19CH201 - ENGINEERING CHEMISTRY

UNIT-1 – ELECTROCHEMISTRY

Single electrode potential (E)

It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt.

Standard electrode potential (E°)

It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of 1 molar concentration at 25°C.

Measurement of Single Electrode Potential

It is impossible to determine the absolute value of a single electrode potential. But, we can measure the potential difference between two electrodes potentiometrically, by combining them to form a complete cell. For this purpose,'reference electrode' is used.

Standard hydrogen electrode (SHE) is the commonly used reference electrode, whose potential has been arbitrarily fixed as zero. The emf of the cell is measured and it is equal to the potential of electrode.In some cases saturated calomel electrode is used as reference electrode.

REFERENCE ELECTRODES (STANDARD ELECTRODES)

The electrode potential is found out by coupling the electrode with another reference electrode, the potential of which is known or arbitrarily fixed as zero. The important primary reference electrode used is a standard hydrogen electrode, standard electrode potential of which is taken as zero.

It is very difficult to set up a hydrogen electrode. So other electrodes called secondary reference electrodes like calomel electrodes are used.

Primary Reference Electrode (Standard Hydrogen electrode)

Construction

Hydrogen electrode consists of platinum foil, that is connected to a platinum wire and sealed in a glass tube. Hydrogen gas is passed through the side arm of the glass tube. This electrode, when dipped in a 1N HCl and hydrogen gas at 1 atmospheric pressure is passed forms a standard hydrogen electrode. The electrode potential of SHE is zero at all temperatures. (Fig. 1.2).

It is represented as,

Pt , H_2 (1 atm)/H^+ (1 M); E° = 0 V

In a cell, when this electrode acts as anode, the electrode reaction can be written as

$$H_2 (g) \text{ -----> } 2H^+ + 2e-$$

When this electrode acts as cathode, the electrode reaction can be written as

$$2H^+ + 2e^- \text{ -----> } H_2(g)$$

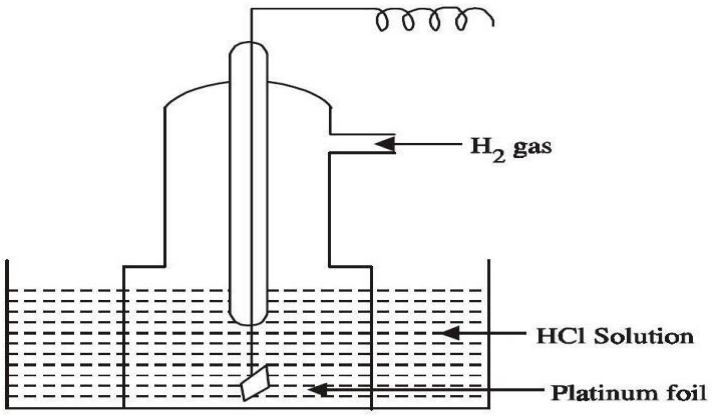

Fig. 1.2 Hydrogen electrode

Limitations

i. It requires hydrogen gas and is difficult to set up and transport.
ii. It requires considerable volume of test solution.
iii. The solution may poison the surface of the platinum electrode.
iv. The potential of the electrode is altered by changes in barometric pressure.

Measurement of single electrode potential of Zn using saturated calomel electrode

The saturated calomel electrode is coupled with another Zn electrode, the potential of which is to be determined (Fig. 1.4). Since the reduction potential of the coupled Zn electrode is less than E° of calomel electrode (+ 0.2422 V), the calomel electrode will act as cathode and the reaction is

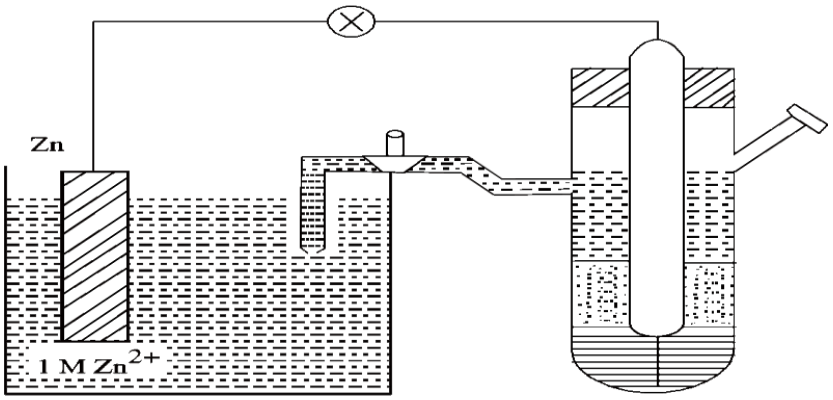

Fig. 1.4 Measurement of electrode potential (Zn)

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

$$E_{cell} = E°_{right} - E°_{left}$$
$$E_{cell} = E°_{cal} - E°_{Zn}\ E°_{Zn}$$
$$= E°_{cal} - E_{cell}$$
$$= + 0.2422 - 1.0025$$
$$E°_{Zn} = - 0.7603 \text{ volt .}$$