UNIT-IV th

Redox Titrations

- **Oxidation**: (i) Loss of electorns
  (ii) Loss of hydrogen
  (iii) Gain of oxygen
  (iv) Increase the valancy

- **Reduction**: (i) Gain of electorns
  (ii) Gain of Hydrogen
  (iii) Loss of oxygen
  (iv) Decrease the valancy

[Note: Oxygen, Hydrogen, Electorn, Valancy]

The oxidation and reduction reactions occurs simultaneously. They may also be refeered to as electorn transfer reactions.

Consider the oxidation of Ferrous Sulphate by cerium,

$$Fe^{2+} + Ce^{4+} \longrightarrow Fe^{3+} + Ce^{3+}$$

(Reducing agent) (oxidizing agent)

Oxidation half reaction : $Fe^{2+} \longrightarrow Fe^{3+} + e^-$

Reduction half Reaction : $Ce^{4+} + e^- \longrightarrow Ce^{3+}$

Oxidizing agent:

Those molecule which reduce itself but oxidize other is called oxidizing agent.
It is also called as Oxidant.

Example : (i) Potassium permanganate ($KMnO_4$)

(ii) Potassium dichromate ($K_2Cr_2O_7$)

(iii) Potassium bromate ($KBrO_3$)

(iv) Potassium iodate (KIO_3)

(v) Hydrogen peroxide (H_2O_2)

Reducing agent

Those molecule which oxidize itself but reduce other is called reducing agent.
It is also called as Reductant.

Example : (i) Metals

(ii) Fe^{2+} salts

(iii) Iodide ion (I^-)

(iv) Hydrogen peroxide (H_2O_2)

NOTE: Hydrogen peroxide acts as both a oxidizing agent and reducing agent.

Titration:

Titrations
- Known — Standard
- Unknown — Test / Sample

There are mainly 5 types of titrations. They are listed as following —

(i) Acid base titration
(ii) Redox titration
(iii) precipitation titration
(iv) Complexometric titration
(v) Gravimetric titration

Redox Titration :-

The titration in which we determine the concentration of unknown reducing and oxidizing agent by using known oxidizing and reducing agent is called Redox titration.

Redox titration is also known as oxidation-reduction titration.

Type of redox titration

There are mainly 6 types of redox titration. They are listed as following —

(i) Cerimetry
(ii) Iodimetry } Iodine (I_2)
(iii) Iodometry }
(iv) Bromatometry
(v) Dichrometry
(vi) Titration with potassium iodate

(i) Cerimetry:

Principle:

→ Analysis involving the use of cerium (IV) Solutions are known as Cerimetry.

→ The element cerium exists in two oxidation State, They are +3 (cerrous) and +4 (cerric)

→ In the +4 state it is a powerful oxidizing agent.

$$Ce^{4+} + e^- \rightarrow Ce^{3+}$$

→ The Stadard reduction potential (E°) in 1M Solutions of common acid of Ce^{4+} salts vary from 1.61 – 1.87 volts.

→ It is used in Solutions of high acidity, since in alkaline Solutions cerium hydroxide precipitation occurs.

→ Solutions of Ce^{4+} are Unstable as,

$$2Ce^{4+} + 2Cl^- \longrightarrow 2Ce^{3+} + Cl_2$$

→ Ammonium ceric Sulphate serves as a powerful oxidizing agent in acidic medium.

→ On reduction, the resulting cerrous salt obtained is colourless in appearance and therefore strong solutions may be considered as self indicating.

→ In general practice, 0.05 N solutions are employed for estimations.

Applications:

① Determination of % purity of $FeSO_4$

$$Ce^{4+} + Fe^{2+} \longrightarrow Ce^{3+} + Fe^{3+}$$

② Determination of total iron content (% iron)

③ Determination of the % purity of $NaNO_2$ (Sodium Nitrite)

$$2Ce^{4+} + NO_2^- + H_2O \longrightarrow 2Ce^{3+} + NO_3^- + 2H^+$$

Titration involving Iodine (I_2)

Iodine titrations

Iodimetry	Iodometry
direct titration with I_2	indirect titration with I_2
Iodine acts as an mild oxidizing agent : $I_2 + 2e^- \rightarrow 2I^-$ (reduction)	Iodide acts as reducing agent $2I^- \rightarrow I_2 + 2e^-$ (Oxidation)

Freshly prepared Starch Solution is used as indicator

→ Iodine is an oxidizing agent

→ Titration, which involve iodine is known as Iodine Titration

Iodine can be used in oxidation reduction in two ways —

Iodimetry: In this method a standard solution of Iodine is directly used.

Iodometry: In this method iodine solution is not directly used as an oxidizing agent but iodine is liberated during Chemical reaction.

Principle

Iodine is a weak oxidant and it is used for the redox titrations of easily oxidized substances.

Iodine is reduce by the reductants like Stannous Chloride, Sodium thiosulphate and arsenious oxide.

In Iodimetry know volume of standard iodine solution is titrated directly with the reducta-nt which is to be determined using starch as an indicator. End point is detected by change of blue to colourless.

In all iodimetric titration iodine is reduced to form iodin ion.

(i) $I_2 + 2e \longrightarrow 2I^-$

(ii) $Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^-$

(iii) $S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I$

(iv) $H_3ASO_3 + I_2 + H_2O \longrightarrow H_3ASO_4 + 2H^+ +$

Applications

Iodimetry

Determination of Sulphur dioxide (SO_2) in wine.

$$SO_2 + I_2 + H_2O \longrightarrow 2I^- + SO_3 + 2H^+$$

Iodometry

Determination of concentration of hydroperoxides in any given lipid matrix (e.g. oils, facts for human consumption)

$$RCOOH + 2H^+ + 2I^- \longrightarrow ROH + I_2 + H_2O$$

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

- **Nernst equation:**

Equation showing relation between potential of a non standard electrochemical cell and concentration of solution is known as Nernst equation.

$$E = E^{\circ} - \frac{RT}{nF} \log_e \frac{[Oxi]}{[Red]}$$

where, E = Electrode potential

E° = Standard electrode potential

R = Universal gas contant

T = Absolute temperature

n = no of e^- transfer

F = Farady constant