

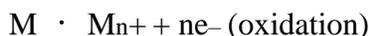


ELECTRODE POTENTIAL

Origin of electrode potential - Nernst's solution pressure theory.

Nernst's theory of electrode potential explains how electrode potential develops. According to this theory, a metal (M) consists of metal ions (M_{n+}) with valence electrons. When the metal (M) is placed in its own salt solution, any one of the following reactions occurs.

(i) Metal passes into the solution as metal ion with the liberation of electrons.



(ii) Positive metal ion from the solution may deposit over the metal.



Examples:

1) When a zinc rod is dipped in a zinc sulphate solution, due to the solution pressure of the metal, zinc passes into the solution as Zn^{2+} ions. Now, the zinc electrode attains a negative charge, due to the accumulation of valence electrons on the metal. The negative charge developed on the electrode attracts the positive ions from the solution. Due to this attraction, the positive ions remain close to the metal.

2) When a copper rod is dipped in a copper sulphate solution, due to the osmotic pressure of the solution, Cu^{2+} ions deposit over the metal. Now, the copper electrode attains a positive charge, due to the accumulation of Cu^{2+} ions on the metal. The positive charges developed on the electrode attract negative ions from the solution. Due to this attraction, the negative ions remain close to the metal. Thus, a sort of layer (positive or negative ions) is formed all around the metal. This layer is called the Helmholtz electrical double layer. This layer prevents further passing of positive ions from the metal or deposition of positive ions from the solution. A difference of potential is consequently set up between the metal and the solution. At equilibrium, the potential difference becomes a constant value, which is known as the electrode potential of a metal.

Thus, *the tendency of an electrode to lose electrons is called the oxidation potential and the tendency of an electrode to gain electrons is called the reduction potential.*

Single Electrode Potential (E)

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

Standard Electrode Potential (E_0)

It is the tendency of a metallic electrode to lose or gain electrons, when it is dipped in its one molar own salt solution at $25^\circ C$.



Measurement of Single Electrode Potential

It is impossible to determine the absolute value of single electrode potential. But, we can measure the potential difference between two electrodes potentiometric ally by combining them to form a complete cell. For this purpose, reference electrode is used. Standard hydrogen electrode (SHE) is the commonly used reference electrode whose potential has been arbitrarily fixed as zero. The emf of the cell is measured and it is equal to the potential of single electrode.

NERNST EQUATION FOR ELECTRODE POTENTIAL

Consider the following electrode reaction: aq



The emf of a reversible cell can be measured by free energy change (ΔG) of a reaction takes place in the reversible cell. If the reaction involves the transfer of 'n' electrons, 'F' Faradays of electricity will flow and E is the emf of the cell, then the total electrical energy produced by the cell is given by following equation

$$-\Delta G = n FE \quad \text{.....(1)}$$

Where, $-\Delta G$ is decrease in free energy change.

In other way,

$$-\Delta G^0 = n FE^0 \quad \text{.....(2)}$$

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

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

$$\Delta G = \Delta G^0 + RT \ln K \quad \text{.....(3)}$$

It can be written as,

$$\Delta G = \Delta G^0 + RT \ln [\text{Product}] / [\text{Reactant}] \quad \text{.....(4)}$$

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

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

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

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

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

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

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



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

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

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

This equation is known as the Nernst equation

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

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



Then, the Nernst equation (10) becomes

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

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.