

Electro Chemistry BSC. (II) sub

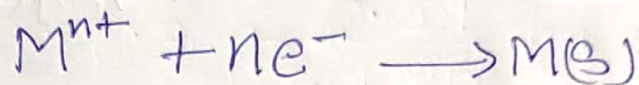
D.B. College (Jaynagar)

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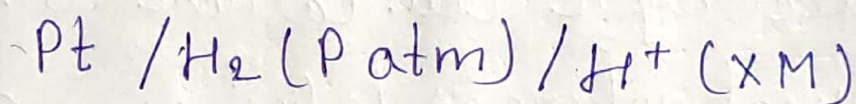
## □ DIFFERENT TYPES OF ELECTRODES:

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



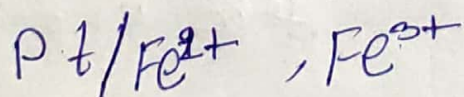
$$E = E^{\circ} + \frac{0.0591}{n} \log [M^{n+}]$$

2. Gas - ion Electrode

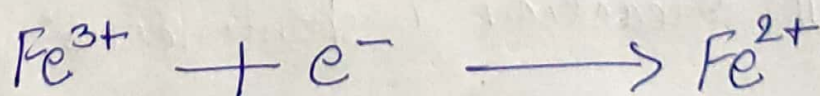


$$E = E^{\circ} - 0.0591 \log \frac{P_{H_2}^{1/2}}{[H^{+}]}$$

3. Oxidation - Reduction Electrode



as a reduction electrode

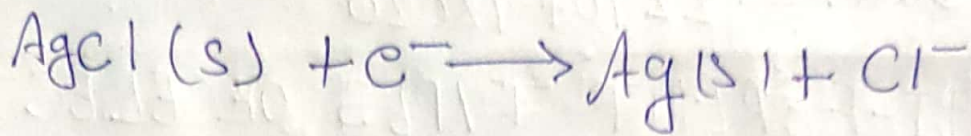


$$E = E^{\circ} - 0.0591 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

4. Metal - Metal insoluble salt electrode

Ex. Ag / AgCl, Cl<sup>-</sup>

as a reduction electrode



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

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 electrochemical cell -  
Free energy of cell  
$$\Delta G = -nFE_{\text{cell}} \quad \Delta G = -nFE_{\text{cell}}$$
4. Cell reaction is spontaneous, if  
$$\Delta G = -ve \quad \text{or} \quad E_{\text{cell}} = +ve$$
5. Cell reaction will be in equilibrium.

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

G In Nernst equation

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

If  $E_{\text{cell}} = 0$ , then

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

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

$$\text{or, } E_{\text{cell}}^{\circ} = \frac{RT}{nF} \log_e K$$

Put the value of  $E_{\text{cell}}^{\circ}$  in

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

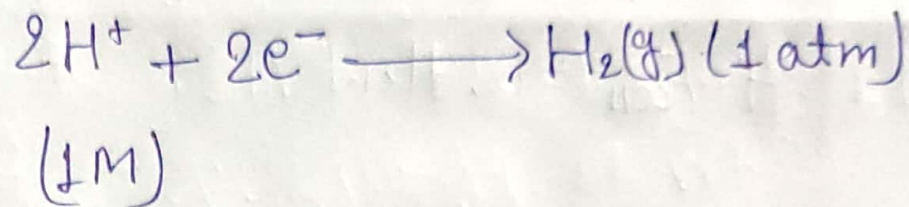
$$\text{we get } \Delta G^{\circ} = -nF \frac{RT}{nF} \log_e K \Rightarrow \Delta G^{\circ} = -RT \log_e K$$

## □ Reference Electrode

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

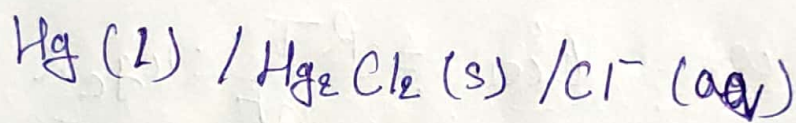
(a) Standard Hydrogen Electrode (SHE):

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 1M in  $H^+$  at 25C.

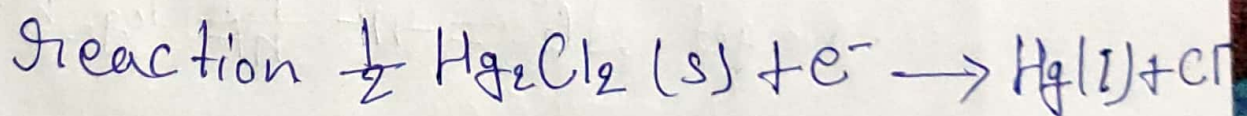


the potential of this electrode at 25C is taken as Zero Volt.

(b) Calomel Electrode :



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



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