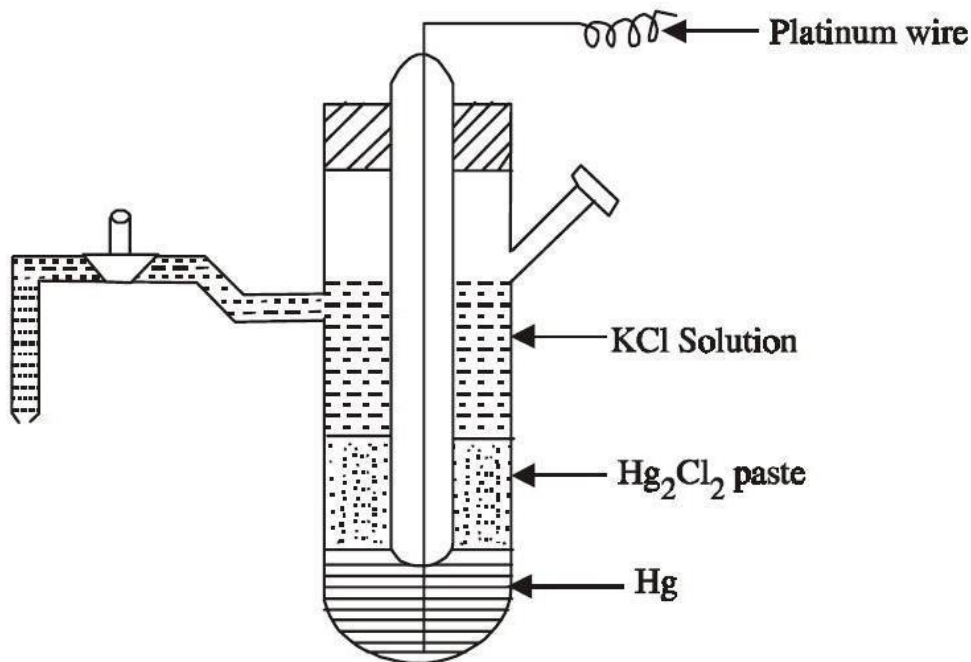## 19CH201 - ENGINEERING CHEMISTRY

UNIT-1 - ELECTROCHEMISTRY

Secondary Reference Electrode - Saturated Calomel Electrode.
Construction

Calomel electrode consists of a glass tube containing mercury at the bottom over which mercurous chloride is placed. 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. 1.3). The side tube is used for making electrical contact with a salt bridge. The electrode potential of the calomel electrode is + 0.2422 V.
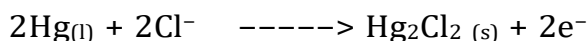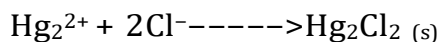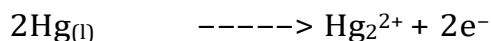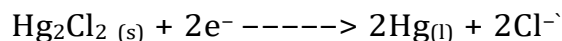

Fig. 1.3 Calomel electrode

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It is represented as,

$Hg , Hg_2Cl_2 (s) , KCl (sat.solution); E° = 0.2422 V$

If the electrode acts as anode the reaction is

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

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

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

If the electrode acts as cathode the reaction is

$Hg_2 Cl_2 (s) ----->Hg_2^{2+} + 2Cl^-$

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

$Hg_2Cl_{2\ (s)} + 2e^- -----> 2Hg_{(l)} + 2Cl^-`$
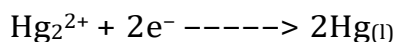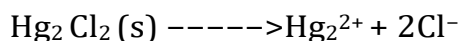
The electrode potential is given by (for example cathode)

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

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

$\qquad$ 0.1 N KCl $\quad = \quad$ + 0.3338 V

$\qquad$ 1.0 N KCl $\quad = \quad$ + 0.2800 V

$\quad$ Saturated KCl $\quad = $ + 0.2422 V.