23CHT101-Engineering Chemistry

Unit- I Electrochemistry

ELECTROCHEMICAL SERIES OR EMF SERIES

- The increasing value of standard reduction potentials are called as electrochemical series.
- The standard electrode potential of a number of electrodes is given in table. The values are determined potentiometrically by combining the electrode with another standard electrode, whose electrode potential is zero.

Electrode	Half cell reaction	E^0 volts (standard reduction potential
Li^+/Li	$Li^+ + e^- \rightarrow Li$	-3.04
K^+/K	$K^+ + e^- \rightarrow K$	-2.9
Ca^{+2}/Ca	$Ca^{+2} + 2e^- \rightarrow Ca$	-2.8
Na^+/Na	$Na^+ + e^- \rightarrow Na$	-2.7
Mg^{+2}/Mg	$Mg^{+2} + 2e^- \rightarrow Mg$	-2.3
Zn^{+2}/Zn	$Zn^{+2} + 2e^- \rightarrow Zn$	-0.76
Fe^{+2}/Fe	$Fe^{+2} + 2e^- Fe$	-0.4
$H^+/H_2,Pt$	$H^+ + e^- \rightarrow \frac{1}{2}H_2$	+ 0
Cu^{+2}/Cu	$Cu^{+2} + 2e^- \rightarrow Cu$	+0.15
Ag^+/Ag	$Ag^+ + e^- \rightarrow Ag$	+ 0.7
$Pt,Cl_2/Cl^-$	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+ 1.3
$Pt,F_2/F^-$	$F_2 + 2e^- \rightarrow 2F^-$	+ 2.8

APPLICATION OF ELECTROCHEMICAL SERIES

1. CALCULATION OF STANDARD EMF OF THE CELL:

The standard emf of the cell (E^o) can be calculated if the standard electrode potential values are known using the following reaction.

$$E^o \text{ cell} = E^o_{RHE} - E^o_{LHE}$$

2. RELATIVE CASE OF OXIDATION OR REDUCTION

Higher the value of standard reduction potential (+ve value) greater is the tendency to get reduced. (i.e metals on the top (- ve value) are more easily ionized).

a. The fluorine has higher positive value of standard reduction potential (+ 2.87 V) and shows higher tendency towards reduction.

b. The lithium has higher negative value (- 3.01 V) and shows higher tendency towards oxidation

3. DISPLACEMENT OF ONE ELEMENT BY THE OTHER

Metals which lie higher in the emf series can displace those elements which lie below them in the series.

For example: We may know whether Cu will displace Zn from the solution or vice versa. We know that standard reduction potential of Cu and Zn i.e

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

So, Cu^{2+} has a great tendency to acquire Cu form than Zn 2+ has acquiring Zn form

4. DETERMINATION OF EQULIBRIUM CONSTANT FOR THE REACTION.

Standard electrode potential can also be used to determine the standard free energy charge (G) and equilibrium constant (K) for the reaction. We know that

$$G^o = RT \ln k = 2.303\ RT \log K$$

$$\log K = - G^o / 2.303\ RT$$

$$\log K = nF E^o / 2.303\ RT \quad \text{i.e} - G^o = nF E^o$$

From the value of E^o, the equilibrium constant for the cell reaction can be calculated.

5. DISPLACEMENT BEHAVIOR OF HYDROGEN

Metals with negative reduction potential will displace the hydrogen form an acid solution.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

$$E^o_{Zn} = - 0.76V$$

From the value of E^o, the equilibrium constant for the cell reaction can be calculated.

The metal with positive reduction potential will not displace the hydrogen from an acid solution.

$$Ag + H_2SO_4 \longrightarrow \text{no reaction}$$

$$E^o_{Ag} = +0.80\ V$$