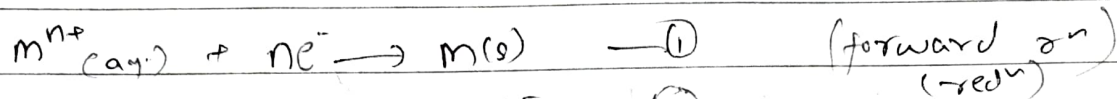


## ★ Nernst Equation

It is a quantitative relationship b/w electrode potential and concentration of the electrolyte species.

- Consider a general redox rxn



we know that  $\Delta G = -nFE$  --- (2)

$$\Delta G^\circ = -nFE^\circ \quad \text{--- (3)}$$

② Standard conditions.  
298K, 1atm, 1M

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

$$\text{for (1), } K = \frac{[M]}{[M^{n+}]} = \frac{1}{[M^{n+}]}$$

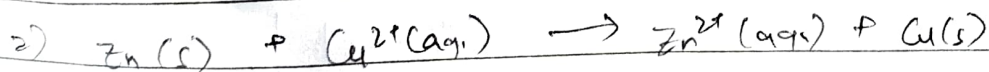
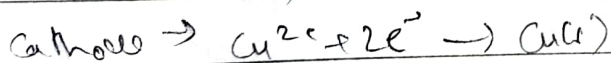
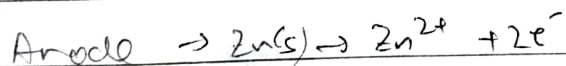
$$\Rightarrow \Delta G = \Delta G^\circ + RT \ln \left( \frac{[M]}{[M^{n+}]} \right)$$

$$-nFE = -nFE^\circ + RT \ln \left( \frac{1}{[M^{n+}]} \right)$$

$$\Rightarrow E = E^\circ - \frac{RT}{nF} \ln \left( \frac{1}{[M^{n+}]} \right) = E^\circ - \frac{2.303 RT}{nF} \log_{10} \left( \frac{1}{[M^{n+}]} \right)$$

$$\text{At } 298K, E = E^\circ - \frac{0.0592}{n} \log_{10} \left( \frac{1}{[M^{n+}]} \right)$$

eg Zn-Cu in CuSO<sub>4</sub>



## \* Energetics of Cell Reactions

- Net Electrical Work performed by the cell reaction of a galvanic cell:

$$W = QE \quad \text{--- (1)}$$

Charge on 1 mol.  $e^-$  is  $F$  (96500) ~~times~~ Coulombs.

When  $n$  moles of  $e^-$ ,  $q = nF$ .

$$\Rightarrow W = nFE \quad \text{--- (2)}$$

But, the cell does net work @ the expense of  ~~$\Delta G$~~   $G$   
( $\Delta G \downarrow$ )

$$\Rightarrow \boxed{\Delta G = -nFE}$$

$$\rightarrow G = H - TS \quad , H = U + PV$$

$$= (U + PV) - TS$$

Differentiating

$$dG = dU + PdV + VdP - TdS - SdT \quad \text{--- (1)}$$

from SL of Thermo,  $dQ_T = dS$

from FL of Thermo,  $dQ = dU + dW$

$$\Rightarrow dU + PdV = TdS$$

$$\Rightarrow dG = dU + PdV + VdP - TdS - SdT \quad \text{--- (2)}$$

$$\Rightarrow dG = dU + PdV + VdP - \overset{dU + PdV}{TdS} - SdT$$

$$\boxed{dG = VdP - SdT} \quad \text{--- (3)}$$

At const.  $P$   $dG = -SdT$

$$\Rightarrow \boxed{\left( \frac{\partial G}{\partial T} \right)_P = -S} \quad \text{--- (4)}$$

Lower SRP  $\rightarrow$  anode  
Lower Higher SRP  $\rightarrow$  cathode

Page No.:

Date:

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

$$\Rightarrow \Delta G = \Delta H - T\Delta S$$
$$= \Delta H + T(-\Delta S)$$

$$\Delta G = \Delta H + T \left( \frac{\partial(\Delta G)}{\partial T} \right)_P \rightarrow \text{Gibbs-Helmholtz Eq}^n$$

$$\Delta G = -nFE$$

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

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

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

we know that  $\left[ \frac{\partial(\Delta G)}{\partial T} \right]_P = -\Delta S$

$$\Rightarrow \Delta S = nF \left( \frac{\partial E}{\partial T} \right)_P$$

Q Calc. Standard EMF of a cell containing  
 $\text{Sn}^{2+}/\text{Sn}$  &  $\text{Br}_2/\text{Br}^-$  electrodes,

$$E^\circ(\text{Sn}^{2+}/\text{Sn}) = -0.14 \text{ V}, E^\circ(\text{Br}_2/\text{Br}^-) = 1.08 \text{ V}$$

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

$$= 1.08 - (-0.14)$$

$$= \boxed{1.22 \text{ V}}$$

Higher SRP  
(cathode)

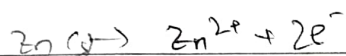
Q Write the electrode rxn, cell rxn & calculate std. EMF @ 298K for the foll. cell: Zn & Fe.

Standard  $E^\circ$  values Zn & Fe are  $-0.76$  &  $-0.44$  V

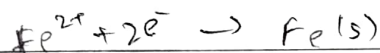
$\Rightarrow$  Zn  $\rightarrow$  anode, Fe  $\rightarrow$  Cathode

$\Rightarrow$  Zn | Zn<sup>2+</sup> || Fe<sup>2+</sup> | Fe  $\rightarrow$  cell rep.

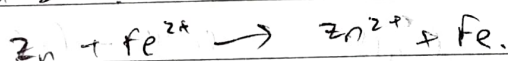
Anode rxn



Cathode



cell rxn:



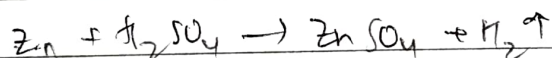
$$\text{EMF of cell} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$= -0.44 - (-0.76)$$

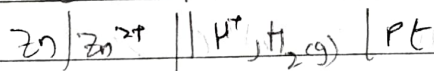
$$= \boxed{0.32}$$

Q Using the Electrochemical series, predict whether Zn & Ag would react with dil. H<sub>2</sub>SO<sub>4</sub> or not.

Rxn of Zn w/ dil. H<sub>2</sub>SO<sub>4</sub>:



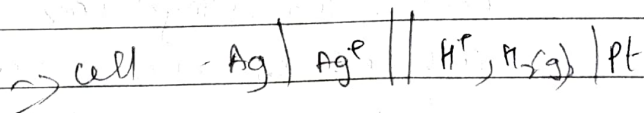
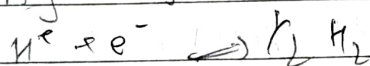
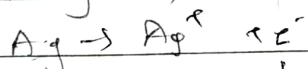
Galvanic cell repn.



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0 - (-0.763) = 0.763 \text{ V}$$

$\therefore E^\circ_{\text{cell}} > 0$   $\Rightarrow$  rxn is feasible.

Rxn of Ag w/ dil. H<sub>2</sub>SO<sub>4</sub>

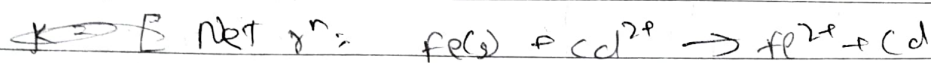
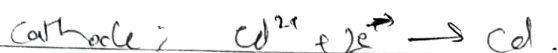
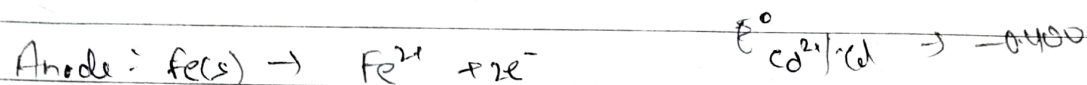


$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0 - (0.80) = -0.80$$

$\therefore E^\circ_{\text{cell}} < 0$ , rxn is not feasible



Q Using electrochemical series, calc. EMF of the cell  
 $\text{Fe(s)} / \text{Fe}^{2+}(0.1\text{M}) \parallel \text{Cd}^{2+}(0.2\text{M}) / \text{Cd}$  @ 298 K. write cell rxn.



$$K = \frac{[\text{Fe}^{2+}]}{[\text{Cd}^{2+}]}$$

$$E^\circ_{\text{cell}} = -0.40 - (-0.44) \\ = 0.04$$

$$E = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln K = 0.04 - \frac{0.0592}{2} \log \left( \frac{[\text{Fe}^{2+}]}{[\text{Cd}^{2+}]} \right)$$

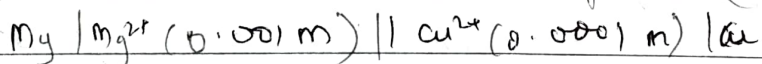
$$E = 0.04 - \frac{0.0592 \times 298}{2 \times 96500}$$

$$= 0.04 - \frac{0.0592}{2} \log_{10} \left[ \frac{0.1}{0.2} \right]$$

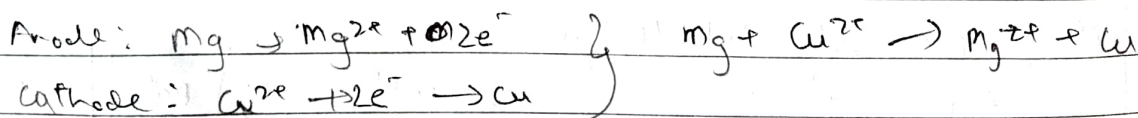
$$= 0.04 - 0.02955 \log_{10} \left( \frac{1}{2} \right)$$

$$= \boxed{0.0488}$$

Q write cell rxn + calc. EMF of cell @ 298 K.



$E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34\text{V}$ ,  $E^\circ_{\text{Mg}^{2+}/\text{Mg}} = -2.37\text{V}$



$$E^\circ_{\text{cell}} = 0.34 - (-2.37) = 2.71$$

$$E^\circ_{\text{cell}} = 2.71 - \frac{0.0591}{2} \log_{10} \left( \frac{0.001}{0.0001} \right)$$

$$= 2.71 - 0.2955 = \boxed{2.4145}$$