

4.4 SOME DEFINITIONS

4.4.1 Electrode Potential

The tendency of the electrode to lose or gain electrons which it is in contact with its own ions in the electrolytic solution is called electrode potential.

4.4.2 Oxidation Potential

It is defined as the tendency of the electrode to lose electrons with respect to normal hydrogen electrode.

4.4.3 Reduction Potential

It is defined as the tendency of the electrode to gain electrons with respect to normal hydrogen electrodes.

4.4.4 Standard Electrode Potential

If in the half cell, the metal rod is suspended in a solution of unit activity and the temperature is maintained at 25°C, the electrode potential is called Standard Electrode Potential.

It is a common practice to express all the electrode potentials as reduction potentials since the reduction half reaction is always just the reverse of the oxidation half reaction. Therefore, reduction potential is obtained from the oxidation potential by simply changing the sign.

i.e. \checkmark Reduction potential = - Oxidation potential

4.5 EMF OF A CELL

EMF means electromotive force. The force which causes the flow of electrons from one electrode to the other and thus results in the flow of current is called electromotive force. EMF is measured in *volts*.

This flow of the electrons mentioned above is because of difference in electrode potential of the two electrodes. As one with oxidation potential results into oxidation, which means release of electrons. The other electrode with reduction potential, accepts these electrons and hence flow of electrons takes place. Hence electromotive force can also be defined as the difference of potential which causes the current to flow from an electrode at higher potential to an electrode at a lower potential. If all the reactants and products are present in their standard state at 25°C, the EMF is called standard EMF. EMF is usually represented as 'E'.

EMF of the cell is sum of the oxidation potential of the electrode where oxidation takes place and reduction potential of the electrode where reduction takes place.

EMF of the cell = Oxidation potential of the oxidation half reaction

+ Reduction potential of the reduction half reaction

Standard EMF of the cell = Standard oxidation potential of the oxidation half reaction

+ Standard reduction potential of the reduction half reaction

4.8 ELECTROCHEMICAL SERIES

The standard electrode potentials of large number of electrodes have been determined using standard hydrogen electrode as reference electrode. (Electrode potential for SHE is arbitrarily fixed as zero). Electrode potential is expressed as reduction potential conventionally. The various electrodes have thus been arranged in order of their increasing values of standard reduction potential as shown in Table 4.1. This arrangement is called Electrochemical series.

If at an electrode reduction takes place w.r.t. SHE, its standard reduction potential is given positive sign. If at an electrode, oxidation takes place w.r.t. SHE, its standard reduction potential is given negative sign.

Table 4.1 Electrochemical series standard reduction potential at 25°C.

Reduction half-reaction	Standard Reduction Potential E° (in volts)
$\text{Li}^+ + e^- \longrightarrow \text{Li}$	-3.05
$\text{K}^+ + e^- \longrightarrow \text{K}$	-2.93
$\text{Ba}^{2+} + 2e^- \longrightarrow \text{Ba}$	-2.90
$\text{Ca}^{2+} + 2e^- \longrightarrow \text{Ca}$	-2.87
$\text{Na}^+ + e^- \longrightarrow \text{Na}$	-2.71
$\text{Mg}^{2+} + 2e^- \longrightarrow \text{Mg}$	-2.37
$\text{Al}^{3+} + 3e^- \longrightarrow \text{Al}$	-1.66
$\text{Mn}^{2+} + 2e^- \longrightarrow \text{Mn}$	-1.18
$\text{Zn}^{2+} + 2e^- \longrightarrow \text{Zn}$	-0.76
$\text{Cr}^{3+} + 3e^- \longrightarrow \text{Cr}$	-0.74
$\text{Fe}^{2+} + 2e^- \longrightarrow \text{Fe}$	-0.44
$\text{Cd}^{2+} + 2e^- \longrightarrow \text{Cd}$	-0.40
$\text{PbSO}_4 + 2e^- \longrightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.31
$\text{Co}^{2+} + 2e^- \longrightarrow \text{Co}$	-0.28
$\text{Ni}^{2+} + 2e^- \longrightarrow \text{Ni}$	-0.25
$\text{Sn}^{2+} + 2e^- \longrightarrow \text{Sn}$	-0.14
$\text{Pb}^{2+} + 2e^- \longrightarrow \text{Pb}$	-0.13
$2\text{H}^+ + 2e^- \longrightarrow \text{H}_2$	0.00
$\text{Sn}^{4+} + 2e^- \longrightarrow \text{Sn}^{2+}$	0.13
$\text{Cu}^{2+} + e^- \longrightarrow \text{Cu}^+$	0.15
$\text{AgCl} + e^- \longrightarrow \text{Ag} + \text{Cl}^-$	0.22
$\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$	0.34
$\text{I}_2 + 2e^- \longrightarrow 2\text{I}^-$	0.53
$\text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{2+}$	0.77
$\text{Ag}^+ + e^- \longrightarrow \text{Ag}$	0.80
$\text{Br}_2 + 2e^- \longrightarrow 2\text{Br}^-$	1.09

4.9 NERNST EQUATION FOR ELECTRODE POTENTIAL AND CELL EMF

If in a reversible cell, the cell reaction is represented as :



The free energy change of this reaction is given as :

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_X^x \cdot a_Y^y \dots}{a_A^a \cdot a_B^b \dots}$$

$$T = 298 \text{ K}$$

ΔG = Free energy change

ΔG° = Standard free energy change

R = Gas constant = $8.314 \text{ K}^{-1} \text{ mol}^{-1}$

a_A, a_B, a_X, a_Y etc. represents activities of A, B, X and Y in any state other than standard state. Transference of 1 mole of electrons corresponds to flow of 1 F (faradays) of electricity and transference of n moles of electrons corresponds to flow of nF , faradays of electricity. If E is the EMF of the cell, then electrical energy produced in the cell = nFE .

$$1F = 96500 \text{ C}$$

As electrical energy produced is equal to the decrease in free energy ($-\Delta G$) of the cell reaction.

Hence

$$-\Delta G = nFE \quad \dots(2)$$

and

$$-\Delta G^\circ = nFE^\circ \quad \dots(3)$$

E° = standard EMF of the cell

Substituting the value of ΔG and ΔG° from (2) and (3) in equation (1).

$$-nFE = -nFE^\circ + RT \ln \frac{a_X^x \cdot a_Y^y \dots}{a_A^a \cdot a_B^b \dots}$$

$$E = E^\circ + \left(\frac{1}{-nF} \right) RT \ln \frac{a_X^x \cdot a_Y^y}{a_A^a \cdot a_B^b}$$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_X^x \cdot a_Y^y \dots}{a_A^a \cdot a_B^b \dots} \quad \dots(4)$$

Equation (4) is called Nernst Equation for calculation of EMF of the cell.

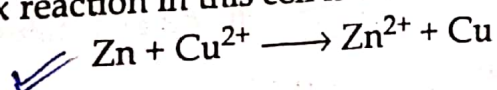
In terms of concentrations

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[X]^x [Y]^y}{[A]^a [B]^b}$$

$[X]$ represents concentration of X.

Activities and Concentrations of pure liquids and pure solids are taken as unity

How to apply Nernst equation? To answer this question let us take one example of Daniell cell. The redox reaction in this cell is :



Here $n = 2$

So, Nernst equation is

$$E = E^\circ - \frac{RT}{2F} \ln \frac{[\text{Zn}^{2+}][\text{Cu}]}{[\text{Zn}][\text{Cu}^{2+}]} = E^\circ - \frac{RT}{2F} \ln K$$

$$[\text{Cu}] = 1 \text{ and } [\text{Zn}] = 1$$

$$E = E^\circ - \frac{0.0591}{2} \log K$$

[Conc. of pure solids is unity]

$$E = E^\circ - \frac{RT}{2F} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

4.9.1 Applications of Nernst Equation

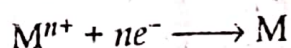
(i) In Calculation of EMF of a Cell

Nernst equation is very helpful in calculation of EMF of a cell (as explained above by taking example of Daniell cell).

(ii) In Calculation of Single Electrode Potential

For any type of reversible electrodes, the expression for electrode potential can be derived from Nernst equation. In this case, E° will refer to standard electrode potential. We know that by saying standard electrode potential we mean standard reduction potential. Hence to apply Nernst equation for electrode potential, the electrode reaction must be written as reduction reaction.

For any metal electrode, consisting of metal in equilibrium with its ions (M^{n+}), the electrode reaction written as reduction is



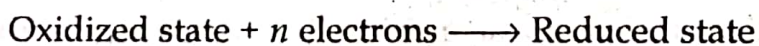
Hence electrode potential can be written as :

$$E_{M^{n+},M} = E^\circ_{M^{n+},M} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

$$[M] = 1$$

$$E_{M^{n+},M} = E^\circ_{M^{n+},M} + \frac{RT}{nF} \ln \frac{[M^{n+}]}{1}$$

But there are different types of reversible electrodes. Hence for any type of electrode the electrode reaction can be written in general as:



On applying Nernst equation

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Reduced state}]}{[\text{Oxidized state}]}$$

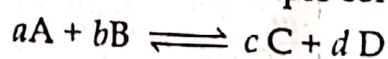
$$E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{Oxidized state}]}{[\text{Reduced state}]}$$

E = electrode potential for given concentrations of the ions involved.

E° = standard electrode potential.

(iii) In Calculation of Equilibrium Constant

At the equilibrium, there is no potential difference between the two electrodes and hence emf of cell becomes zero. Let us for example consider the following equilibrium



$$\text{Equilibrium constant} = K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

On applying Nernst equation to above equation.

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$E = E^\circ - \frac{RT}{nF} \ln K$$

At equilibrium, emf (E) of the cell becomes zero.

$$0 = E^\circ - \frac{RT}{nF} \ln K$$

$$E^\circ = \frac{RT}{nF} \ln K$$

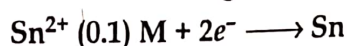
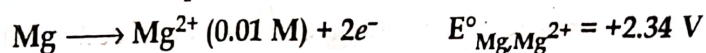
$$= \frac{RT}{nF} 2.303 \log K$$

E° = standard e.m.f. of the cell

Hence equilibrium constant 'K' can be calculated.

Solved Examples

Example 1. Represent the cell made up of following half cell reactions.



$$E^\circ_{\text{Sn}^{2+}, \text{Sn}} = -0.136 \text{ V}$$

Calculate EMF of this cell at 25°C.

Solution. The cell is represented as $\text{Mg}/\text{Mg}^{2+} (0.01 \text{ M}) \parallel \text{Sn}^{2+} (0.1 \text{ M}) \mid \text{Sn}$

$$\text{Std. EMF of the cell } E^\circ = E^\circ_{\text{Mg}, \text{Mg}^{2+}} + E^\circ_{\text{Sn}^{2+}, \text{Sn}}$$

$$2.34 + (-0.136) \text{ V} = 2.204 \text{ V}$$

The cell reaction is $\text{Mg} + \text{Sn}^{2+} \longrightarrow \text{Mg}^{2+} + \text{Sn}$

So $n = 2$

$$\text{Hence at } 25^\circ\text{C}, \quad \text{EMF of the cell} = E = E^\circ - \frac{0.0591}{2} \log \frac{\text{Mg}^{2+}}{\text{Sn}^{2+}}$$

$$= 2.204 - \frac{0.0591}{2} \log \frac{0.01}{0.1} = 2.234 \text{ V}$$

$$\frac{RT}{F}$$

Example 2. Calculate the electrode potential of a copper wire dipped in 0.1 molar copper sulphate solution at 25°C. At this temperature, the standard electrode potential of copper is 0.34 volt. ($F = 96500$ coulombs, $R = 8.314$ joules/degree/mol). Assume CuSO_4 to be completely ionized and take the activity of copper ions equal to the molar concentration.

Solution. The electrode reaction as reduction reaction may be written as :



Here

$$n = 2$$

By Nernst equation, the electrode potential will be given by

$$\begin{aligned} E &= E^\circ + \frac{RT}{nF} \cdot \ln \frac{[\text{Cu}^{2+}]}{[\text{Cu}]} \\ &= E^\circ + \frac{2.303RT}{nF} \cdot \log [\text{Cu}^{2+}] \quad [\because [\text{Cu}] = 1] \\ &= 0.34 + \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \log (0.1) \\ &= 0.34 + (-0.0296) = 0.3104 \text{ volt} \end{aligned}$$

Example 3. Calculate the equilibrium constant for the reaction :



Solution. According to the relationship between standard e.m.f. (E°_{cell}) and equilibrium constant (K_c),

$$E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K$$

$$E^\circ_{\text{cell}} = \frac{0.0591}{n} \log K \text{ at } 298 \text{ Kelvin}$$

Here, $n = 2$ and $E^\circ_{\text{cell}} = 0.46 \text{ V}$

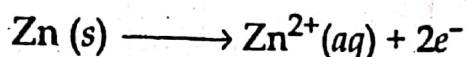
$$\log K = \frac{n E^\circ_{\text{cell}}}{0.0591} = \frac{2 \times 0.46}{0.0591} \quad \text{or } \log K = 15.5668$$

$$K = \text{antilog } 15.5668 = 3.688 \times 10^{15}$$

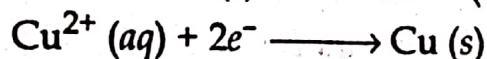
Example 5. Calculate the ΔG of the following galvanic cell :
 $\text{Zn} \mid \text{Zn}^{2+} (1.0 \text{ M}) \parallel \text{Cu}^{2+} (0.175 \text{ M}) \mid \text{Cu} (s)$ at 25°C .

($E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$, $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$)

Solution. The half cell reaction are :

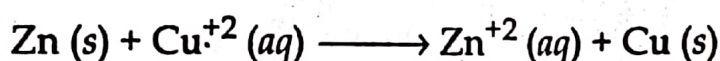


oxidation



reduction

The overall cell reaction is



From nernst equation

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log \frac{[\text{Zn}^{2+}][\text{Cu}]}{[\text{Cu}^{2+}][\text{Zn}]}$$

So

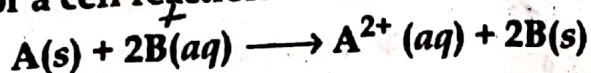
$$E_{\text{cell}} = 1.1 - \frac{0.059}{2} \log \frac{0.1}{0.175} = 1.107 \text{ V}$$

As

$$E^\circ = E^\circ_{\text{Cathode}} - E^\circ_{\text{Anode}} = 0.34 - (-0.76) = 1.1$$

$$\Delta G = -nFE_{\text{cell}} = -2 \times 96500 \times 1.107 = -213.68 \text{ KJ Ans.}$$

Example 6. For a cell reaction



at 298 K , the value of Equilibrium constant is 1.0×10^4 . Calculate E°_{cell} .

(PTU May 2007)

Solution.

$$n = 2, K = 1.0 \times 10^4$$

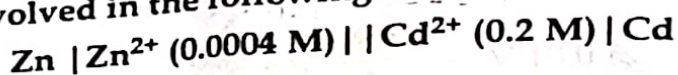
$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log K$$

$$E_{\text{cell}} = 0$$

$$E^{\circ}_{\text{cell}} = \frac{0.0591}{n} \log K$$

$$E^{\circ}_{\text{cell}} = \frac{0.0591}{2} \log 1 \times 10^4 = \frac{0.0591}{2} \times 4 = 0.1182 \text{ Ans.}$$

Example 7 Calculate the cell e.m.f., write the cell reaction and calculate the value of free energy change involved in the following cell at 25°C.



(PTU Dec. 2008)

Solution. $\text{Zn} | \text{Zn}^{2+} (0.0004 \text{ M}) || \text{Cd}^{2+} (0.2 \text{ M}) | \text{Cd}$

Cell reaction :



$$\text{Std emf of cell} = E^{\circ}_{\text{R}} - E^{\circ}_{\text{L}} = E^{\circ}$$

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{[P]}{[R]}$$

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[P]}{[R]}$$

$$E = E^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cd}^{2+}]}$$

$$E = E^{\circ} - \frac{0.0591}{2} \log \frac{.0004}{.2}$$

$$E = E^{\circ} - .0295 \log .002$$

$$\text{Free energy change} = \Delta G = -nFE$$

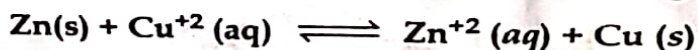
$$= -2 \times 96500 \times (E^{\circ} - .0295 \log .002)$$

$$= -2 \times 96500 \times (E^{\circ} - 0.295 \times (-2.7))$$

$$= -2 \times 96500 \times 0.295 \times 2.7 \times E^{\circ}$$

$$= -153724 E^{\circ} \text{ Ans.}$$

Example 8. The standard EMF of the Daniell cell involving cell reaction



is 1.10 volts. Calculate the equilibrium constant of the cell reaction at 25°C.

Solution.

$$E^{\circ} = 1.10 \text{ V}$$

$$E = E^0 - \frac{0.0591}{n} \log K$$

$$E^0 = \frac{0.0591}{n} \log K$$

$$1.10 = \frac{0.0591}{2} \log K$$

$$\frac{1.10 \times 2}{0.0591} = \log K$$

$$\text{antilog} \left(\frac{2.20}{0.0591} \right) = K \Rightarrow \text{antilog } 37.2 = K \Rightarrow K = 1.58 \times 10^{37} \text{ Ans.}$$

Example 9. The standard electrode potential for $\text{Hg}_2^{2+}/\text{Hg}$ and Hg^{2+}/Hg are 0.799 V and 0.855 V respectively. Calculate at 25°C, the equilibrium constant for the reaction.

Solution. For cell ; $\text{Hg}_2^{2+} | \text{Hg} || \text{Hg}^{2+} | \text{Hg}$

Cell reaction is $2 \text{Hg} + 2 \text{Hg}^{2+} \longrightarrow 2 \text{Hg}_2^{2+}$

i.e. $\text{Hg} + \text{Hg}^{2+} \longrightarrow \text{Hg}_2$

At equilibrium, $E_{\text{cell}} = 0$

$$E^0_{\text{cell}} = \frac{0.059}{n} \log K$$

$$E^0_{\text{cell}} = 0.855 - 0.799 = 0.056$$

$$\log K = 0.056 / 0.059 = 0.9491$$

$$K = 8.89 \text{ Ans.}$$

Example 10. Write the electrode reaction and calculate the oxidation potential of each of the following at 298 K.

(i) $\text{Ag}, \text{AgCl} (s) / \text{Cl}^- (a = 0.0001)$; $E^0_{\text{Ag}/\text{Ag}^+} = -0.025 \text{ V}$

(ii) $\text{Pt}, \text{H}_2 (1 \text{ atm}) | \text{H}^+ / a = 0.15$

Calculate the potential of the cell by combining (i) and (ii) above.

Ans. (i) $\text{Ag}, \text{AgCl} (s) | \text{Cl}^- (a = 0.0001)$

Oxidation half reaction

