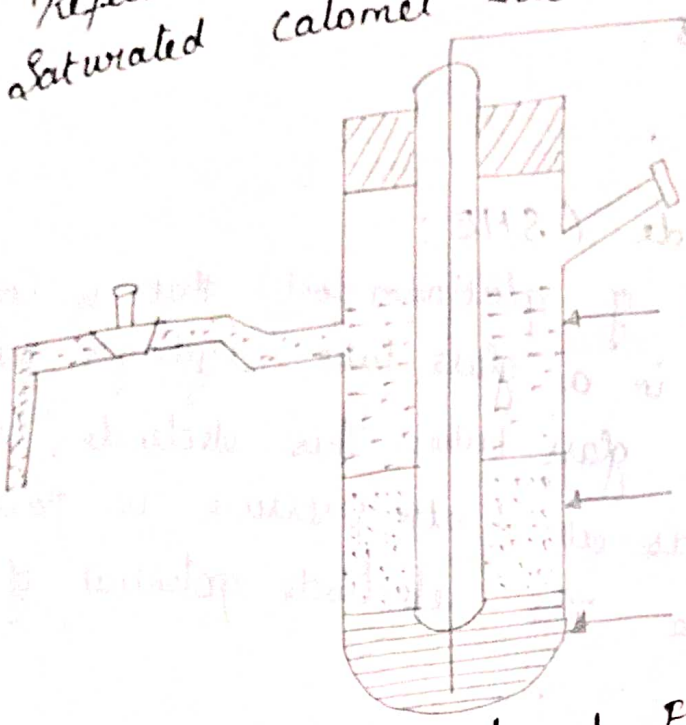
* pressure

Secondary Reference Electrode :

Ex - Saturated calomel Electrode.



Calomel Electrode

Construction :

To overcome the limitations of hydrogen electrode, the calomel electrode is developed. This is called the Secondary reference electrode. It consists of a glass tube. Pure mercury is placed at the bottom of the tube and is covered with a paste of mercurous chloride. The remaining portion of the tube is filled with a Saturated solution of KCl. The bottom of the tube is sealed with a Platinum wire.

It is represented as.

$Hg, Hg_2Cl_2(s), KCl$ (sat. solution) : $E^0 = 0.2422\ V$.

If the electrode acts as anode, the reaction is

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

$$Hg_2^{2+} + 2Cl^- \longrightarrow Hg_2Cl_2(s)$$

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

If the electrode acts as Cathode the reaction is

$$Hg_2Cl_{2(s)} \longrightarrow Hg_2^{2+} + 2Cl^-$$

$$Hg_2^{2+} + 2e^- \longrightarrow 2Hg_{(l)}$$

$$Hg_2Cl_{2(s)} + 2e^- \longrightarrow 2Hg_{(l)} + 2Cl^-$$

The electrode potential is given by

$$E_{(calomel)} = E^\circ_{(calomel)} - \frac{RT}{2F} \ln a_{Cl^-}$$

The electrode potential depends on the activity of the chloride ions and it decreases as the activity of the chloride ions increases.

The Single electrode potential of the three calomel electrodes on the hydrogen Scale at 298 K are given as

0.1 N KCl = + 0.3338 V

1.0 N KCl = + 0.2800 V

Saturated KCl = + 0.2422 V

Measurement of Single electrode potential of Zn using Saturated Calomel electrode.

The Saturated Calomel electrode is coupled with another ~~ele~~ electrode whose potential is to be determined. If the reduction Potential of the Unknown Zn electrode is less than E° of calomel electrode (+ 0.2422 V), the calomel electrode will act as cathode & the reaction is

$$E_{cell} = E^\circ_{right} - E^\circ_{left}$$

$$E_{cell} = E^\circ_{cal} - E^\circ_{Zn}$$

$$E^\circ_{Zn} = E^\circ_{cal} - E^\circ_{cell}$$

$$= +0.2422 - 1.0025 \quad \text{Where } E^\circ_{Zn} = -0.7603 \text{ volt}$$