Chapter 10

ELECTROCHEMICAL CELLS

Redox Reaction :- The reaction in which oxidation and reduction takes place simultaneously.

Gain of 2 electron (Reduction)

Ex. :- $Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$

Loss of 2 electron (Oxidation)

Oxidation :- The loss of electron or increase in oxidation number of a substance

Reduction :- The gain of electron or decrease in oxidation number of a substance.

Oxidising Agent or Oxidant :- The substance which oxidise others and itself gets reduced.

Reducing Agent or Reductant :- The substance which reduces others and itself get oxidised.

Oxidation Number (ON):- It is the hypothetical charge that an atom would have if all bonds to atoms of different elements were 100% ionic.
It represents the number of electrons lost (if O.N is positive) and gain (if O.N is negative) by an atom of that element in the compound.

Rules to Determine Oxidation Number :-

1. All atomic and molecular species have oxidation number of zero

   Ex. : Mg, H_2, N_2, Ca, H
2. All element of group one (except H) in a compound has ON of +1
3. All element of group two in a compound have ON of +2.
4. Al has +3 oxidation number in a compound.
5. For an ion, charge number is equal to oxidation number

   Ex. : Fe^{3+}, ON = +3

   Mg^{2+}, ON = +2

   CO_3^{2-}, ON of a anion is –2
6. Flourine has oxidation number of –1
7. Hydrogen will always be +1 except in metal hydrides like NaH, MgH_2.
8. Oxygen has ON of –2 except in peroxide $O_2^{2-}(ON = -1)$, superoxide $O_2^{-}(ON = -½)$ and OF_2 $(ON = +2)$.

   Ex. : $Cr_2O_7^{2-}$

   $2x + 7x(-2) = -2$

   $2x = 12$

   $x = +6$

   MnO_4^{-}

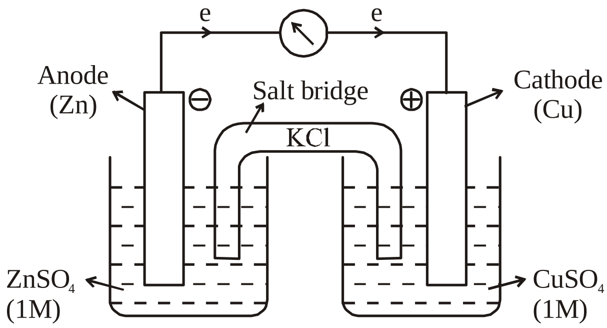
   $x + 4(-2) = -1$

   $x = +7$

Electro Chemical Cells

- Galvanic Cells (Chemical Energy $\rightarrow$ Electrical Energy)
- Electrolytic Cells (Electrical Energy $\rightarrow$ Chemical Energy)

Galvanic Cell :-



Anode (Oxidation) : $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Cathode (Reduction) : $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Net Reaction : $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu$

Salt Bridge : It is a U-shaped tube containing a solution of an inert electrolyte such as KCl, KNO_3 or NH_4NO_3.

Characteristics : (i) Mobilities of ions should be same
(ii) Ions should not get oxidised or reduced during the process.

Function : (i) Maintain the flow of current
(ii) Maintain the electrical neutrality of anodic and cathodic compartment

Potential difference develops between electrodes and the electrolyte is called electrode potential.

When half cells are connected by a wire, the difference in the reduction potential of cathode and the reduction potential of anode is called cell potential.

$$E_{cell} = E_{r_{cathode}} - E_{r_{anode}}$$

When pressure is 1 bar, temperature is 298K and the concentration of solution is 1M, the cell potential is called standard cell potential $\left(E^0_{cell}\right)$

$$E^0_{cell} = E^0_{r_{(cathode)}} - E^0_{r_{(anode)}}$$

$E^0_{red} \uparrow O \cdot A \uparrow$ $\qquad$ $E^0_{red} \downarrow R \cdot A \uparrow$

Reduction Potential : Tendency to reduce. Higher the reduction potential, more easily the species will reduced

Ex.: $E^0_{Ag^+|Ag} = 0.80V$ $\qquad$ $E^0_{Cu^{2+}|Cu} = 0.34V$ $\qquad$ $E^0_{Zn^{2+}|Zn} = -0.76V$

Reduction Tendency : $Ag > Cu > Zn$

Oxidation Potential : Tendency to oxidise. Lower the reduction potential, more easily the species will oxidise.

Oxidation Tendency : $Zn > Cu > Ag$

Strength of Oxidizing Agent :- Higher the reduction potential, strongest the oxidizing agent.

O.A. : $Ag > Cu > Zn$.

Strength of Reducing Agent :- Lower the reduction potential, strongest the reducing agent

R.A :- $Zn > Cu > Ag$.

Note :- $E^0_{red} = -E^0_{oxid}$ $\quad M^+ + e^- \rightarrow M\left(E^0_{red}\right)$

$M \rightarrow M^+ + e^- \left(E^0_{oxid}\right)$

Problem: In which of the following $CuSO_4$ can be stored

(a) Zn pot (b) Ag pot

(c) Fe pot (E° = –0.44) (d) Al pot (–1.66 v)

Soln. $CuSO_4$ can be stored in Ag pot as $E^0_{Ag^+|Ag} > E^0_{Cu^{2+}|Cu}$.

Correct option is (b)

Problem: Given that $I_2 + 2e^- \rightarrow 2I^-$ $\quad E^0 = 0.54$ V

$Br_2 + 2e^- \rightarrow 2Br^-$ $\quad E^0 = 1.69$ V

Predict which of the following is true

(a) I^- ions will be able to reduce bromine (b) Br^- ions will be able to reduce iodine

(c) Iodine will be able to reduce bromine (d) Bromine will be able to reduce iodide ions

Soln. Since reduction potential of $Br_2 | Br^-$ is greater than reduction potential of $I_2 | I^-$, so I^- will reduce Br_2.

Correct option is (a)

Problem: $E^0_{A^+/A} = 0.3$ V $\quad E^0_{B^+/B} = 0.7$ V $\quad E^0_{C^+/C} = -0.7$ V

The correct statement is

(a) B can reduce both A and C (b) C can oxidise both A and B

(c) A can oxidise C and reduced B (d) A can oxidise both B and C

Soln. Order of reductional potential :- $C < A < B$

$\Rightarrow$ order of strength reducting agent :- $C > A > B$

So, C can reduce both A and B

B can oxidise both A and C

A can oxidise C but will reduce B

Correct option is (c)

Problem: A 19th century iron bridge is protected from corrosion by connecting it to a block of metal (sacritificial anode), which is replaced annually. The corrosion of iron, represented by the chemical equation :

$$2Fe(s) + 2H_2O(\ell) + O_2(g) \rightarrow 2Fe(OH)_2$$

Which of the following metals is best suited as sacrificial anode ?

(a) Ag : $Ag^+ + e^- \longrightarrow Ag(s)$, $\quad E^0 = +0.80$ V

(b) Cd : $Cd^{2+} + 2e^- \longrightarrow Cd(s)$, $\quad E^0 = -0.40$ V

(c) Cu : $Cu^{2+} + 2e^- \longrightarrow Cu(s)$, $\quad E^0 = +0.34$ V

(d) Mg : $Mg^{2+} + 2e^- \longrightarrow Mg(s)$, $\quad E^0 = -2.36$ V

Soln. In rusting oxidation of iron takes place. Sacrificial anode is a metal which can act as anode inplace of iron and itself get oxidised and iron gets protected.

Metal with highest oxidation potential is the most suitable metal for sacrificial anode.

Since Magnesium has lowest reduction potential or highest oxidation potential. So, Mg will be used as sacrifical anode

Correct option is (d)

Types of Half Cess :-

1. **Metal-Metal ion Half Cell :-** It consist of a metal rod dipped in a solution of metal ion

Representation :- $M^{n+}|M$