Nernst Equation

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

- Consider a general redox r^n

$M^{n+}(aq.) + ne^- \rightarrow M(s)$ — ① (forward r^n) (redn)

we know that $\Delta G = -nFE$ — ②

$\Delta G^0 = -nFE^0$ — ③ @ Standard conditions. 298K, 1atm, 1M

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

for ①, $K = [M]/[M^{n+}] = 1/[M^{n+}]$

$\Rightarrow \Delta G = \Delta G^0 + RT \ln\left([M]/[M^{n+}]\right)$

$-nFE = -nFE^0 + RT \ln\left(1/[M^{n+}]\right)$

$$\Rightarrow \boxed{E = E^0 - \frac{RT}{nF} \ln\left(\frac{1}{M^{n+}}\right) = E^0 - \frac{2.303\,RT}{nF} \log_{10}\left(\frac{1}{[M^{n+}]}\right)}$$

At 298 K, $E = E^0 - \frac{0.0592}{n} \log_{10}\left(1/[M^{n+}]\right)$

eg Zn - Cu in $CuSO_4$

Anode $\rightarrow Zn(s) \rightarrow Zn^{2+} + 2e^-$

Cathode $\rightarrow Cu^{2+} + 2e^- \rightarrow Cu(s)$

$\Rightarrow Zn(s) + Cu^{2+}(aq.) \longrightarrow Zn^{2+}(aq.) + Cu(s)$

Energetics of Cell Reactions

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

$$W = QE \quad - (1)$$

Charge on 1 mol. $\bar{e}$'s is F (96 500) Coulombs.

When n moles of $\bar{e}$'s, $q = nF$.

$\Rightarrow W = nFE \quad - (2)$

But, the cell does net work at the expense of G ($G \downarrow$)

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

→ $G = H - TS$, $H = U + PV$

$= (U + PV) - TS$

Differentiating

$\Delta G = \Delta U + P\Delta V + V\Delta P - T\Delta S - S\Delta T \quad - (1)$

from SL of Thermo, $dQ/T = dS$

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

$= dU + PdV$

$\Rightarrow dU + PdV = TdS \quad - (2)$

$\Rightarrow dG = \cancel{dU} + \cancel{PdV} + VdP - \underbrace{TdS}_{dU + PdV} - SdT$

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

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

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

Lower SRP → anode
~~Lower~~ Higher SRP → cathode

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

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

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

$\Delta G = -nFE$

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

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

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

we know that $[\delta(\Delta G)/\delta T]_P = -\Delta S$

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

Q Calc. Standard EMF of a cell containing Sn^{2+}/Sn & Br_2/Br^- electrodes

$E^\circ(Sn^{2+}/Sn) = -0.14\ V$, $E^\circ(Br_2/Br^-) = 1.08\ V$
↳ Higher SRP (cathode)

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$
$= 1.08 - (-0.14)$
$= \boxed{1.22V}$

Page No.:
Date:

Q. Write the electrode r^n, cell r^n & calc. Std. EMF @ 298K for the foll. cell: Zn & Fe.
Standard E^0 values Zn & Fe are -0.76 & -0.44 V

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

$\Rightarrow Zn | Zn^{2+} || Fe^{2+} | Fe$ $\rightarrow$ cell rep.

Anode r^n

$Zn(s) \rightarrow Zn^{2+} + 2e^-$

Cathode

$Fe^{2+} + 2e^- \rightarrow Fe(s)$

cell r^n:

$Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe.$

EMF of cell $= E^0_{cathode} - E^0_{anode}$
$= -0.44 - (-0.76)$
$= \boxed{0.32}$

Q. Using the Electrochemical series, predict whether Zn & Ag would react with dil. H_2SO_4 or not.

R^n of Zn w/ dil H_2SO_4:

$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2\uparrow$

Galvanic cell rep^n.

$Zn | Zn^{2+} || H^+, H_{2(g)} | Pt$

$E^0_{cell} = E^0_{cathode} - E^0_{anode} = 0 - (-0.763) = 0.763$ V.

$\because E^0_{cell} > 0$, r^n is feasible.

R^n of Ag w/ dil H_2SO_4

$Ag \rightarrow Ag^+ + e^-$

$H^+ + e^- \rightarrow \frac{1}{2} H_2$

$\rightarrow$ cell $Ag | Ag^+ || H^+, H_{2(g)} | Pt$

$E^0_{cell} = E^0_{cathode} - E^0_{anode} = 0 - (0.80) = -0.80$

$\therefore E^0_{cell} < 0$, r^n is not feasible

Q Using electrochemical series, calc. EMF of the cell $Fe(s) / Fe^{2+}(0.1m) \| Cd^{2+}(0.2m) | Cd$ @ 298 K. write cell r^n's.

$E^{\circ}_{Cd^{2+}/Cd} \rightarrow -0.400$

Anode: $Fe(s) \rightarrow Fe^{2+} + 2e^-$

Cathode: $Cd^{2+} + 2e^- \rightarrow Cd$.

Net r^n: $Fe(s) + Cd^{2+} \rightarrow Fe^{2+} + Cd$

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

$E^{\circ}_{cell} = -0.40 - (-0.44)$

$= 0.04$

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

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

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

$= 0.04 - 0.0295 \log_{10}\left(\frac{1}{2}\right)$

$= \boxed{0.0488}$

Q Write cell r^n + calc. EMF of cell @ 298 K.

$Mg / Mg^{2+}(0.001 m) \| Cu^{2+}(0.0001 m) | Cu$

$E^{\circ}(Cu^{2+}/Cu) = 0.34 V$, $E^{\circ}_{Mg^{2+}/Mg} = -2.37 V$

Anode: $Mg \rightarrow Mg^{2+} + 2e^-$

Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$

$Mg + Cu^{2+} \rightarrow Mg^{2+} + Cu$

$E^{\circ}_{cell} = 0.34 - (-2.37) = 2.71$

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

$= 2.71 - 0.02955 = \boxed{2.68045}$