NERNST EQUATION FOR ELECTRODEPOTENTIAL

Consider the following electrode reaction:aq

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

The emf of a reversible cell can be measured by free energychange (ΔG) of a reaction takes place in the reversible cell. Ifthe reaction involves the transfer of 'n' electrons, 'F' Faradays of electricity will flow and E is the emf of the cell, then the totalelectrical energy produced by the cell is given by followingequation

$$-\Delta G = n FE \ldots\ldots (1)$$

Where, -ΔG is decrease in free energy change.

In other way,

$$-\Delta G^0 = n FE^0 \cdots\cdots (2)$$

Where, $-\Delta G^0$is standard free energy change and Eo is thestandard emf of a cell.

For a reversible reaction, the interrelationship of free energy change and equilibrium constant (K) is given by the following gequation :

$$-\Delta G = -\Delta G^0 + RT ln\ K \ldots\ldots (3)$$

It can be written as,

$$-\Delta G = -\Delta G^0 + RT ln\ [Product] / [Reactant] \ldots. (4)$$

The equation (4) is called as Van't Hoff isotherm.

Substituting the value of products and reactants inequation (4), we get

$$\Delta G = \Delta G^0 + RT ln\ [M] / [M^{n+}] \ldots. (5)$$

Substituting the equation (1) and (2) in (5), we get

$$nFE_{red} = nFE^0_{red} + RT\ ln\ [M] / [M^{n+}] \ldots\ldots (6)$$

$$E_{red} = \frac{nFE^0_{red}}{nF} + \frac{RT\ ln\ [M]}{nF\ [M^{n+}]}$$

$$E_{red} = E^0_{red} + \frac{RT\ ln\ [M]}{nF\ [M^{n+}]} \ldots. (7)$$

$$E_{red} = E^0_{red} + \frac{2.303RT\ log\ [M]}{nF\ [M^{n+}]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

T = 298 K

R = 8.314 J K^{-1} mol^{-1}

F = 96500 coulombs [M] = 1
Substituting all the values in equation (8), we get

$$E_{red} = E^0_{red} + \frac{0.0591}{n} \log \frac{1}{[M^{n+}]} \quad \text{.....(9)}$$

This equation is known as the Nernst equation

$$E_{red} = E^0_{red} - \frac{0.0591}{n} \log [M^{n+}] \quad \text{..... (10)}$$

Nernst equation for this equation is the reduction potential of single electrode
Consider the following oxidation reaction:

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

Then, the Nernst equation (10) becomes

$$E_{oxi} = E^0_{red} + \frac{0.0591}{n} \log [M^{n+}] \quad \text{..... (11)}$$

Equation (11) is Nernst equation for oxidation potential of single electrode.

Applications of Nernst Equation

- It is used to calculate the emf of a given cell.
- It is also used to calculate the electrode potential of a given
- Corrosion tendency of metals can be predicted.
- Spontaneity of a given cell reaction can be predicted.