Lecture No - 33

Electrochemistry

Nernst Equation and Applications

The electrode potential of an electrode depends upon the concentration of the electrolyte solution and the temperature.

~~Standard~~ When the concentration of an electrolyte solution is fixed at 1 M and the temperature is 298 K, the electrode potential is termed as the standard electrode potential.

Nernst equation gives the relationship between the electrode potential and the concentration of the electrolyte solutions.

Consider a general cell reaction -

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

For a reversible reaction, the free energy change (ΔG) and its equilibrium constant (K) are related by the Vant's Hoff reaction isotherm as -

$$\Delta G = RT \ln K + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$= \Delta G^\circ + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]} \quad \text{-----} (1)$$

where - $\Delta G^\circ \Rightarrow$ Standard Free energy (i.e. the change in free energy when the concentration of the reactants and products are unity)

R → Gas constant

T → Temperature

The electrical energy produced at the expense of the decrease in free energy, i.e.

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

<u>where</u>. $n \rightarrow$ no of electrons liberated at one electrode.

$F \rightarrow$ Faraday's Constant

$E \rightarrow$ Electrode Potential

$E^\circ \rightarrow$ Standard electrode potential

Substituting the values in eq.-(1).

$$-nFE = -nFE^\circ + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$\boxed{E = E^\circ - \frac{2.303\,RT}{nF} \log \frac{[\text{Product}]}{[\text{Reactant}]}} \quad \text{---} (2)$$

Eq. (2) is called the Nernst equation and gives the dependence of electrode potential on the concentration of the electrolyte.

AT - $T = 298\,K$, $F = 96500$ coulombs, $R = 8.314\ J K^{-1} mol^{-1}$

eq. (2) will be -

$$E = E^\circ - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log \frac{[\text{Product}]}{[\text{Reactant}]}$$

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

For the cell reaction -

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

the eq^n becomes -

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[M_{(s)}]}{[M^{n+}_{(aq)}]}$$

For Pure Solids $[M_{(s)}] = 1$

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

$$E = E^\circ + \frac{0.0591}{n} \log [M^{n+}_{(aq)}]$$

For a cell reaction -

$$aA + bB \longrightarrow cC + dD$$

the eq^n becomes -

$$\cancel{E = E^\circ - \frac{0.0591}{n}}$$

$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Applications of Nernst Equation

(1). **Calculation of cell potential of the cell** - This eqⁿ is used to calculate the cell potential at given electrolytic concentration.

$C_1 \rightarrow$ conc of anodic electrolyte
$C_2 \rightarrow$ conc of cathodic electrolyte

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[C_1]}{[C_2]}$$

(2). **Calculation of equilibrium constant** - This eq. can be used to find K_c.

For a reaction $aA + bB \longrightarrow cC + dD$

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

$K_c \rightarrow$ equilibrium constant.

By Nernst eq.

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

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log K_c$$

At equilibrium $E_{cell} = 0$,

$$0 = E^\circ_{cell} - \frac{0.0591}{n} \log K_c$$

$$\boxed{\log K_c = \frac{n E^\circ_{cell}}{0.0591}}$$ at equilibrium

(3) To find the concentration of one ionic species in a cell if the concentration of the other species is known.

(4) To find the pH of a solution.

$$-\log[H^+] = pH$$