Pharmaceutical Analysis Unit 5: Electrochemical Methods

Introduction to Electrochemical Methods

Welcome to the world of electrochemical methods! This unit will introduce you to powerful analytical techniques that rely on the interplay between electricity and chemical reactions. These methods are crucial for understanding and quantifying substances in various fields, from pharmaceuticals to environmental science.

Conductometry

Conductometry is an electrochemical analytical method primarily based on measuring the **electrical conductance** of a solution. The core idea behind a **conductometric titration** is that the conductance of a solution changes during a chemical reaction, particularly when one type of ion is replaced by another. This change in conductance allows us to pinpoint the **equivalence point** of a titration, which is the point where the titrant has completely reacted with the analyte.

The **conductivity** of a solution is directly related to the movement of **charged particles**, or ions, within it. Different ions have different abilities to carry an electric charge, known as their **ionic conductivity**. Therefore, as the types and concentrations of ions change during a reaction, the overall conductivity of the solution will also change.

To measure this, two platinum electrodes are immersed in an electrolytic solution and connected to an electricity source. The **current (I)** that flows through the solution is determined by the **applied voltage (E)** and the **electrical resistance (R)** of the portion of the solution between the electrodes. This fundamental relationship is described by **Ohm's Law**:

I = E/R

Where:

- **I** is the current in amperes
- **E** is the applied voltage in volts
- **R** is the resistance in ohms

Basics of Conductometry

To fully grasp conductometry, it's essential to understand some key terms:

- **Conductance (G):** This is a measure of how easily electricity flows through a solution. Mathematically, it is the **reciprocal of electrical resistance (1/R)**. The unit of conductance is **Siemens (S)**, or sometimes **mhos** (ohm spelled backwards), or **ohms^{-1}**. A higher conductance means the solution allows current to flow more readily.
- **Electrical Conductivity:** This refers to the ability of a material to conduct electricity. In conductometry, this value is obtained by multiplying the measured conductance (G) by a **cell constant**.
- **Cell Constant:** (This additional detail helps in understanding the concept but is not directly from the provided materials.) The cell constant accounts for the specific geometry of the conductivity cell, including the area of the electrodes and the distance between them. It ensures that the measured conductance is standardized for the cell being used.
- **Specific Conductance (Kappa, K):** This is a more fundamental property, defined as the conductance of a cube of the liquid solution with one centimetre (1 cm) sides. Since conductance (L) is the reciprocal of resistance, specific conductance is proportional to the cross-sectional area of the conductor and inversely proportional to its length. The unit of specific conductance is **Ohm^{-1} cm^{-1}** or **Mho/cm**. The formula is **K = L * (A/l)**, where L is conductance, A is the cross-sectional area, and l is the length of the conductor. *It's important to understand that the source defines specific conductance as K = L/A. This may be a simplification or different notation where L is length and A is area, implying K = L / (area/length), but the standard definition is K = G * (l/A), where G is conductance, l is distance between electrodes, and A is electrode area, with the unit Ohm^{-1} cm^{-1}.*
- **Equivalent Conductance (Λeq):** This represents the specific conductance of a solution containing **one gram equivalent of solute** dissolved in **1000 ml of solution**. It takes into account the charge of the ions. The unit is **Mhos^2 / gram equivalent**. The formula is **Λeq = (1000 * K) / Ceq**, where K is specific conductance and Ceq is the equivalent concentration.
- **Molar Conductance (Λm or Λ):** This is the conductance of a solution containing **one mole of solute** dissolved in **1000 ml of solution**, when placed between two parallel electrodes 1 cm apart. It is denoted by capital lambda (Λ). The concentration of the solution is denoted by C. The unit of molar conductance is **Siemens cm^2 / mole**. The formula is **Λ = 1000 / C**. (Note: *The provided source states Λ = 1000/C directly, implying K is absorbed or simplified in this specific context, or that C here refers to molar concentration in a specific unit. For clarity, a more complete formula is Λm = (K * 1000) / Molarity, where K is specific conductance and Molarity is in mol/L.*)
    - The source provides some examples of molar conductance for common ions:
        - Hydrogen (H^+): 349.6 Siemens cm^2/mole
        - Hydroxide (OH^-): 199.1 Siemens cm^2/mole
        - Chloride (Cl^-): 76.35 Siemens cm^2/mole
        - Ammonium (NH_4^+): 73.5 Siemens cm^2/mole

        - Nitrate (NO_3^-): 71.5 Siemens cm²/mole
        - Silver (Ag^+): 61.9 Siemens cm²/mole
        - Sodium (Na^+): 50.1 Siemens cm²/mole
        - Acetate (CH_3COO^-): 40.9 Siemens cm²/mole
    - *These values highlight that H^+ and OH^- ions have exceptionally high molar conductances, which is a key factor in how conductometric titrations behave.*

Instrument for Conductometry

The instrument used to measure conductance is called a **conductometer**. It typically consists of three main parts:

- **Current Source:** Conductometers employ an **alternating current (AC) source**, often a mechanical high-frequency AC generator. Using AC is crucial because it **prevents polarization effects** at the electrodes, which can occur with direct current (DC) as ions accumulate and react at the electrode surfaces, changing the electrode potential and affecting measurements.
- **Conductivity Cells:** These are typically **wide-mouthed cells** or **dip type cells**, often made of **Pyrex or quartz**. They are designed to hold the experimental solution and are fitted with two platinum electrodes. It is important to keep the cell in a constant temperature environment, often a **thermostat**, because **conductivity is temperature-dependent**.
- **Electrodes:** These are usually **platinum sheets**, each with a surface area of **one cm²**, fixed at a distance of 1 cm apart. The surface of these electrodes is coated with **platinum black**.
    - **Platinum black** is a finely divided, porous form of platinum. Its purpose is twofold:
        1. To **avoid polarization effects**: The rough, high surface area of platinum black minimises the buildup of reaction products and maintains a stable electrode-solution interface.
        2. To **increase the effective surface area**: A larger surface area allows for more efficient charge transfer, leading to more accurate conductance measurements.
    - **Platinization** is the process of coating the electrodes, usually done by applying a solution of **3% chloroplatinic acid and lead acetate** to achieve a uniform coating.
    - The proper usage and packing of electrodes depend on the **conductivity and concentration** of the solution. If the concentration is low, the electrodes should be positioned closer together and be larger.
- *(For students, it's helpful to visualize a Wheatstone bridge circuit, often employed in older conductometers.*
  This circuit allows for precise measurement of an unknown resistance (the solution's resistance) by balancing it against known resistances. Modern conductometers use more advanced electronic circuitry but follow the same principle of measuring resistance or its inverse, conductance.)

Types of Conductometric Titrations

Conductometric titrations are versatile and used for a variety of reactions to determine the equivalence point. Different types of titrations result in distinct changes in conductivity profiles. The difference in **ionic conductivity** of the H^+ and OH^- ions, which are much higher than most other ions, plays a significant role in these profiles.

1. **Acid-Base or Neutral Titrations:** These are among the most common applications.
   - **Strong Acid-Strong Base Titration (e.g., HCl vs NaOH):**
     - Consider titrating strong acid (HCl) with strong base (NaOH).
     - **Initially:** The solution contains a high concentration of highly mobile **hydrogen ions (H^+)** from HCl, resulting in **high conductance**.
     - **During Titration:** As NaOH is slowly added, H^+ ions react with **hydroxide ions (OH^-)** from NaOH to form water (H_2O). The H^+ ions are replaced by less mobile **sodium ions (Na^+)**. Since H^+ ions have a much higher conductivity than Na^+ ions, the overall **conductance of the solution decreases** steadily.
     - **At the Equivalence Point:** All hydrogen ions have reacted with hydroxide ions. The solution contains only NaCl (a salt), and the conductance is at its **lowest point**.
     - **After the Equivalence Point:** Excess NaOH is added. The solution now contains increasing concentrations of highly mobile **hydroxide ions (OH^-)** and additional Na^+ ions. Since OH^- ions also have a very high conductivity, the **conductance of the solution increases rapidly**.
     - The plot of conductance versus volume of titrant will show a V-shape, with the equivalence point at the minimum.
     - Reaction: $HCl + NaOH \rightarrow NaCl + H_2O$
   - **Strong Acid-Weak Base Titration (e.g., HCl vs NH_4OH):**
     - Consider titrating strong acid (HCl) with weak base (NH_4OH).
     - **Initially:** High conductance due to H^+ ions from HCl.
     - **During Titration:** H^+ ions react with NH_4OH to form **ammonium ions (NH_4^+)** and water. H^+ ions are replaced by NH_4^+ ions, which have a lower conductivity than H^+. Therefore, the **conductance decreases**.
     - **At the Equivalence Point:** Conductance reaches its **minimum** as most H^+ ions have reacted.
     - **After the Equivalence Point:** Addition of excess **weak base (NH_4OH)** does not significantly increase the conductance because NH_4OH is a weak electrolyte and

dissociates only slightly. The common ion effect from the already formed NH_4Cl also suppresses the dissociation of NH_4OH. Thus, the conductance **remains relatively constant or increases very slowly**.

- The plot shows a sharp decrease followed by a nearly flat line.
- Reaction: $HCl + NH_4OH \rightarrow NH_4Cl + H_2O$

○ **Weak Acid-Strong Base Titration (e.g., CH_3COOH vs NaOH):**

- Consider titrating weak acid (CH_3COOH) with strong base (NaOH).
- **Initially:** Weak acid dissociates only slightly, so the initial conductance is **low but slightly increasing** due to the presence of some H^+ ions.
- **During Titration:** As NaOH is added, it reacts with CH_3COOH to form **sodium acetate (CH_3COONa)** and water. The undissociated weak acid is replaced by the salt (CH_3COONa), which is a strong electrolyte. The acetate ions (CH_3COO^-) and sodium ions (Na^+) have a higher conductivity than the undissociated weak acid. Thus, the **conductance slowly increases** due to the formation of the salt.
- **At the Equivalence Point:** All the weak acid has reacted, and the conductance has increased steadily.
- **After the Equivalence Point:** Addition of excess **strong base (NaOH)** introduces highly mobile OH^- ions. The **conductance increases rapidly** due to the presence of these excess OH^- ions.
- The plot shows an initial slow increase followed by a sharp increase.
- Reaction: $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

○ **Weak Acid-Weak Base Titration (e.g., CH_3COOH vs NH_4OH):**

- Consider titrating weak acid (CH_3COOH) with weak base (NH_4OH).
- **Initially:** Low conductance from the weak acid.
- **During Titration:** The weak acid reacts with the weak base to form **ammonium acetate (CH_3COONH_4)**, which is a salt. This salt is a strong electrolyte, so its formation causes the **conductance to increase slowly**.
- **At the Equivalence Point:** The conductance continues to rise slowly.
- **After the Equivalence Point:** Addition of excess **weak base (NH_4OH)**, like excess weak acid, does not significantly increase conductance because it is a weak electrolyte and dissociates minimally. Therefore, the **conductance remains relatively constant or increases very slightly**.
- The plot shows a continuous slow increase followed by a nearly flat line.
- Reaction: $CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O$

2. **Precipitation Titrations (e.g., NaCl with $AgNO_3$):**

    - Consider titrating sodium chloride (NaCl, a strong electrolyte) with silver nitrate ($AgNO_3$, a strong electrolyte).
    - **Initially:** High conductance due to the presence of Na^+ and Cl^- ions from NaCl.
    - **During Titration:** As $AgNO_3$ is added, Ag^+ ions react with Cl^- ions to form **silver chloride (AgCl) precipitate**. In this reaction, the Cl^- ions are replaced by **nitrate ions (NO_3^-)** from the titrant.
    - *For students, it's worth noting that the ionic conductivities of Cl^- and NO_3^- are quite similar. Therefore, as one is replaced by the other, the overall conductance might not change dramatically, or might even remain relatively constant if their conductivities are nearly identical.*
    - **At the Equivalence Point:** Most of the Cl^- ions have precipitated.
    - **After the Equivalence Point:** Excess $AgNO_3$ is added. This introduces additional Ag^+ and NO_3^- ions into the solution, which are not involved in precipitation. Consequently, the **conductance of the solution starts increasing rapidly** due to the accumulation of these excess ions.
    - The plot shows a relatively constant or slightly changing conductance followed by a sharp increase.
    - Reaction: $NaCl + AgNO_3 \rightarrow AgCl\ (s) + NaNO_3$
3. **Redox Titrations:**

    - **Redox titrations are generally not well-suited for conductometric measurements.** This is because most redox reactions require a **large excess of acid or base** to complete the reaction or to provide the necessary conditions. The high concentration of these highly conductive H^+ or OH^- ions interferes significantly by masking any smaller changes in conductance caused by the actual redox species. Therefore, conductometric titrations are typically **not performed for redox reactions**.
4. **Replacement or Displacement Titrations:**

    - The provided sources list this as a type of conductometric titration. *However, they do not offer specific explanations or examples for this category.* Generally, these titrations involve the replacement of one ion in a compound with another, leading to a change in conductance.
5. **Complexometric Titrations:**

    - The provided sources list this as a type of conductometric titration. *However, they do not offer specific explanations or examples for this category.* In complexometric titrations, a complexing agent reacts with metal ions, and if the complex formation alters the number or mobility of charged species, it can be monitored conductometrically.
6. **Non-Aqueous Titrations:**
    - The provided sources list this as a type of conductometric titration. *However, they do not offer specific explanations or examples for this category.* These titrations are performed in non-aqueous solvents, which can be useful for substances that are insoluble in water or for enhancing the acidity/basicity of very weak acids/bases. Conductometric methods can be applied if there are sufficient ions in the non-aqueous medium.

Applications of Conductometry

Conductometric titrations are highly useful in various analytical applications:

- **Water Quality Monitoring:** They are used to determine **water pollution** levels in rivers, lakes, and other natural water resources, as pollution often increases ionic content and thus conductivity.
- **Alkalinity of Water:** Conductometry can determine the **alkalinity of fresh water**, which is important for understanding its buffering capacity.
- **Salinity of Seawater:** This method is employed to determine the **salinity of seawater**, a study that falls under the field of **oceanography**.
- **Deuterium Ion Concentration:** It can be used to determine the **concentration of deuterium ions** in water-deuterium mixtures.
- **Food Microbiology:** Conductometry helps in **tracing microorganisms** in food samples, as microbial growth can alter the conductivity of the medium.
- **Ash Content in Sugar Juices:** It is used to **estimate the ash content** in sugar juices, which is an indicator of inorganic impurities.
- **Purity of Water:** Conductometric titrations are used to find out the **purity of distilled and deionized water**, as pure water has very low conductivity.
- **Solubility of Sparingly Soluble Salts:** The solubility of salts that dissolve only slightly, such as **silver chloride ($AgCl$)** and **barium sulphate ($BaSO_4$)**, can be determined.
- **Atmospheric SO_2 Determination:** This method can be used for the **determination of atmospheric sulphur dioxide (SO_2) levels**.
- **Vanillin Estimation:** Conductometry can be used for the **estimation of vanillin** in vanilla flavour extracts.

Unit 5: Potentiometry & Polarography

Introduction to Potentiometry

Potentiometry is a significant field within **electroanalytical chemistry**. It involves measuring the **potential (voltage)** of an electrochemical cell **under conditions of no current flow**. This measured potential is then used to determine the **analytical quantity of interest**, most commonly the **concentration of a specific component (analyte)** in a solution.

The potential generated in an electrochemical cell arises from the **free energy change** that would occur if the chemical reactions within the cell were to proceed to equilibrium. Potentiometric methods rely on the measurement of the cell's electromotive force (Ecell) for quantitative analysis.

Electrochemical Cell

An **electrochemical cell** is a fundamental arrangement in electrochemistry. It consists of **two electrodes** immersed in an **electrolytic solution**, and it is capable of producing a chemical reaction by the passage of electricity through it, or generating electricity from a chemical reaction. Each cell is made of two distinct electrodes:

- One electrode **liberates electrons** and is called the **oxidizing electrode** (anode).
- The other electrode **absorbs electrons** and is called the **reducing electrode** (cathode).

Example: A classic example is the **Voltaic cell** or **Daniell cell**, which uses zinc and copper electrodes in solutions of their respective sulphates, connected by a salt bridge.

Electrode Potential (E): In electrochemistry, the **electromotive force (EMF)** of a cell built from two electrodes is known as the electrode potential. Conventionally:

- The **left-hand side** is the **standard hydrogen electrode (SHE)**, which is assigned a potential of zero volts by international agreement.
- The **right-hand side** is the electrode whose potential is being defined or measured.

By convention, the cell potential (**Ecell**) is calculated as:

Ecell = Ecathode - Eanode

If the standard hydrogen electrode is used as the anode (Eanode = 0), then **Ecell = Eright = Eelectrode**. The left-right convention is consistent with the international agreement that redox potentials are given for reactions written in the form of **reduction half-reactions**.

The electrode potential, measured in volts (V), appears at the interface between an electrode and an electrolyte solution. It results from the **transfer of charged species** across this interface, specific adsorption of ions, and the orientation of polar molecules of the solvent.

Nernst Equation

The **Nernst Equation** is a vital equation that relates the **electrode potential (E)** to the **standard electrode potential (E^0)**, temperature, and the activities (effective concentrations) of the electroactive species. It quantifies how the potential of an electrode varies with the concentrations of the ions involved in the electrode reaction.

The equation is:

$E = E^0 - (RT / nF) * \ln(a\_products / a\_reactants)$

Where:

- **E** = Electrode potential (in Volts)
- **E^0** = Standard potential of the electrode (in Volts), measured under standard conditions (1 M concentration, 1 atm pressure, 25 °C)
- **R** = Universal gas constant (8.314 J/(K·mol))
- **T** = Temperature in Kelvin
- **n** = Number of electrons transferred in the half-reaction
- **F** = Faraday constant (96485 C/mol), representing the charge of one mole of electrons
- **ln(a)** = Natural logarithm of the activity (a) of the species. For dilute solutions, activity can be approximated by concentration.

(For students, it's helpful to remember that the Nernst equation is crucial because it allows us to calculate the potential of an electrode under non-standard conditions and to relate measured potentials directly to analyte concentrations, which is the basis of potentiometric analysis.)

Salt Bridge

A **salt bridge** is a critical component in many electrochemical cells, particularly galvanic (voltaic) cells. It is a **laboratory device** used to:

- **Connect the oxidation and reduction half-cells** of a galvanic cell.
- **Maintain electrical neutrality** within the internal circuit of the cell.

Importance: If a salt bridge is not present, one half-cell would accumulate a negative charge (due to excess electrons or accumulation of anions) and the other half-cell would accumulate a positive charge (due to consumption of electrons or accumulation of cations) as the reaction proceeds. This charge imbalance would quickly halt the reaction and prevent the production of electricity. The salt bridge prevents this by allowing **ion migration** to balance the charges in each half-cell.

Types of Salt Bridges:

- **Glass Tube Type:** This type consists of a **U-shaped glass tube** filled with a relatively **inert electrolyte**, most commonly **potassium chloride (KCl)** or sodium chloride (NaCl). The electrolyte is often solidified with an agar gel to prevent it from flowing out.
- **Filter Paper Type:** Another common type uses **filter paper** (e.g., Whatman filter paper) soaked in a relatively inert electrolyte, typically **potassium chloride or sodium chloride**. No gelling agent is required here because the filter paper itself provides a solid medium for ion conduction.

Standard Potential

In electrochemistry, the **standard electrode potential (E^0 or E)** is defined as the measure of the **individual potential of a reversible electrode** under **standard state conditions**. These conditions include:

- Solutes at an effective concentration (activity) of **1 mole per cubic decimetre (1 mol dm^{-3})**.
- Gases at a pressure of **1 atmosphere (1 ATM)**.
- A specific temperature, usually 25 °C (298.15 K).

The standard potential represents the tendency of a half-reaction to occur as a reduction relative to the standard hydrogen electrode (SHE), which is arbitrarily assigned a standard potential of 0 volts.

Reference Electrodes

A **reference electrode** is an electrode that maintains a **known, constant half-cell potential** and is **completely insensitive to the composition of the solution being studied (analyte solution)**. They are essential for potentiometric measurements because they provide a stable baseline against which the potential of an indicator electrode (which responds to the analyte) can be measured.

Ideal qualities of a reference electrode:

- **Reversible:** It should quickly reach equilibrium and follow the Nernst equation.
- **Obeys the Nernst Equation:** Its potential should be predictable.
- **Exhibits a potential that is constant with time:** Stability is key for reproducible measurements.
- **Returns to its original potential** after being subjected to small currents.
- **Exhibits little hysteresis** with temperature cycling, meaning its potential doesn't drift after temperature changes.

Examples of common reference electrodes:

- Standard Hydrogen Electrode (SHE)
- Saturated Calomel Electrode (SCE)
- Silver-Silver Chloride (Ag-AgCl) Electrode

Standard Hydrogen Electrode (SHE): The SHE is considered the **primary standard for pH measurement** and for establishing the standard potential scale.

- **Components:** It consists of a small **platinum wire or sheet** coated with finely divided **platinum black**. This electrode is immersed in a solution with a hydrogen ion activity of one (1 M H^+).
- **Hydrogen Gas: Hydrogen gas (H_2)** is continuously bubbled over the platinum electrode surface at a pressure of 1 atmosphere. This gas ensures saturation of the solution interface and represents the bulk of the solution.
- **Function:** The platinum surface acts as an inert site for the **electron transfer** for the hydrogen half-reaction but does not participate in the electrochemical reaction itself.
- **Half-cell Reaction:** H_2 (g) $\rightleftharpoons$ $2H^+$ (aq) + $2e^-$
- **Potential:** The potential at 25 °C is given by the equation: **Ecell = 0.0591 * log ([H^+]_std / [H^+]_unknown)** *As mentioned, the standard potential of SHE is defined as 0 V, serving as the reference point for all other electrode potentials.*

Saturated Calomel Electrode (SCE): The SCE is one of the **most commonly used reference electrodes** in analytical chemistry due to its ease of use and stable potential.

- **Temperature Dependence:** The **solubility of potassium chloride (KCl)**, which is a key component, is **temperature dependent**. Therefore, the operation of the SCE usually requires **temperature regulation** to maintain a stable potential.
- **Components:** It consists of **two concentric glass tubes**. The inner tube contains a **platinum wire** that is amalgamated (alloyed) with mercury and connected to an external circuit. This is surrounded by a thick paste of **metallic mercury (Hg)**, **mercurous chloride (Hg_2Cl_2) – known as calomel**, and **potassium chloride (KCl)**. The outer tube contains a saturated KCl solution.
- **Porous Connection:** A small pinhole in the inner tube and a **porous asbestos fibre** sealed into the tip of the outer tube provide an electrical contact with the sample solution while preventing mixing.
- **Stability:** The paste of Hg, Hg_2Cl_2, and saturated KCl ensures a **constant and reproducible potential**, provided the temperature is stable.
- *(For students, the key advantage of SCE is its stability and ease of construction, making it a robust laboratory reference electrode.)*

Silver Chloride (Ag-AgCl) Electrode: The Ag-AgCl electrode is another widely used and stable reference electrode, particularly common in compact pH probes.

- **Function:** It functions as a **redox electrode** where the equilibrium exists between **silver metal (Ag)** and its **salt silver chloride (AgCl)**.
- **Corresponding Equations:** $Ag^+ + e^- \rightleftharpoons Ag\ (s)$ $AgCl\ (s) \rightleftharpoons Ag^+ + Cl^-$ Overall: $AgCl\ (s) + e^- \rightleftharpoons Ag\ (s) + Cl^-$
- **Characteristics:** This reaction is characterised by **fast electrode kinetics**, allowing for efficient electron transfer. It can sustain sufficiently high currents for reliable measurements. The reaction is known to obey the Nernst equation in solutions with pH values between 0 and 13.5.
- **Nernst Equation for Ag-AgCl:** The potential of the Ag-AgCl electrode depends on the **activity or effective concentration of chloride ions (Cl^-)**, as shown by the Nernst equation: **$E = E^0 - (RT / nF) * \ln(a\_Cl^-)$** *Where a_Cl^- is the activity of chloride ions.*

Indicator Electrode

An **indicator electrode** is the working electrode in a potentiometric measurement whose **potential is governed by the concentration of the analyte** (the substance being measured). It develops a potential (E_ind) that is dependent on the analyte concentration, providing a selective, rapid, and reproducible response.

- **Metallic Indicator Electrodes:** These are typically metal wires that participate in a redox reaction with the analyte.
  - Examples: Copper (Cu) for $CuSO_4$, Zinc (Zn) for $ZnSO_4$ solutions.
- **Membrane Indicator Electrodes:** These electrodes use a selective membrane that generates a potential difference across it depending on the analyte concentration.
  - Example: **Glass electrode** (for pH measurement).

Glass Electrode: The glass electrode is the most common type of membrane electrode, widely used for **pH measurements**.

- **Construction:** It consists of a **very thin-walled glass bulb**, made from a special type of **low-melting point glass** that is sensitive to hydrogen ions.
- **Internal Components:** Inside the bulb, a **dilute HCl solution** is present, into which an **internal reference electrode** is immersed. This internal reference electrode is usually an **Ag-AgCl electrode** or a **saturated calomel electrode**.
- **Purpose of Internal Solution:** The dilute HCl solution provides an **unchanging hydrogen ion concentration** and a **constant chloride ion concentration** (if Ag-AgCl is used internally). The tube is permanently sealed at the top.

- **Instrumentation Principle:** The operation of the glass electrode is based on the principle that the **potential difference developed across the thin glass membrane** is directly proportional to the **pH difference** (and thus the hydrogen ion concentration difference) between the internal solution and the external sample solution.
- **Modern pH Probe (Combination Electrode):** A typical modern pH probe is a **combination electrode**, which cleverly integrates both the **glass (indicator) electrode** and the **reference electrode** into a **single body**.
    - **Sensing Part:** The sensing element is the glass bulb, made of a **thin glass membrane** that is specific to hydrogen ions.
    - **Internal Electrode:** The internal electrode within the glass bulb is usually a **silver chloride electrode** or a **calomel electrode**.
    - **Internal Solution:** The internal solution is typically a **pH 7 buffered solution** of 0.1 mol/L HCl (for pH electrodes) or 0.1 mol/L MeCl (for pMe electrodes). If a silver chloride electrode is used internally, a small amount of AgCl precipitate might be present inside the glass electrode to maintain equilibrium. If a calomel electrode is used, the internal solution is typically 0.1 mol/L KCl.
    - **Electrode Body:** The main body of the electrode is made from **non-conductive glass or plastics**.
    - **pH Bulb Structure:** The bottom of the pH electrode swells out into a round, thin glass bulb. The pH electrode itself is a tube within a tube. The inner tube contains the unchanging 1 x 10 mol/L HCl solution.
    - **Anodic Terminus:** The anodic terminus (part of the internal reference) wraps around the outside of the inner tube and ends as a sort of reference probe inside the inner tube.
    - **Reference Solution Contact:** The electrode is filled with a reference solution of KCl, and it makes contact with the external sample solution through a **porous plug**, which effectively acts as a salt bridge.

Polarography

Introduction and Principle: Polarography is a specialized subfield of **voltammetry**, which is an electrochemical technique where current is measured as a function of applied potential. In polarography, the distinguishing feature is the use of a **dropping mercury electrode (DME)** as the working electrode.

The principle involves recording the **current versus potential** (a voltammogram) as the applied potential across the cell is gradually changed. The current response arises from the **electrolysis of a solution** at a **polarizable microelectrode**.

The simple principle of polarography involves studying solutions or electrode processes by electrolysis with two electrodes:

1. **One polarizable electrode:** This is the DME, whose potential can be easily changed, causing a current to flow.
2. **One unpolarizable electrode:** This is a reference electrode (like SCE), whose potential remains constant regardless of the current.

The polarizable electrode is typically formed by mercury continuously dropping from a capillary tube.

Ilkovic Equation: The **Ilkovic equation** is a fundamental relationship in polarography, named after the Slovak chemist Dionýz Ilkovič, who derived it. This equation relates the **diffusion current (id)**, which is the limiting current caused by the diffusion of the depolarizer to the electrode surface, to various parameters of the dropping mercury electrode and the analyte. The depolarizer (c) is the substance that is reduced or oxidized at the dropping mercury electrode.

The Ilkovic equation is:

id = 607 * n * C * D^(1/2) * m^(2/3) * t^(1/6)

Where:

- **id** = Diffusion current (in microamperes)
- **n** = Change in valency (number of electrons transferred per molecule of depolarizer)
- **C** = Concentration of the depolarizer (in mmol/L)
- **D** = Diffusion coefficient of the depolarizer (in cm^2/s)
- **m** = Flow rate of mercury dropping from the capillary (in mg/s)
- **t** = Life time of a single mercury drop (in seconds)

(For students, this equation is important because it shows that the diffusion current, which is directly measurable, is proportional to the concentration of the analyte (C). This linear relationship is what allows polarography to be a quantitative analytical technique.)

Dropping Mercury Electrode (DME)

The **Dropping Mercury Electrode (DME)** is the defining working electrode in classical polarography. It is an electrode where **mercury continuously flows and forms fresh droplets** at the tip of a capillary tube, which then fall into the solution.

- **Mercury Drop Formation:** A flow of mercury passes through an insulating capillary, producing a droplet that grows and then detaches in a reproducible manner.
- **Electrode Assembly:** The collected mercury at the bottom of the cell typically serves as the **auxiliary electrode** in some designs, or a separate auxiliary electrode is used. Each released

mercury drop is immediately followed by the formation of another, usually at a rate of around **0.2 Hz** (about 5 drops per minute).
- **Operating Conditions:** Mercury is usually dropped at a stable flow rate of **5-30 drops per minute**. The system operates typically at an applied voltage range of **50-200 mV/min**. The drop life is usually **2-12 seconds**, and the potential range for measurements is generally from **+0.4 V to -2 V**.
- *(For students, experiments conducted with mercury electrodes, even if slightly varied, are broadly referred to as forms of polarography or voltammetry using solid working electrodes if not strictly DME.)*

Advantages of DME: The unique properties of the DME offer several significant advantages:

- **Reproducible, Smooth, and Continuously Renewed Surface:** Each new mercury drop presents a fresh, clean, and highly reproducible electrode surface. This is a major advantage as it **eliminates the poisoning effect** that can occur on solid electrodes where reaction products or impurities can accumulate and alter the electrode's behaviour.
- **Amalgam Formation with Many Metals:** Mercury can form **amalgams** (alloys) with many metals. This property is beneficial because it can facilitate the reduction of certain metal ions by forming an amalgam, thus expanding the range of analytes that can be studied.
- **Steady Diffusion Current:** The diffusion current assumes a **steady value immediately after each change of applied potential** and is highly reproducible. This stability allows for accurate current measurements.
- **Calculable Surface Area:** The **surface area of the mercury drop can be calculated** from its weight and density, which is useful for fundamental electrochemical studies.

Disadvantages of DME: Despite its advantages, the DME also has some limitations:

- **Anodic Polarographic Wave Masking:** At potentials more positive than approximately **+0.4 V (versus a Saturated Calomel Electrode, SCE)**, mercury itself begins to **dissolve (oxidize)**, producing an anodic polarographic wave. This mercury oxidation wave can **mask or obscure the waves of other easily oxidizable substances**, limiting the useful anodic potential range. Therefore, DME is primarily used for the analysis of **reducible substances** (those that undergo reduction).
- **Capillary Blockage:** The capillary tube through which mercury flows is very small and delicate. It can be **easily blocked** by particulate matter or impurities in the solution, leading to **malfunction of the electrode**.
- **Toxicity and Oxidation of Mercury:** Mercury is a **very toxic substance**, posing safety and environmental concerns. It is also **easily oxidized**, especially in the presence of oxygen, which further limits its use and requires careful handling and deaeration of samples.

Rotating Platinum Electrode (RPE)

The **Rotating Platinum Electrode (RPE)** is another type of working electrode used in certain electrochemical titrations and polarography, especially when the limitations of the DME are a concern.

- **Construction:** It consists of a **platinum wire** sealed into a soft-glass tubing. This glass tubing is then connected to and rotated by a **constant-speed motor**. The platinum wire itself is extended to the outer edge of a bell-shaped glass tube at the bottom of the electrode.
- **Application:** RPE is used in polarography and electrochemical titrations where a **high speed of operation** is desired. The glass tube and the glass wall act as a **stationary electrode** in conjunction with the rotating platinum wire.
- **Operation:** The electrode operates at **high rotational speeds**. This high-speed rotation performs several functions:
    - **Greater Mass Transfer:** Rotation significantly increases the rate at which analyte species are transported from the bulk solution to the electrode surface (mass transfer). This is important for obtaining higher and more stable currents.
    - **Sharpens the End Point:** By enhancing mass transfer, the RPE can produce **sharper and more distinct endpoints** in titrations, making them easier to identify.
    - **Greatly Reduced Residual Current:** Due to the condenser effect and low hydrogen overpotential on platinum, the RPE exhibits a **greatly reduced residual current**. Residual current is the small current that flows even in the absence of the analyte, and a lower residual current improves the sensitivity of the measurement.

Applications and Advantages of Polarography

Polarography, particularly when employing the Dropping Mercury Electrode (DME), offers several advantages that lead to its applications. While the provided sources explicitly detail the advantages of the DME, these advantages directly translate into reasons for polarography's utility in chemical analysis.

The primary **advantages of the Dropping Mercury Electrode (DME)**, which contribute to polarography's effectiveness, include:

- **High Reproducibility:** The continuous renewal of the mercury drop surface ensures highly reproducible measurements. This is critical for reliable quantitative analysis.
- **Prevention of Electrode Poisoning:** The fresh surface of each mercury drop prevents the accumulation of reaction products or impurities, which can "poison" solid electrodes and lead to inaccurate results.
- **Formation of Amalgams:** Mercury's ability to form amalgams with many metals can enhance the reduction processes of certain metal ions, making them easier to detect and quantify.

- **Quantitative Analysis:** The Ilkovic equation demonstrates a direct proportionality between the diffusion current and the analyte concentration, making polarography a powerful tool for **quantitative determination** of various substances.
- **Qualitative Analysis:** The specific potential at which a substance is reduced or oxidized (the half-wave potential) is characteristic of that substance, allowing for **qualitative identification** in certain cases.

(While the sources focus on the DME's characteristics, polarography itself has found applications in diverse fields, including determining trace metals in environmental samples, analyzing organic compounds, and studying reaction mechanisms due to its sensitivity and ability to differentiate between various species based on their reduction/oxidation potentials. However, these broader application areas are not detailed in the provided materials.)