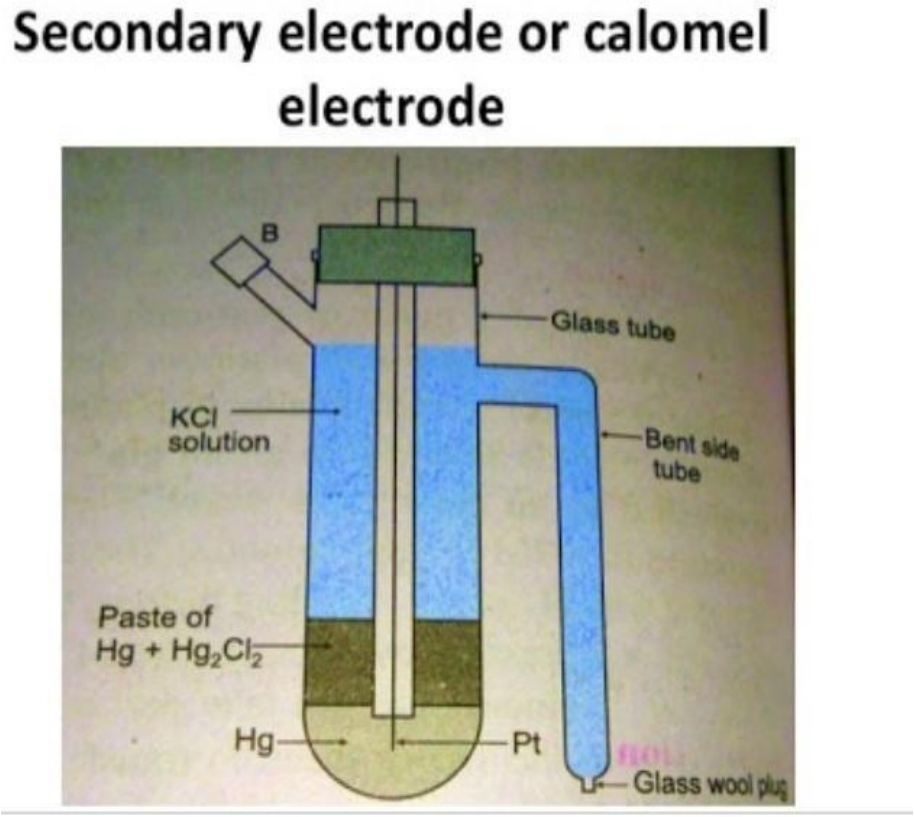
Need for Secondary Reference Electrode

- It is very difficult to maintain the H+ ion concentration at 1 M and hydrogen gas pressure at 1 atm.
- 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 (Fig. 2.4).

If the electrode acts as anode, the reaction is

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

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

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

Mercury undergo oxidation to produce mercurous ion (Hg_2^{2+})and combines with chloride ion to give mercurous chloride(Hg_2Cl_2). Hence, the concentration of chloride ions is decreased.

Calomel electrode 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 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

0.1 N KCl = 0.3338 V
1 N KCl = 0.2800 V
Saturated KCl = 0.2422 V

2) The potential of calomel electrode is temperature dependent.

Measurement of Single Electrode Potential using Saturated Calomel Electrode

The saturated calomel electrode is coupled with another electrode whose potential is to be determined. If the reduction

potential of the unknown electrode (E_x) is less than the single **: Electrochemical Series** electrode potential of calomel electrode (+ 0.2422 V), calomel electrode will act as cathode. We know that,

$$E^o_{cell} = E^o_{right} - E^o_{left}$$

$$E_{cell} = E_{cal} - E_x$$

E_{cell} can be determined experimentally by using potentiometer, then E_x can be calculated as follows :

$$E_x = E_{cal} - E_{cell}$$