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Electrometric Methods

Electrometric Methods

Definition:

- **Electrometric methods** involve the **measurement of electrical quantities**—such as **potential (voltage), current, or conductivity**—to study and quantify chemical systems.
- These techniques are highly sensitive, non-destructive, and suitable for detecting trace amounts of substances.

Electrometric methods are mainly used for:

- Quantitative analysis
- Qualitative analysis
- Studying reaction kinetics
- Determining equilibrium constants

Types of Electrometric Methods:

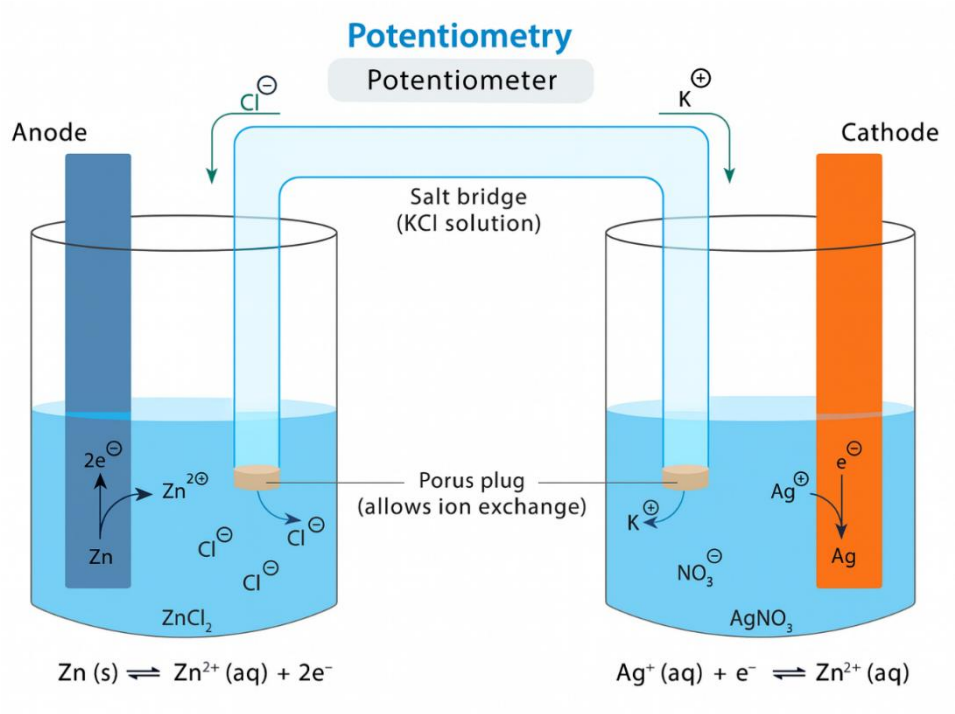


1. **Potentiometry**
2. **Conductometry**
3. **Polarography**
4. **Amperometric Titrations**

Potentiometry

Potentiometry

Definition:



- Potentiometry is an electrochemical technique in which the electrode potential (voltage) of a cell is measured without drawing any significant current.
- It is mainly used to determine the concentration of an ion in solution by measuring the electrical potential difference between a reference electrode and an indicator (sensing) electrode.

Principle:

- The working principle is based on the Nernst equation, which relates the measured electrode potential to the ion activity (or concentration):

$$E = E^\circ - \frac{0.0591}{n} \log a_{ion}$$

- Where:
  - E= measured electrode potential
  - E°= standard electrode potential
  - n= number of electrons involved in the reaction
  - a_{ion}= activity of the ion
- Since no significant current flows through the system, the chemical equilibrium is not disturbed.

Instrumentation:

1. **Reference Electrode:**
   - Maintains a constant potential.
   - Examples: **Standard Hydrogen Electrode (SHE), Calomel Electrode, Ag/AgCl Electrode**

2. Indicator Electrode:

- Responds to the activity of a specific ion.
- Examples:
  - **Glass electrode** for H^+ (pH)
  - **Metal electrodes** for metal ions (Cu, Zn, etc.)
  - **Ion-selective electrodes (ISEs)** for specific ions (F^-, Na^+, K^+)

3. High-impedance Voltmeter or Potentiometer:

- Measures the potential difference without allowing significant current to flow.

Applications:

- **pH measurement** using glass electrode
- Determination of **fluoride, nitrate, calcium, etc.** using ion-selective electrodes
- Used in **potentiometric titrations**, where the equivalence point is detected by a sharp change in potential
- Monitoring of **redox reactions**

Advantages:

- Highly selective when using ion-selective electrodes
- Minimal disturbance to the system
- Applicable over a wide concentration range

Limitations:

- Electrode calibration is necessary
- Slower response in low-conductivity solutions
- Potential affected by interfering ions

Electrical Potential

Definition:

- Electrical potential (or electric potential) refers to the amount of electric potential energy per unit charge at a point in a field.
- It represents the **capacity of an electric field to do work** on a charged particle.
- **Formula**:

$$V = \frac{W}{q}$$

- **Where:**
  - V = electrical potential (volts, V)
  - W = work done (joules, J)
  - q = charge (coulombs, C)

Importance in Electrochemistry:

- In electrochemical systems, electrical potential is the **driving force** behind the movement of electrons between two half-cells.
- **It helps determine:**
  - The direction of electron flow
  - The feasibility of redox reactions
  - The strength of an oxidizing/reducing agent

Measurement:

- Electrical potential cannot be measured absolutely but only as a difference between two points, typically using a reference electrode and a working/indicator electrode.

Units:

- **Volt (V):** 1 Volt = 1 Joule/Coulomb
- Measured using voltmeters or potentiometers in circuits

Role in Potentiometry:

- In potentiometry, changes in electrical potential are measured to:
  - Detect equivalence points in titrations
  - Determine ion concentration (like pH, metal ions)
  - Monitor chemical reactions

Electrochemical Cell

Definition:

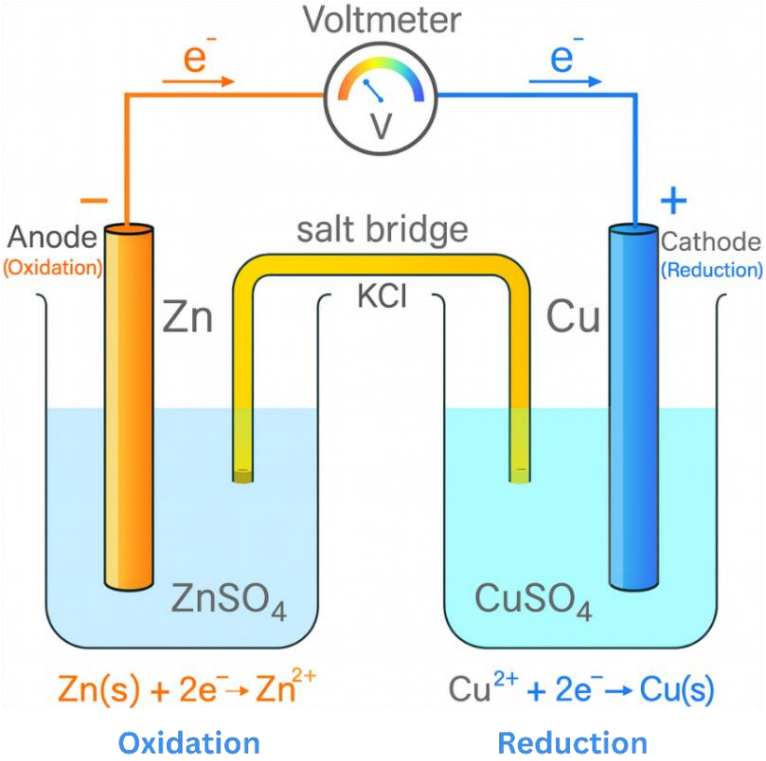
- An electrochemical cell is a device that converts chemical energy into electrical energy (galvanic/voltaic cell) or uses electrical energy to drive chemical reactions (electrolytic cell).

Types of Electrochemical Cells

1. Galvanic Cells

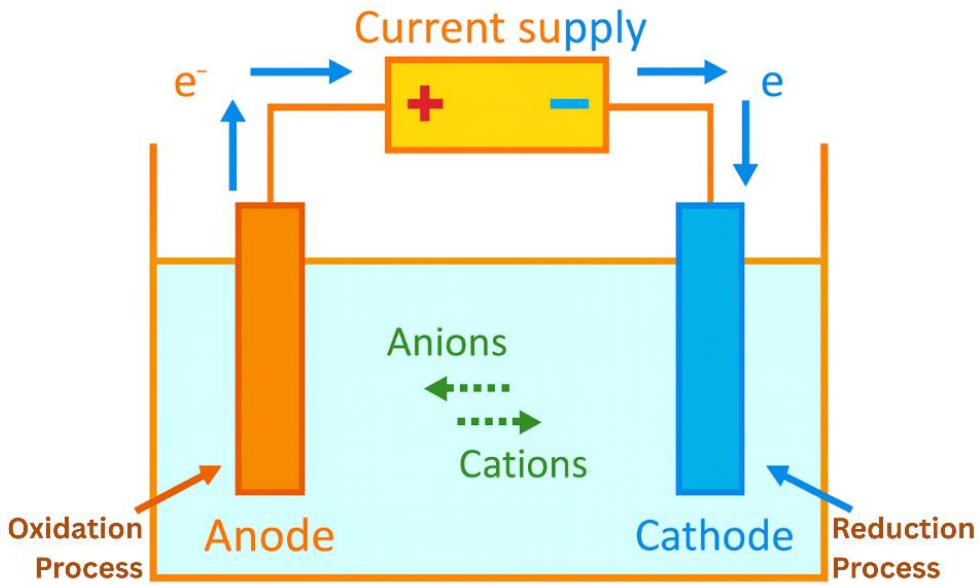
➢ In a galvanic cell, a spontaneous redox reaction occurs between the anode (site of oxidation) and cathode (site of reduction).

- Electrons flow from the anode to the cathode through an external circuit, generating electric current, while the electrolyte maintains charge neutrality by allowing ion movement.
- **Example:** The Daniell cell, with a zinc anode in zinc sulfate and a copper cathode in copper sulfate, connected by a salt bridge.



2. Electrolytic Cells

- In electrolytic cells, an external voltage source drives a non-spontaneous redox reaction.
- The anode (connected to the positive terminal) is the site of oxidation, and the cathode (negative terminal) is the site of reduction.
- Applications include electroplating, electrorefining, and the electrolysis of water to produce hydrogen and oxygen.



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