19CH201 - ENGINEERING CHEMISTRY

UNIT-1 - ELECTROCHEMISTRY

1.2 Electrode potential - Nernst equation and problems

Single electrode potential (E)

It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt.

Standard electrode potential (E°)

It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of 1 molar concentration at 25°C.

Nernst equation for electrode potential

Consider the following redox reaction

$$M^{n+} + ne^- \longrightarrow M$$

For such a redox reversible reaction, the free energy change (ΔG) and its equilibrium constant (K) are inter related as

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

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

where,

ΔG° = Standard free energy change

The above equation (1) is known as Van't Hoff isotherm. The decrease in free energy (− ΔG) in the above reaction involves transfer of 'n' number of electrons, then 'n' faraday of electricity will flow. If E is the emf of the cell, then the total electrical energy (nEF) produced in the cell is

$$-\Delta G = nEF$$

or)

$$-\Delta G^\circ = nE^\circ F \quad \text{........ (2)}$$

where,

$-\Delta G$ = decrease in free energy change.

(or) $-\Delta G°$ = decrease in standard free energy change. Comparing equation 1 and 2, it becomes

$$-nEF = -nE°F + RT \ln \frac{[M]}{[M^{n+}]} \quad ....(3)$$

Dividing the above equation (3) by $-nF$

[the activity of solid metal [M] = 1]

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

$$\text{In general, } E = E° - \frac{RT}{nF} \ln \frac{[Product]}{[Reactant]}$$

(or)

$$E = E° + \frac{RT}{nF} \ln [M^{n+}]$$

(or)

$$E = E^o + \frac{2.303RT}{nF} \log[M^{n+}]$$

When, R = 8.314 J/K/mole; F = 96500 coulombs ;

T = 298 K (25°C), the above equation becomes

$$E = E^o_{red} + \frac{0.0591}{n} \log[M^{n+}]$$

In general,

$$E = E^o_{oxi} + \frac{0.0591}{n} \log C$$

Similarly for oxidation potential

$$E = E^o_{oxi} + \frac{0.0591}{n} \log[M^{n+}]$$

The above equation 5&6 are known as "Nernst equation for single electrode potential".

Applications of Nernst equations

Nernst equation is used to calculate electrode potential of unknown metal.

Corrosion tendency of metals can be predicted.