23CHT101-Engineering Chemistry

Unit- I Electrochemistry

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

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

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

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

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

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) $- \Delta G^\circ$ = 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]

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

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

(or)

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

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

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

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

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

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^0 = -0.13 volt)

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Standard Oxidation potential is given as $Pb^{2+} + 2e^- \rightarrow Pb$; E^0 = -0.13v

Concentration of Pb^{2+} = 0.015M

Solution

The Nernst equation for reduction potential is

$$E = E^0_{red} + 0.0591/n \log(Pb^{2+})$$

$$E = -0.13 + .o2955(-1.824)$$

$$E = -0.1839V$$

Oxidation potential of Pb = -0.1839V