

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

Temp. in 'K' We can get it by measuring ΔG @ different temperature

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

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 ~~var~~ different Temperature

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

if Case 1

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

then

$$nFE = -\Delta H$$

Case 2:-

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

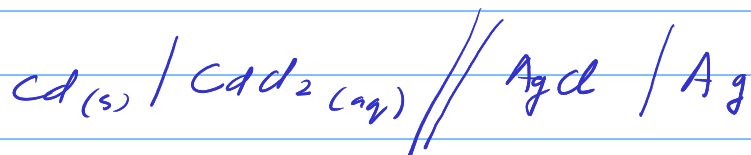
$$nFE > -\Delta H$$

Case 3:-

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

$$nFE < -\Delta H$$

eg 1.



@ anode



$$E_{an} @ 25^\circ\text{C} = 0.6753\text{V}$$

@ cathode



$$E_{cat} @ 0^\circ\text{C} = 0.6915\text{V}$$



Calculate ΔG , ΔS , ΔH @ 25°C

$\Delta G @ 25^\circ\text{C}$

$$\begin{aligned}\Delta G &= -nFE \\ &= -2 \times 96500^{(1)} \times 0.6753 \text{ (V)} \\ &= -130319 \text{ C}\cdot\text{V} \\ &= -130.319 \text{ kJ}\end{aligned}$$

$\Delta S @ 25^\circ\text{C}$

$$\begin{aligned}\left(\frac{\partial E}{\partial T}\right)_P &= \left(\frac{0.6753 - 0.6915}{298 - 273}\right) = \frac{-0.0162}{25} \text{ V K}^{-1} \\ &= -0.00065 \text{ V K}^{-1}\end{aligned}$$

$$\begin{aligned}-\Delta S &= \left(\frac{\partial \Delta G}{\partial T}\right)_P \quad (1) \quad -\Delta S = -nF\left(\frac{\partial E}{\partial T}\right)_P \\ \Delta S &= 2 \times 96500 \times -0.00065 \text{ V K}^{-1} \\ &= -125 \text{ J K}^{-1}\end{aligned}$$

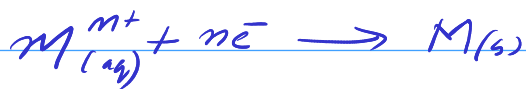
$\Delta H @ 25^\circ\text{C}$

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

$$\begin{aligned}-\Delta H &= nFE - TnF\left(\frac{\partial E}{\partial T}\right)_P \\ &= nF\left(E - T\left(\frac{\partial E}{\partial T}\right)_P\right)\end{aligned}$$

$$\begin{aligned}&= 2 \times 96500 \left(0.6753 - 298 \times 0.00065\right) \\ &= 167515 \text{ J} \\ \Delta H &= -167.5 \text{ kJ}\end{aligned}$$

Emf cell @ non-std conditions! -



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

Change in
free energy

Change in Free energy in
Std conditions

Reaction Quotient

$$\Delta G = -nFE$$

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

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

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

$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Temp in K

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

96500 C/mol

@ $T = 298 \text{ K}$

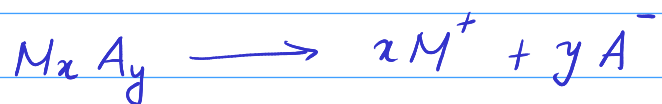
$$= E^\circ - \frac{0.0592}{n} \log \frac{a_{M(s)}}{a_{M^{n+}}}$$

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

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

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

Activity & mean ionic activity:



Let us say

$a_+ \rightarrow$ activity of M^+

$a_- \rightarrow$ activity of A^-

a = activity of electrolyte

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

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

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

$$(a_{\pm})^{x+y} = \underbrace{a_+^x \cdot a_-^y}_{\text{activities}}$$

for example HCl

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



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

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

We

$$a = \gamma m \quad \begin{array}{l} \nearrow \text{activity co-efficient} \\ \searrow \text{concentration} \end{array}$$

\swarrow activity

$$\begin{array}{l} m_+ \rightarrow x m \quad \text{concentration of cations} \\ m_- \rightarrow y m \quad \text{concentration of anions} \end{array} \quad \begin{array}{l} \nearrow \text{concentration of electrolyte} \\ \searrow \text{concentration of anion} \end{array}$$

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

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

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

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

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

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

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

Significance of Nernst eqn:-

(1) We predict concentration of electrolyte



$$E^{\circ}_{\text{Fe}^{2+}/\text{Fe}} = -0.45 \text{ V}$$

$$E^{\circ}_{\text{Cd}^{2+}/\text{Cd}} = -0.40 \text{ V}$$

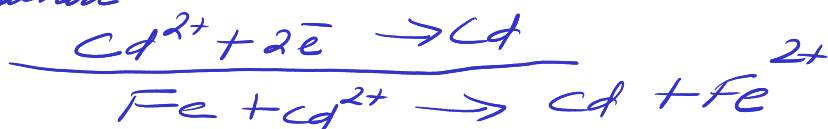
$$E = 0.02 \text{ V @ } 25^{\circ}\text{C}$$

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

@ anode :-



@ Cathode



$$E_{\text{cell}}^{\circ} = E_{\text{cath}} - E_{\text{anod}}$$

$$= -0.40\text{V} - (-0.45\text{V})$$

$$= 0.05\text{V}$$

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

$$0.02 = 0.05 - \frac{0.0592}{2} \log \left[\frac{0.1}{[\text{Cd}^{2+}]} \right]$$

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

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

-1

11

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

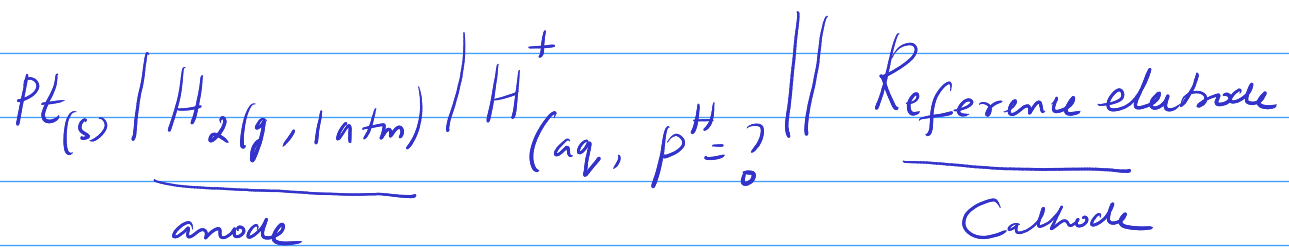
$$- \log([\text{Cd}^{2+}]) = 2.014$$

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

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

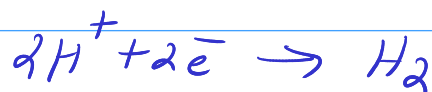
$$[\text{Cd}^{2+}] = 0.00\text{M}$$

2) Calculation of p^H



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

@



activity of gas @ 1 atm
 $a = 1$

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

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

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

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

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

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

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

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

$\Downarrow \text{pH}$

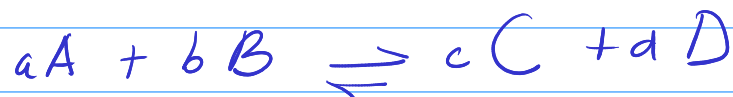
$$E_{\text{cell}} = E_{\text{ref}} + 0.0592 \text{pH}$$

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

if H_2 electrode is used as Cathode.

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

3) Calculation of K



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

(a) equilibrium

$$E = 0$$

$$Q = K$$

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

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

$$K = e^{\left(\frac{n F E^0}{RT} \right)}$$