Relation b/w Change in Enthalpy, Entropy & E

$\Delta G = \Delta H - T\Delta S$ ⟶ $G = H - TS$

↳ Gibbs function

$-S = \left(\frac{\partial G}{\partial T}\right)_P$

$-\Delta S = \left(\frac{\partial \Delta G}{\partial T}\right)_P$

↳ temperature co-efficient of Change in free energy @ constant pressure

↓

We can get it by measuring ΔG @ different temperature

temp in 'K'

↑

$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$ → Gibbs Helmholtz eqn

↓ Change in free energy @ Const. pressure

↓ Change in Enthalpy @ Const. pressure

$\Delta G = -nFE$

$-nFE = \Delta H + T\left(\frac{\partial -nFE}{\partial T}\right)_P$

$nFE = -\Delta H + Tnf\left(\frac{\partial E}{\partial T}\right)_P$

↓

temperature co-efficient of emf of cell at constant pressure

↓

We get this by measuring E of cell at different Temperature

$$E = -\frac{\Delta H}{nF} + T\left(\frac{\partial E}{\partial T}\right)_P$$

Case : 1

if $\left(\frac{\partial E}{\partial T}\right)_P = 0$

then

$$nFE = -\Delta H$$

Case 2 :-

if $\left(\frac{\partial E}{\partial T}\right)_P$ is +ve

$$nFE > -\Delta H$$

Case 3 :-

$\left(\frac{\partial E}{\partial T}\right)_P$ is −ve

$$nFE < -\Delta H$$

eg :

$$Cd_{(s)} \,|\, CdCl_{2(aq)} \,//\, AgCl \,|\, Ag$$

@ anode

$$Cd \rightarrow Cd^{2+} + 2e^- \qquad E_{cell}\,@\,25^\circ C = 0.6753V$$

@ cathode

$$2AgCl + 2e^- \rightarrow 2Ag + 2Cl^- \qquad E_{cell}\,@\,0^\circ C = 0.6915V$$

$$Cd + 2AgCl \rightarrow 2Ag + Cd^{2+} + 2Cl^-$$

Calculate ΔG, ΔS, ΔH @ 25°C

ΔG @ 25°C

$$\Delta G = -nFE$$

$$= -2 \times 96500^{(C)} \times 0.6753(V)$$

$$= -130319 \quad C.V$$

$$= -130.319 \quad KJ$$

ΔS @ 25°C

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{0.6753 - 0.6915}{298 - 273}\right) = \frac{-0.0162}{25} \quad VK^{-1}$$

$$= -0.00065\ VK^{-1}$$

$$-\Delta S = \left(\frac{\partial \Delta G}{\partial T}\right)_P \quad (i) \quad -\Delta S = -nF\left(\frac{\partial E}{\partial T}\right)_P$$

$$\Delta S = 2 \times 96500^{(C/mol)} \times -0.00065\ VK^{-1}$$

$$= -125\ JK^{-1}$$

ΔH @ 25°C

$$nFE = -\Delta H + T nF\left(\frac{\partial E}{\partial T}\right)_P$$

$$-\Delta H = nFE - T nF\left(\frac{\partial E}{\partial T}\right)_P$$

$$= nF\left(E - T\left(\frac{\partial E}{\partial T}\right)_P\right)$$

$$= 2 \times 96500\left(0.6753 - 298 \times^{(-)} 0.0006\right)$$

$$= 167515\ J$$

$$\Delta H = -167.5\ kJ$$

Emf Cell @ ~~Std~~ non-Std conditions:-

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

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

ΔG: Change in free energy

ΔG°: Change in Free energy in Std conditions

Q: Reaction Quotient

$$\Delta G = -nFE$$

$$Q = \frac{a_{M(s)}}{a_{M^{n+}}}$$

$$-nFE = -nFE^\circ + RT \ln Q$$

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

R: 8.314 J K^{-1} mol^{-1}, T: Temp in K

$$= E^\circ - \frac{2.303 \times R \times T}{nF} \log Q$$

nF: 96500 C/mole

@ $T = 298$ K

$$= E^\circ - \frac{0.0592}{n} \log \frac{a_{M(s)} \Rightarrow 1}{a_{M^{n+}}}$$

$$= E^\circ - \frac{0.0592}{n} \log \frac{1}{a_{M^{n+}}}$$

$$\boxed{E = E^\circ + \frac{0.0592}{n} \log a_{M^{n+}}}$$

$E \propto a_{M^{n+}}$

Activity & mean ionic activity:

$$M_x A_y \longrightarrow x M^+ + y A^-$$

Let us say

$a_+ \rightarrow$ activity of M^+

$a_- \rightarrow$ activity of A^-

a = activity of electrolyte

$$a = a_+^x \cdot a_-^y$$

$$a_\pm = \sqrt[x+y]{a_+^x \times a_-^y}$$

$$\boxed{a = (a_\pm)^{x+y}}$$

$$(a_\pm)^{x+y} = a_+^x \cdot a_-^y$$

activity

for example HCl

$$a = (a_\pm)^2$$

Na_2SO_4

$$a_\pm = \sqrt[3]{a_+^2 \times a_-}$$

$$a = (a_\pm)^3$$

We

$$a = \gamma m$$

a: activity; γ: activity co-efficient; m: concentration

$m_+ \rightarrow x m$ → Concentration of electrolyte

Concentration of cation

$m_- \rightarrow y m$ → Concentration anion

$$a = (a_\pm)^{x+y}$$

$$= (\gamma_\pm m_\pm)^{x+y}$$

$$= (\gamma_+ m_+)^x (\gamma_- m_-)^y$$

$$= (\gamma_+ \times x m)^x (\gamma_- \times y m)^y$$

$$= x^x y^y (\gamma_+ m)^x (\gamma_- m)^y$$

$$\boxed{a = x^x y^y (\gamma_\pm m)^{x+y}}$$

$$\gamma_+^x \cdot \gamma_-^y = \gamma_\pm^{x+y}$$

Significance of Nernst eqn:-

(1) We predict concentration of electrolyte

$$Fe_{(s)} | Fe^{2+}_{(aq, 0.1M)} || Cd^{2+}_{(aq,\ ?M)} | Cd_{(s)}$$

$$E^\circ_{Fe^{2+}/Fe} = -0.45V$$

$$E^\circ_{Cd^{2+}/Cd} = -0.40V$$

$$E = 0.02V \ @\ 25^\circ C$$

$$[Cd^{2+}] = ?$$

@ anode :-

$$Fe \rightarrow Fe^{2+} + 2e^-$$

@ Cathod

$$Cd^{2+} + 2e^- \rightarrow Cd$$

$$Fe + Cd^{2+} \rightarrow Cd + Fe^{2+}$$

$$E^\circ_{cell} = E_{cathode} - E_{anode}$$

$$= -0.40V - (-0.45V)$$

$$= 0.05V$$

$$E = E^\circ - \frac{0.0592}{2} \log \left(\frac{[Fe^{2+}]}{[Cd^{2+}]} \right)$$

$$0.02 = 0.05 - \frac{0.0296}{2} \log \left[\frac{0.1}{[Cd^{2+}]} \right]$$

$$-\log \left[\frac{0.1}{[Cd^{2+}]} \right] = -\frac{0.02 - 0.05}{0.0296}$$

$$\log \left[\frac{0.1}{[Cd^{2+}]} \right] = 1.014$$

$$\log(0.1) - \log[Cd^{2+}] = 1.014$$

$$-1 - \log[Cd^{2+}] = 2.014$$

$$\log[Cd^{2+}] = -2.014$$

$$[Cd^{2+}] = 10^{-2.014}$$

$$[Cd^{2+}] = 0.01 \text{ M}$$

2) Calculation of p^H

$$Pt_{(s)} \mid \underbrace{H_{2(g,\,1atm)} \mid H^+_{(aq,\,p^H=?)}}_{\text{anode}} \parallel \underbrace{\text{Reference electrode}}_{\text{Cathode}}$$

$$E = E_{Ref} - E_{anod}$$

@

$$2H^+ + 2e^- \rightarrow H_2$$

activity of gas @ 1 atm is = 1

$$E_{anod} = \underset{0}{\overset{\parallel}{E^0}} - \frac{0.0592}{2} \log \frac{1}{[H^+]^2}$$

$$= \frac{-0.0592}{2} \log \frac{1}{[H^+]^2}$$

$$= \frac{0.0592}{2} \log [H^+]^2$$

$$= \frac{0.0592}{2} \times 2 \times \log [H^+]$$

$$= 0.0592 \log [H^+]$$

$$E_{cell} = E_{ref} - E_{anode}$$

$$= E_{ref} - 0.0592 \log [H^+]$$

$$E_{cell} = E_{ref} + 0.0592(-\log[H^+])$$

$$\Downarrow pH$$

$$E_{cell} = E_{ref} + 0.0592\, pH$$

$$\boxed{pH = \frac{E_{cell} - E_{ref}}{0.0592}}$$

if H_2 electrode is used as Cathode

$$pH = -\left(\frac{E_{cell} + E_{ref}}{0.0592}\right)$$

3) Calculation of K

$$aA + bB \rightleftharpoons cC + dD$$

$$E = E^0 - \frac{RT}{nF} \ln Q$$

@ equilibrium

$$E = 0$$

$$Q = K$$

$$E^0 = \frac{RT}{nF} \ln K$$

$$\ln K = \frac{E^0 nF}{RT}$$

$$K = e^{\left(\frac{nFE^0}{RT}\right)}$$