the **assay of drugs**, especially those that are oxidizable (e.g., ascorbic acid, dopamine).

Limitations:

- Requires **precise instrumentation** and calibration.
- Platinum may **adsorb impurities**, requiring regular cleaning.
- Not suitable for systems requiring **amalgam formation** (mercury electrodes preferred in such cases).

Rotating Platinum electrode

