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PHARMACEUTICAL ANALYSIS I

UNIT 5

TOPIC :

- **Potentiometry –** Electrochemical cell, construction and working of reference (Standard hydrogen, silver chloride electrode and calomel electrode) and indicator electrodes (metal electrodes and glass electrode), methods to determine end point of potentiometric titration and applications.

Potentiometry

- Potentiometry is an electroanalytical method used to determine the concentration of an analyte in solution by measuring the electrical potential (voltage) of a solution without drawing any significant current.
- The measurement is done using a reference electrode (constant potential) and an indicator electrode (responsive to ion concentration).

Principle:

The principle of potentiometry is based on the Nernst equation, which relates the electrode potential to the concentration (or activity) of the ions involved in the redox reaction.

- The potential difference (voltage) between the indicator electrode (which responds to changes in analyte concentration) and the reference electrode (which maintains a constant potential) is measured.
- This potential difference is proportional to the logarithm of the ion concentration in the solution.
- No significant current is allowed to flow during the measurement, ensuring the chemical composition remains unchanged.

Key Equation – Nernst Equation:

$$E = E^0 + \frac{0.0591}{n} \log[\text{Ion concentration}]$$

Where:

- E = electrode potential
- E^0 = standard electrode potential
- n = number of electrons transferred
- Ion concentration = activity of the ion being measured

Electrochemical Cell

- An electrochemical cell is a device that generates electrical energy from chemical reactions (or vice versa) through oxidation-reduction (redox) processes. These cells are fundamental in batteries, fuel cells, and electrolysis systems.

Types of Electrochemical Cells:

1. **Galvanic (Voltaic) Cell**
   - Converts **chemical energy into electrical energy**.
   - Based on **spontaneous redox reactions**.
   - Generates electric current as electrons flow from anode to cathode.
   - Example: **Daniel Cell**, batteries.

Working of a Galvanic Cell (e.g., Daniel Cell):

Setup:

- Two half-cells:
  - **Zinc rod** in **$ZnSO_4$** solution
  - **Copper rod** in **$CuSO_4$** solution
- Connected by a **salt bridge** and an external wire.

Reactions:

- **Anode (Zinc):**

$$Zn\ (s) \rightarrow Zn^{2+}(aq) + 2e^-$$

(Oxidation – loss of electrons)

- **Cathode (Copper):**

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

- (Reduction – gain of electrons)
- **Electrons flow** from Zn → Cu through the external circuit.
- **Salt bridge** allows anions and cations to flow, maintaining charge balance.

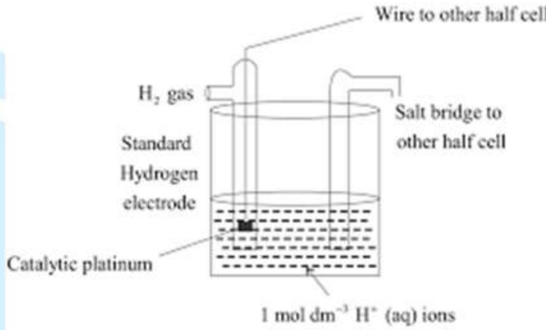
2. **Electrolytic Cell**
   - Converts **electrical energy into chemical energy**.
   - Involves **non-spontaneous redox reactions**.
   - Requires an external power source to drive the reaction.
   - Example: **Electrolysis of water**, electroplating, extraction of metals like aluminum.

Applications of Electrochemical Cells:

1. **Batteries** – Dry cells, lithium-ion cells, lead-acid batteries.
2. **Electroplating** – Depositing metal layers on surfaces.
3. **Electrolysis** – Splitting water or extracting metals.
4. **Fuel Cells** – Clean energy source for vehicles.
5. **Corrosion Studies** – Understanding how metals degrade.

Construction and working of Standard hydrogen electrode

- The **Standard Hydrogen Electrode (SHE)** is the **primary reference electrode** with a defined electrode potential of **0.00 V** under standard conditions. It is used to measure the electrode potentials of other electrodes.



Construction of Standard Hydrogen Electrode

The SHE is constructed using the following components:

Parts of SHE:

1. **Platinum Electrode (Pt)**
   - A thin platinum strip or foil coated with platinized platinum (for high surface area).
   - Inert and conducts electrons without participating in the reaction.
2. **Hydrogen Gas (H_2)**
   - Pure hydrogen gas is bubbled at 1 atm pressure over the platinum electrode.
3. **Acidic Solution**
   - Contains H^+ ions (usually 1.0 M HCl or H_2SO_4).
   - Ensures $[H^+]$ = 1 mol/L as per standard conditions.
4. **Gas Inlet Tube**
   - Delivers hydrogen gas at a constant rate into the solution.
5. **Porous Junction or Salt Bridge**
   - Connects to the second half-cell and allows ion flow.

Working Principle of SHE:

- The SHE works on the redox equilibrium:

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

- The platinum electrode serves as a conductor for the electron exchange between H_2 gas and H^+ ions.
- At equilibrium, the potential developed is defined as **0.00 V** under standard conditions:
  - H_2 gas at 1 atm
  - H^+ concentration = 1 M
  - Temperature = 25°C (298 K)
- The SHE can act as:
  - **Anode** when connected to an electrode with higher reduction potential.
  - **Cathode** when connected to a lower reduction potential electrode.

Advantages of SHE:

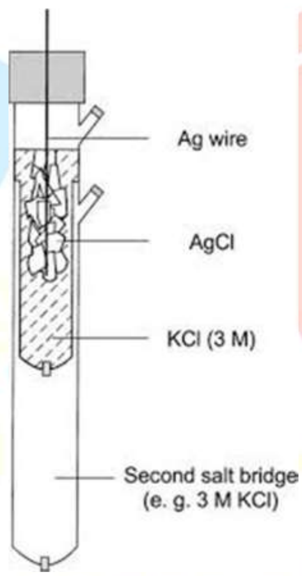
- Universal standard (reference).
- Can act as both anode and cathode.
- Accurate and reproducible under controlled conditions.

Limitations of SHE:

- Difficult to maintain standard conditions (1 atm gas, 1 M acid).
- Platinum surface may get poisoned by impurities.
- Not convenient for routine use—other reference electrodes like Calomel Electrode or Silver-Silver Chloride Electrode are often preferred in practice.

Construction and working of silver chloride electrode

- The Silver-Silver Chloride electrode is a reference electrode that provides a constant and known potential. It is made of a silver wire coated with silver chloride, immersed in a chloride ion solution (e.g., KCl).
- It is widely used in electrochemical measurements as a stable and safe alternative to the Standard Hydrogen Electrode (SHE).



Construction:

1. **Silver Wire (Ag):**
   - A clean silver wire acts as the base electrode.
2. **Coating of Silver Chloride (AgCl):**
   - The silver wire is coated with **AgCl** either chemically or electrochemically.
   - The coating is white in color and slightly porous to allow ion exchange.
3. **Chloride Ion Solution:**
   - The electrode is immersed in a solution containing **KCl or HCl**, usually:
     - Saturated KCl
     - 3.5 M KCl
     - 1.0 M KCl
4. **Glass Tube or Housing:**

- The silver wire and AgCl coating are enclosed in a glass container with an outlet at the bottom for ionic contact.

5. **Porous Plug or Salt Bridge:**
    - A small opening or porous plug at the end of the electrode allows contact with the test solution while preventing rapid mixing.

Working Principle:

The Ag/AgCl electrode works based on the equilibrium between silver metal (Ag), silver chloride (AgCl), and chloride ions (Cl^-):

$$AgCl\,(s) + e^- \rightleftharpoons Ag\,(s) + Cl^-(aq)$$

- When connected in an electrochemical cell, this electrode maintains a constant potential determined by the concentration of Cl^- in the electrolyte.
- It serves as a reference point to measure the potential of other electrodes (indicator electrodes).

Advantages:

- Easy to handle and construct.
- Stable and reproducible potential.
- Safer than mercury-containing reference electrodes (like the calomel electrode).
- Suitable for biological and environmental studies.

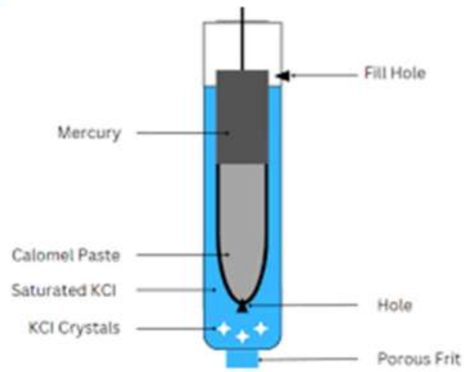
Limitations:

- Not suitable in systems that react with chloride ions.
- The potential depends on the Cl^- concentration — must be precisely maintained.
- Over time, AgCl layer may degrade or be contaminated.

Construction and working of calomel electrode

→ The Calomel Electrode is a type of reference electrode used in electrochemical measurements, especially in potentiometry.

→ A calomel electrode is a secondary reference electrode based on the redox reaction between mercury (Hg) and mercurous chloride (Hg_2Cl_2, calomel) in the presence of potassium chloride (KCl).



Construction of Calomel Electrode

The Calomel Electrode consists of the following components:

1. **Glass Tube** – Holds the electrode assembly.
2. **Mercury (Hg)** – Placed at the bottom of the tube.
3. **Calomel Paste (Hg_2Cl_2)** – A paste of **mercury and mercurous chloride** (Hg_2Cl_2).
4. **Potassium Chloride (KCl) Solution** – Saturated KCl acts as the electrolyte.
5. **Porous Plug or Salt Bridge** – Allows ionic contact with the test solution while preventing mixing.

Working Principle of Calomel Electrode:

The working of the calomel electrode is based on the **redox equilibrium**:

$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$$

The electrode maintains a constant potential depending on the chloride ion concentration.

It acts as a reference electrode by providing a stable and known electrode potential.

Advantages:

- Stable and reproducible potential
- Easy to prepare and use
- Widely used as a reference standard

Indicator Electrodes

→ Indicator electrodes (also known as **working electrodes**) are electrodes whose potential **depends on the concentration of a specific ion** in the solution. They respond to changes in analyte concentration and are used to measure unknown ionic activity.

Types of Indicator Electrodes:

1. **Metal Electrodes**
2. **Glass Electrode**

1. Metal Electrodes

➢ These are electrodes made from metals that can either participate in a redox reaction or act as inert conductors.

Types of Metal Electrodes:

A. Electrodes of the First Kind

- Metal is in direct contact with a solution of its own ions.
- Potential depends on the metal ion concentration.
- **Example**:
    - Cu/Cu^{2+}

B. Electrodes of the Second Kind

- Metal is in contact with a sparingly soluble salt and a solution containing the common ion.
- Often used as reference electrodes.
- **Example**:
    - Ag/AgCl

2. Glass Electrode

- A glass electrode is a hydrogen ion-selective electrode, mainly used for pH measurements.

Construction:

- **Glass bulb**: Made of special pH-sensitive glass.
- **Internal solution**: Usually contains 0.1 M HCl.
- **Internal electrode**: Silver–silver chloride (Ag/AgCl).
- **Connected to reference electrode** (like calomel or Ag/AgCl).

Working Principle:

- The potential develops due to the exchange of H^+ ions between the glass membrane and solution.
- The potential is directly related to pH**:**

$$E - E^o - 0.0591 \times pH$$

Applications:

→ Measurement of pH in labs and industries.

→ Used in acid-base titrations.

→ Preferred when solutions are colored or turbid.

Methods to determine end point of potentiometric titration

➢ In potentiometric titration, the end point is determined by monitoring the change in potential (E) between an indicator electrode and a reference electrode as the titrant is added.
The end point corresponds to the equivalence point, where the amount of titrant exactly reacts with the analyte.

Methods of End Point Determination

1. Graphical Method (Titration Curve Method)

Principle:

→ As the titrant is added, the potential (E) changes gradually.
→ Near the equivalence point, the change becomes very rapid.
→ A plot of electrode potential (E) vs. volume of titrant (V) shows an S-shaped curve.

Procedure:

- Record potential after each small addition of titrant.
- Plot E (mV) on the Y-axis and V (mL) on the X-axis.
- Identify the inflection point (steepest part of the curve) — this is the end point.

Advantages:

- Simple and widely used.
- Gives a visual representation of titration.

Suitable for:

- Strong acid–strong base titrations
- Redox titrations (e.g., $KMnO_4$ vs Fe^{2+})

2. First Derivative Method

Principle:

→ Measures the rate of change of potential with volume ($\Delta E/\Delta V$).

→ The maximum value of this derivative indicates the steepest change in potential — i.e., the equivalence point.

Procedure:

- From the titration data, calculate $\Delta E/\Delta V$ between successive points.
- Plot the first derivative vs. volume.
- The peak of the curve corresponds to the end point.

Advantages:

- More accurate than simple graphical method.
- Eliminates ambiguity in locating inflection point.

Used for:

- Acid–base titrations
- Redox titrations

3. Second Derivative Method

Principle:

→ The second derivative (d^2E/dV^2) measures the rate of change of the first derivative.

→ At the equivalence point, the second derivative crosses zero (changes sign).

Procedure:

- Calculate the second derivative from titration data.
- Plot d^2E/dV^2 vs. volume.
- The point where curve crosses the zero line is the end point.

Advantages:

- Very precise.
- Ideal when the titration curve is not sharp or well-defined.

Used in:

- Weak acid–weak base titrations
- Non-aqueous titrations

Applications of Potentiometry

- **Determination of End Point in Titrations**
  - Used in acid–base, redox, precipitation, and complexometric titrations.
  - No need for a visual indicator.
- **pH Measurement**
  - Glass electrode in potentiometry is used to measure pH accurately.
- **Determination of Ion Concentration**
  - Ion-selective electrodes (like fluoride or nitrate electrodes) help detect specific ions.
- **Assay of Drugs in Pharmaceuticals**
  - Accurate determination of active ingredients in drug formulations.
  - Example: Ascorbic acid, ibuprofen.
- **Mixture Analysis**
  - Can differentiate and determine multiple components in a mixture.
  - Example: HCl and CH_3COOH mixture.
- **Non-Aqueous Titrations**
  - Used in titrations where water is not a suitable solvent.
  - Example: Titration of amines in glacial acetic acid.
- **Determination of pKa Values**
  - Helps in studying the dissociation of weak acids and bases.