CHEMISTRY STUDY MATERIALS FOR CLASS 12
(NCERT BASED NOTES OF CHAPTER -03)
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Electrochemistry

Nernst Equation

Nernst proposed an equation to relate the electrode potential of an electrode (or, emf of a cell) with the electrolytic concentration.

He showed that for the electrode reaction:

$$M^{n+}_{(aq)} + ne^- \longrightarrow M_{(s)}$$

the electrode potential can be given by:

$$E_{(M^{n+}/M)} = E^0_{(M^{n+}/M)} + \frac{RT}{nF} \ln \frac{[M^{n+}]}{[M]}$$

Since the concentration of any solid is taken as unity, the above equation becomes:

$$E_{(M^{n+}/M)} = E^0_{(M^{n+}/M)} + \frac{RT}{nF} \ln [M^{n+}]$$

Or, $E_{(M^{n+}/M)} = E^0_{(M^{n+}/M)} + \frac{2.303RT}{nF} \log [M^{n+}]$

or, $\boxed{E_{el.} = E^0_{el.} + \frac{2.303RT}{nF} \log [M^{n+}]}$

Where

E^0 is the standard electrode potential; *R* is the gas constant (8.314 $JK^{-1}\,mol^{-1}$).

F is Faraday constant (96500 C mol^{-1}), *T* is temperature in Kelvin and

$[M^{n+}]$ is the concentration of the species, M^{n+}.

In Daniel cell, the electrode reactions are:

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

The electrode potentials are given as

For Cathode:

$$E_{(Cu^{2+}/Cu)} = E^0_{(Cu^{2+}/Cu)} + \frac{RT}{2F} \ln [Cu^{2+}]$$

For anode: $E_{(Zn^{2+}/Zn)} = E^0_{(Zn^{2+}/Zn)} + \frac{RT}{2F} \ln [Zn^{2+}]$

The cell potential, $E_{cell} = E_{(Cu^{2+}/Cu)} - E_{(Zn^{2+}/Zn)}$

$$= \{E^0_{(Cu^{2+}/Cu)} + \frac{RT}{2F} \ln [Cu^{2+}]\} - \{E^0_{(Zn^{2+}/Zn)} + \frac{RT}{2F} \ln [Zn^{2+}]\}$$

$$= [E^0_{(Cu^{2+}/Cu)} - E^0_{(Zn^{2+}/Zn)}] + \frac{RT}{2F} \ln \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

Or, $$E_{cell} = E^0_{cell} + \frac{RT}{2F} \ln \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

On changing the base of logarithm, we get

$$E_{cell} = E^0_{cell} + \frac{2.303RT}{2F} \log \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

On substituting the values of R (8.314 $JK^{-1} mol^{-1}$), *F* (96500 C mol^{-1}) at 298K, the above equation becomes,

$$E_{cell} = E^0_{cell} + \frac{0.0591}{2} \log \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

For a general electrochemical reaction of the type:

$$aA + bB -- ne^- - \rightarrow cC + dD$$

Nernst equation can be written as:

$$\boxed{E_{cell} = E^0_{cell} + \frac{0.0591}{n} \log \frac{[A]^a[B]^b}{[C]^c[D]^d}}$$

Equilibrium Constant from Nernst Equation

For a Daniel cell, the emf of the cell at 298K is given by:

$$E_{cell} = E^0_{cell} + \frac{0.0591}{2} \log \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

When the cell reaction attains equilibrium, $E_{cell} = 0$

So, $$0 = E^0_{cell} + \frac{0.0591}{2} \log \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

Or, $$E^0_{cell} = -\frac{0.0591}{2} \log \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

$$= \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

But at equilibrium, $\frac{[Zn^{2+}]}{[Cu^{2+}]} = Kc$

So the above equation becomes,

$$E^0_{cell} = \frac{0.0591}{2} \log Kc$$

In General, $$E^0_{cell} = \frac{2.303RT}{nF} \log Kc$$

or, $$\boxed{E^0_{cell} = \frac{0.0591}{n} \log Kc \text{ at } 298\,K}$$

Electrochemical Cell and Gibbs Energy of the Reaction

Electrical work done in one second is equal to electrical potential multiplied by total charge passed. Also the reversible work done by a galvanic cell is equal to decrease in its Gibbs energy. Therefore, if the emf of the cell is *E* and *nF* is the amount of charge passed,

then the Gibbs energy of the reaction, $\Delta G = -nFE_{cell}$

If the concentration of all the reacting species is unity, then $E_{cell} = E^0_{cell}$.

So, $\Delta G^0 = -nFE^0_{cell}$

Thus, from the measurement of E^0_{cell}, we can calculate the standard Gibbs energy of the reaction.

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