Reference Electrodes

Standard Hydrogen Electrode:

The potential of unknown electrode can be measured by coupling it with another electrode, called reference electrode whose potential is already known or arbitrarily fixed as zero. The important reference electrode is standard hydrogen electrode, whose standard electrode potential is taken as zero at all temperature. So, it is called primary reference electrode. It is very difficult to set up a hydrogen electrode. So, other electrode called secondary reference electrode (like calomel electrode) is used.

Standard Hydrogen electrode is called a primary reference electrode because 1) The emf developed by the standard hydrogen electrode is arbitrarily fixed as zero at 1 atm pressure and the value of which is treated as constant at all temperature. 2) It is an only electrode with which the potential of all other electrodes are compared.

The typical standard hydrogen electrode is shown in the figure

Construction of Standard Hydrogen Electrode.

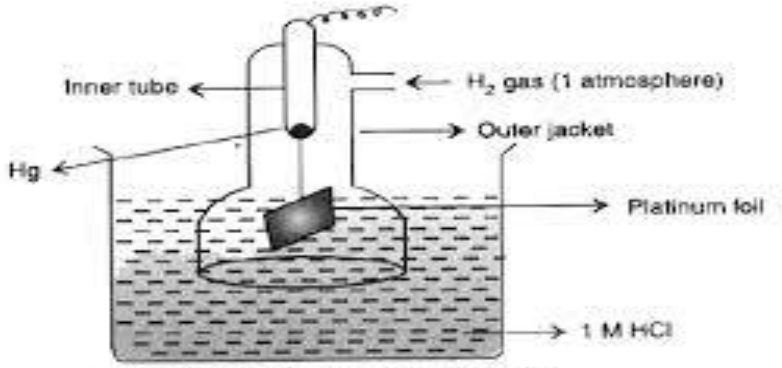

Fig. Standard hydrogen electrode

It consists of rectangular platinum foil which is connected to a platinum wire and sealed in a glass tube. A glass jacket surrounds the tube carrying the platinum foil. The jacket is closed at the top and opened at the bottom. A side tube attached to the outer jacket is used for the injection of hydrogen gas into the cell. This electrode, when dipped in a 1 M HCl solution at 25 ^{0}C and hydrogen gas at 1 atm is passed, forms a standard hydrogen electrode.

When this electrode acts as anode, the electrode reaction is as follows:

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

When this electrode acts as cathode, the electrode reaction is as follows:

$$2H^+ + 2e^- \longrightarrow H_2(g) \text{ (reduction)`}$$ The standard hydrogen electrode is represented as,
Pt, $H_2(1atm)/H^+(1M);E^o= 0V$

Development of EMF of SHE

When hydrogen gas is bubbled through the solution, it is adsorbed by the platinum foil. Due to the adsorption ofhydrogen gas, the equilibrium is established between hydrogen molecules and H^+ ions. The electrode potential developed during this equilibrium is taken as zero and treated as constant at all temperature.

Limitation

- It requires H_2 gas and is difficult to setup and transport.
- It requires considerable volume of test solution.
- The solution may affect the surface of the platinum electrode.
- The potential of the electrode is altered by changing the pressure of H_2 gas.

Need for Secondary Reference Electrode

1. It is very difficult to maintain the H^+ ion concentration at 1 M and hydrogen gas pressure at1 atm.

2. Platinum electrode is poisoned by the presence of impurities in the solution or gas.