

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:

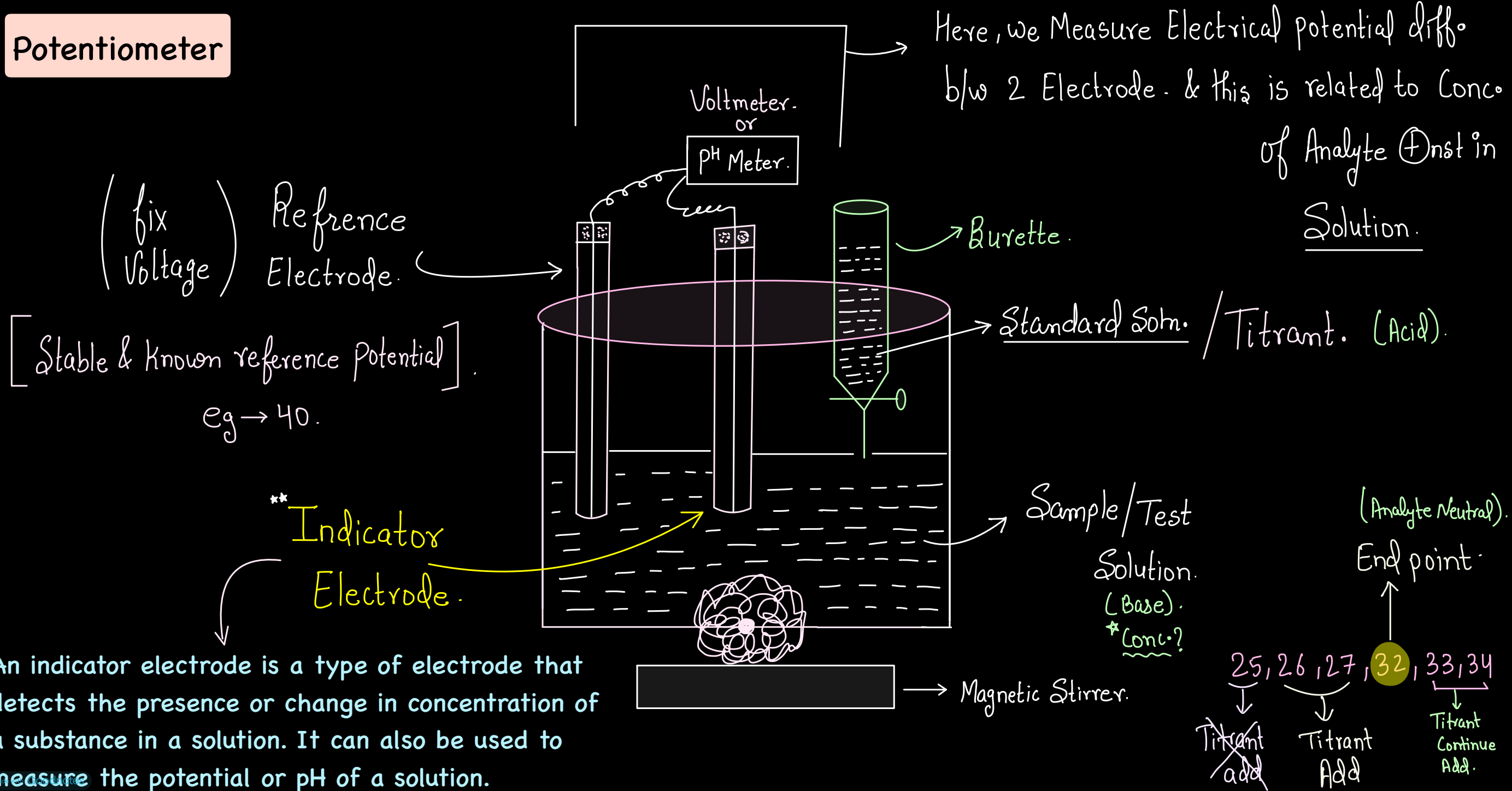
Potentiometry is based on the principle that the potential difference between two electrodes in an electrochemical cell is related to the concentration of the analyte (the substance being measured).

Measurement:

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

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Potentiometer



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.

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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

Electrochemical Cell / Dielectric or Galvanic cell

↪ Consist of 2 Half Cell.

Generate Voltage
or
E.M.F

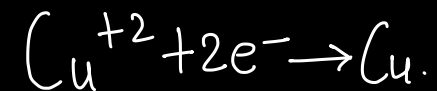
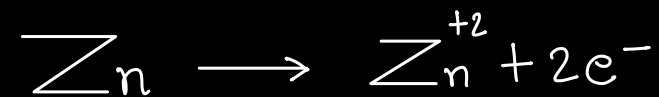
An electrochemical (or galvanic) cell converts chemical energy into electrical energy through spontaneous redox reactions.

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:

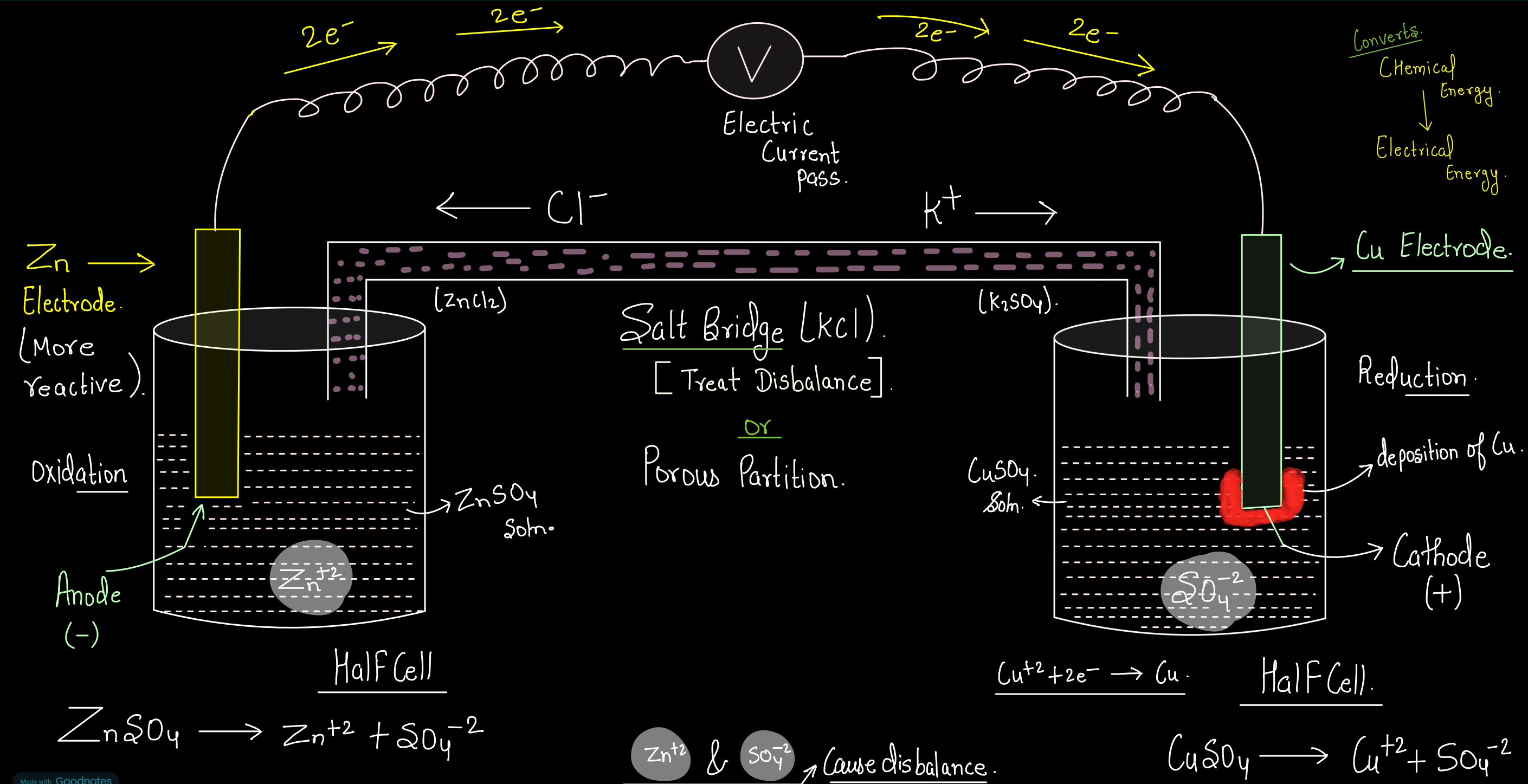
The reactions occurring in a galvanic cell involve the transfer of electrons from one species (oxidation at the anode) to another species (reduction at the cathode).

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



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

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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.

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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.

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2. Glass Electrode

Measure the activity of Specific Ion.

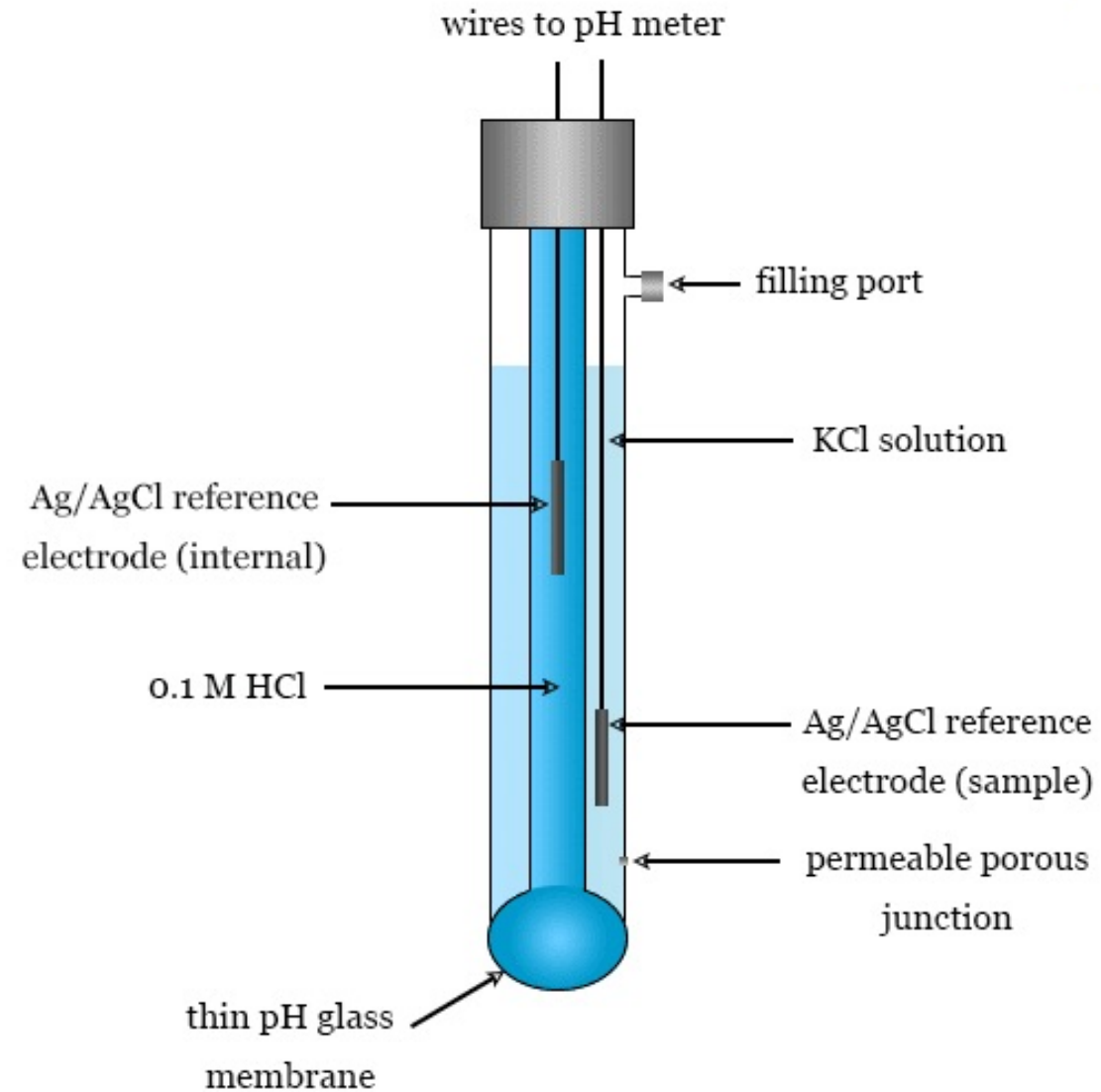
A glass electrode is a type of ion-selective electrode (ISE) used primarily to measure the pH of a solution.

[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.]

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Glass Electrode



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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.

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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.

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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:

Applications of Potentiometry

1. pH Measurement

Determining acidity or alkalinity of solutions (pH) using glass electrode.

Controlled pH in pharmaceuticals, food, biotechnology, and water treatment.

2. Acid–Base Titrations

Determining acid or base concentration by following potential change during the addition of a standard solution.

Examples: Titration of weak acid with strong base or vice versa.

3. Redox Titrations (Redox Potentiometric Method)

Determining the concentration of an oxidizing or reducing agent.

Example: Fe^{2+} by dichromate, I^- , or SO_2 .

4. Precipitation Titrations

Determining chloride (Cl^-) or halide ions with silver nitrate (AgNO_3) by following potential change at a silver electrode.

Example: Volhard or Fajans methods.

5. Complexometric Titrations

Determining metal ions (Ca^{2+} , Mg^{2+} , Pb^{2+} , etc) using complex formation.

Example: EDTA complexometric titrations with indicator electrode.

6. Indicator Electrode Applications

Fluoride ion determination with Fluoride ISE (ion-selective electrode).

Calcium, sodium, or potassium ion determination with respective ISEs.

7. Pharmaceutical Applications

Determining drug purity or content (active ingredients) by acid-base or redox potentiometric methods.

Controlled release formulation pH and ion content.

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8. Water Quality Control

Determining pH, chloride, or heavy metal ions in water.
Analysis for water treatment and pollution control.

9. Clinical and Biological Applications

Determining electrolyte levels in blood or urine.
pH control in biotechnology and enzyme assays.