ELECTROCHEMISTRY

Is the branch of physical chemistry that deals with the study of the relation between the chemical changes & electricity.

Electrochemical cell

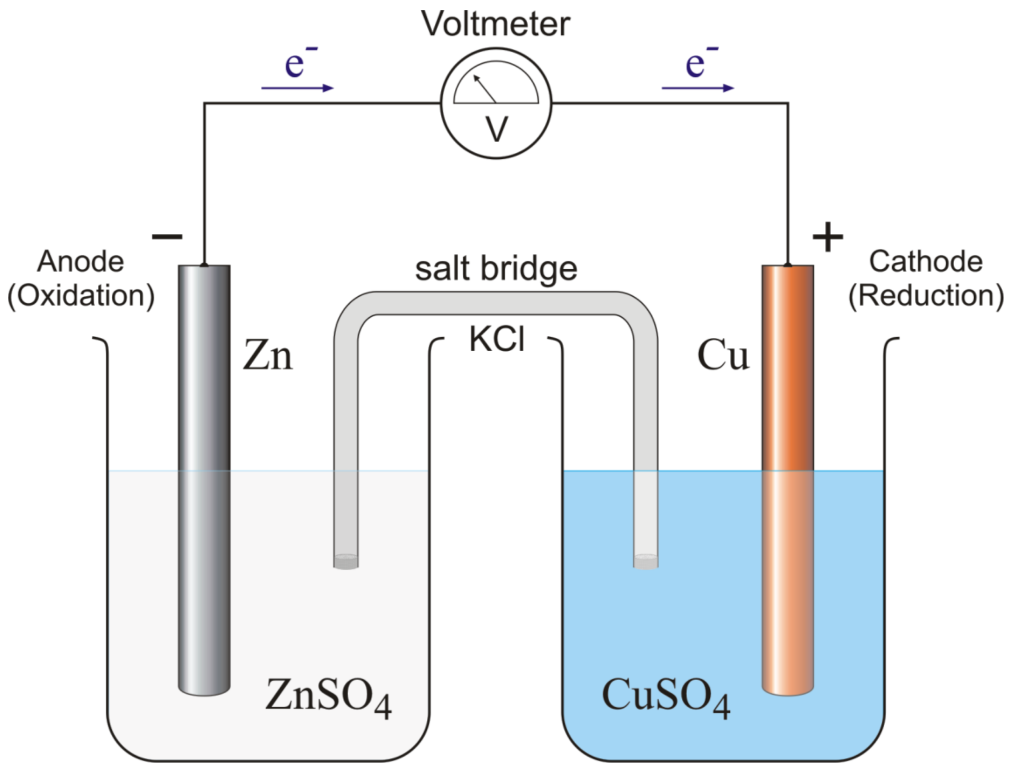
- Is a device used to study the chemical reactions electrically. It consist of two electrodes, each in contact with a solution of its own ions & transforms the free energy change of the redox reaction at the electrodes into electrical energy. In a redox reaction, the energy released in a reaction due to the movement of charged particles gives rise to a potential difference.

- The maximum potential difference produced is called electromotive force (EMF) in volts.

Types of electrochemical cell

- 1) Voltaic cell (Galvanic cell)
- Converts chemical energy produced due to spontaneous redox reaction into electrical energy.
- 2) Electrolytic cell
- Converts electrical energy supplied from an external source into chemical energy.
- (write differences between voltaic & electrolytic cell)

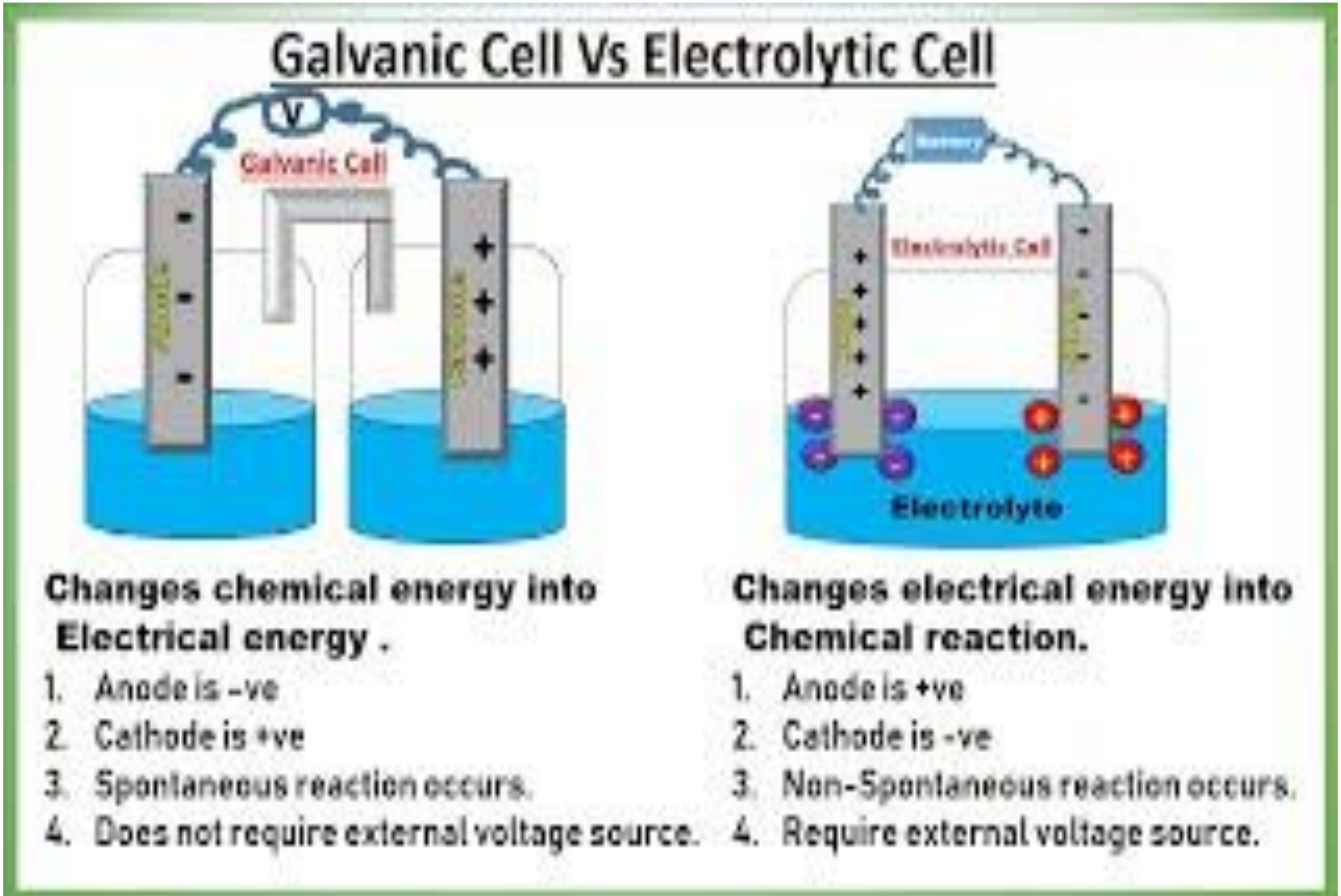
Galvanic cell



$Zn(s) + 2e^- \longrightarrow Zn^{2+}$ $\quad$ $Cu^{2+} + 2e^- \longrightarrow Cu(s)$

$$Zn(s)\,|\,ZnSO_4(aq)\,||\,CuSO_4(aq)\,|\,Cu(s)$$

Galvanic & Electrolytic cell



- 3) Concentration cell
- Is also an electrochemical device that generates electrical energy when two electrodes of the same metal are in contact with solution of its ions at different concentrations.
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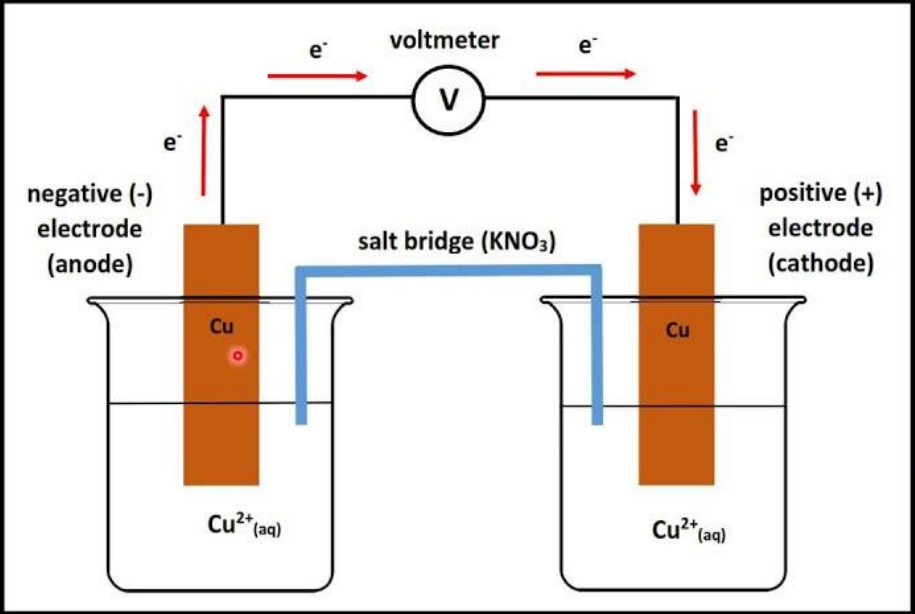
Concentration cells

A concentration cell has the same electrodes in each half-cell but the concentration of the electrolyte in each half-cell is different.

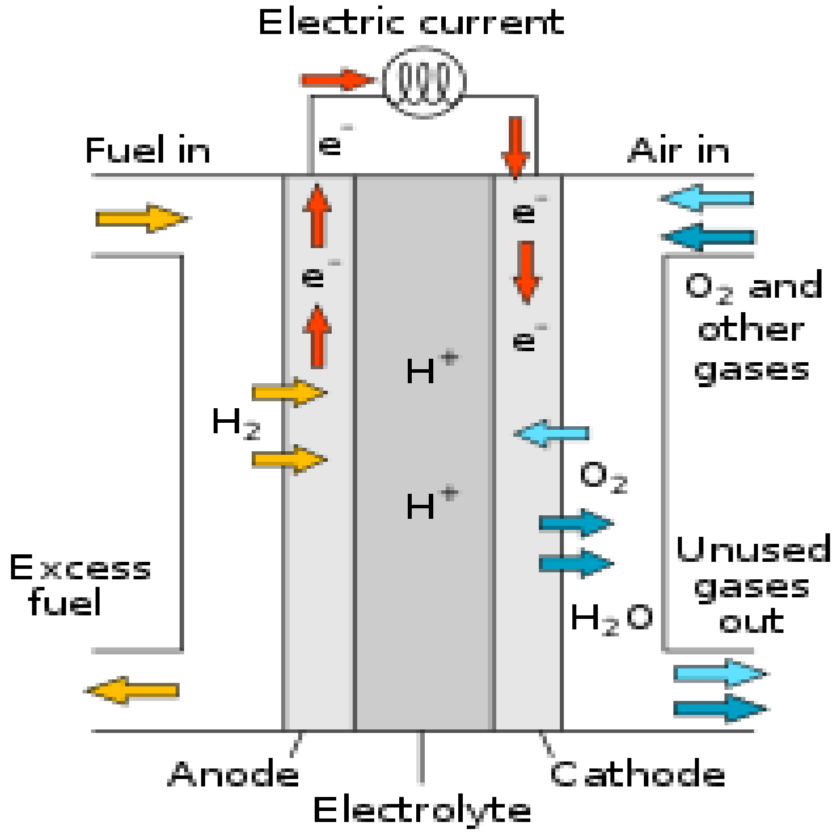
$[Cu^{2+}]$
0.0100 mol dm^{-3}



$[Cu^{2+}]$
0.100 mol dm^{-3}

- 4) **Fuel Cell**
- Is also electrochemical device , which operates with continuous replenishment of the fuel at the electrode & no charging is required. In a fuel cell, the free energy change of electrode redox reactions is converted into electric energy.

Fuel cell



Electric current
Fuel in
Air in
e⁻
H⁺
H₂
O₂ and other gases
O₂
H₂O
Unused gases out
Excess fuel
Anode
Electrolyte
Cathode

- Electrode Potential
- It is defined as the potential that exists between the metal or the gas & its ions in aqueous solution, at their equilibrium when they are in contact with each other.
- The electrode potential of a metal is thus a measure of its tendency to loose or gain electrons when in contact with a solution of its own salt.

Standard Electrode Potential (E^o)

- It is defined as the potential that exists between the metal or the gas & its aqueous solution of unit concentration at 298^oK when the sum of all partial pressures of the gaseous reactants & products , if any is equal to 1 atm pressure.

Electrochemical Series

- The elements arranged in the increasing order of their standard electrode potential constitute a series called electrochemical series.

Element	Electrode Reaction (Reduction)	Standard Electrode Reduction potential E^0, volt
Li	$Li^+ + e^- = Li$	−3.05
K	$K^+ + e^- = K$	−2.925
Ba	$Ba^{++} + 2e = Ba$	−2.90
Sr	$Sr^{++} + 2e = Sr$	−2.89
Ca	$Ca^{2+} + 2e^- = Ca$	−2.87
Na	$Na^+ + e^- = Na$	−2.714
Mg	$Mg^{2+} + 2e^- = Mg$	−2.37
Al	$Al^{3+} + 3e^- = Al$	−1.66
Mn	$Mn^{++} + 2e = Mn$	−1.18
Zn	$Zn^{2+} + 2e^- = Zn$	−0.7628
Cr	$Cr^{3+} + 3e^- = Cr$	−0.74
Fe	$Fe^{2+} + 2e^- = Fe$	−0.44
Cd	$Cd^{2+} + 2e^- = Cd$	−0.403
Co	$Co^{++} + 2e = Co$	−0.27
Ni	$Ni^{2+} + 2e^- = Ni$	−0.25
Sn	$Sn^{2+} + 2e^- = Sn$	−0.14
Pb	$Pb^{++} + 2e = Pb$	−0.12
H_2	**$2H^+ + 2e^- = H_2$**	**0.00**
Cu	$Cu^{2+} + 2e^- = Cu$	+0.337
I_2	$I_2 + 2e^- = 2I^-$	+0.535
Hg	$Hg^{2+} + 2e^- = Hg$	+0.885
Ag	$Ag^+ + e^- = Ag$	+0.799
Br_2	$Br_2 + 2e^- = 2Br^-$	+1.08
Pt	$Pt^{++} + 2e = Pt$	+1.20
Cl_2	$Cl_2 + 2e^- = 2Cl^-$	+1.36
Au	$Au^{3+} + 3e^- = Au$	+1.50
F_2	$F_2 + 2e^- = 2F^-$	+2.87

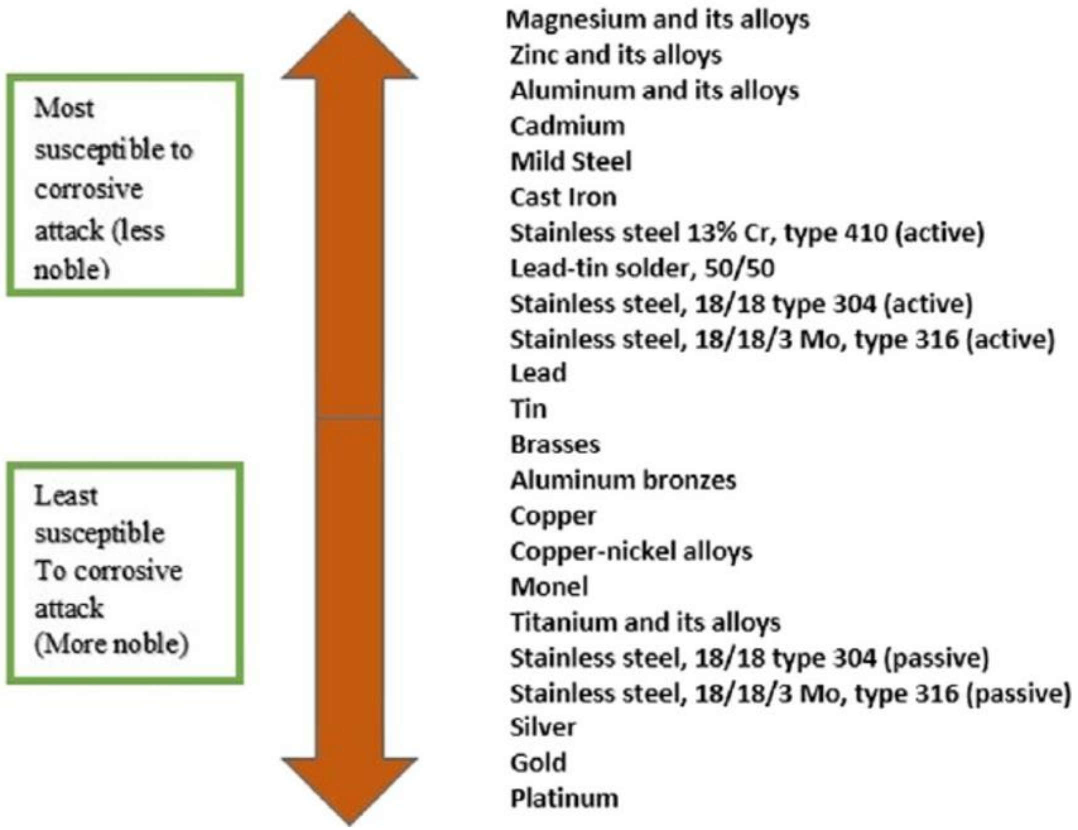
Galvanic series

- Metals & their alloys are arranged in decreasing order of their corrosion tendencies.
- In this, their elctrode potential is measured by immersing them in sea water / salt water.

- (Write difference between electrochemical & Galvanic series)

Galvanic Series

Corrosion Susceptibility of metals



Difference between electrochemical & galvanic series

Electrochemical series	Galvanic series
The arrangement of metals and non-metals in increasing order their standard reduction potential is known as electrochemical series	The arrangement of metals and alloys in decreasing order of their corroding tendency in an unpolluted sea water is known as galvanic series.
It contains metals and non-metals	It contains metals and alloys.
It is an ideal series	It is a practical series
ECS is based upon the electrode potential which is determined by using Nernst equation	This series is based on actual corrosion rate
Position of metals is fixed in ECS	Galvanic Position of a given metal in series may change
It gives no idea about the position of alloys	It gives clear idea about the position of alloys
It gives information about the displacement tendencies	It gives information about the relative corrosion tendencies

NERNST EQUATION

$$E_{redn.} = E^{\circ}_{redn.} - \frac{RT}{nF} \ln \frac{[\text{Reduced species}]}{[\text{Oxidised species}]}$$

($E_{redn.}$ or $E^{\circ}_{redn.}$ will be expressed as E or E°).

For a general reaction with respect to standard hydrogen electrode.

$$M^{n+} + ne^{-} \longrightarrow M$$

Nernst equation will be as follows :

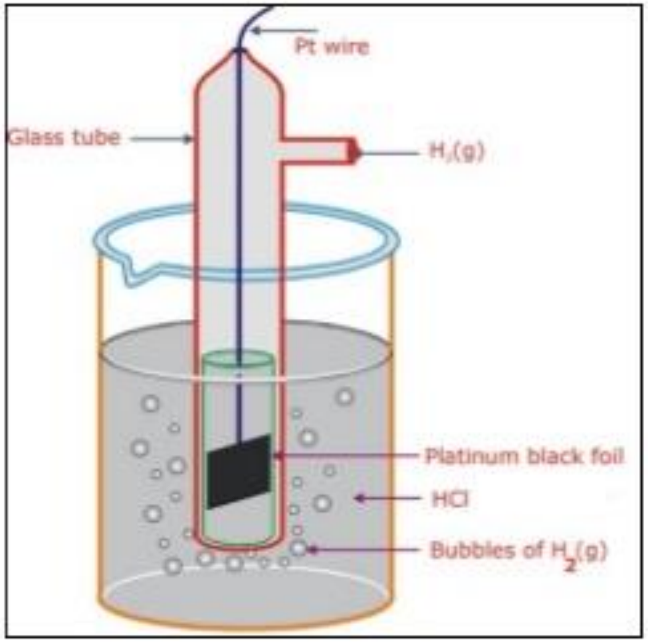
$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$ (For a solid metal M concentration is unity.)

$$E = E^{\circ} - \frac{RT}{nF} \ln [M^{n+}]$$

or $$E = E^{\circ} + \frac{2 \cdot 303RT}{nF} \log_{10} [M^{n+}] \qquad ...(1)$$

Standard hydrogen electrode(SHE)

It consists of a platinum wire in a inverted glass tube. Hydrogen gas is passed through the tube at 1 atm. A platinum foil is attached at the end of the wire. The electrode is immersed in 1M H^+ ion solution at 25°C. The electrode potential of SHE is zero at all temperatures.



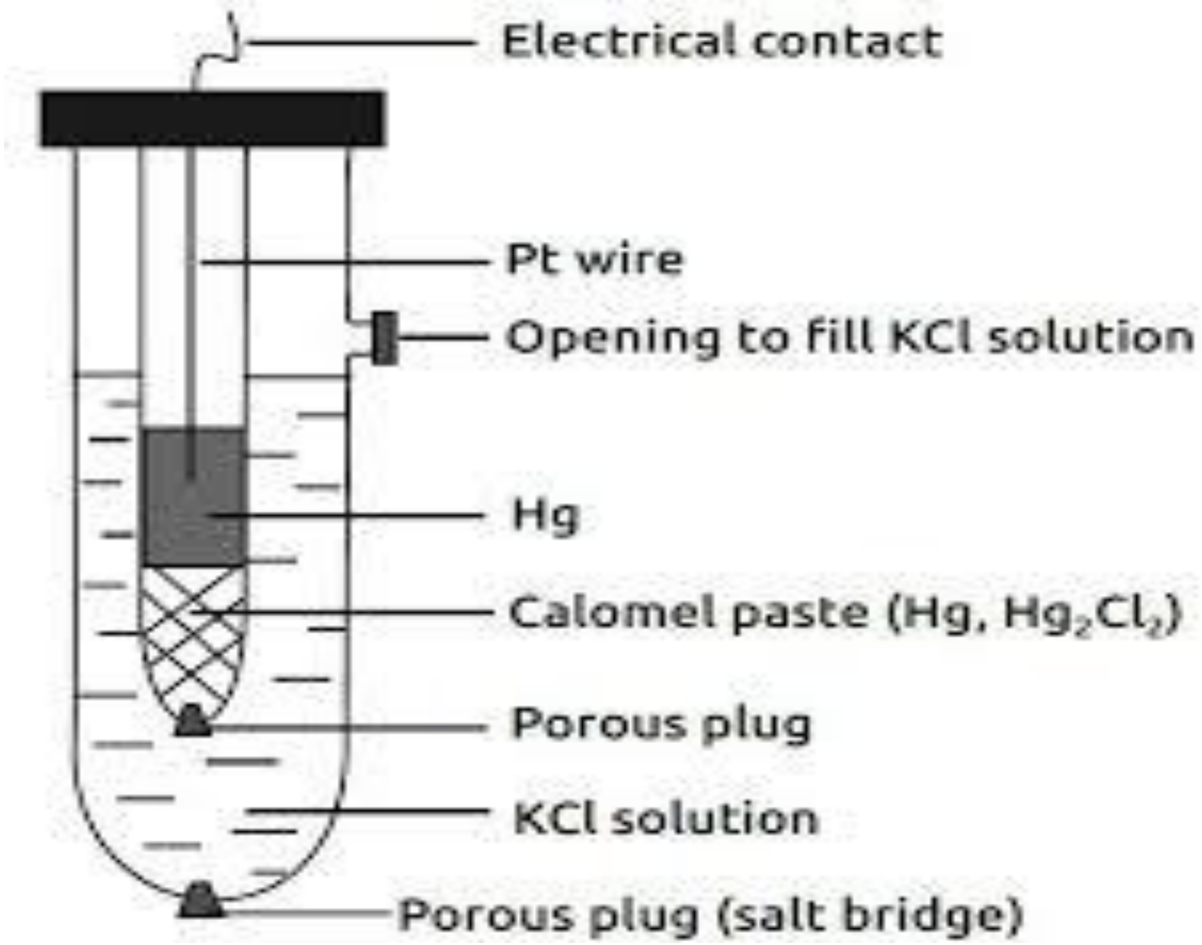
SHE equation

- Standard hydrogen electrode forms reversible electrode & can be represented as:
- Pt, H2 (1 atm) | (1.0 M) HCl
- If reduction occurs at the electrode, the reaction will be:
- $2H^+ + 2e^- \leftrightarrow H_2\uparrow$
- E^o of SHE is assumed to be zero.

Limitations of SHE

- 1.SHE cannot be used in the presence of strong oxidizing & reducing agent.
- 2. It is difficult to maintain unit molar concentration of hydrogen throughout & to pass hydrogen at 1 atm pressure.
- 3. Presence of arsenic compounds would get adsorbed on platinum foil & poisons the surface thereby affecting equilibrium of the reaction.

Calomel Electrode



Construction of calomel electrode

- It consists of a thin layer of pure mercury at the bottom of the container. It is covered with a paste of Hg, $HgCl_2$, & KCl solution of known concentration. The rest of the container is filled with KCl solution of known concentration, saturated with Hg_2Cl_2 as shown in the figure.

Calomel electrode equation

13B-1 Calomel Reference Electrodes

- A calomel electrode

$$Hg \,|\, Hg_2Cl_2(\text{sat'd}),\ KCl(x\ M)\ \|$$

- The *electrode potential* of the saturated calomel electrode is 0.2444 V at 25°C

$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-(aq)$$

The electrode reactions are represented as follows.

As anode:

$$2Hg — Hg_2^{2+} + 2e^-$$

$$Hg_2^{2+} + 2Cl^- — Hg_2Cl_2$$

$$2Hg + 2Cl^- — Hg_2Cl_2 + 2e^-$$

As cathode:

$$Hg_2Cl_2 — Hg_2^{2+} + 2Cl^-$$

$$Hg_2^{2+} + 2e^- — 2Hg$$

$$Hg_2Cl_2 + 2e^- — 2Hg + 2Cl^-$$

Nernst equation for calomel electrode

Saturated Calomel Electrode (SCE)

- Calomel half-cell

$$Hg \,|\, Hg_2Cl_2 \,|\, KCl\ (sat'd)$$

- Mercurous chloride is reduced and elementary Hg is oxidised in the reversible electrode half-reaction:

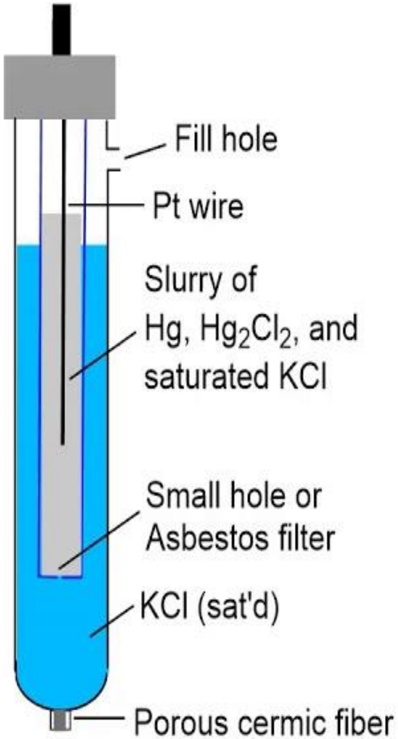
$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$$

$$\text{Oxidised state} + n e^- \rightleftharpoons \text{Reduced state}$$

$$E_{el} = E^o_{el} - \frac{RT}{nF} ln \frac{[Reduced\ state]}{[Oxidised\ state]}$$

- Since the activities of liquid Hg and solid Hg_2Cl_2 are both unity, the potential of the electrode is described by the Nernst equation:

$$E = E^o_{Hg_2Cl_2/Hg} - \frac{0.0591}{2} \log \frac{(1)[Cl^-]^2}{1}$$



Saturated calomel electrode

- Calomel electrode with saturated KCl & 1.0 M KCl have electrode potential values of 0.2412V & 0.28 V respectively.

Advantages of Calomel electrode

- 1. It is used in corrosion studies.
- 2. It is easy to construct & easy to transport.
- 3. It provides constant potential value with varying temperature.
- 4. It finds application in laboratories for measuring potential of an electrode.