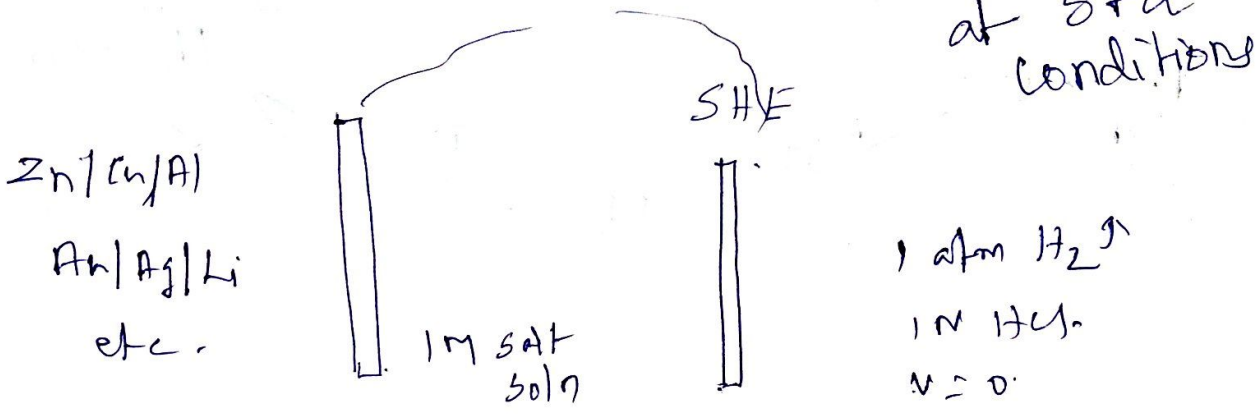
EMF - series

at Std conditions



oxidative ⟶ Zn = 0.76 V

Reductive ⟶ Cu = 0.36 V

Uniformity

Reduction potential (Standard)

Zn ⟶ oxidation potential $E_{Zn/Zn^{2+}} = 0.76$

$[Zn \rightleftarrows Zn^{2+} + 2e^-]$ Reduction potential. $E_{Zn^{2+}/Zn} = -0.76$

Accordingly

Z

Y

X

1.5 An

0.8 Ag

0.36 Cu $Cu^{2+} + 2e^- \rightarrow Cu$

V = 0 SHE $H_2 \rightleftharpoons 2H^+ + e^-$

Reduction Potential increasing order

−0.13 Pb $Pb^{2+} + 2e^- \rightarrow Pb^0$

−0.4 Cd $Cd^{2+} + 2e^- \rightarrow Cd^0$

−0.76 Zn $Zn^{2+} + 2e^- \rightarrow Zn$

−2.71 Ra

−3.5 Li $Li^+ + e^- \rightarrow Li^0$

NERNST EQN

ΔG = Free Energy Change

ΔG = Electrical Energy produced

$\Delta G = -nFE$

Single Electrode + EMF of a cell

↓

Reduction rexn.

$M^{n+} + ne^- \longrightarrow M_{(s)}$ ——— (1)

As per thermodyanamic law

the Free Energy Change

$\Delta G = \Delta G^\circ + RT \ln Q$ ——— (2)

Q = Rxn quotient

$$= \frac{\text{Product of Rxn Products}}{\text{Product of Rxn Reactants}}$$

Eqn - 2 becomes

$$\Delta G = \Delta G^{\circ} + RT \ln \frac{[M]}{[M^{n+}]}$$

Pure solid = 1

$$\Delta G = \Delta G^{\circ} + RT \ln \frac{1}{[M^{n+}]}$$

$$\Delta G = -nFE \; ; \quad \Delta G^{\circ} = -nFE^{\circ}$$

Now

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

$$\div -nF \qquad E = E^{\circ} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

$$E = E^{\circ} - \frac{2.303\,RT}{nF} \log \frac{1}{M^{n+}}$$

Where

$$\frac{2.303\,RT}{F} = 0.0591 \text{ at } 25^{\circ}C$$

$R = 8.31$

$F = 96500$

Thus,

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$

$$E \propto \frac{1}{[M^{n+}]}$$

$$E \propto [M^{n+}]$$

$\downarrow$

Concentration

Ily For EMF

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

$$Q = \frac{\text{Rexn Pdt}}{\text{Rexn React}}$$

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \left(\frac{[C]^c [D]^d}{[A]^a [B]^b} \right)$$

For Example

Zn / Cu

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

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{Zn^{2+}[Cu]_s}{[Zn]_s Cu^{2+}}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$E_{cell} \propto$ Concentrations.