

SNS COLLEGE OF TECHNOLOGY

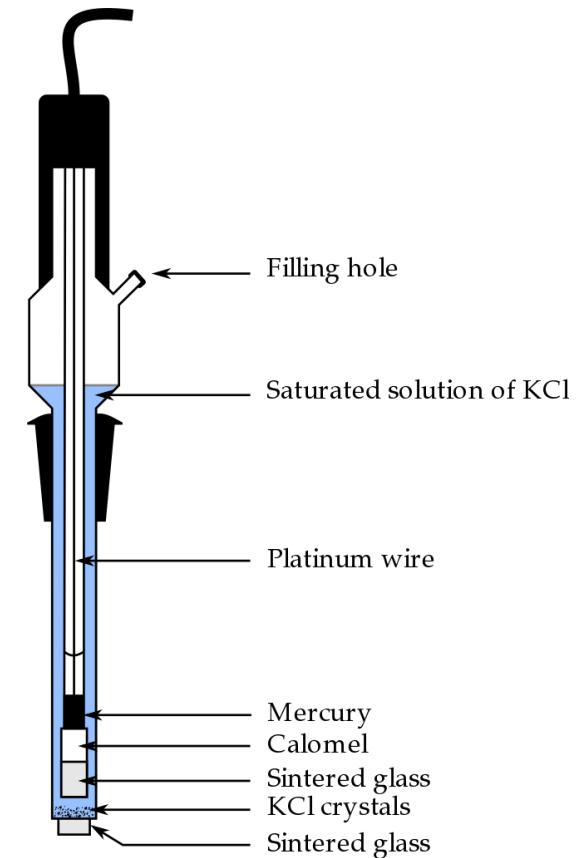
AN AUTONOMOUS INSTITUTION

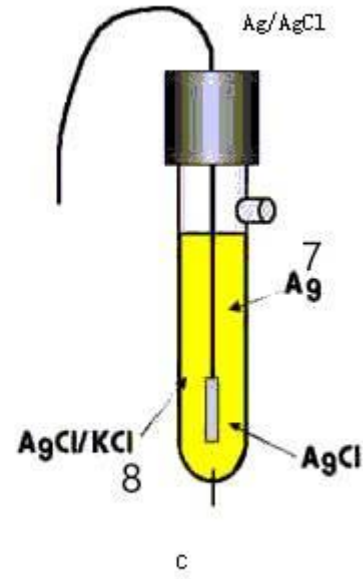
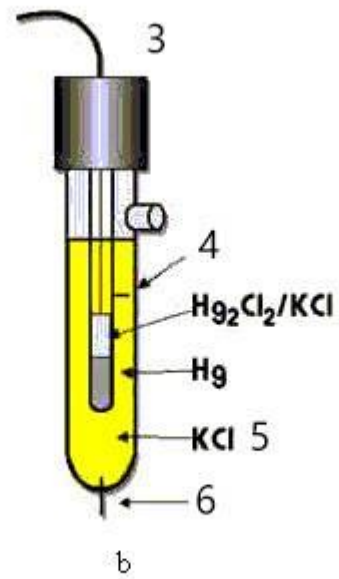
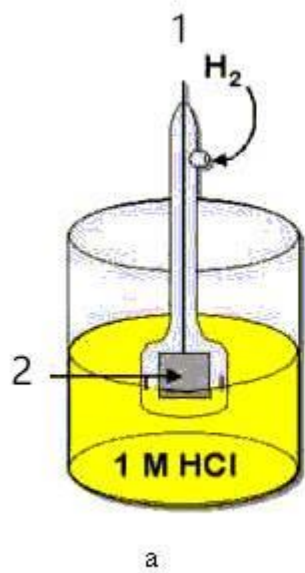
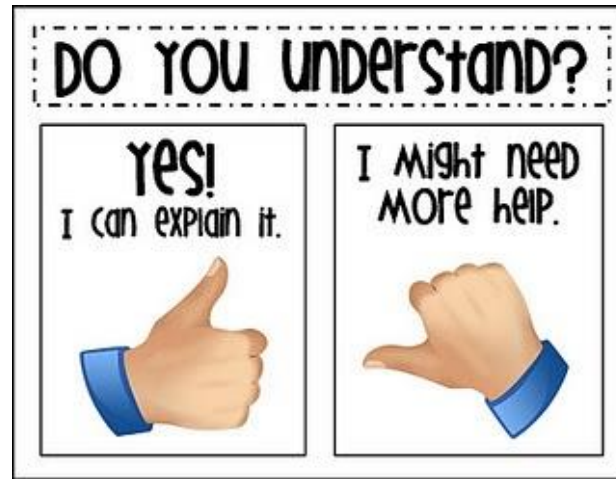
Coimbatore – 641035

23CHT101-ENGINEERING CHEMISTRY

UNIT 1 - ELECTROCHEMISTRY

1.4 Standard Hydrogen Electrode

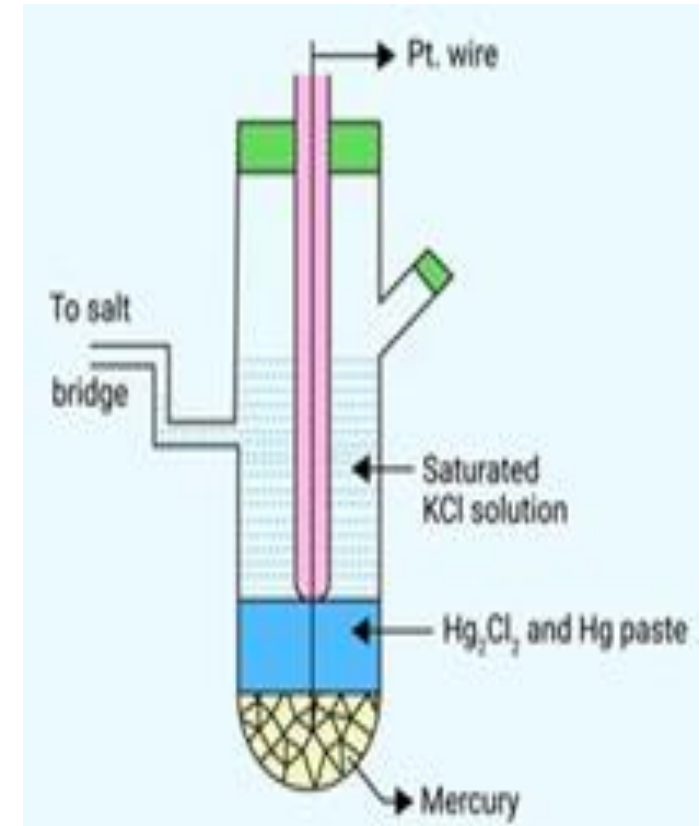




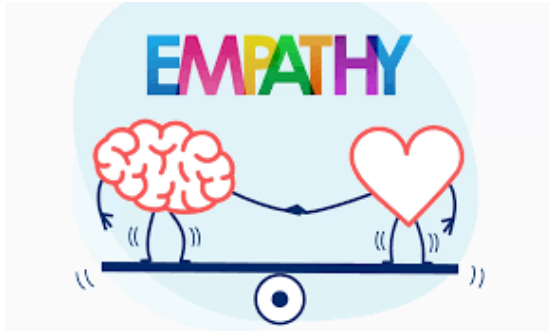
Concentration of KCl	Oxidation potential at 298 K
0.1 M or 0.1N	-0.3338 V
1 M or 1N	-0.2800 V
Saturated	-0.2415 V

CALOMEL ELECTRODE

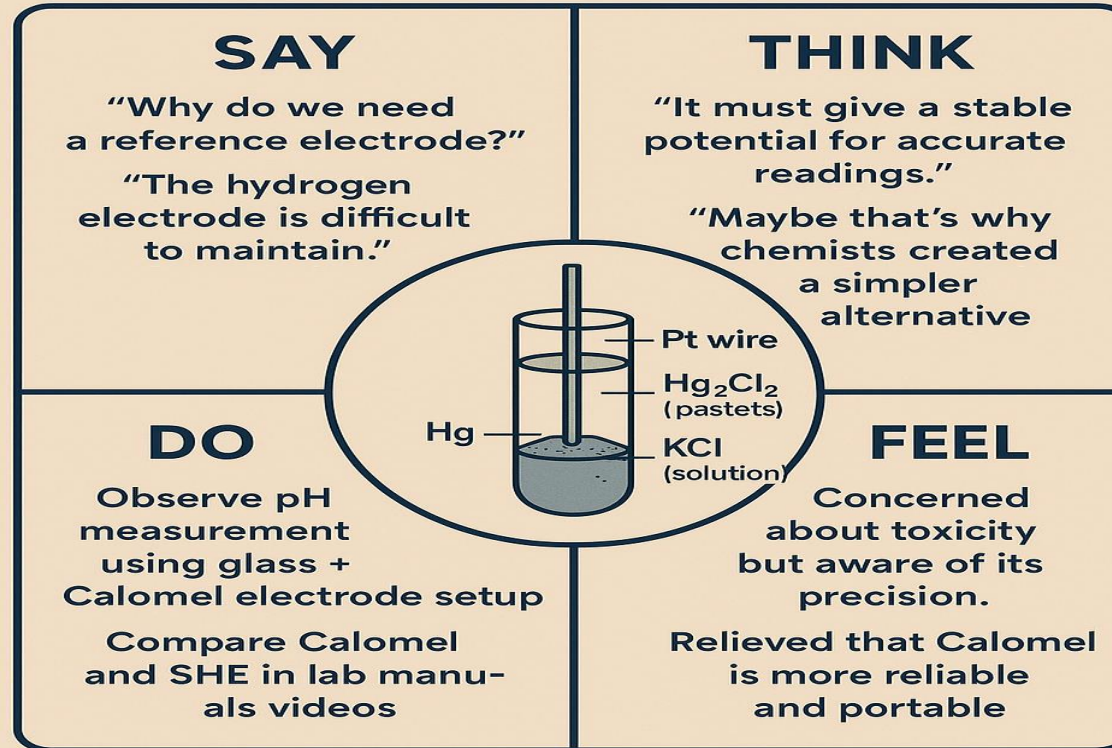
Parameter	Standard Condition
A glass tube containing	Hg at the bottom
A paste of mercurous chloride-calomel, placed over the mercury	Hg_2Cl_2
The tube is filled with a KCl) solution of known concentration	Usually saturated, 1 N, or 0.1 N
Electrode potential	Vary with concentration



CALOMEL ELECTRODE - Why?

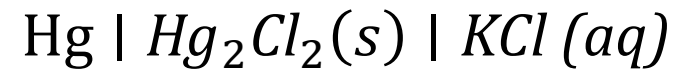


EMPATHY FOR CALOMEL ELECTRODE

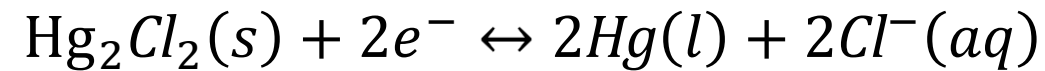




Symbolic representation:



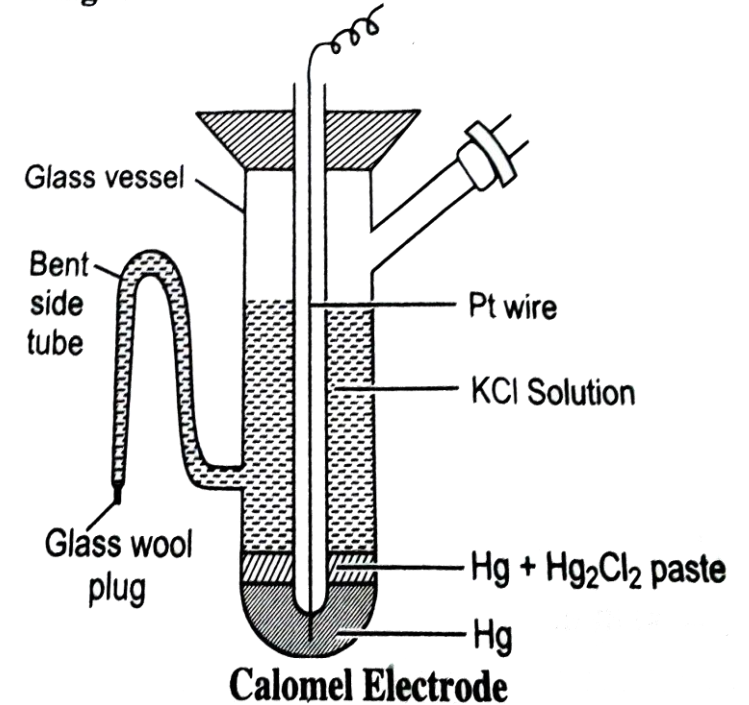
Half-cell reaction:

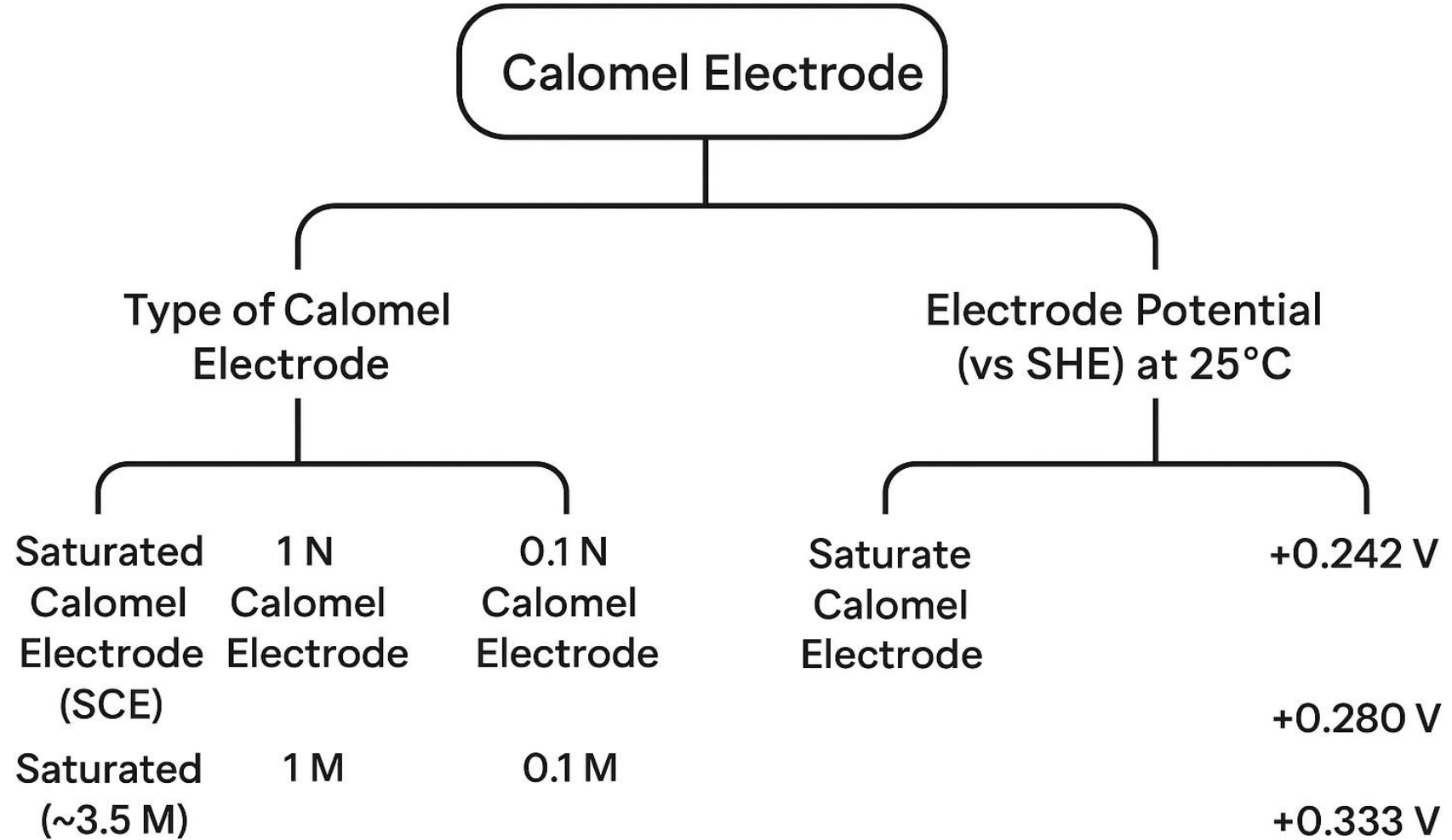




A Calomel Electrode is a secondary reference electrode consisting of mercury (Hg) in contact with a paste of mercurous chloride (Hg_2Cl_2 , calomel) and a solution of potassium chloride (KCl) of known concentration.

Diagram of calomel electrode





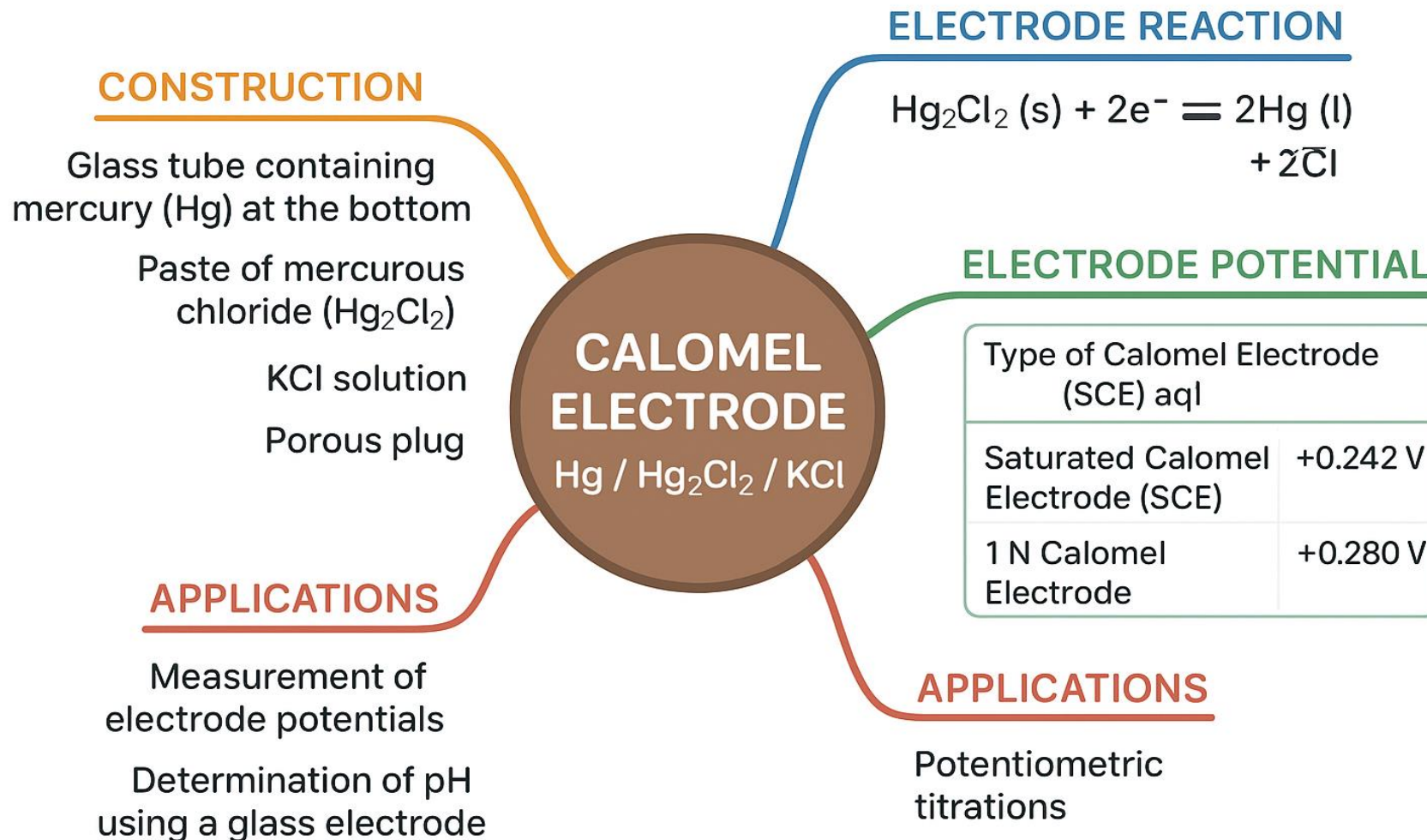


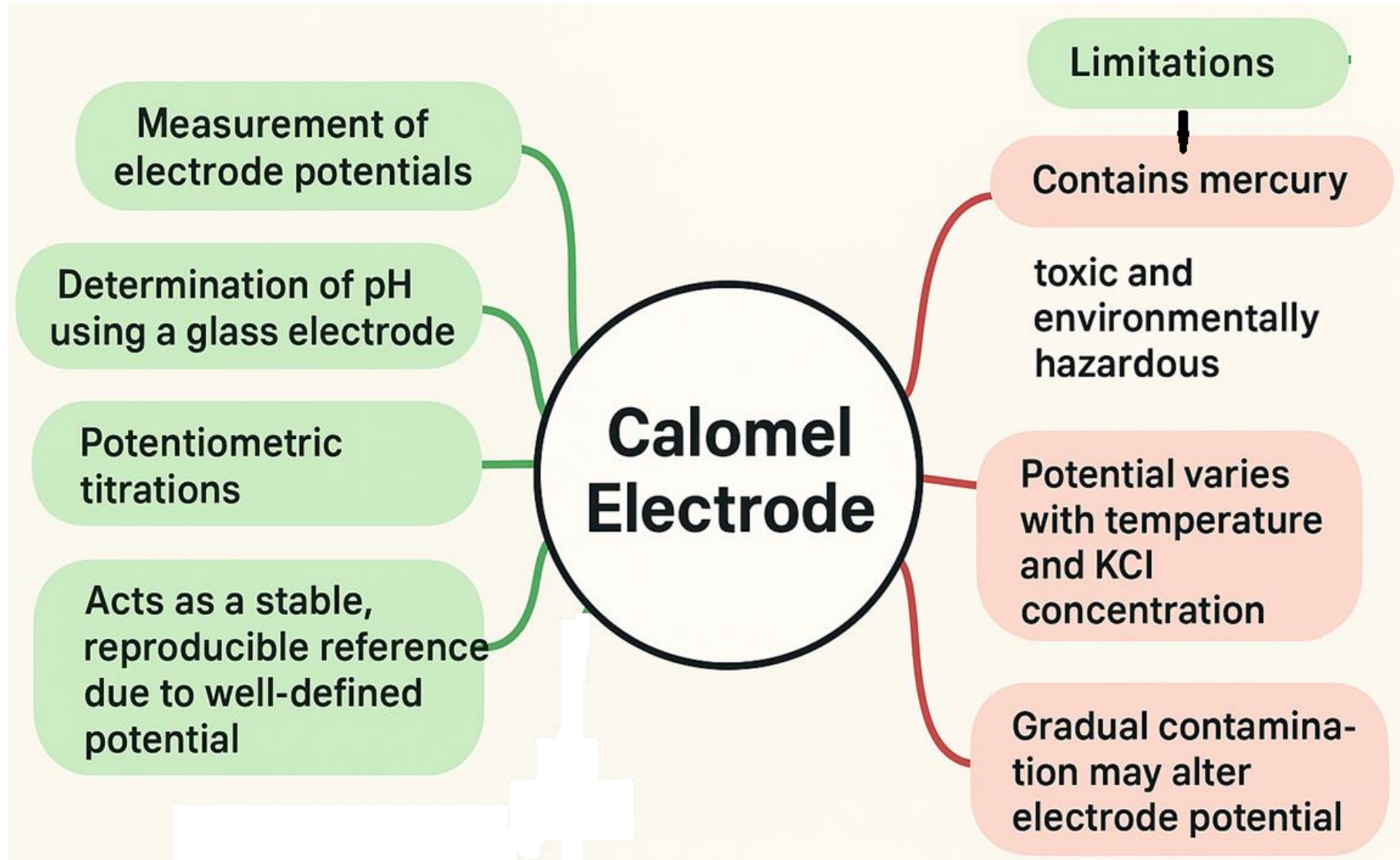
Working Principle

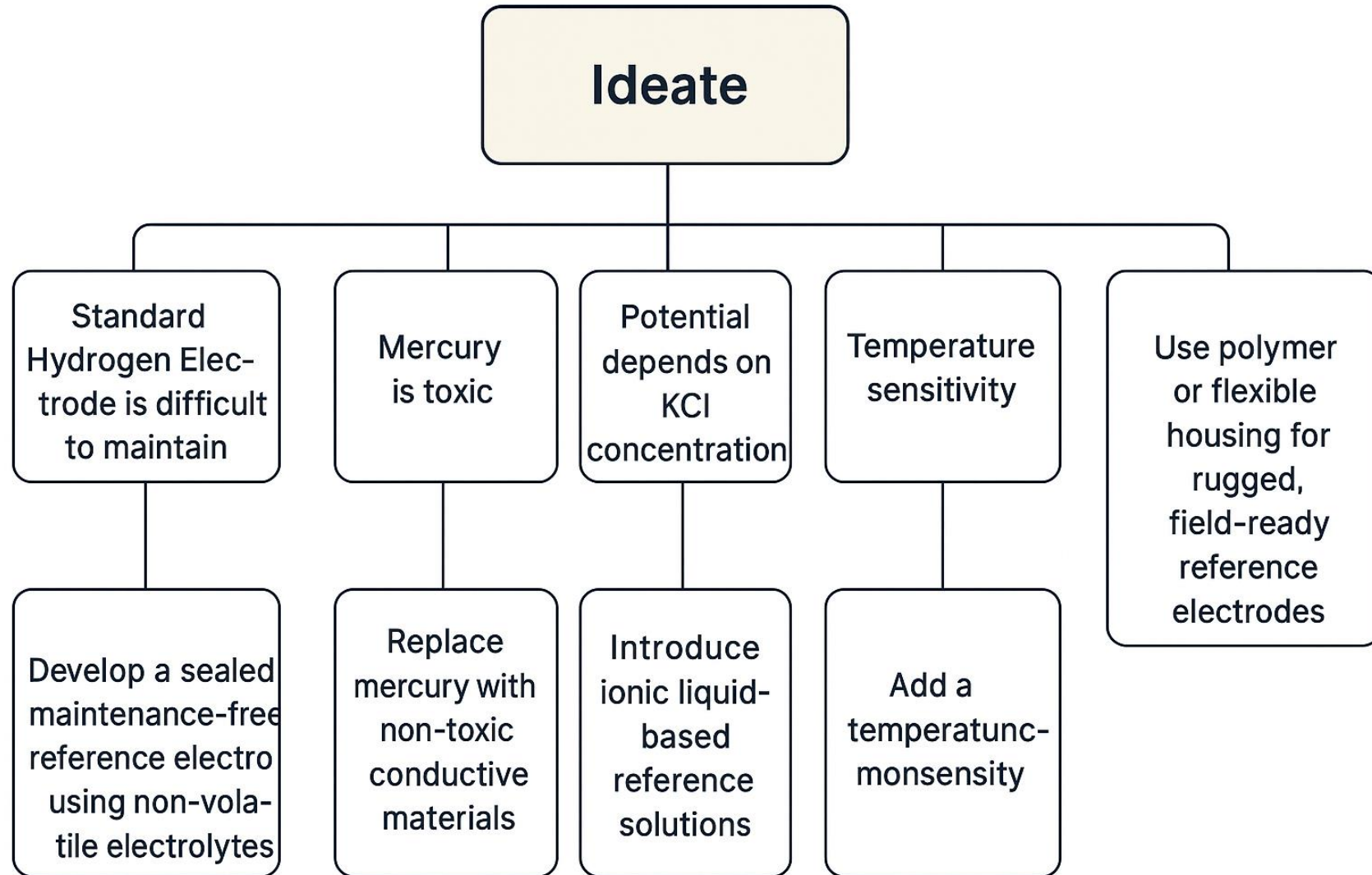
The electrode potential is established by the redox equilibrium between mercury and mercurous chloride in the presence of chloride ions.

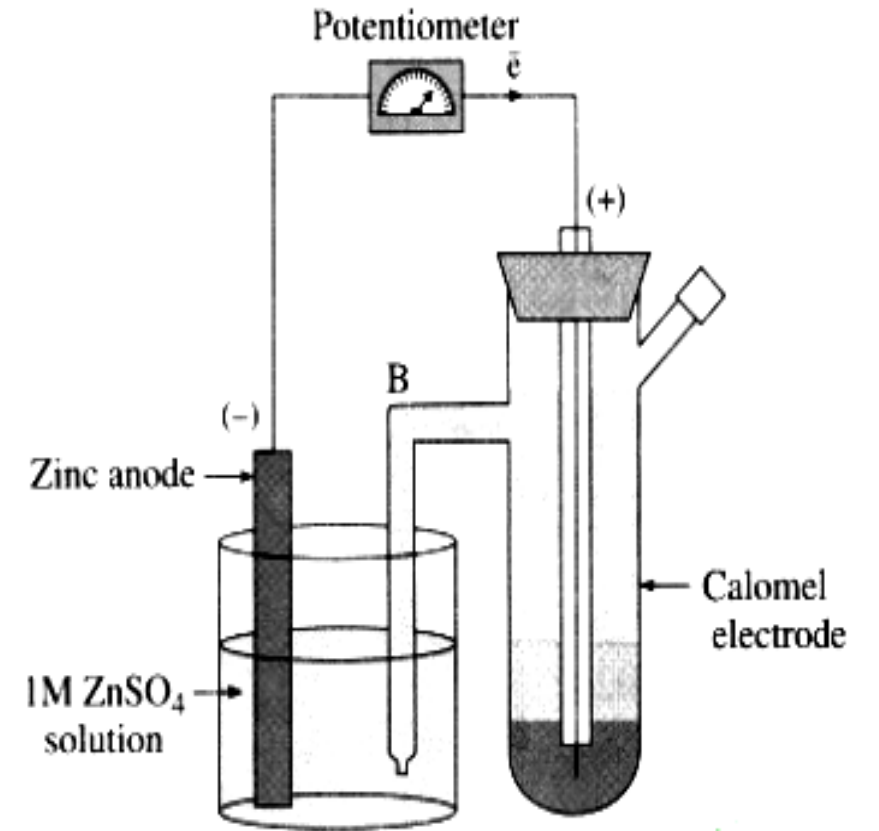
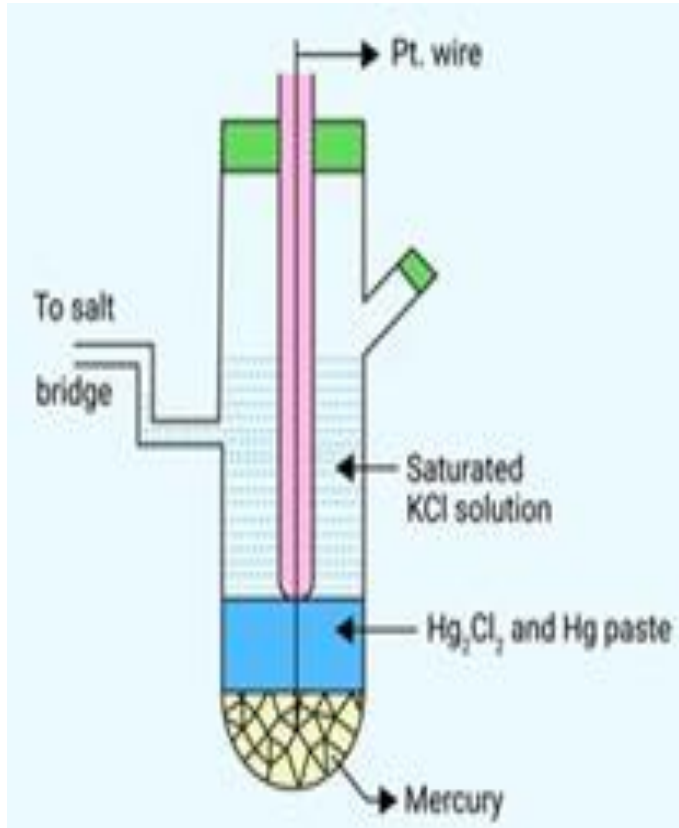
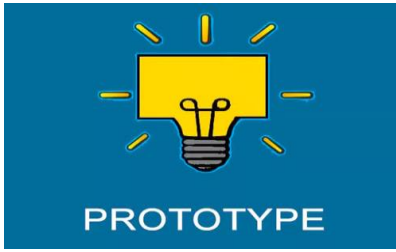
When connected to another electrode, the EMF of the cell can be measured and the potential of the other electrode can be calculated using the Nernst equation

$$\begin{aligned} E_{\text{cell}} &= E_{\frac{1}{2} \text{ cathode}} - E_{\frac{1}{2} \text{ anode}} \\ &= E_{\text{Hg}_2\text{Cl}_2/\text{Hg}_2^{2+}, \text{Cl}^-}^0 - \frac{RT}{2F} \ln \frac{1}{[\text{Hg}_2^{2+}] \cdot [\text{Cl}^-]^2} \\ &= E_{\text{Hg}_2\text{Cl}_2/\text{Hg}_2^{2+}, \text{Cl}^-}^0 - \frac{RT}{2F} \ln \frac{1}{K_{sp}} \quad \text{in which} \quad E_{\text{Hg}_2\text{Cl}_2/\text{Hg}_2^{2+}, \text{Cl}^-}^0 = +0.53 \text{ V} \end{aligned}$$









References

<https://www.aakash.ac.in/important-concepts/chemistry/calomel-electrode>

[https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Instrumental_Analysis_\(LibreTexts\)/23%3A_A_Potentiometry/23.01%3A_Reference_Electrodes](https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Instrumental_Analysis_(LibreTexts)/23%3A_A_Potentiometry/23.01%3A_Reference_Electrodes)