Electrochemistry B.Sc.(II) Sub.
D.B. College (Jaynagar)
Guest Leactuere — Akhilesh Kumar Singh
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9. NERNST EQUATION :

With the help of Nernst equation, we can calculate the electrode potential of electrode or EMF of cell

$$E_{cell} = E^{\circ} - \frac{RT}{nF} \log_e \frac{[Product]}{[Reactant]}$$

where - E° = Standard electrode Potential

R = gas Constant

T = temperature (in K)

F = Faraday (96500 Coulomb mol^{-1})

n = no. of e^- gained or loosed in balanced equation.

or, $$E_{cell} = E^{\circ} - \frac{0.591}{n} \log_{10} \frac{[Product]}{[Reactant]} = E - \frac{0.0591}{n} \log Q$$

Let, in the Cell:

at Anode : $M_1 \longrightarrow M_1^{n+} + ne^-$

for this reaction —

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$$E_{oxi} = E^\circ_{oxi} - \frac{0.0591}{n} \log_{10} \frac{[M_1^{+n}]}{[M_1]} \quad --- (1)$$

at Cathode: $M_2^{+n} + ne^- \rightarrow M_2$

for this reaction —

$$E_{red.} = E^\circ_{red.} - \frac{0.0591}{n} \log_{10} \frac{[M_2]}{[M_2^{+n}]}$$

Note: Concentration of Solid taken as unity. --- (2)

So $[M_1] = [M_2] = 1$

We know that EMF of Cell is

$$EMF = \underset{(Anode)}{E_{oxi}} + \underset{(cathode)}{E_{red}}$$

By adding equation (1) and (2) we get,

$$EMF = E^\circ_{oxi} - \frac{0.0591}{n} \log [M_1^{+n}] + E^\circ_{red} - \frac{0.0591}{n} \log \frac{1}{[M_2^{+n}]}$$

$$= (E^\circ_{oxi} + E^\circ_{red}) - \frac{0.0591}{n} [\log [M_1^{+n}] - \log [M_2^{+n}]]$$

$$EMF = E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[M_1^{+n}]}{[M_2^{+n}]}$$

Ex: The 0.1M copper sulphate solution in which copper electrode is dipped at 25 C. Calculate the electrode potential of copper electrode [Given E° $Cu^{+2}/Cu = 0.34V$]

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

$$E_{red} = E^0_{red} - \frac{0.0591}{n} \log \frac{[Product]}{[Reactant]}$$

here $n = 2$

So $E = 0.34 - \frac{0.0591}{2} \log_{10}$

$= 0.34 - 0.03 = 0.31$ Volts

Ex: The EMF of Cell

$Cr / Cr^{+3} (0.1M) // Fe^{+2} (0.01M) / Fe$

(Given $E\ Cr^{+3}/Cr = -0.75V$

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

Sol.: Half Cell reactions are:

At Anode $- [Cr \rightarrow Cr^{+3} + 3e]\ 2$

At Cathode $- [Fe^{+2} + 2e^- \rightarrow Fe]\ 3$

Over all reaction $2Cr + 3Fe^{+2} \rightarrow 2Cr^{+3} + 3Fe$

E cell = oxidation Pot. + Reduction Pot.

$= 0.75 + (-0.45) = 0.30$

$$E_{cell} = E^\circ - \frac{0.0591}{n} \log \frac{[Product]}{[Reactant]}$$

$$= 0.30 - \frac{0.0591}{6} \log \frac{[Cr^{+3}]^2}{[Fe^{+2}]^3}$$

$$= 0.30 - \frac{0.0591}{6} \log \frac{[0.1]^2}{[0.01]^3}$$

$$= 0.30 - \frac{0.24}{6}$$

$= 0.26$ Volt.