Lecture-3

Reference Electrode

The electrodes of known potential, with reference to which the potential of any other electrode can be measured, are called reference electrodes.

• There are two types of reference electrodes, namely
  1. Primary reference electrode, Example: Hydrogen gas electrode
  2. Secondary reference electrode, Example: Calomel electrode and silver-silver electrode

Limitations of Primary Reference Electrode
• The electrode cannot be easily setup.
• The equilibrium between the two processes is not reached quickly.
• It is difficult to control the pressure of hydrogen gas at 1 atm.
• The electrode gets poisoned by impurities

Secondary Reference Electrodes
For the sake simplicity and to overcome the above difficulties, there was a need for the development of secondary reference electrodes. The potentials of these electrodes are known on the hydrogen scale and are used in place of hydrogen electrode. These electrodes can be easily setup.

Types of Electrodes :-

I. Metal-metal ion electrode: A metal is dipped in a solution containing its own ions.
   Ex: Zn/Zn^{2+}; Cu^{2+}/Cu; Ag/Ag^{+}

II. Metal – Metal salt electrode[Metall-insoluble salt electrode]
   A metal is in contact with a sparingly salt solution containing anion of the salt.
   Ex: Calomel electrode: Hg/Hg₂Cl₂/Cl⁻(sat)
   Silver- silver chloride electrode: Ag/AgCl/Cl⁻

III. Gas electrode: It consists of a gas, which is in contact with an inert metal dipped in an ionic solution of the gas molecules.
    Ex: Hydrogen electrode: Pt/H₂/H^+
    Chlorine electrode: Pt/Cl₂/Cl⁻

IV. Amalgam electrode: Amalgam electrode is similar to metal-metal ion electrode except for the fact that in a amalgam electrode, metal amalgam is in contact with a solution containing its own ions.
    Ex: Lead amalgam electrode: PbHg/Pb^{2+}
V. Oxidation-Reduction electrode: An oxidation-reduction electrode is one in which the potential arises from the presence of oxidized and reduced forms of the same substance in solution. The potential developed is picked up by an inert electrode like platinum.  
Ex: Pt/Fe^{2+},Fe^{3+};  Pt/Ce^{3+},Ce^{4+};  Pt/Sn^{2+}, Sn^{4+}

VI. Ion selective electrode [membrane electrode] A membrane is in contact with an ionic solution, with which it can exchange their ions.  
Ex: Glass electrode [exchange H+ ions with metal ion by ion-exchange metal- ion process].

Limitations of Standard Hydrogen Electrode (SHE):-

1. Difficulty in setting up of the electrode.  
2. The electrode becomes inactive in presence of impure gases present in hydrogen.  
3. It cannot be used in solutions containing redox systems.  
4. It cannot be used in the presence of ions of many metals.

Construction and working of calomel electrode

Calomel electrode is the mercury-mercurous chloride electrode. It consists of glass vessel having bent side tube. Pure mercury is placed at the bottom of the tube. Which is covered with a paste of mercury- mercurous chloride (Hg+HgCl₂) i.e., calomel. The remaining portion of the cell is filled with a solution of normal (1N) or decinormal (0.1N) or saturated KCl. A platinum wire sealed into a glass tube is dipped into mercury layer is used to provide the external electrical contact. The side tube is used for making electrical contact with a salt bridge.  

The electrode can be represented as  
Hg(l)/Hg₂Cl₂ (s) / Cl⁻

The calomel electrode can act as anode or cathode depending on the nature of other electrode of the cell.  
When it acts anode, the electrode reaction is  
2Hg(l) → Hg₂²⁺ + 2e⁻

Hg₂²⁺ + 2Cl⁻ → Hg₂Cl₂

2 Hg + 2Cl⁻ → Hg₂Cl₂ + 2e⁻  (Oxidation reaction)

When it acts as cathode, the electrode reaction is,  
Hg₂²⁺ + 2e⁻ → 2 Hg
Hg₂Cl₂ → Hg₂²⁺ + 2Cl⁻
The net reversible electrode reaction is,
\[ \text{Hg}_2\text{Cl}_2 (s) + 2e^- \rightleftharpoons 2 \text{Hg (l)} + 2 \text{Cl}^- \]

Electrode potential is given by
\[ E = E^o - \frac{2.303 \text{RT}}{2F} \log [\text{Cl}^-]^2 \]
\[ = E^o - 0.0591 \log [\text{Cl}^-] \text{ at 298 K} \]

The electrode potential is decided by the concentration of chloride ions & the electrode is reversible with chloride ions at 298K, the electrode potentials are as follows.

- 0.1N KCl electrode (0.334V)
- 1 N KCl electrode (0.281 V)
- Saturated KCl electrode (0.2422 V)

**Uses:**
i) It is used as a secondary reference electrode in the measurement of single electrode potential. It is the most commonly used reference electrode in all potentiometric determinations.

**For example:** The test electrode, \( \text{Zn}^{(s)} / \text{Zn}^{2+} \text{(aq)} \) is coupled with a saturated calomel electrode.

\[ \text{Zn}^{(s)} / \text{Zn}^{2+} \text{(aq)} \bigg| \bigg| \text{Cl}^- \text{(saturated soln)} / \text{Hg}_2\text{Cl}_2(s) / \text{Hg (l)} \]

The emf of the so formed cell is determined experimentally by potentiometric method.

Then \( E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \)
\[ = 0.2422 - E_{\text{zn}} \quad \text{OR} \quad E_{\text{zn}} = 0.2422 - E_{\text{cell}} \]

**Advantages**
- It is simple to construct.
- The cell potential is reproducible and constant over a long period.
- The cell potential does not vary with temperature

**Uses**

It is used as a secondary reference electrode the measurement of single electrode potential by potentiometric method.
**Determination of single electrode potential**

For ex: test electrode Zn/Zn$^{2+}$ coupled with saturated calomel electrode.

\[
\text{Zn/Zn}^{2+}//\text{Cl}^-//\text{Hg}_2\text{Cl}_2(\text{s})/\text{Hg(1)}
\]

EMF is determined by potentiometric method

\[
E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}
= E_{\text{calomel}} - E_{\text{Zn}^{2+}/\text{Zn}}
= 0.2422 - E_{\text{Zn}^{2+}/\text{Zn}}
\]

\[
E_{\text{Zn}^{2+}/\text{Zn}} = 0.2422 - E_{\text{cell}}
\]