



SNS COLLEGE OF TECHNOLOGY (An Autonomous Institution)



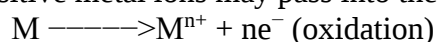
Electrode potential

Empathy question:

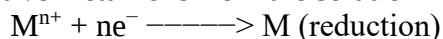
1. How chemical reactions occur in electrochemical cells, such as batteries, fuel cells, and corrosion processes.

A metal (M) consists of metal ions (M^{n+}) 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.



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



Example 1) Zn electrode dipped in $ZnSO_4$ solution.

When Zn electrode dipped in $ZnSO_4$ solution, Zn goes into the solution as Zn^{2+} ions due to oxidation.



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

→ Cu electrode dipped in $CuSO_4$ Solution

When Cu electrode is dipped in $CuSO_4$ solution, Cu^{2+} ions from the solution deposit over the metal due to reduction



Now, the Cu electrode attains a positive charge, due to the accumulation of Cu^{2+} ions on the metal. The positive charges developed on the electrode attract the negative ions from the solution due to this attraction the negative ions remain close to the metal.

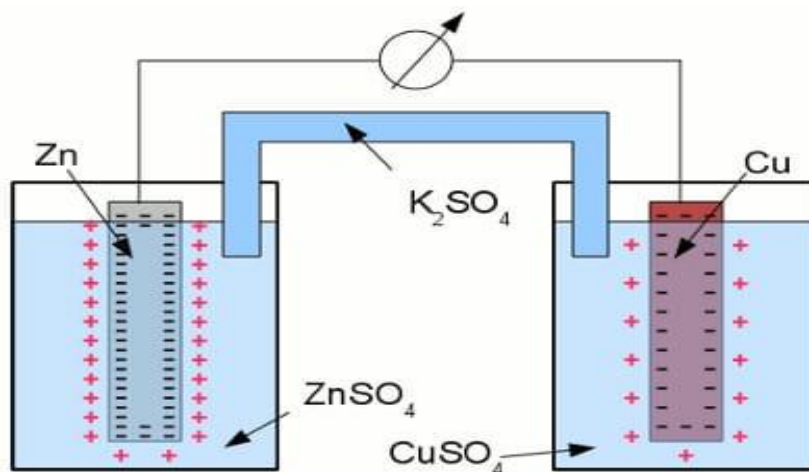
→ Zn electrode in $ZnSO_4$ solution

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 from 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 metallic electrodes to lose or gain electrons, when it is in contact with a solution of its own salt.

STANDARD ELECTRODE POTENTIAL (E)

The tendency of metallic electrodes to lose or gain electrons when it is in contact with a solution of its own salt of 1 molar concentration at 298K

NERNST EQUATION FOR ELECTRODE POTENTIAL

Empathy Question:

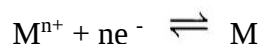
1. Studying the Nernst equation is important because it provides crucial insights into the behavior of ions in electrochemical systems and biological membranes.
2. Here's why it's essential and where it's applied?
3. To understand how neurons communicate and generate electrical signals.
4. To predict how different ion concentrations in the electrolytes affect the voltage and efficiency of these devices.



5. Corrosion: To assess and mitigate the effects of ion concentration on the corrosion of metals and materials.

Nernst equation for electrode potential

Consider the following redox reaction



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

$$\begin{aligned}\Delta G &= -RT \ln K + RT \ln \frac{[Product]}{[Reactant]} \\ &= \Delta G^{\circ} + RT \ln \frac{[Product]}{[Reactant]} \quad \text{..... (1)}\end{aligned}$$

where,

ΔG° = Standard free energy change

The above equation (1) is known as ***Van't Hoff isotherm***. The decrease in free energy ($-\Delta G$) 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

$$\begin{aligned}-\Delta G &= nEF \\ \text{(or)} \\ -\Delta G^{\circ} &= nE^{\circ}F \quad \text{..... (2)}\end{aligned}$$

where,

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

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

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

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

[Activity of solid metal $[M] = 1$]

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



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

(or)

$$E = E^\circ + \frac{2.303RT}{nF} \log [M^{n+}] \text{ -----(4)}$$

When, $R = 8.314 \text{ J/K/mole}$; $F = 96500 \text{ coulombs}$; $T = 298 \text{ K (25}^\circ\text{C)}$, the above equation becomes

$$E = E^\circ_{\text{red}} + \frac{0.0591}{n} \log [M^{n+}] \text{ -----(5)}$$

$$E = E^\circ_{\text{oxi}} - \frac{0.0591}{n} \log C$$

$$E = E^\circ_{\text{oxi}} - \frac{0.0591}{n} \log [M^{n+}] \text{ -----(6)}$$

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.

PROBLEM BASED ON NERNST EQUATION

Calculate the reduction potential of lead electrode in contact with a solution of 0.015M Pb^{2+} ions.

($E^\circ = -0.13 \text{ volt}$)

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Standard Oxidation potential is given as $\text{Pb}^{2+} + 2 \text{e}^- \rightarrow \text{Pb}$; $E^\circ = -0.13\text{v}$

Concentration of $\text{Pb}^{2+} = 0.015\text{M}$

Solution

The Nernst equation for reduction potential is

$$E = E^\circ_{\text{red}} + \frac{0.0591}{n} \log (\text{Pb}^{2+})$$

$$E = -0.13 + \frac{0.0591}{2} \log (0.015)$$

$$E = -0.1839\text{V}$$

Oxidation potential of Pb = -0.1839V