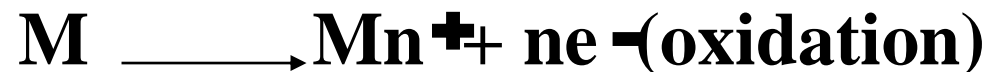# ELECTRODE POTENTIAL

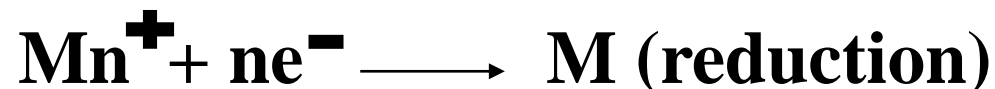## ORIGIN OF ELECTRODE POTENTIAL

A metal (M) consists of metal ions (Mn+) with valence electrons when the metal (M) is placed in a solution of its own salt , any one of the following reactions will occur

1.Positive metal ions may pass into the solutions.

$$M \longrightarrow Mn^+ + ne^- \text{(oxidation)}$$

2.Positive metal ions from the solution may deposit over the metal

$$Mn^+ + ne^- \longrightarrow M \text{ (reduction)}$$

Example 1)Zn electrode dipped in $ZnSo_4$ solution .

When Zn electrode id dipped in $ZnSo_4$ solution , Zn goes into the solution as Zn2+ ions due to oxidation .

$$Zn \longrightarrow Zn2+ + 2e-$$

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Now the Zn electrode attains a negative charge ,due to the accumulation of valence electrons on the metal . The negative changes developed on the electrode attracts the positive ions solution. Due to   this attraction the positive ions remain close to the metal.

➡ Cu ELECTRODE DIPPED IN CuSo4 SOLUTION

 When Cu electrode is dipped in CuSo4 solution,Cu2+ ions from the solution deposit over the metal due to reduction
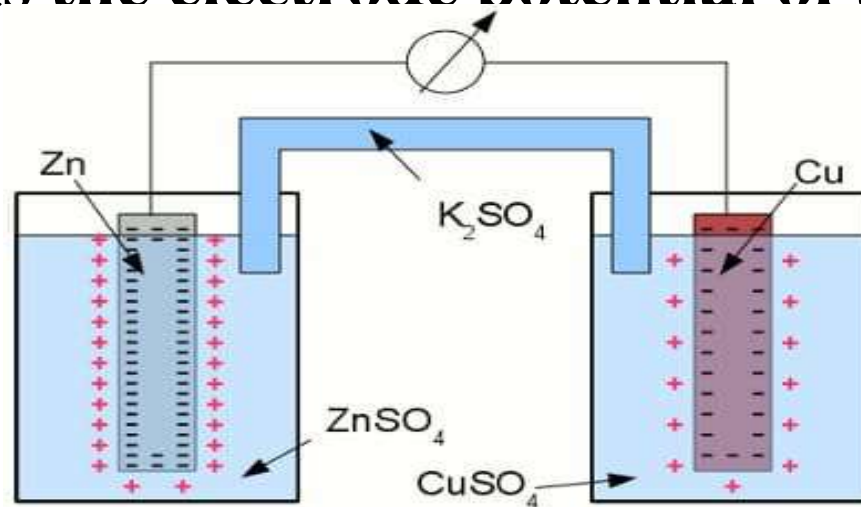
$$Cu \rightleftharpoons Cu^{2+} + 2e^-$$

Now ,the Cu electrode attains a positive charge ,due to the accumulation of Cu2+ ions thye metal .The positive charge charges developed on the electrode attract the negative ions from the solution due to this attraction the negative ions remain close to the metal.

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➡Zn electrode in ZnSo4 solution

Thus , a sort of layer (+)or (-) ions is formed all around the metal . This layer is called Helmholtz electrical double layer .This layer prevents passing of the positive ions form or to the metal . A difference of potential is consequently set up between the metal and the solution .

At equilibrium ,the potential difference between constant value , which is known as the electrode potential of a metal

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OXIDATION POTENTIAL

If oxidation occurs at the electrode ,at equilibrium ,the potential of the electrode is oxidation potential . The tendency of an electrode to lose electrons is oxidation potential.

REDUCTION POTENTIAL

The tendency of an electrode to gain electrons is called reduction potential.

SINGLE ELECTRODE POTENTIAL(E)

It is a measure of tendency of a metallaic electrodes to lose or gain electrodes , when it is in contact with a solution of its own salt.

STANDARD ELECTRODE POTENTIAL   E$^{\circ}$)

The tendency of a metallic electrodes to lose or gain electrodes when it is in contact with a solution of its own salt of 1 molar concentration at 25° c.

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NERNST EQUATION

Consider the following electrode reaction

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

The emf of a reversible cell can be measured by few energy change (Δ_G) 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

$$-\Delta G = -nFE \qquad\qquad\qquad \dots\dots\dots.1$$

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

In other way,

$$\Delta G^0 = nFE^0 \; \boldsymbol{or} \; \Delta G^0 = nFE^0 \qquad \dots\dots\dots\dots\dots 2$$

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

$$-\Delta G = -\Delta G^0 + RT \ln K$$

$$\Delta G = -RT \ln K + RT ln \frac{[product]}{[reactant]}$$

But $\quad \Delta G^0 = -RT \ln k$

Sub

$$\Delta G = \Delta G^0 + RT ln \frac{[product]}{[reactant]}$$

- Where,
- E_0 denotes the cell potential
- F is the Faraday constant

$- \text{nFE}_{\text{red}} = - \text{nFE}°_{\text{red}} + \text{RT} \ln [product] / [reactant]$

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$$- nEF = - nE°F + RT \ln [M]/ [Mn+] \ldots\ldots (3)$$

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

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

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

In general, $E = E° - RT \, nF \ln [Product]/[Reactant]$

$$(or) \; E = E° + 2.303RT/nF \log [Mn+] \text{-----------------}(4)$$

When, R = 8.314 J/K/mole; F = 96500 coulombs; T = 298 K (25°C), the above equation becomes

$$E = E^0 \, red + \frac{0.0591 \log [Mn+]}{n} \text{——————} (5)$$

$$E = E^0 \, oxi - \frac{0.0591 \log [Mn+]}{n} \text{————} (6)$$

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

Applications of Nernst equations

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

2. Corrosion tendency of metals can be predicted.

3. It is used to calculate the EMF of a cell.

4. pH of a solution can be calculated by measuring emf

. 5. Concentration of solution in galvanic cell can be determined