Electro Chemistry BSC. (II) Sub

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☐ DIFFERENT TYPES OF ELECTRODES:

1. Metal – Metal ion electrode M/M^{n+}

$$M^{n+} + ne^- \longrightarrow M(s)$$

$$E = E + \frac{0.0591}{n} \log [M^{n+}]$$

2. Gas – ion Electrode

$Pt / H_2 (P\ atm) / H^+ (x\ M)$

$$E = E - 0.0591 \log \frac{P_{H_2}^{\frac{1}{2}}}{[H^+]}$$

3. Oxidation – reduction Electrode

$Pt / Fe^{2+}, Fe^{3+}$

as a reduction electrode

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}$$

$$E = E - 0.0591 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

4. Metal – Metal insoluble salt electrode

Ex. $Ag / AgCl, Cl^-$

as a reduction electrode

$$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-$$

$$E_{Cl^-/AgCl/Ag} = E^\circ_{Cl^-/AgCl/Ag} - 0.0591 \log[Cl^-]$$

Note:

1. The Value of electrode potential does not depend on stoichiometry of half reactions

2. In electrolytic Cell, cathode is negative terminal whereas in Galvanic Cell Cathode is positive terminal.

3. Work obtained by electro chemical Cell – free energy of Cell

$$\Delta G = -nFE_{cell} \qquad \Delta G = nFE_{cell}$$

4. Cell reaction is spontaneous, if

$$\Delta G = -Ve \text{ or } E_{cell} = +Ve$$

5. Cell reaction will be in equilibrium.

Ex. $\Delta G = 0$ or $-nFE_{cell} = 0$ or $E_{cell} = 0$

6. In nernst equation

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} \log_{10} \frac{[Product]}{[Reactant]}$$

If $E_{cell} = 0$, then

$$E_{cell} = \frac{0.0591}{n} \log_{10} \frac{[Product]}{[Reactant]}$$

or, $$E^{\circ}_{cell} = \frac{0.0591}{n} \log_{10} K$$

or, $$E^{\circ}_{cell} = \frac{RT}{nF} \log_e K$$

Put the value of E°_{cell} in

$$\Delta G = -nFE_{cell}$$

we get $\Delta G^{\circ} = -nF \frac{RT}{nF} \log_e K \Rightarrow \Delta G = -RT \log_e K$

Reference Electrode

An electrode used to calculate the electrode Potential of other electrodes.

(a) Standard Hydrogen Electrode (SHE):

It consist of a Platinum electrode over which H_2 gas (1 atm pressure) is bubbled and the electrode is immersed in a solution that is 1 M in H^+ at 25C.

$$2H^+ + 2e^- \longrightarrow H_2(g)\ (1\ atm)$$
$$(1M)$$

the potential of this electrode at 25 C is taken as Zero Volt.

(b) Calomel Electrode :

$$Hg(l) / Hg_2Cl_2(s) / Cl^-(aq)$$

It is prepared by a Pt wire in Contact with a paste of Hg and Hg_2Cl_2 present in a KCl solution.

Reaction $\frac{1}{2} Hg_2Cl_2(s) + e^- \longrightarrow Hg(l) + Cl^-$

$$E = E - 0.0591 \log [Cl^-].$$