3.3 Electrodes:

Electrodes are conductors by which electrons flow through to generate a current.

It is impossible to determine the value of a single electrode potential. But we can always measure the potential difference between two electrodes using a potentiometer, by combining the two electrodes to form a cell.

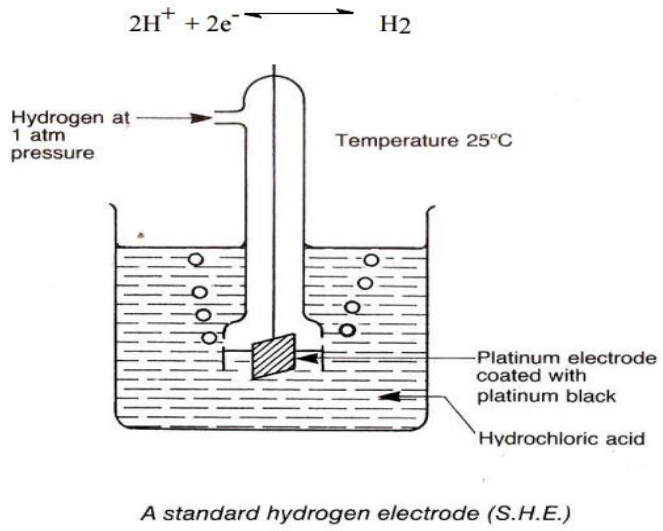
For this purpose, we use reference electrode. Standard hydrogen electrode is called primary reference electrode. Calomel electrode is called secondary reference electrode.

3.3.1 Standard hydrogen electrode (SHE) (Primary Reference Electrode)

It has a platinum foil connected to platinum wire and sealed in a glass tube. The platinum foil is dipped in 1M HCl. Hydrogen gas 1 atm pressure is passed through the side arm of glass tube as shown in the figure. The standard electrode potential of SHE is taken as zero. The electrode is represented,

$$Pt \mid H_2(g)\ (1\ atm) \mid H^+\ (1M)$$

The electrode reaction is,



A standard hydrogen electrode (S.H.E.)

3.3.2 Calomel Electrode (Secondary reference electrode):

It consists of a glass tube containing pure mercury at the bottom. A paste of mercurous chloride covers the mercury. A solution of potassium chloride is present over the paste. The bottom of the tube is sealed with a platinum wire. There is a side tube for electrical contact. The electrode is represented as, $Hg \mid Hg_2Cl_2(s) \mid KCl\ (aq)$

The electrode reaction is,

$$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$$

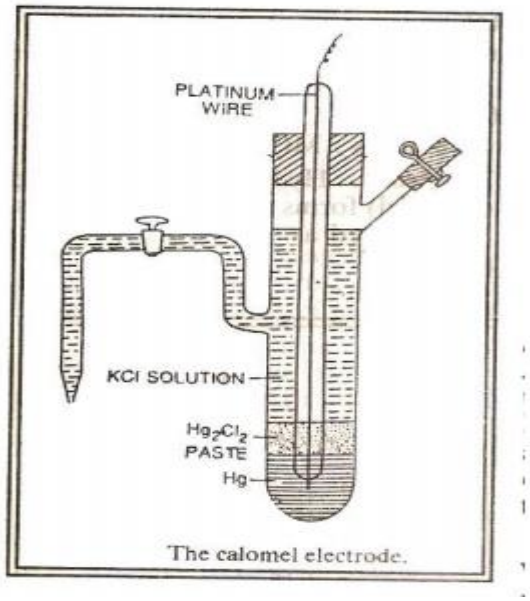
The electrode potential is,

$$E = E^\circ - \frac{RT}{2F} \ln [Cl^-]^2$$

$$E = E^\circ - \frac{RT}{F} \ln [Cl^-]$$

At 25°C, $E = E - 0.0591 \log (Cl^-)$

For saturated KCl, E = +0.242 volt.



The calomel electrode.

Measurement of single electrode potential using a reference electrode (saturated calomel electrode):

The given electrode, say zinc electrode, is coupled with saturated calomel electrode as in the figure. Since the reduction potential of zinc electrode less than that of calomel electrode, zinc acts as anode and calomel as cathode. The cell reaction will be,

$Zn/ ZnSO_4$ (1 M) // KCl (satd)/ Hg_2Cl_2/Hg

$$Zn/ ZnSO_4 \text{ (1 M) // KCl (satd)/ } Hg_2Cl_2/Hg$$

$$Zn + Hg_2Cl_2 \longrightarrow Zn^{2+} + 2Hg + 2Cl^-$$

The emf of the cell is measured using a potentiometer. The value of Ecell = 1.002 volt.

Now, $E_{cell} = E^O_{right} - E^0_{left}$

$= E^O_{cal} - E^O_{Zn}$

$1.002 = 0.242 - E^0_{Zn}$

$E_{Zn} = 0.242 - 1.002$

E_{Zn} = - 0.76 volt.

Advantages of Reference Electrode (Calomel Electrode):

- Easy to set up.
- Easily transportable
- Long shelf life
- Reproducibility of emf
- Low temperature coefficient
- Electrode can be used in a variety of solutions.
- E^o value is accurately known.