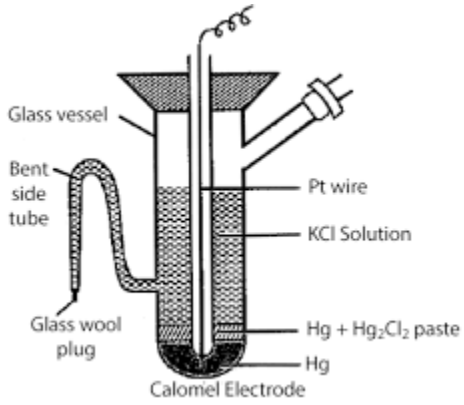
Need for Secondary Reference Electrode

1. It is very difficult to maintain the H^+ ion concentration at 1 M and hydrogen gas pressure at1 atm.

2. Platinum electrode is poisoned by the presence of impurities in the solution or gas.

Calomel Electrode or Secondary Reference Electrode



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.

If the electrode acts as anode, the reaction is

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

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

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

Mercury undergoes oxidation to produce mercurous ion (Hg^{2+}) and combines with chloride ion to give mercurous chloride (Hg_2Cl2). Hence, the concentration of chloride ions is decreased. Calomel electrode the electrode acts as cathode, the reaction is

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

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

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

The mercurous ion present in the mercurous chloride undergoes reduction to give mercury. Hence the concentration of chloride ions is increased.

Calomel electrode is represented by Hg | Hg_2Cl_2(s), KCl (sat.solution).

Characteristics of calomel electrode:

1) The electrode potential of calomel electrode depends on the activity of the chloride ions. When the concentration of chloride ion decreases, the electrode potential of calomel Electrode increases. The single electrode potential of calomel electrode with various concentration of KCl on the hydrogen scale at 298 K are given below
2) 0.1 N KCl = 0.3338 V
3) 1 N KCl = 0.2800 V
4) Saturated KCl = 0.2422 V

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/ ZnSO4 (1 M) // KCl (satd)/ Hg2Cl2/Hg

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

The emf of the cell is measured using a potentiometer. The value of E_{cell} = 1.002 volt.

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

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

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

$EZn = 0.242-1.002$

$EZn = -0.76$ 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.