Unit – IV

Oxidation – Reduction (Redox) Titration

Definitions :-

* **Oxidation** :- It can be defined as loss of electrons or increase in oxygen content.

* **Reduction** :- It can be defined as gain of electrons or increase of hydrogen content.

* **Oxidizing agent** :- Substance which get reduced.

* **Reducing agent** :- Substance which get oxidized.

→ Both processes are combined and occur together so we combine them in one word as REDOX reaction.

Oxidation – Reduction (Redox) :-

Reaction of ferrous ion with ceric ion

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

$Fe^{+2} - e \rightleftharpoons Fe^{+3}$ (loss of electrons : Oxidation)
$Ce^{+4} + e \rightleftharpoons Ce^{+3}$ (Gain of electrons : Reduction)

→ In every redox reaction, both reduction & oxidation must occur.

→ Substance that gives electrons is the reducing agent or reductant.

→ Substance that accepts electrons is the oxidizing agent or oxidant.

Overall, the no. of electrons lost in the oxidation half reaction must equal the no. gained in the reduction half equation.

Oxidation Number (O.N.) :-

→ The O.N. of a monoatomic ion = its electrical charge.
→ The O.N. of atoms in free un-combined elements = zero
→ The O.N. of an element in a compound may be Calculated by assigning the O.N. to the remaining elements of the compound using the a fore mentioned basis & the following additional rules:-

(a) The O.N. for Oxygen = −2 (in peroxides = −1).
(b) The O.N. for Hydrogen = (−1)

For e.g.:-

NaCl	Na = +1 , Cl = −1.
K_2CrO_4	K = +1 , Cr = +6 , O = −2
SO_4^{-2}	O = −2 , S = +6
H_2	H = 0
NH_3	N = −3 ; H = +1 , etc.

Nernst Equation for electrode potential (E)

$$E_T = E^0 + \frac{RT}{nf} \log [M^{n+}]$$

or

$$E_{25^\circ C} = E^0 + \frac{0.0591}{n} \log [M^{n+}]$$ { Standard electrode potential E^0

Factors Affecting Oxidation Potential :-

1. Common Ion :- $E_{25^\circ C} = E^0 + \frac{0.0591}{n} \log \frac{[\text{oxidation}]}{[\text{Reduction}]}$

→ The potential of MnO_4^- / Mn^{+2} varies with ratio $[MnO_4^-] / [Mn^{+2}]$.

→ If ferrous is titrated with MnO_4^- in presence of Cl^-, chloride will interfere by reaction with MnO_4^- & gives higher results.

2. **Effect of pH :-**

$$E_{MnO_4^-/Mn^{+2}} = E^0 + \frac{0.0591}{5} \log \frac{[MnO_4^-][H^+]}{[Mn^{2+}]}$$

→ The oxidation potential of an oxidizing agent containing oxygen increases by increasing acidity & vice versa.

3. **Effect of Complexing Agents :-**

Iodine :- $I_2 + 2e^- \longrightarrow 2I^-$

$$E_{I_2/I^-} = E^0 + \frac{0.0591}{2} \log \frac{[I_2]}{[I^-]^2} \quad \left\{ \begin{matrix} E^0 (I_2/2I^-) \\ = 0.54 \end{matrix} \right\}$$

Ferric ⇒ $Fe^{+3} + e^- \rightarrow Fe^{+2}$

$$E_{Fe^{+3}/Fe^{+2}} = E^0 + \frac{0.0591}{1} \log \frac{[Fe^{+3}]}{[Fe^{+2}]} \quad \left\{ E^0_{Fe^{+3}/Fe^{+2}} = 0.77 \right.$$

4. **Effect of Precipitating agents :-**

Ferri cyanide :-

$$[Fe(CN)_6]^{-3} + e^- \longrightarrow [Fe(CN)_6]^{-4}$$

$$E_{ferri/ferro} = E^0 + \frac{0.0591}{1} \log \frac{[Fe(CN)_6^{-3}]}{[Fe(CN)_6^{-4}]}$$

Addition of Zn^{+2} salts which precipitates ferrocyanide.

$$[Fe(CN)_6]^{+4} + Zn^{+2} \longrightarrow Zn_2[Fe(CN)_6]\downarrow$$

Copper →

$$2\,Cu^{+2} + 4I^{-} \longrightarrow 2\,Cu_2I_2\ (ppt.) + I_2$$

$$E_{Cu^{+2}/Cu^{+}} = E^{\circ} + \frac{0.0591}{1} \log \frac{[Cu^{+2}]}{[Cu^{+}]}$$

Properties of Oxidising Agent :-

(a) Potassium Permanganate ($KMnO_4$)
(b) Potassium dichromate ($K_2Cr_2O_7$)
(C) Iodine (I_2), Potassium Iodate (KIO_3)
(d) Bromate - bromide mixture.

(a) Potassium Permanganate ($KMnO_4$) :- Very strong oxidising agent not a primary standard self indicator.

In Acid Medium :-

$$MnO_4^{-} + 8H^{+} + 5e^{-} \rightleftharpoons Mn^{+2} + 4H_2O$$

It can oxidize : Oxalate, Fe^{+2}, ferrocyanide, As^{+3}, H_2O_2 & NO_2^{-}

In Alkaline Medium :-

$$MnO_4^{-} + e^{-} \rightleftharpoons MnO_4^{-2}$$

In neutral medium :-

$$4\,MnO_4^{-} + 2H_2O \rightleftharpoons MnO_2 + 4OH + 3O_2$$

(b) Potassium dichromate ($K_2Cr_2O_7$) :-

It is a primary standard (highly pure & stable).

$$Cr_2O_7^{-2} + 14H^{+} + 6e^{-} \rightleftharpoons 2Cr^{+3} + 7H_2O$$

(C.) **Iodine (I_2)** :- Salubility of Iodine in water is very small.

Its aqueous solution has appreciable vapour pressure. Prepared in I^-.

$$I_2 + I^- \rightleftharpoons I_3^- \quad \text{(Triiodide ion)}$$

Potassium Iodate (KIO_3) :- It is a strong oxidizing agent, highly pure, its solution is prepared by direct weighing.

$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$ (in 0.1N HCl) Eq. wt = M/w=

$IO_3^- + 2I_3 + 6H^+ \longrightarrow 5I^- + 3H_2O$ (in 4-6N HCl) Eq. wt = M/w=

$IO_3^- + 2I^- + 6H^+ \quad 3I^- + H_2O$ Eq. w. = M/w=4

Andrew's Reaction :-

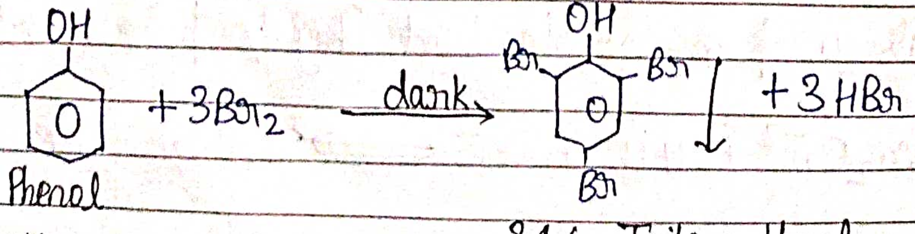
Determination of Iodide with potassium iodate in 4-6N HCl (Chloroform as indicator)

→ Starch can not be used.
→ Potassium iodate prepared in molar.

(d) **Bromate - bromide mixture** :- Upon acidification of bromate/bromide mixture, bromine is produced.

$$BrO_3^- + 5Br^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

Used for the determination of Phenol & primary aromatic amines.



Phenol

2,4,6 – Tribromophenol

The excess Br_2 is determined:-

$Br_2 + 2I^- \longrightarrow I_2 + 2Br^-$ & $I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2I^-$

Chloroform is added (dissolve TBP & indicator). Starch can be used.

Detection of End Point in Redox Titrations :-

1.) Self Indicator (No indicator):-

$\underset{\text{(violet)}}{KMnO_4} + Fe^{+2} + H^+ \longrightarrow Mn^{+2}\text{(colourless)} + Fe^{+3}$

2.) External Indicator :-

In Titration of Fe^{+2} by $Cr_2O_7^{-2}$

$Cr_2O_7^{-2} + 3Fe^{+2} + 14H^+ \longrightarrow 2Cr^{+3} + 3Fe^{+3} + 7H_2O$

The reaction proceeds until all Fe^{+2} is converted into Fe^{+3}.

Fe^{+2} + ferricyanide (indicator) ⟶ Ferrous ferricyanide (blue)
$Fe^{+2} + [Fe(CN)_6]^{-3} \longrightarrow Fe_3[Fe(CN)_6]^{-2}$

3.) Internal Redox Titrations :-

$In_{ox} + ne^- = In_{red.}$

Indicator colours may be detected when $[In_{oxd}]/[In_{red.}] = 1/10$ or
hence,

Indicator range : $E = E^0_{In} \pm 0.0591/n$

(a.) Diphenylamine :- $E^0 = 0.76$, $n = 2$

Range $= 0.73 - 0.79$ V

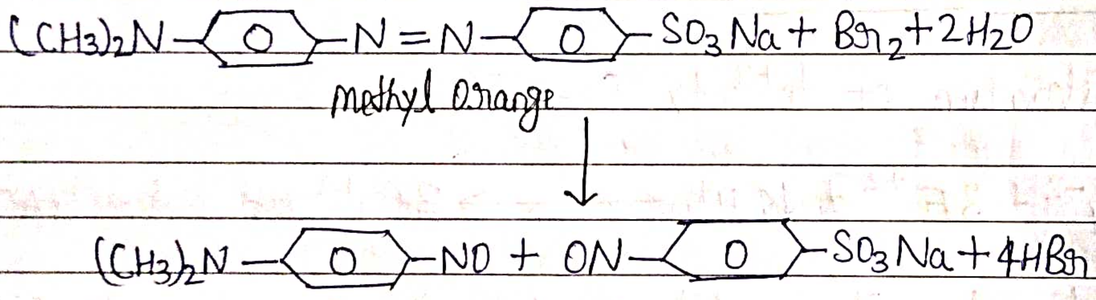
$E < 0.73$ V, colourless (red.)
$E > 0.79$ V, bluish violet (oxi.)

(b) Ferroin Indicator :- (1,10 - phenanthroline - ferrous chelate)

$E^\circ = 1.147$, $n = 1$
Range = 1.088 – 1.206 V
$E < 1.088$V, red (red.)
$E > 1.206$ V, pale blue (oxid.)

4.) Irreversible Redox Indicators :- Some highly coloured compound that undergo irreversible oxidation or reduction.

* Methyl orange :-



→ In acid solutions, methyl orange is red.
→ Addition of strong oxidants (Br_2) would destroy the indicator & thus it changes irreversibly to pale yellow colour.

Types of Oxidation – Reduction Titration :-

1.) Cerimetry :-

Oxidation → $e^- \downarrow$, $H \downarrow$, $O \uparrow$, Oxidation No. ↑

Reduction → $e^- \uparrow$, $H \uparrow$, $O \downarrow$, Oxidation No. ↓

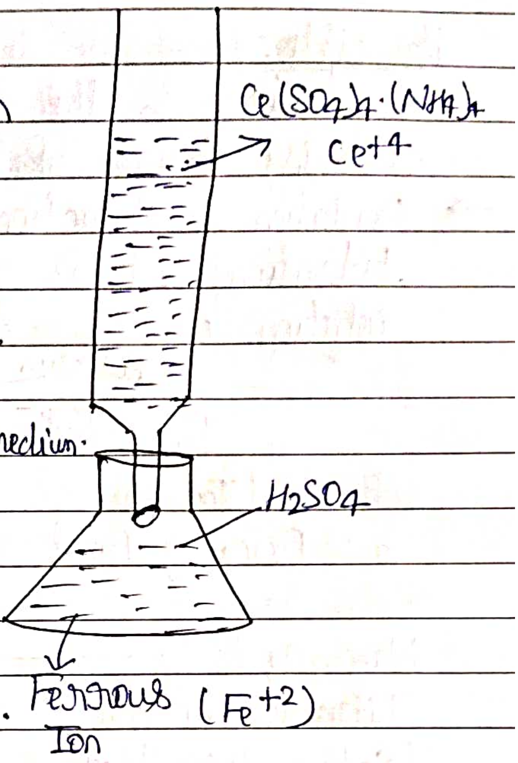
Principle :-

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

(Analyte) (Titrant)

Ferrous Ceric Ferric Cerium

(Reducing Agent) (Oxidising Agent)



* 0.5 M H_2SO_4 is used to prepare Ceric ammonium sulphate solution.

* Titration is carried out in acidic medium.

* 100 ml of 0.1 M Fe^{2+} solution (Analyte) is titrated with 0.1 M Ce^{4+} solution (Titrant).

* Fe^{+2} ion is worked as self indicator. The colour change occurs from yellow colour to colourless.

* There is no need to use external indicator because Fe^{+2}, ion itself works as self Indicator.

Application :-

- Estimation of $FeSO_4$.

$2\,Ce(SO_4)_2 + 2\,FeSO_4 \longrightarrow Ce_2(SO_4)_3 + Fe_2(SO_4)_3$

- Estimation of ferrous gluconate & ferrous fumerate.
- Estimation of Ascorbic acid.
- Estimation of TiO_2.
- Estimation of Paracetamol.

2.1 Iodimetry :-

Principle:-

→ Iodimetry is the direct titration with Iodine (I_2) due to oxidising power of Iodine.

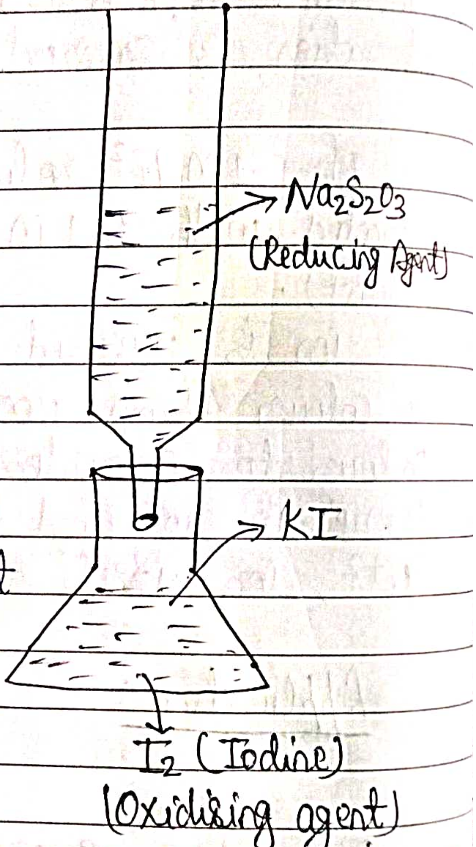
→ Oxidation & Reduction process involving I_2 is called as Iodimetr titration. It is a direct titration with a standard solution of I_2 :

$$\underset{\text{(Iodine)}}{I_2} \xrightarrow{+2e^-} \underset{\text{(Iodide)}}{2I^-}$$

Reduction

Oxidising Agent.

$$\underset{\substack{\text{Titrant}\\\text{(Sodium Thiosulphate)}}}{Na_2S_2O_3} + \underset{\text{Analyte}}{I_2} \longrightarrow Na_2S_4O_6 + NaI$$



→ Iodimetry is direct titration method.

→ Sodium thiosulphate is a reducing agent which is used as titrant for titration of Iodine. Here, Sodium thiosulphate reduce Iodine into Iodide form.

→ Iodine (I_2) is insoluble in water hence to enhance solubility of Iodine (I_2) generally KI is used.

→ The indicator used in Iodimetry is "Starch indicator". Which gives Blue / Purple Colour.

Application :- (Antidote for cyanide poisoning)

- Estimation of $Na_2S_2O_3$ (Sodium hypo sulphite).
- Estimation of Sodium metabisulfide.

3.] Iodometry :-

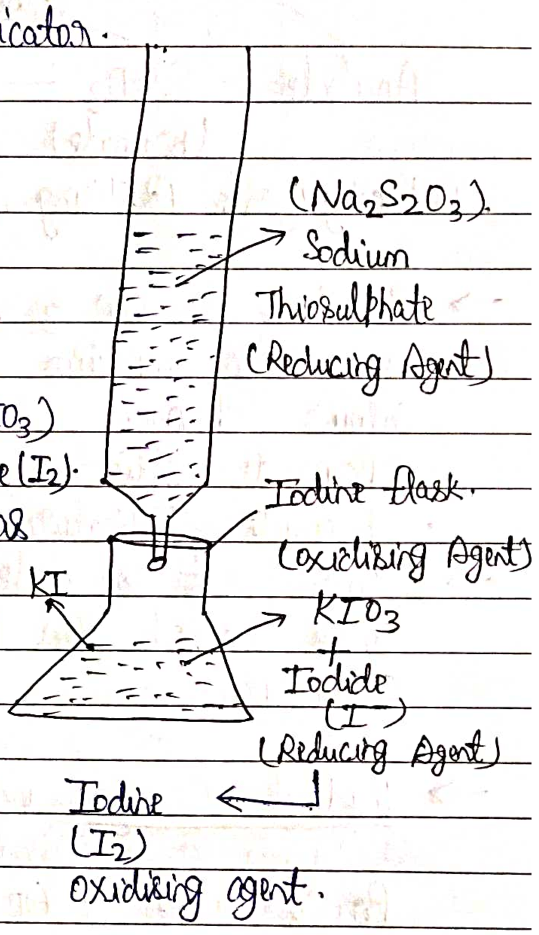
→ The titration in which the equivalent amount of I_2 (Iodine) is liberated from KI & the liberated I_2 is titrated against Sodium thiosulphate solution, such type of indirect (Back) titration is called Iodometry.

→ Starch - mucilage is used as an indicator.

$$\underset{\text{(Reducing agent)}}{\underset{\text{Iodide}}{2I^-}} \xrightarrow[\text{Oxidation}]{} \underset{\text{Iodine}}{I_2} + 2e^-$$

→ Iodometry is a back titration method.

→ Here, sample is an oxidising agent (KIO_3) which convert Iodide (I^-) into Iodine (I_2). Now, Iodine (I_2) will form as much as the Oxidising agent (KIO_3) is present in the sample. Thus, to determine Conc. of sample (KIO_3), Iodine (I_2) is titrated with Sodium thiosulphate ($Na_2S_2O_3$).



Application :-

→ Estimation of KIO_3, $CuSO_4$, Bleeching powder, H_2O_2, Ceric Sulphate, Chloramine, etc.

→ The titration occurs in Absence of Acid.

$$KIO_3 + 3H_2SO_4 + 5KI \longrightarrow 3K_2SO_4 + 3I_2 + 3H_2O$$

$$3I_2 + 6Na_2S_2O_3 \longrightarrow 6Na_2S_4O_6 + 6NaI$$

→ The colour change is Yellow to colourless.

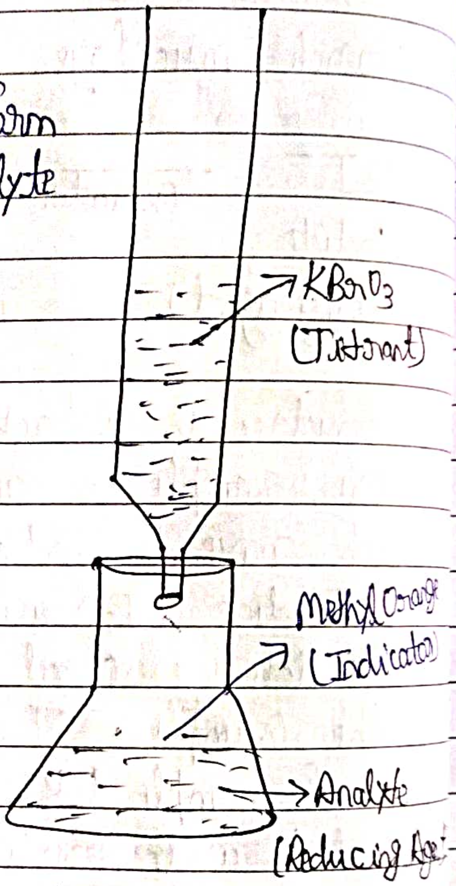
4.) Bromatometry :-

→ when any analyte (Redaxing Agent) is titrated with potassium bromate (KBO$_3$) [Oxidising Agent], it is called Bromatometry.

Oxidation.

Reduction.

$$\underset{\text{Reducing Agent}}{\text{Analyte}} + \underset{\substack{\text{(Bromate)}\\ \text{Oxidising Agent}}}{BrO_3^-} \longrightarrow \underset{\text{(Bromide)}}{Br^-} + \text{Oxidized form of Analyte}$$



→ Solution of KBrO$_3$ is prepared in acidic medium to find sharp colour change.

- Bromate Indicator → Colourless
- Bromide Indicator → Red Colour.

→ End point is detected by the conversion of Red solution to Colourless.

→ Methyl Orange indicator is generally used.

$$\underbrace{BrO_3^-}_{} + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O$$

↳ Available in pure form, hence used as 1° standard.

Application :-

* Estimation of Isoniazid
* Estimation of Antimony.
* Estimation of Arsenic.
* Estimation of Hydroxylamine.

} REDUCING AGENT.

5.] Dichrometory :-

Prinaiple:-> When Ferrous ion (Analyte & as a Reducing Agent) is titrated with potassium dichromate ($K_2Cr_2O_7$), it is called dichrometry.

oxidation

Reduction

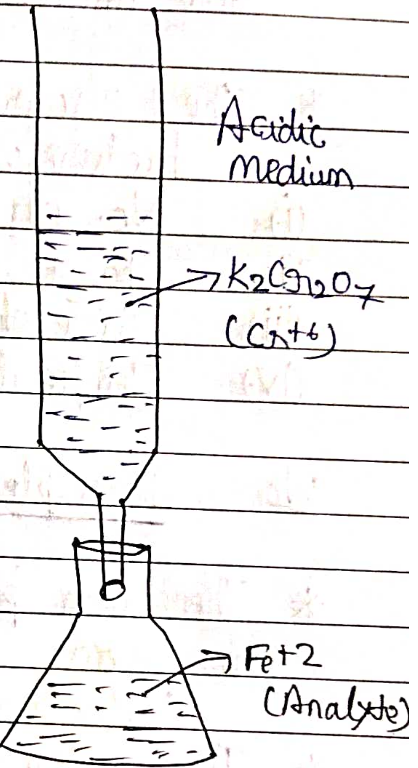
$Fe^{+2} + K_2Cr_2O_7 \longrightarrow Fe^{+3} + Cr^{+3}$

(Analyte) Reducing Agent

(Titrant) Oxidising Agent

Ferric Ion

Cranium Ion.



→ $K_2Cr_2O_7$ is strong oxidising Agent.

→ The indicator used is : Diphenyl Amine, Diphenyl benzidene & Diphenyl amine. Sulfonate or N-phenyl-anthranilic Acid.

→ The colour change is from Green to Voilet / Pink.

→ $KMnO_4$ (Pot. Permanganate) is more strong oxidising agent than $K_2Cr_2O_7$ (Potassium dichromate), but generally, it is not used because $KMnO_4$ is less stable easily degradable & show error in titration due to impurity.

$CrO_7^{-} + 14H^+ + 6e^- \longrightarrow 2Cr^{+3} + 7H_2O$.

Application :-

→ Estimation of ferrous ion.
→ Estimation of fe in ferric alum, haematite etc.