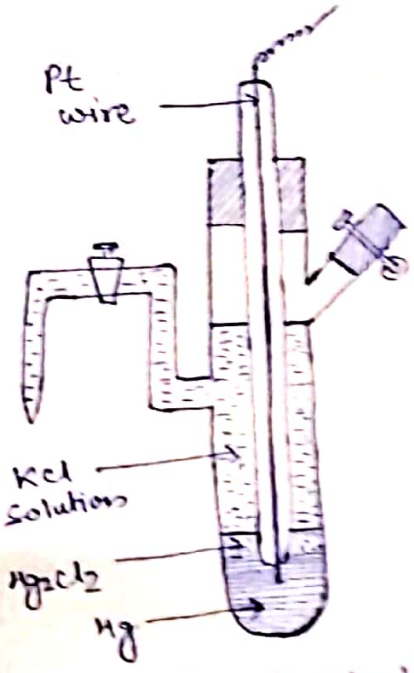
TDC-II
Paper-III
Unit-4

Calomel Electrode :-

It consists of mercury, solid mercurous chloride and a solution of KCl. The electrode is represented as:

$$Hg.Hg_2Cl_2(s); KCl(soln)$$

Mercury of high grade purity is placed at the bottom of a glass tube having a side tube on each side. Mercury is covered by a paste of mercurous chloride (calomel). A solution of KCl is introduced above the paste through the side tube. The concentration of the solution is either decinormal, normal or else the solution is fully saturated. The solution is also fills the side tube ending in a jet on the left. A Pt wire sealed into a glass tube serves to make electrical contact of the electrode with the circuit. If the electrode reaction involves reduction, the Hg_2^{2+} ions furnished by the sparingly soluble mercurous chloride would be discharged at the electrode. Hence, more and more of calomel would pass into solution.



Calomel Electrode

The reactions may be represented as follows:

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

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

If the electrode reaction involves oxidation then —

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

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

In case of calomel electrode, the electrode reaction may be represented as:

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

The electrode, therefore, is reversible with respect to Cl^- ion.

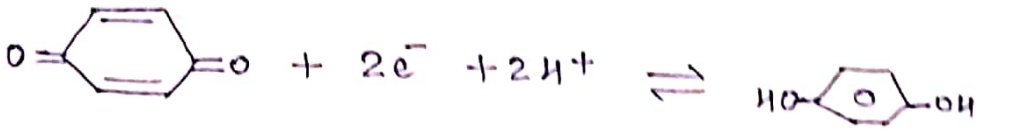
The calomel electrode with saturated KCl solution is most commonly used and is reffered to as saturated calomel electrode (SCE).

—x—

Quinhydrone Electrode :-

The term oxidation-reduction electrode is used for those electrode in which the potential is developed due to the presence of ions of the same substance in two different valence.

Quinhydrone electrode is a type of oxidation-reduction electrode. It consists of a Pt-wire placed in a solution containing Hydroquinone (QH_2) and quinone (Q) in equimolar amounts. The electrode reaction in this case is represented as follows:



Quinone (Q)

Hydroquinone (QH_2)

This electrode, which may be represented as:

$$Pt, Q, QH_2 ; H^+(aq)$$

It is reversible with respect to H^+ ions.

—x—

[Dr A.K. Gupta
Chemistry (L.S College)]