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19CH201 - ENGINEERING CHEMISTRY

UNIT-1 - ELECTROCHEMISTRY

1.4 Calomel electrode - Ion selective electrode
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.
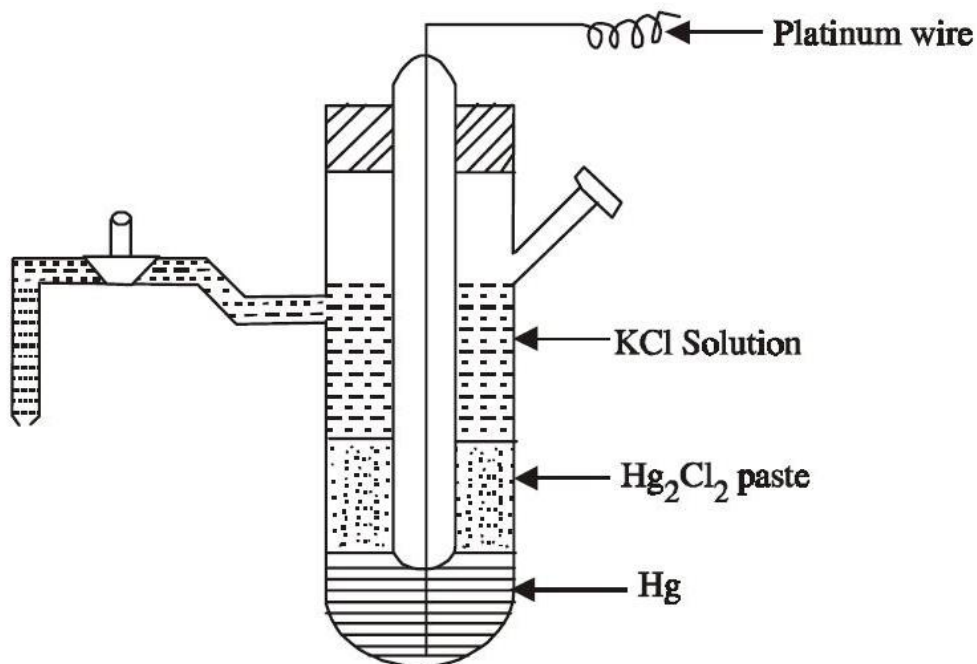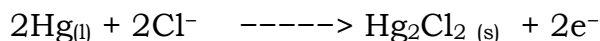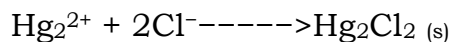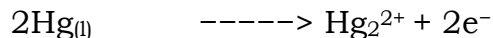

Fig. 1.3 Calomel electrode

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It is represented as,

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

If the electrode acts as anode the reaction is

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

$\quad\quad Hg_2^{2+} + 2Cl^- ---->Hg_2Cl_2\ _{(s)}$

$\quad\quad$ ---

$\quad\quad 2Hg_{(l)} + 2Cl^- \quad ----> Hg_2Cl_2\ _{(s)}\ + 2e^-$

$\quad\quad$ ---

If the electrode acts as cathode the reaction is

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

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

$\quad\quad$ --

$\quad\quad Hg_2Cl_2\ _{(s)}\ + 2e^- ----> 2Hg_{(l)} + 2Cl^-$

$\quad\quad$ ---
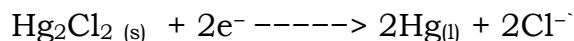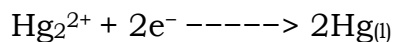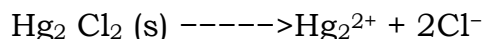
The electrode potential is given by (for example cathode)

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

$\quad$ 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

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

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

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

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Ion-Selective Electrodes (ISE)

Ion-selective electrodes are the electrodes having the ability to respond only to a particular ions, and develop potential, ignoring the other ions in a mixture totally. The potential developed by an ion-selective electrode depends only on the concentration of particular ions.

Example: Glass Electrode

The glass membrane of the glass electrode is only selective to H^+ ions only in a mixture.

Glass Electrode (Internal Reference Electrode)

Construction

A glass electrode consists of thin-walled glass bulb (the glass is a special type having low melting point and high electrical conductivity) containing a Pt wire in 0.1M HCl (Fig.1.5). The glass electrode is represented as

Pt, 0.1 M HCl / Glass

HCl in the bulb furnishes a constant H^+ ion concentration.

Fig. 1.5 Glass electrode

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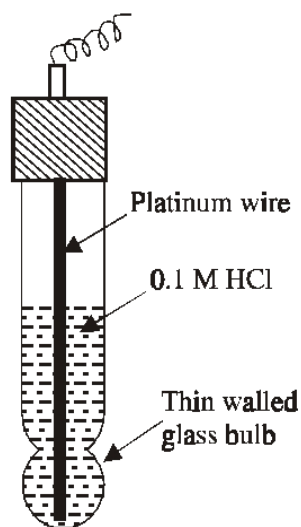
Glass electrode is used as the "internal reference electrode". The pH of the solutions, especially coloured solutions containing oxidizing or reducing agents can be determined. The thin walled glass bulb called glass membrane functions as an ion-exchange resin, and an equilibrium is set up between the Na^+ ions of glass and H^+ ions in solution. The potential difference varies with the H^+ ion concentration, and its emf is given by the expression

$$E_G = E°_G + 0.0592\ pH$$