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CONSTRUCTION AND WORKING OF REFERENCE ELECTRODES

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REFERENCE ELECTRODE

Reference electrode having the fixed potential and the value does not change.

- 1. Standard Hydrogen electrode**
- 2. Calomel electrode**
- 3. Silver-Silver Chloride electrode**



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1. STANDARD HYDROGEN ELECTRODE

The standard H₂ electrode potential is defined as the potential that is developed between the H₂ gas adsorbed on the Pt metal and H⁺ of the solution when the H₂ gas at a pressure of 760 mm of Hg is in equilibrium with H⁺ of unit concentration

- **Working: Pt foil: coated with black Pt**
- **1 molar HCl solution**
- **Pure H₂ gas bubbled continuously at 1 atm.**
- **Pt act as conductor, inert and facilitate in attaining equilibrium**
- **Electrode Potential is 0.00 volts**
- **H₂ (gas) ↔ 2H⁺ (ions) + 2e⁻ (electrons) SHE**



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LIMITATIONS :

- 1. Can't be used in solution containing strong oxidizing agents.**
- 2. Difficult and expensive to maintain.**
- 3. Excess of H₂ bubbling out carries little HCl with it and hence the H⁺ concentration decreases. In such a system, it is difficult to maintain the concentration of HCl at 1M.**



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2. CALOMEL ELECTRODE

- **Most commonly used electrode in potentiometry**
- **Tube 5-15cm long, 0.5-1 cm in diameter.**
- **Slurry of mercury & mercurous chloride with saturated soln of KCl**
- **Connected by a small opening with saturated solution of KCl.**
- **Pt metal is placed inside the slurry**
- **Ceramic fiber act as salt bridge**
- **$2\text{Hg} + 2\text{Cl}^- \rightarrow \text{Hg}_2\text{Cl}_2 + 2\text{e}^-$**
- **$E = 0.2444$ at 25°**



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ADVANTAGES:

- **Concentration of chloride ions don't change even some of the solvent get evaporated.**
- **Generates small junction potential so more accurate**

LIMITATIONS :

- **Mostly saturated solution of KCl is used and that is temperature dependent.**



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3. SILVER-SILVER CHLORIDE ELECTRODE

• It consist of silver wire coated with AgCl

- Coating may be electroplating or Physical.
- This coated wire is placed in 1M solution of AgCl.
- $\text{Ag} + \text{Cl}^- \leftrightarrow \text{AgCl} + 1\text{e}^-$
- $E = 0.199\text{V}$

Advantages

Easy handling, and cost effective

Limitation:

sometimes show reactivity



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THANK YOU