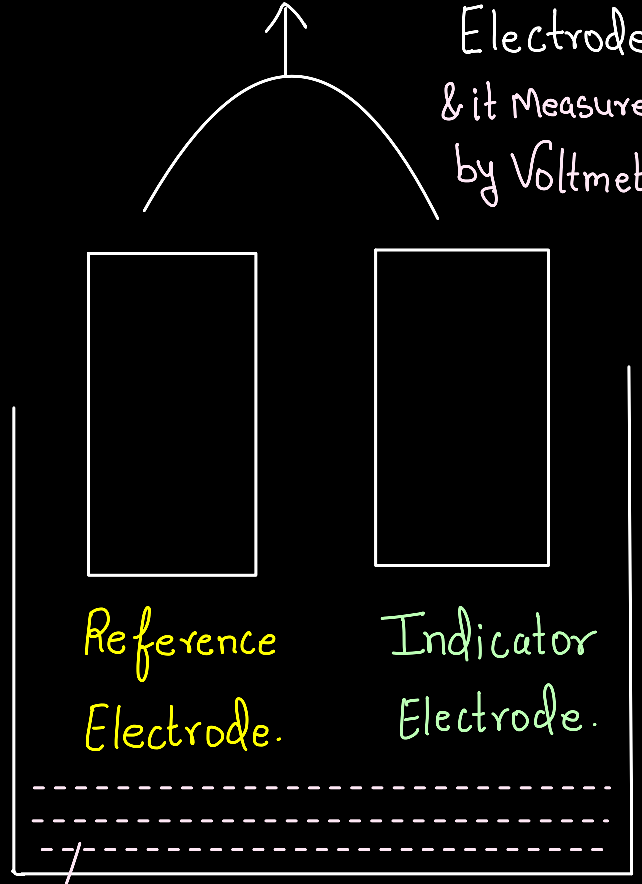
UNIT-5

Electrochemical methods of analysis

-Conductometry- Introduction, Conductivity cell, Conductometric titrations, applications.

-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.

-Polarography- Principle, Ilkovic equation, construction and working of dropping mercury electrode and rotating platinum electrode, applications



Potentiometry

Potentiometry is an analytical technique that measures the electrical potential difference between two electrodes (a reference and an indicator electrode) in an electrochemical cell to determine the concentration of a solute in a solution.

Principle:

Potentiometry is based on the principle that the potential difference between two electrodes in an electrochemical cell is related to the concentration of the analyte (the substance being measured).

Measurement:

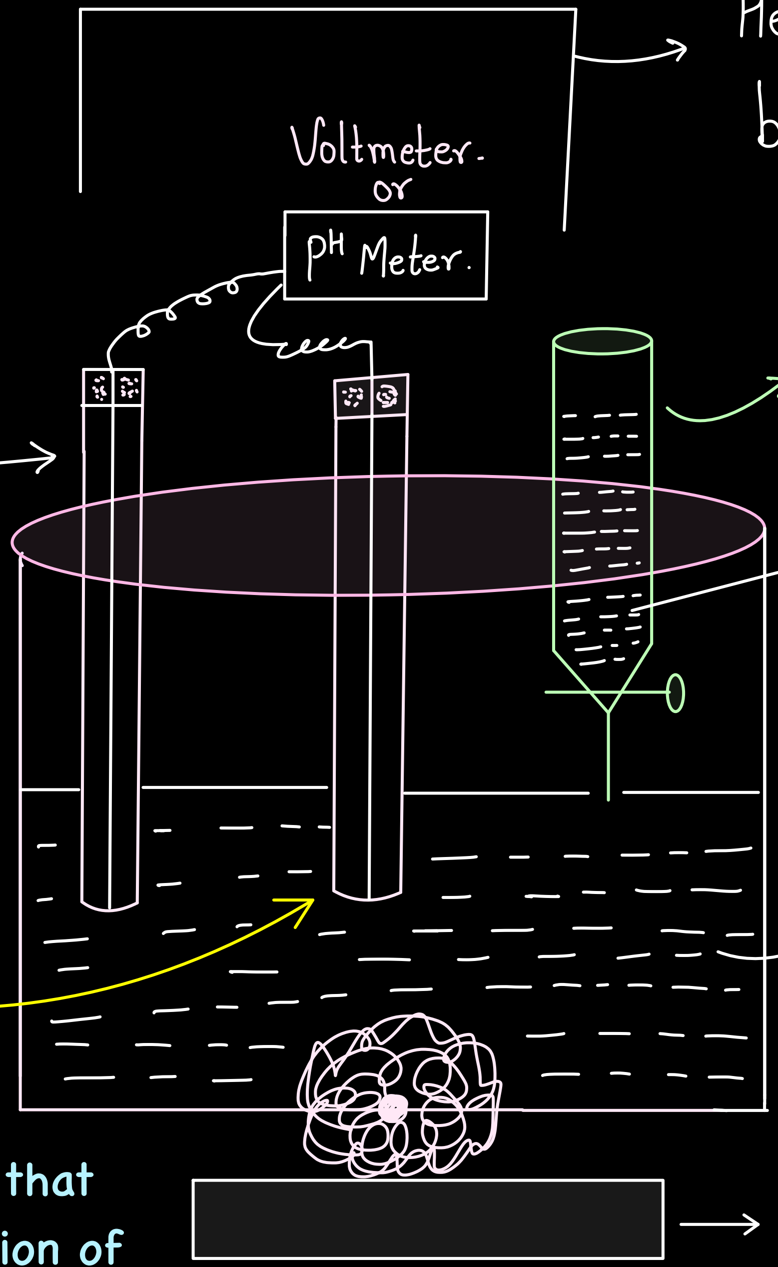
The potential difference between the two electrodes is measured using a voltmeter or other suitable instrument.

Potentiometer

(fix Voltage) Refrence Electrode.

[Stable & Known reference Potential].

eg → 40.



Here, we Measure Electrical potential diff. b/w 2 Electrode. & this is related to Conc. of Analyte Inst in Solution.

Burette.

Standard Soln. / Titrant. (Acid).

** Indicator Electrode.

Sample / Test Solution. (Base). * Conc.?

Magnetic Stirrer.

(Analyte Neutral).

End point.

25, 26, 27, 32, 33, 34

~~Titrant add~~ | Titrant Add | Titrant Continue Add.

An indicator electrode is a type of electrode that detects the presence or change in concentration of a substance in a solution. It can also be used to measure the potential or pH of a solution.

This electrode potential is measured by Nernst equation

$$\left[E = E_0 - \frac{2.303RT}{nF} \log K \right]$$

E= Electrode potential

K= Equilibrium constant for half cell reaction as in equilibrium law

E= Standard reduction potential

R= gas constant

T= kelvin temperature

n= number of electrons transfer in the half reaction

F= faraday of electricity

Cell Potential.
Or

Electrochemical Cell / Dielectric or Galvanic cell

→ Generate Voltage
Or
E.M.F

Consist of 2 Half Cell.

An electrochemical (or galvanic) cell converts chemical energy into electrical energy through spontaneous redox reactions.

It consists of two half-cells, each with an electrode and an electrolyte, which are connected by a wire and a salt bridge.

Redox Reactions:

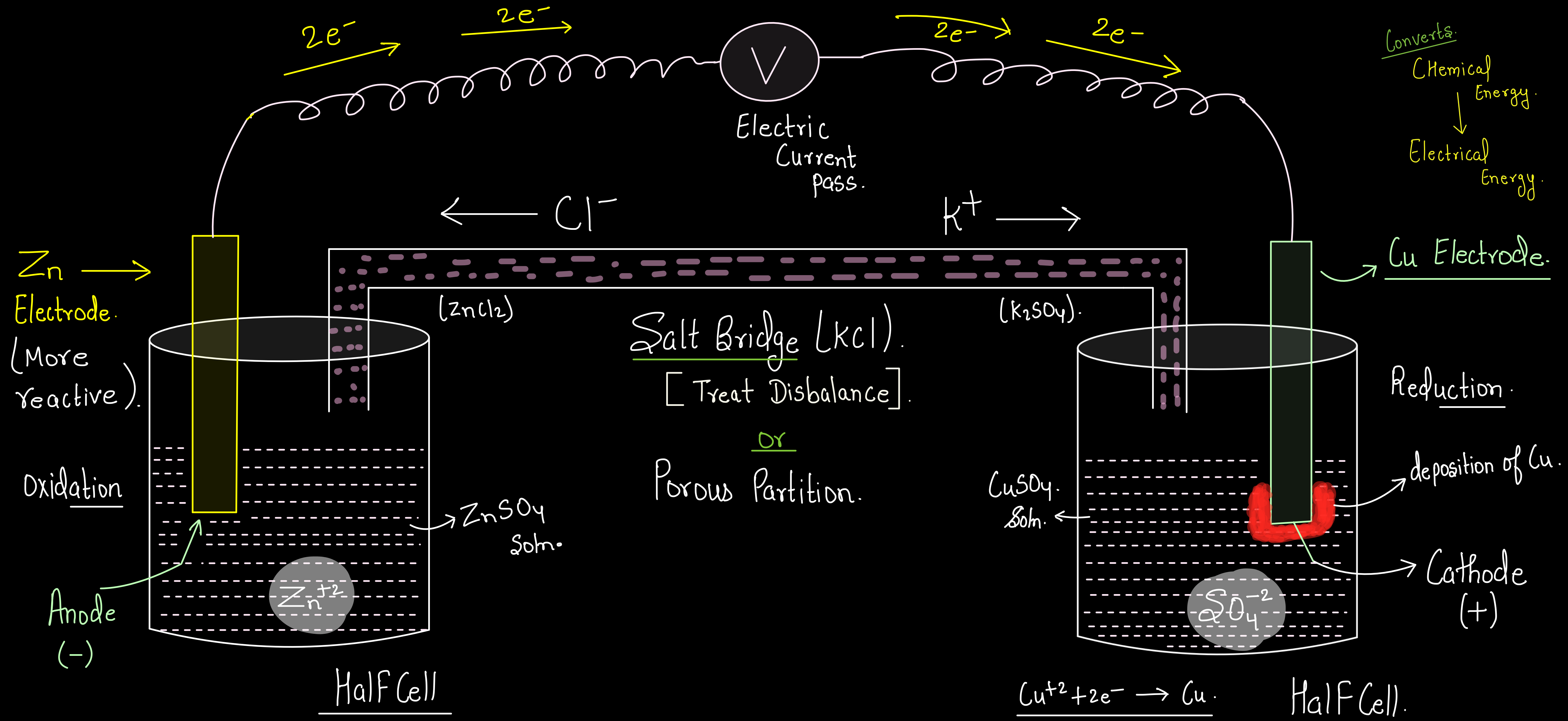
The reactions occurring in a galvanic cell involve the transfer of electrons from one species (oxidation at the anode) to another species (reduction at the cathode).

Oxidation: The loss of electrons. For example, in a zinc-copper cell, zinc undergoes oxidation at the anode:

$$Zn \longrightarrow Zn^{+2} + 2e^-$$

$$Cu^{+2} + 2e^- \rightarrow Cu.$$

Reduction: The gain of electrons. In the same cell, copper ions gain electrons at the cathode:



$ZnSO_4 \longrightarrow Zn^{+2} + SO_4^{-2}$

Zn^{+2} & SO_4^{-2} Cause disbalance.

$CuSO_4 \longrightarrow Cu^{+2} + SO_4^{-2}$

Components:

Anode: The electrode where oxidation occurs (loss of electrons).

Cathode: The electrode where reduction occurs (gain of electrons).

Electrolyte: A substance that allows ions to move between the electrodes.

Salt Bridge or Porous Partition: A medium that maintains the balance of charge by allowing ions to flow between the two half-cells without mixing the electrolytes.
In a galvanic cell, electrons flow from the anode (where oxidation happens) to the cathode (where reduction happens), generating an electric current that can be used to power devices.

Cell Potential (Electromotive Force):

The cell potential (or EMF) is the voltage produced by the cell, which is the difference in electric potential between the anode and cathode.

The greater the difference in reduction potential between the two half-reactions, the higher the EMF.

Applications:

Galvanic cells are used in batteries, such as lithium-ion batteries, alkaline batteries, and zinc-carbon batteries.

They are also used in fuel cells and electrochemical sensors.

Limitations:

Galvanic cells are often limited by factors like voltage decay over time and capacity degradation in batteries.

Their efficiency and performance are affected by temperature, concentration of electrolytes, and other environmental factors.

Construction and working of reference electrode → Measure Voltage.

(Standard hydrogen, silver chloride electrode and calomel electrode)

Reference electrode- A reference electrode is an essential component in electrochemical measurements. It provides a stable and known reference potential against which the potential of another electrode (usually the working electrode) can be measured.

** The reference electrode's potential does not change during the electrochemical process, making it a reliable standard for comparison.

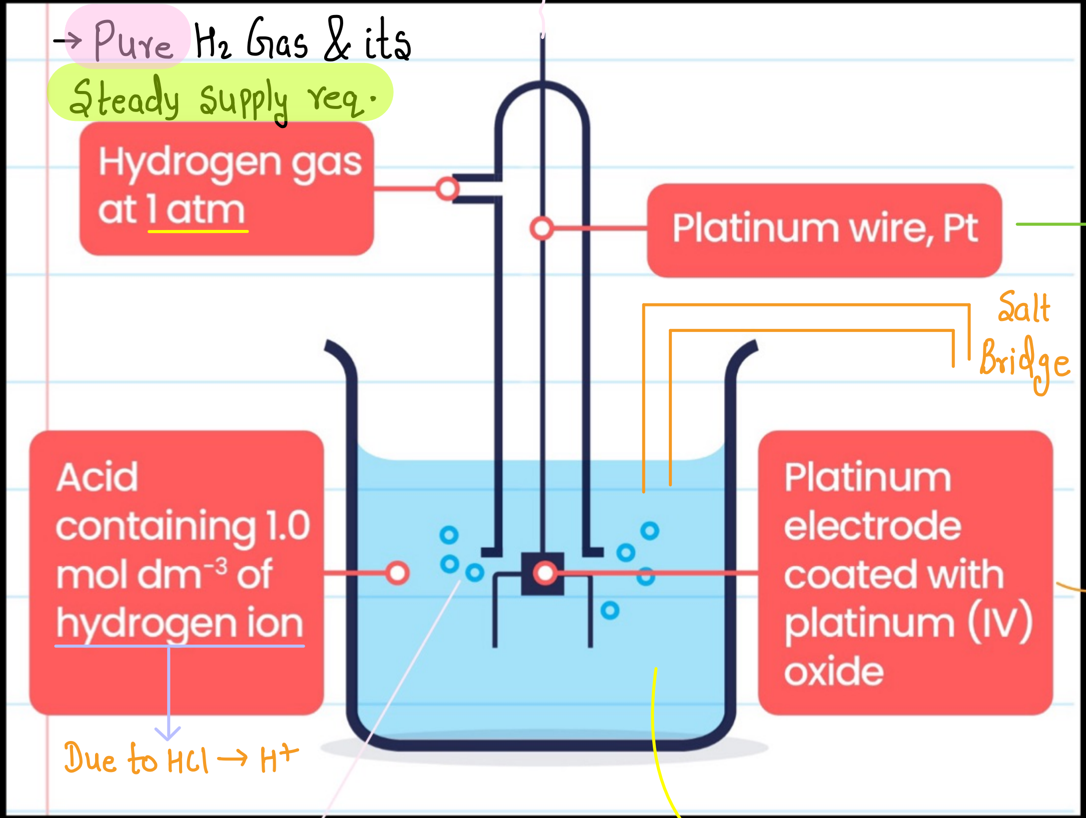
✓ The Standard Hydrogen Electrode (SHE), Calomel Electrode (SCE), and Silver/Silver Chloride Electrode (Ag/AgCl) are the most commonly used reference electrodes

1. Standard Hydrogen Electrode (SHE) Or Normal Hydrogen electrode (NHE).

The Standard Hydrogen Electrode (SHE) is a reference electrode used in electrochemical measurements. It is considered the "universal reference" with a defined potential of 0.00 V at all temperatures.

☆ [Temp. Must be 25°C
Or
298 K.]

Connect with External Circuit



Good Conductor of Electricity.

Chemically Inert [Not react with Electrolyte & Gas.]

to other Half Cell. (To Complete Circuit).

To (↑)se Surface area. (for better Interaction b/w Electrode & H_2 gas).

Bubbles forms due to H_2 Gas.

1M HCl. (H^+ Conc. Must be Constant).

Anode (-) (oxidation).

$$H_2 \rightarrow 2H^+ + 2e^-$$

Cathode (+) (reduction).

$$2H^+ + 2e^- \longrightarrow H_2$$

Electrode Structure:

Construction of Standard Hydrogen Electrode (SHE):

1. Platinum Electrode:

The core of the SHE is a platinum electrode. Platinum is used because it is a good conductor of electricity and is chemically inert, meaning it does not react with the electrolyte or gases. The platinum electrode is usually coated with platinum black, a form of platinum with a high surface area. This increases the electrode's surface area, which allows for better interaction between the electrode and the hydrogen gas.

2. Hydrogen Gas:

Hydrogen gas (H_2) is bubbled over the platinum electrode at a pressure of 1 atm (101.3 kPa). The gas is introduced into the solution in such a way that the platinum electrode is in contact with the hydrogen gas.

3. Electrolyte Solution:

The platinum electrode is immersed in an aqueous solution of H^+ ions (hydrogen ions), typically 1 M HCl (hydrochloric acid) or any other solution containing 1 M H^+ ions.

The concentration of hydrogen ions is kept constant at 1 mol/L to maintain standard conditions. The hydrogen ions in the solution are in equilibrium with hydrogen gas at the surface of the electrode.

4. Half-Reaction:

The half-reaction that occurs at the platinum electrode involves the reduction of hydrogen ions (H^+) to form hydrogen gas (H_2):

$$\boxed{2H^+ + 2e^- \longrightarrow H_2(g).}$$

When Refrence act as Cathode.

(Reduction).

This reaction is reversible, meaning that hydrogen gas can also be oxidized to form hydrogen ions at the electrode, depending on the direction of the current.

5. Temperature:

The temperature of the system is maintained at 25°C (298 K), as this is the standard temperature for defining the electrode potential.

Visual Layout of SHE Construction:

Platinum Electrode (Pt): This is placed in the solution and in contact with hydrogen gas.

Hydrogen Gas Bubbled: Hydrogen gas is bubbled over the platinum electrode at a pressure of 1 atm.

Electrolyte Solution: Typically, a 1 M solution of HCl or other hydrogen ion solutions is used.

External Circuit: The platinum electrode is connected to an external circuit where it can interact with the other half-cell in an electrochemical cell.

Connection to Salt Bridge: The SHE is often connected to a salt bridge or another half-cell that completes the circuit.

Advantages of the Standard Hydrogen Electrode (SHE):

1. Universal Reference Point:

2. Well-Defined Standard Potential:

3. Consistency in Measurements:

4. Widely Accepted:

5. Accurate pH Measurements:

Limitations of Standard Hydrogen electrode

Requires Hydrogen Gas:

The SHE relies on the presence of hydrogen gas at 1 atm pressure, which requires the setup to maintain a steady supply of pure hydrogen gas. This can be impractical in some laboratory or field conditions.

Sensitive to Gas Purity:

The performance of the SHE can be affected by impurities in the hydrogen gas. Any contamination can alter the electrode potential, making the electrode less reliable.

Gas Flow Issues:

Maintaining a constant flow of hydrogen gas and ensuring its even distribution around the platinum electrode can be technically challenging.

Temperature Sensitivity:

While the standard electrode potential is defined at 25°C, any deviations in temperature from the standard can cause variations in the electrode potential, requiring adjustments for accurate readings.

2. Silver Chloride Electrode or silver/silver chloride (Ag/AgCl) electrode

A silver/silver chloride (Ag/AgCl) electrode is a common reference electrode, based on the reduction of AgCl to Ag, with a standard potential of +0.222 V, often used in place of the Standard Hydrogen Electrode (SHE) due to its ease of use and stability

1. Construction:

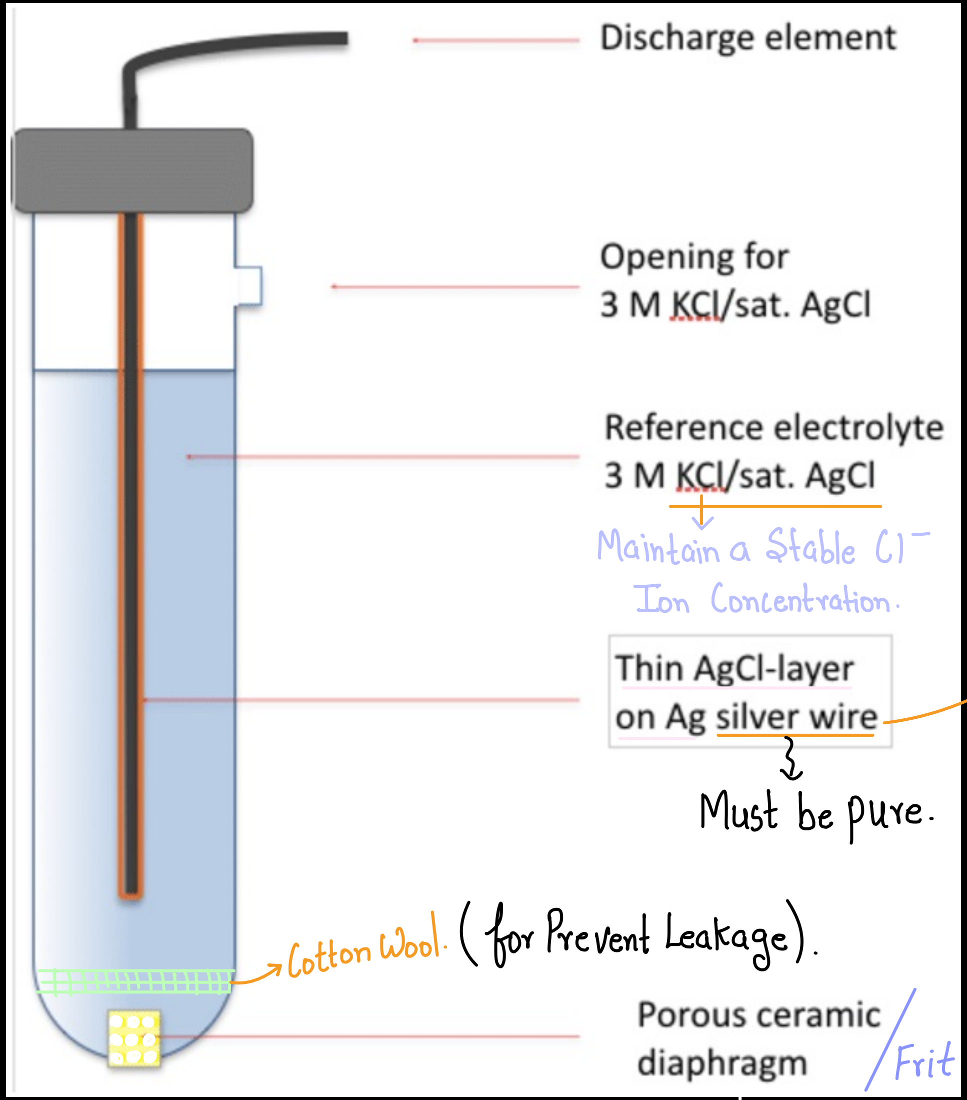
The construction of the silver chloride electrode involves the following key components:

Silver (Ag) wire or rod: A high-purity silver wire or rod is used as the base of the electrode.

Silver chloride (AgCl) coating: The silver wire or rod is coated with a thin layer of silver chloride (AgCl).

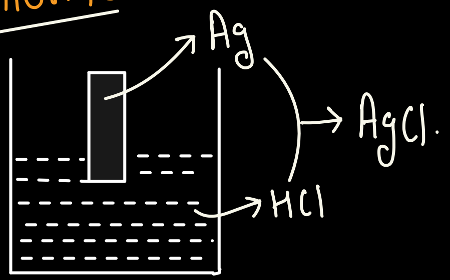
This is typically done by immersing the silver electrode in a solution of hydrochloric acid (HCl) to form AgCl through the reaction:

$$\left[Ag_{(s)} + Cl^-_{(aq.)} \longrightarrow AgCl_{(s)} + e^- \right]$$



* facillate Ion Exchange b/w Electrolyte filling Soln. & Sample Soln.

Also Coated With Silver Chloride.



Act like Anode then.

$$Ag + Cl^- \rightarrow AgCl + e^-$$

Act Like Cathode.

$$Ag^+ + e^- \rightleftharpoons Ag(s).$$

The equilibrium between silver and silver chloride is essential for the electrode's function

Electrolyte solution: The electrode is immersed in an electrolyte solution that is typically a concentrated chloride solution, such as a potassium chloride (KCl) solution.

The concentration of chloride ions in this solution helps maintain the equilibrium between the silver and silver chloride phases.

2. Working Principle:

The silver chloride electrode operates based on the following electrochemical reaction:

$$\left[Ag_{(s)} + Cl^-_{(aq.)} \longrightarrow AgCl_{(s)} + e^- \right]$$

In this reaction:

Silver (Ag) is in contact with chloride ions (Cl^-) in the electrolyte, forming silver chloride (AgCl) at the surface of the electrode.

The equilibrium between silver and silver chloride is essential for the electrode's function. The chloride ion concentration, along with the silver chloride solid phase, governs the potential of the electrode.

3. Function:

The primary function of the silver chloride electrode is to serve as a reference electrode in electrochemical cells. It provides a stable and reproducible reference potential, which is essential for accurate measurements in various electrochemical processes.

Stable Potential: The silver chloride electrode maintains a stable potential due to the equilibrium between silver, silver chloride, and chloride ions in the solution. The potential remains constant as long as the chloride ion concentration is stable.

4. Advantages:

Stability and Reproducibility: The silver chloride electrode offers a very stable and reproducible potential due to the well-defined equilibrium between Ag/AgCl and Cl^- in solution.

Ease of Construction: The electrode is relatively easy to construct and inexpensive compared to other reference electrodes.

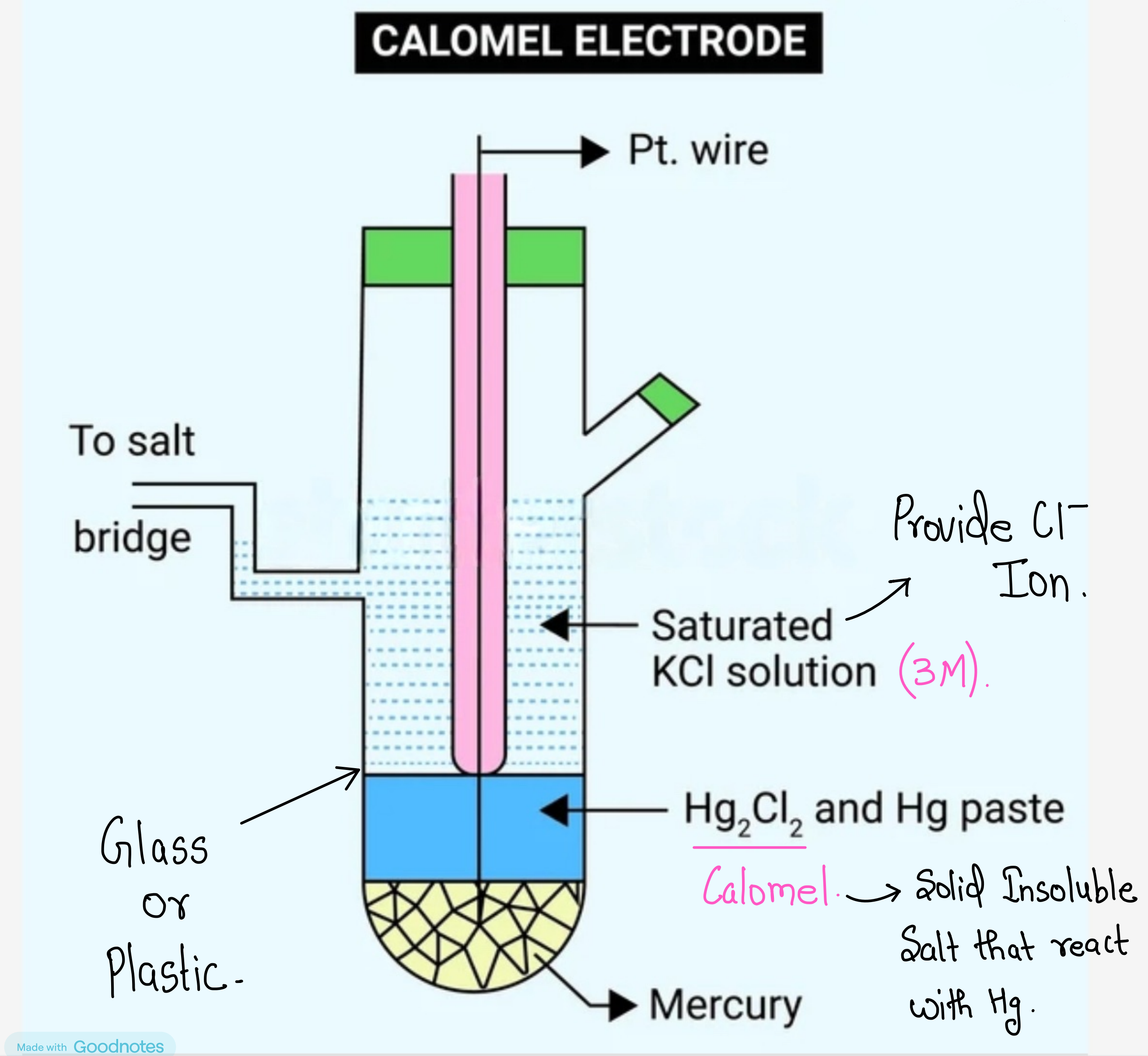
Versatility: It can be used in a wide range of applications, including those requiring precise pH measurements, redox potential measurements, and ion-selective electrode applications.

5. Limitations:

Requires Chloride Ions: The electrode depends on the presence of chloride ions in the solution, so it may not be suitable for use in solutions without chloride ions or for very low chloride ion concentrations.

Potential Drift: Over time, the electrode may suffer from changes in potential due to the formation of silver oxide or other surface reactions.

Saturated calomel electrode



If work as a Cathode

$$Hg_2^{+2} + 2e^- \longrightarrow 2Hg.$$

Anode → (-) (oxidation).

$$2Hg \longrightarrow Hg_2^{+2} + 2e^-$$

Calomel electrode Construction

1. Construction:

The calomel electrode is a reference electrode commonly used in electrochemical measurements. It consists of the following key components:

Mercurous Chloride (Hg_2Cl_2): This is the "calomel" part, a compound of mercury and chlorine. It forms the key active material of the electrode.

Mercury (Hg): A small quantity of mercury is used to maintain the necessary liquid phase for the electrode.

Aqueous KCl Solution: The electrode is immersed in a saturated or fixed concentration of potassium chloride (KCl) solution. The concentration is usually 3 M (3 molar).

Glass or Plastic Tube: The electrode assembly is typically contained in a glass or plastic tube to keep the electrolyte and mercury in place.

Porous Plug: Often a porous ceramic plug or frit is used to maintain electrical contact between the internal electrolyte and the solution being tested.

Calomel electrode Functions

Calomel electrodes are widely used in various electrochemical applications:

Reference Electrode: It provides a stable and known potential against which the potential of a working electrode can be measured. This is crucial for determining the redox potential of a solution.

pH Measurements: In conjunction with a glass electrode, the calomel electrode can be used in pH meters as a reference electrode.

Electrochemical Analysis: It is commonly used in techniques such as potentiometry, voltammetry, and electrolysis for studying redox reactions, corrosion, and other electrochemical properties of materials.

Environmental and Analytical Chemistry: Calomel electrodes are employed in the analysis of substances in solutions, such as in the determination of ion concentrations and the measurement of oxidation-reduction potentials.

Advantages:

Stable Potential: The calomel electrode offers a stable potential that is not significantly affected by temperature or the concentration of the KCl solution.

Widely Used and Reliable: It has been used for many decades and is trusted in scientific research for its reproducibility.

Disadvantages:

Mercury Toxicity: The use of mercury in the electrode can be hazardous, and care must be taken in its handling and disposal.

Limited Temperature Range: Its stability can be affected at high or low temperatures.

Indicator Electrode

An indicator electrode is a type of electrode that detects the presence or change in concentration of a substance in a solution. It can also be used to measure the potential or pH of a solution.

Indicator electrodes

(Metal electrodes and Glass electrode)

1.Metal electrodes - particularly those made of inert metals like platinum or gold, serve as indicator electrodes to measure the potential difference between the solution and the electrode, allowing for the determination of analyte concentrations

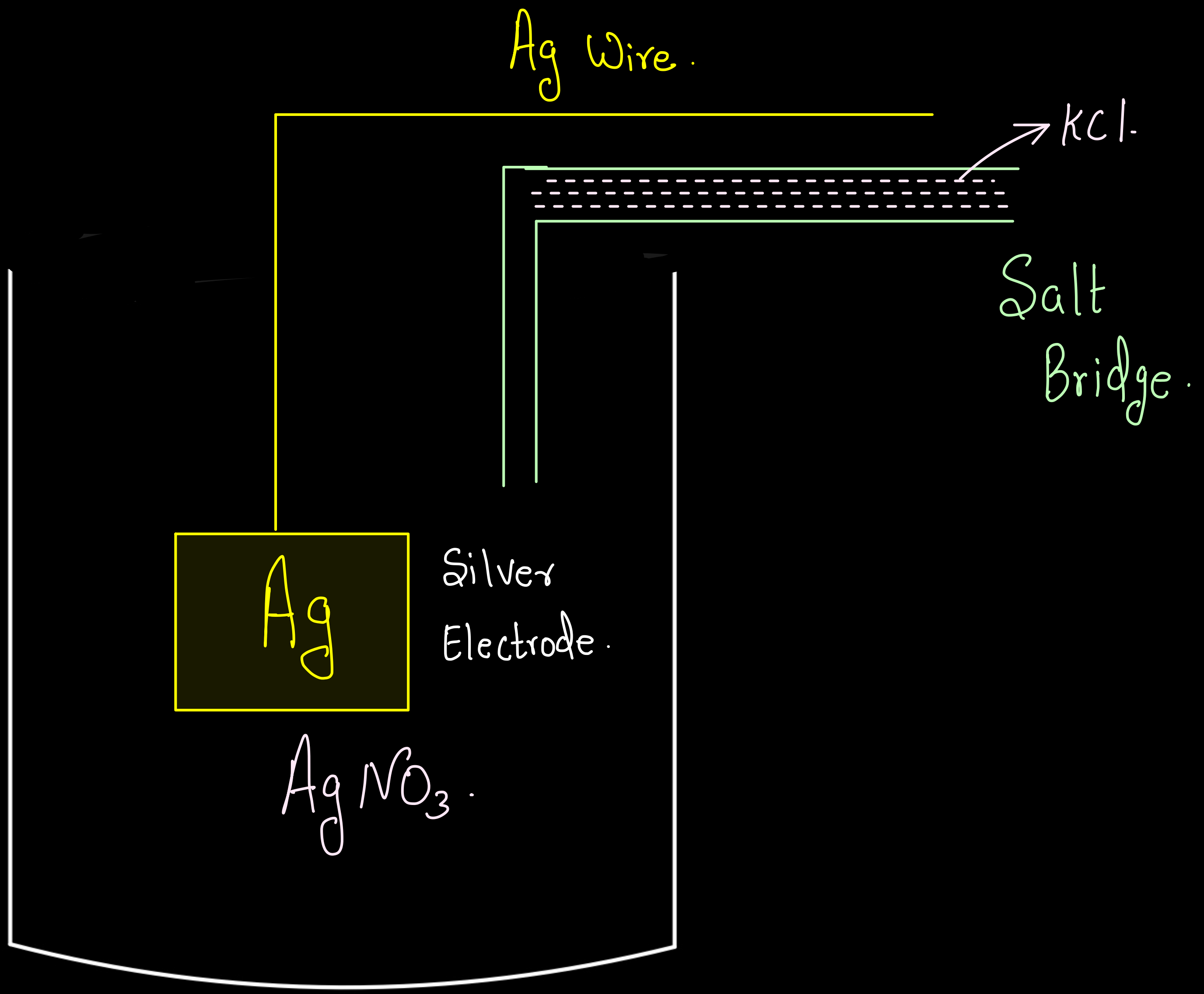
These electrodes are used to detect the potential changes in the solution being analyzed, which are directly related to the concentration of the analyte

Metal Electrodes as Indicator Electrodes:

Metal electrodes, such as platinum or gold, are simple electrodes made from a piece of metal. These metals are chosen for their inertness and high conductivity.
They are used to measure the potential of redox reactions or the activity of specific ions in the solution.

Electrode is made up of the sample element.

Electrode is dipped in solution



Advantages of Metal Electrodes:

High Conductivity:

Metal electrodes are highly conductive, allowing for efficient electron flow between the electrode and the electrolyte or external circuit. This is critical for many electrochemical applications, such as batteries, corrosion studies, and sensors.

Stability:

Many metals, such as platinum, gold, and silver, offer good stability under various conditions (pH, temperature, and chemical environment). This makes them reliable for long-term use in electrochemical measurements.

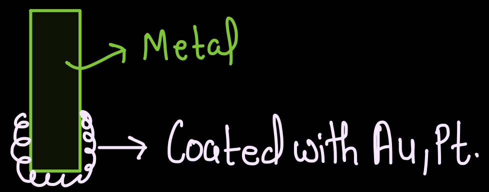
Wide Application Range:

Metal electrodes can be used in a wide range of electrochemical systems, including batteries, fuel cells, corrosion monitoring, and ion-selective electrodes. This versatility makes them valuable in research and industry.

Durability:

Some metal electrodes, like platinum and gold, are chemically inert, meaning they do not easily degrade or corrode under typical working conditions. This durability enhances their performance in harsh environments.

Disadvantages of Metal Electrodes:



Corrosion:

Some metals (like copper or iron) are prone to corrosion, especially in acidic or alkaline environments. This corrosion can degrade the electrode's performance and shorten its lifespan. To mitigate this, certain metals are coated with protective layers (e.g., gold or platinum coatings).

Limited Ion Selectivity:

Metal electrodes generally do not exhibit high ion selectivity. While this can be addressed with ion-selective electrodes (ISEs), many metal electrodes need to be modified or combined with other materials to provide selective ion sensing.

Cost:

High-quality metal electrodes (e.g., platinum or gold) can be expensive, especially for specialized applications. This cost factor may limit their use in certain industries or experiments.

2. Glass Electrode

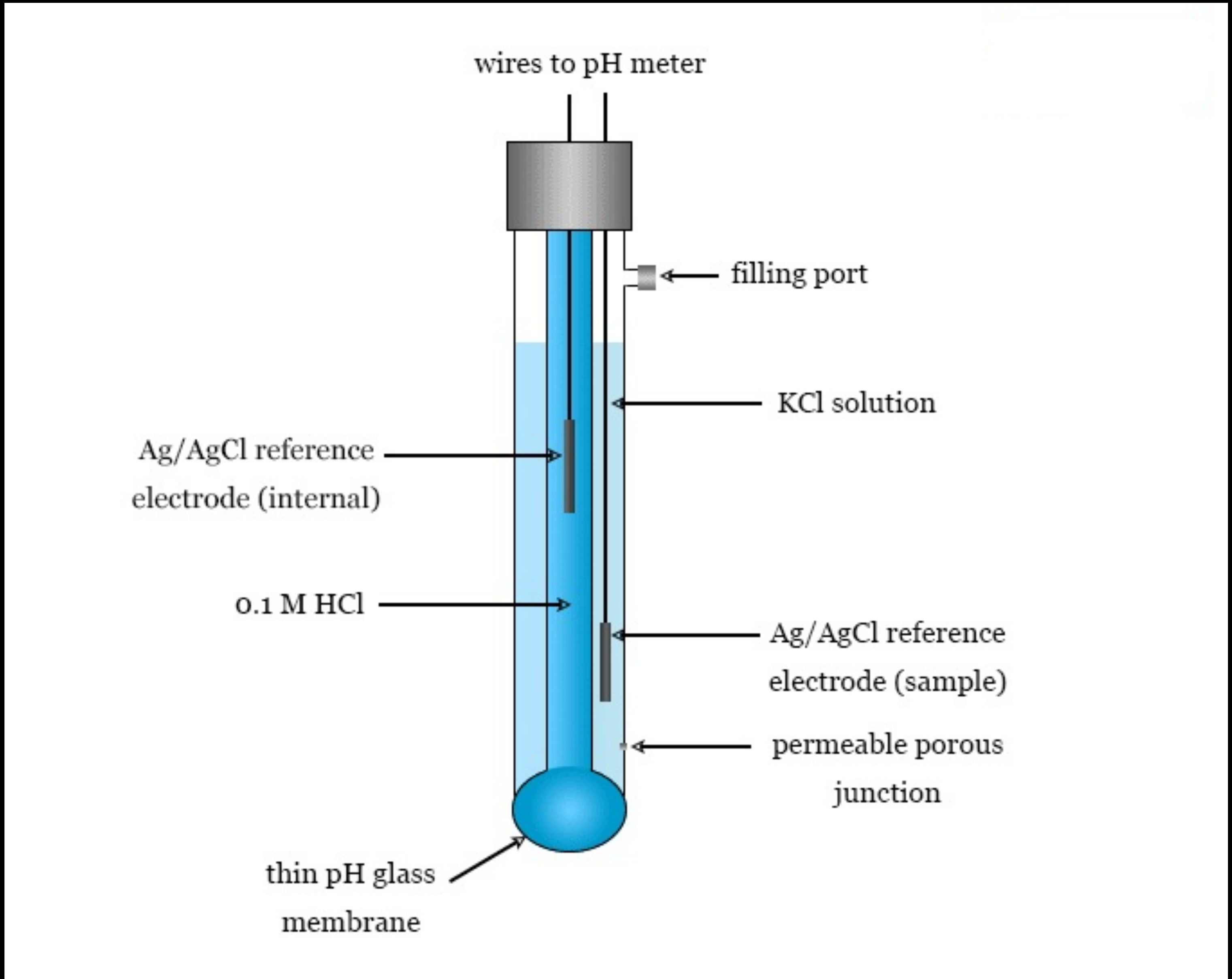
Measure the activity of Specific Ion.

A glass electrode is a type of ion-selective electrode (ISE) used primarily to measure the pH of a solution.

It is a crucial tool in many fields, including chemistry, biology, environmental science, and medicine, due to its ability to provide highly accurate pH measurements.

Glass electrodes work by detecting the hydrogen ion (H^+) concentration in a solution, which is directly related to pH.

Glass Electrode



Internal Reference Solution:
Inside the electrode, there is a reference solution (often potassium chloride, KCl) that is in contact with an internal reference electrode (usually silver/silver chloride, Ag/AgCl). The internal reference provides a stable reference potential.

External Reference Electrode:
The glass electrode is typically used in conjunction with a reference electrode (such as a silver/silver chloride electrode) to form a complete measurement cell. The reference electrode provides a stable, known potential against which the potential of the glass electrode is measured.

Measuring Potential:

The potential difference between the glass electrode and the reference electrode depends on the concentration of hydrogen ions in the solution being measured. This potential is then translated into a pH value based on the Nernst equation.

Advantages of Glass Electrodes:

High Accuracy and Precision:

Glass electrodes are highly accurate and provide precise pH measurements. They are widely used in laboratory and industrial applications where reliable pH data is crucial.

Fast Response Time:

Glass electrodes respond quickly to changes in the hydrogen ion concentration, allowing for real-time monitoring of pH in dynamic systems.

Durability:

They are relatively durable and can be used over a long period with proper maintenance.

Wide Range of Use:

Glass electrodes can measure pH over a broad range, from very acidic to very alkaline solutions (typically from pH 0 to 14).

Low Cost (for General Use):

Sensitive to Hydrogen Ions:

Methods to determine end point of potentiometric titration and applications.

In potentiometric titration, the endpoint is determined by monitoring the changes in the electric potential (voltage) between a reference electrode and a working electrode as the titrant is added to the analyte solution.

Here are the different methods to determine the endpoint in potentiometric titration:

Methods to determine the endpoint

1. Acid-base titration Acids and bases with high solubility are used as standard solutions for neutralization titrations. The titration can be performed either with an acidic or a basic solution, but it is recommended that both acidic and basic standard solutions are available just in case a back-titration is needed to confirm the endpoint. By titrating a solution against a primary standard, one can determine its concentration. By measuring 1.000 mL of the base and the acid concentration in this ratio, we can determine the concentration of the other.

2. Precipitation titration Titrations based on precipitates that form slightly soluble precipitates are called "precipitation titrations". The precipitating titration utilizing silver nitrate establishes the polarity of the precipitates. If it precipitates with (AgNO3) then the process is called argentometric. Titration by precipitation is extremely useful since it allows us to determine the concentration of halogens and some metal ions.

3. Complexometric titration Electron acceptors (electron donors) react with complexions (coordination compounds) to form complex ions. At least one unshared electron pair must be present in the donor species (or ligand) to form a bond. An electrode mixture containing Bi^{3+}, Cd^{2+}, and Ca^{2+} for determining many cations using EDTA and metal electrodes!

4. Oxidation-reduction reaction Titrations performed with redox analytes are based on redox reactions between analytes and titrants. The use of a potentiometer and a redox indicator is commonly used for measuring redox potential. The most common redox titration methods use a reducing agent and starch to determine the redox state of iodine solutions. After being introduced to starch, iodine forms a blue-red complex. It is possible to reduce iodine (I_2) to iodide (I^-) using substances such as thiosulfate ($S_2O_3^{2-}$), and at the end of this process, the blue color will disappear.

Applications of Potentiometry

Potentiometry is a widely used electrochemical technique that measures the potential (voltage) between two electrodes without drawing a current. It has numerous applications in various fields due to its sensitivity, accuracy, and versatility. Here are some key applications of potentiometry:

1. pH Measurement

Application: Potentiometry is commonly used to measure the pH of a solution using a glass electrode (which acts as the indicator electrode) and a reference electrode. The potential difference between the two electrodes is related to the hydrogen ion concentration (pH) of the solution.

Example: pH meters in laboratories, environmental monitoring, and industrial processes.

2. Ion Concentration Determination

Application: Potentiometric titration can be used to determine the concentration of specific ions in a solution. Specialized ion-selective electrodes (ISEs) are designed to measure the concentration of individual ions.

Example: Determining the concentration of ions like Na^+, K^+, Ca^{2+}, Cl^-, and others in biological fluids, water, or industrial samples.

3. Redox Titration

Application: Potentiometry is used in redox titrations to determine the endpoint of titrations between oxidizing and reducing agents. The change in the potential between the working and reference electrodes is monitored to identify the equivalence point.
Example: Titrating a reducing agent (e.g., ascorbic acid) with an oxidizing agent (e.g., potassium permanganate) and using the potential change to determine the endpoint.

4. Water Quality Monitoring

Application: Potentiometric measurements are widely used for monitoring water quality, including measuring pH, ion concentrations (e.g., chloride, nitrate), and redox potential (ORP).
Example: Measuring the concentration of ions such as chloride (Cl^-), nitrate (NO_3^-), or sulfate (SO_4^{2-}) in water bodies or wastewater treatment plants to assess pollution levels and water treatment efficiency.

5. Pharmaceutical and Medical Applications

Application: Potentiometry is used in pharmaceutical analysis for quality control of drugs and formulations. Ion-selective electrodes are employed to measure the concentration of specific ions in biological fluids.

Example: Determining the concentration of potassium ions (K^+) or sodium ions (Na^+) in blood samples, or the analysis of drugs like digoxin (which affects the heart) in blood serum.

6. Food and Beverage Industry

Application: Potentiometry is used to monitor various parameters in food and beverage production, such as pH, acidity, and ion concentrations, which are critical to product quality and safety.

Example: Measuring the pH of beverages (e.g., soft drinks, beer) and foods (e.g., dairy products, sauces) to ensure the desired taste, preservation, and safety.

7. Environmental Monitoring

Application: Potentiometry is used in environmental chemistry to measure parameters like pH, redox potential (ORP), and ion concentrations in soil, air, and water samples.

Example: Monitoring soil pH and ion concentrations to assess agricultural suitability, as well as measuring pollutants like heavy metals in water and air.

8. Corrosion Monitoring

Application: Potentiometric measurements are used to monitor the corrosion potential (also known as the open circuit potential) of metals and alloys in various environments. Corrosion is influenced by the redox potential, and potentiometry can help assess corrosion rates.

Example: Monitoring corrosion in pipes, tanks, or marine structures, and preventing damage by evaluating the electrochemical conditions of the material.