TPC-II
Paper-III

Electrochemistry

Derivation of Nernst Equation for Electrode Potential.

Consider a cell reaction

$$aA + bB \longrightarrow cC + dD$$

when reactants and products are in their standard unit activity state Then, The standard decrease in free Energy is given by Thermo-dynamic Equation (Van't Hoff Equation) is given by $-\Delta G^{\circ}$

$$-\Delta G = -\Delta G^{\circ} + RT \ln Q$$

where $Q = \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b}$ = Reaction Quotient

$$\Delta G = \Delta G^{\circ} - RT \ln Q$$

$$-nFE = -nFE^{\circ} - RT \ln Q$$

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

Replacing the concentration as as an approximation & change Ln to Log10, we have

$$E = E^{\circ} - \frac{2.303RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

At 25°C $\frac{2.303RT}{nF} = \frac{2.303 \times 8.314 \times 298K}{96500}$

$= 0.059$ volt

Hence $E = E^{\circ} - \frac{0.059}{n} \log \frac{[C]^c [D]^c}{[A]^a [B]^b}$

This is required Nernst Equation.

Knowing the active mass of reactants and products of the ~~pro~~ cell reaction, we can find E.m.f. of cell at 25°C conn.

where E° = standard e.m.f of the cell and is equal to the e.m.f of the cell when activity of all reactants and products are unity

$E^{\circ} = E^{\circ}_{Cathode} - E^{\circ}_{Anode}$

Ex- for Galvanic cell $Zn(s) | Zn^{+2}(aq) || Cu^{+2}(aq) | Cu(s)$

$E_{cell} = E^{\circ}_{Cu^{+2}/Cu} - E^{\circ}_{Zn^{+2}/Zn} - \frac{0.059}{2} \log \frac{[Zn^{+2}]}{[Cu^{+2}]}$