

Electrochemistry

If a cell yields ' nF ' coulombs of electricity in a reversible reaction, it is equal to decrease of Gibbs free energy.

$$\therefore -\Delta G = nFE^{\circ} \quad \text{--- (1)}$$

By Gibbs's Helmholtz, (at constant pressure)

$$\Delta G = \Delta H + T \left(\frac{d\Delta G}{dT} \right)_p \quad \text{--- (2)}$$

Using (1) in (2):-

$$-nFE^{\circ} = \Delta H + T \frac{d}{dT} (-nFE)$$

$$\Rightarrow -nFE^{\circ} = \Delta H + nFT \left(\frac{dE}{dT} \right)_p$$

$$\therefore \Delta H = -nF \left[E^{\circ} + T \left(\frac{dE}{dT} \right)_p \right]$$

In terms of E° :-

$$\frac{\Delta H}{nF} = -E^{\circ} + T \left(\frac{dE}{dT} \right)_p$$

$$\therefore E^{\circ} = -\frac{\Delta H}{nF} + T \left(\frac{dE}{dT} \right)_p$$

For standard electrode potential, conditions are:-

1) 25°C

2) 1 M conc

3) 1 atm pressure

Nernst Equation :-

for redox reaction :- $M^{n+} + ne^- \rightleftharpoons M$

Let $K \rightarrow$ Equilibrium constant

$Q \rightarrow$ Non-Equilibrium constant

- ① At Equilibrium, Conc. of products = Conc. of Reactants
At Non-Equilibrium, Conc. of products \neq Conc. of reactants

In terms of Gibbs Free Energy :-

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \left[Q = \frac{[\text{Products}]}{[\text{Reactants}]} \right]$$

At EQ^m , $[Q = K \text{ \& } \Delta G = 0]$

Why $\Delta G = 0$ at EQ^m ?

\hookrightarrow Spontaneity of redox reaction decreases due to increase in the stability of the reaction.
This means $\text{forward rate} = \text{Backward rate}$ (in the stable reaction)

\rightleftharpoons sign \rightarrow symbolizes the reaction can occur forward & backward direction (reverse)

\rightarrow means forward & \leftarrow means backward

In Non- EQ^m , $\Delta G \neq 0$:-

$\Delta G > 0 \rightarrow$ reaction occurs in forward direction

$\Delta G < 0 \rightarrow$ reaction occurs in backward direction

ΔG° value at EQ^m :-

$$\Delta G = \Delta G^\circ + RT \ln Q$$

At EQ^m ,

$$\Delta G = 0 \quad \& \quad Q = K \text{ (equilibrium constant)}$$

$$\Rightarrow 0 = \Delta G^\circ + RT \ln K$$

$$\Rightarrow \Delta G^\circ = -RT \ln K$$

where :- $R = 8314$

$T = 298 K$

* Derivation :-

If cell involves transfer of ' n ' e^- , then ' F ' (Faraday) of electricity will flow.

If E is the e.m.f of cell, total electricity produced in cell :-

$$-\Delta G = nFE$$

$$-\Delta G^\circ = nFE^\circ$$

where :- $F = 96500 C$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\Rightarrow -nFE = -nFE^\circ + RT \ln \frac{[Product]}{[Reactant]}$$

Divide both sides by ' $-nF$ '

$$\Rightarrow E = E^\circ - \frac{RT}{nF} \ln Q$$

$$\ln Q = 2.303 \log_{10} Q$$

(or)

$$E = E^\circ - \frac{0.0591}{n} \log Q$$

$$\rightarrow \frac{RT}{F} = 0.0591$$