



## **19CH201 - ENGINEERING CHEMISTRY**

### **UNIT-1 - ELECTROCHEMISTRY**

#### **1.2 Electrode potential - Nernst equation and problems**

##### **Single electrode potential (E)**

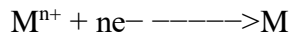
It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt.

##### **Standard electrode potential (E°)**

It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of 1 molar concentration at 25°C.

##### **Nernst equation for electrode potential**

Consider the following redox reaction



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

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

where,

$$\Delta G^{\circ} = \text{Standard free energy change}$$

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

$$-\Delta G = nEF$$

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

$$- nEF = - nE^\circ F + RT \ln \frac{[M]}{[M^{n+}]}$$

.....(3)

Dividing the above equation (3) by - nF

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

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

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

(or)

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

(or)

$$E = E^\circ + \frac{2.303RT}{nF} \log[M^{n+}]$$

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

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

In general,

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

Similarly for oxidation potential

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

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



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### Applications of Nernst equations

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

Corrosion tendency of metals can be predicted.



## **SNS COLLEGE OF ENGINEERING**

**Kurumbapalayam(Po), Coimbatore - 641 107**

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