OXIDATION NUMBER

⇒ The charge present on an atom in a given Compound.

Rules for Calculating Oxidation Number :-

① The O. No. of element present in its native form is Zero.

$O_2(g) = 0$ $Cu(s) = 0$

② The O.No. of Elements of gp 1 and gp-2 are +1 and +2 respectively.

③ The O.No. of ions is equal to charge present on it.

$Na^{+} = +1$ $Mg^{+2} \rightarrow +2$

$Cl^{-} = -1$

④ The O.No. of Hydrogen is always +1 Except metal hydrides.

NaH. $H \rightarrow -1$

⑤ The O. No. of Oxygen is always −2 Except

Peroxide → $O_2^{-2} \rightarrow -\overset{-1}{O}-\overset{-1}{O}-$ & Oxofluoride OF_2

$\rightarrow O \rightarrow +2$

Superoxide → $-1/2$

⑥ The O.No. of Halogens is always −1 Except interhalogen Compounds.

Eg :- $\underbrace{IF_7} \rightarrow x + 7(-1) = 0$ $\quad x = +7$

⑦ The O.No. of Radicals is equal to charge present on it.

$C_2O_4^{-2}$ (Oxalate) $\Rightarrow -2$

CN^- (Cyanide) $\Rightarrow -1$

$SO_4^{-2} \Rightarrow -2$

IF_7

Calculate oxidation state of underlined atoms?

(1) $K\underline{Mn}O_4$

$x + 1 + 4(-2) = 0$

$x + 1 - 8 = 0$

$x = +7$

(2) $\underline{\underline{Cr_2O_7^{-2}}}$

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

$2x - 14 = -2$

$2x = +12$

$x = +6$

(3) $K_4[\underline{Fe}(CN)_6]$

$x + 4(+1) + 6(-1) = 0$

$x + 4 - 6 = 0$

$x = +2$

(4) $\underline{N}_2O_3$

$2x + 3(-2) = 0$

$2x - 6 = 0$

$2x = +6$

$x = +3$

(5) $C_2O_4^{-2}$

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

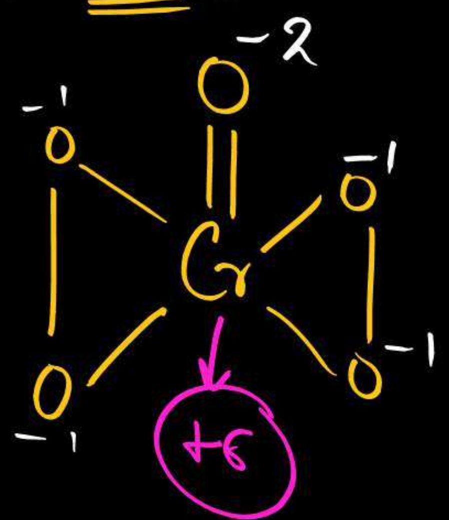
$2x - 8 = -2$

$2x = +6$

$x = +3$

Calculation of oxidation state from structure?

(1) CrO_5

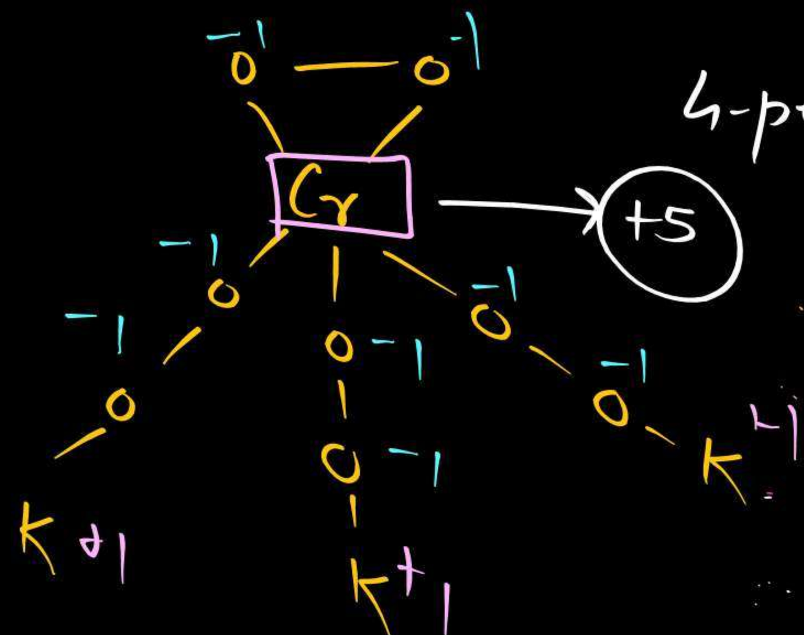


$x-1-1-1-1-2=0$

$x=+6$

(2) K_3CrO_8

4-peroxide bond



(3) Fe_3O_4

⇒ Mixed oxide of

FeO & Fe_2O_3

$+2$ $\quad$ $+3$

$$3x + 4(-2) = 0$$

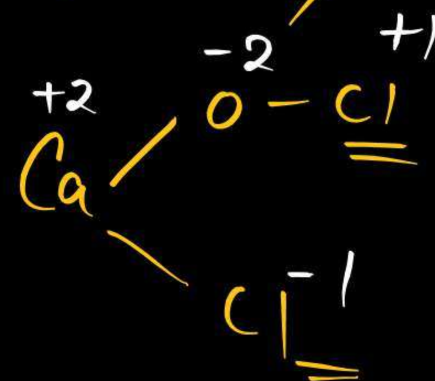
$$3x - 8 = 0$$

Av. Ox. St. of Fe

$$x = +8/3$$

(4) Bleaching Powder

($CaOCl_2$)



(5) OXO acids of sulphuric acid

$$\text{Dithionic acid} \xleftarrow[-H_2O_2]{\times 2} \boxed{H_2SO_4} \xrightarrow{\times 2 \; -H_2O} \text{Pyrosulphuric acid}$$

$$H_2SO_4 \xrightarrow[-H_2]{\times 2} \text{Marshall's acid}$$

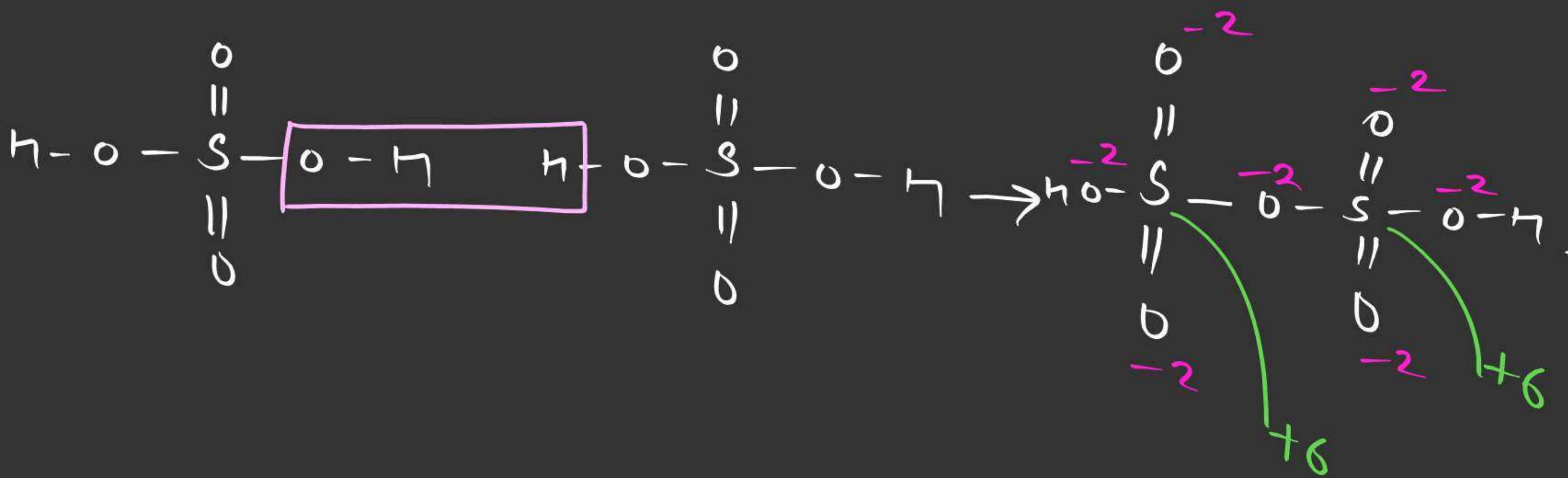
Eg:-

$$\overset{+1}{H}-\overset{-2}{O}-\underset{\underset{\underset{-2}{O}}{\|}}{\overset{\overset{\overset{-2}{O}}{\|}}{S}}-\overset{-2}{O}-\overset{+1}{H}$$

$S \rightarrow +6$

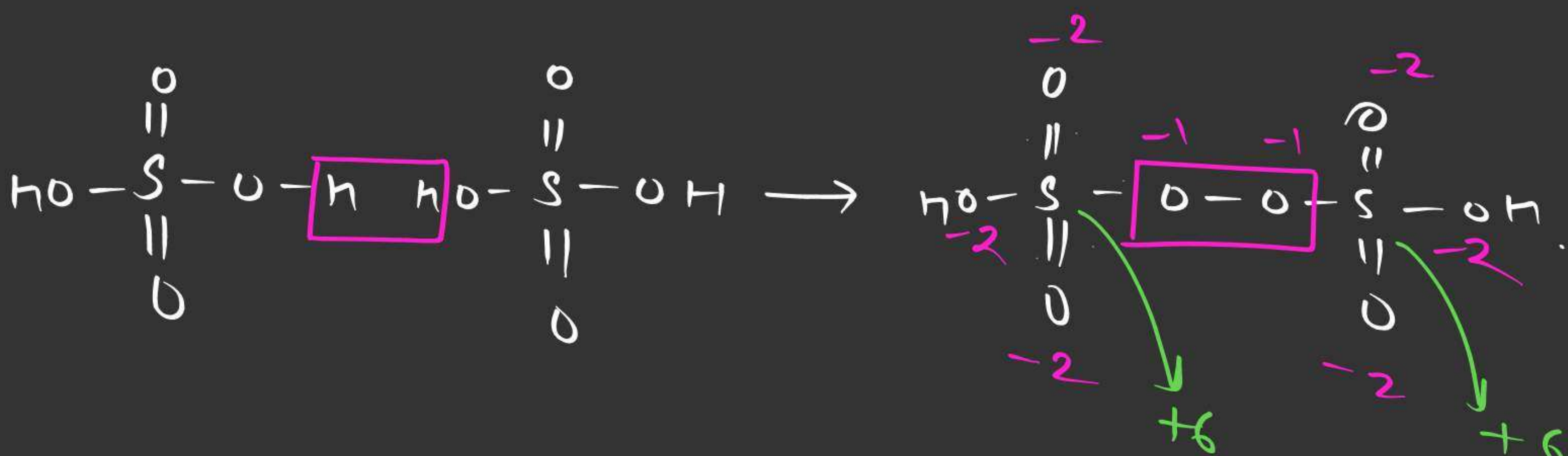
⇒ $H_2S_2O_7$ (Pyrosulphuric acid)

⇒ $H_2SO_4 \times 2 \xrightarrow[-H_2O]{} H_2S_2O_7$



Marshall's Acid ($H_2S_2O_8$)

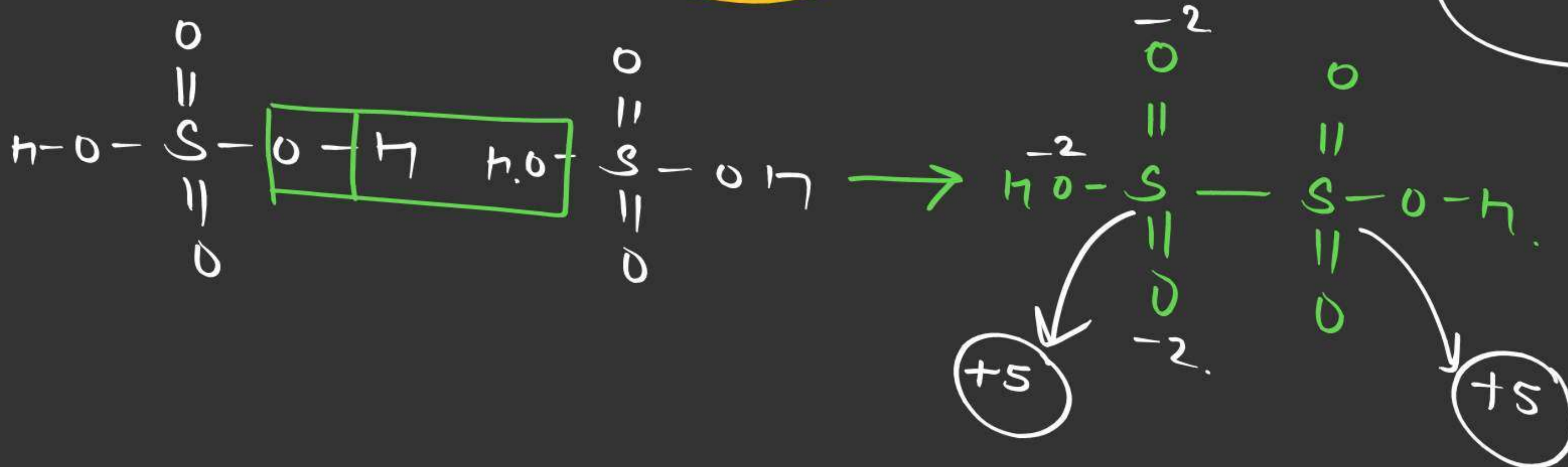
$H_2SO_4 \times 2 - H_2 \rightarrow H_2S_2O_8$



Dithionic acid

$H_2SO_4 \times 2 - H_2O_2 \rightarrow H_2S_2O_6$

1 S–S Bond



(6) OXO acids of phosphoric acid

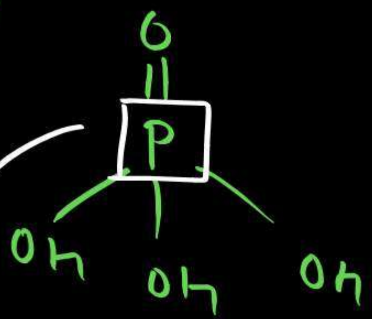
$H_3PO_3 \times 2 - H_2O$

Pyrophosphorous acid

H_3PO_4

(H_3PO_4)
$\times 2$
$-H_2O$

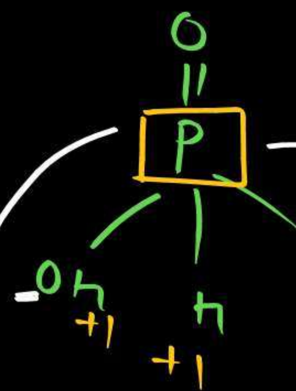
Pyrophosphoric acid



$x - 2 - 1 - 1 - 1$

$x + 5$

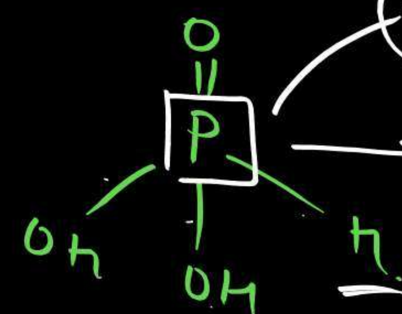
H_3PO_2



$x - 2 - \cancel{1} + \cancel{1} + 1$

$x + 1$

H_3PO_3



$x - 2 - \cancel{1} - 1 + \cancel{1}$

$x + 3$

(7) Carbon suboxide

(C_3O_2)

$$\overset{-2}{O}=C=C=C=\overset{-2}{O}$$

$$\begin{array}{ccc} C & C & C \\ \downarrow & \downarrow & \downarrow \\ +2 & 0 & +2 \end{array}$$

Av. O. state $= \dfrac{0+2+2}{3}$

$+4/3$

(8) $[Fe(CO)_5]$

$x + 0 = 0$

$x = 0$

OXIDATION	REDUCTION
→ Loss of $e^{\ominus}$	→ gain of $e^{\ominus}$
→ Increase in Oxidation No.	→ Decrease in Oxidation no..
→ Addition of 'O'	→ Addition of 'H'
→ Removal of 'H'	→ Removal of 'O'
→ Addition of $\ominus$ EN element	→ Addition of Electropositive element.

OXIDISING AGENT

⇒ Oxidises others and Reduce itself.

REDUCING AGENT

⇒ Reduces others and oxidises itself.

n - factor

ACID

⇒ no. of transferrable H^+ ion.

⇒ (Basicity)

$H_2SO_4 \rightarrow 2H^+ + SO_4^{-2}$

n=2

BASE

⇒ no. of OH^- ion.

$NaOH \rightarrow Na^+ + OH^-$

n=1

SALT

Total +ive / total -ive.

$NaCl \rightarrow Na^+ + Cl^-$

n=1

⇒ $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$.

⇒ +2+6 ⇒ +8

n=8

ELEMENT

⇒ Valency × Atomicity

ORGANIC ACID

⇒ no. of COOH grp.

n-factor in Oxidation :→ $\boxed{\text{Total loss of } e^{\ominus}}$ n_1

n-factor in Reduction :→ $\boxed{\text{Total gain of } e^{\ominus}}$ n_2

n-factor in Disproportionation Rx^n :→ $\boxed{\dfrac{n_1 \times n_2}{n_1 + n_2}}$

Maximum and minimum Oxidation state

Maximum Oxidation State :→ (+) × Valence $e^{\ominus}$

Minimum Oxidation State :→ (−) × Valency

REDOX REACTION

⇒ Rx^n in which Oxidation and Reduction takes place Simultaneously.

Reduction ($n_1 = 5$)

$$\text{Eg } \underset{\downarrow \text{ O.A.}}{\overset{+7}{Mn}}O_4^- + \underset{\downarrow \text{ R.A.}}{\overset{+3}{C_2}}O_4^{-2} \longrightarrow \overset{+2}{Mn^{+2}} + \overset{+4}{C}O_2.$$

Oxidation

($n_2 = 1 \times 2 = 2$)

Identify Oxidising agent and Reducing agent is following and n-factor also.

(1) $\overset{+6}{Cr_2}O_7^{-2} \longrightarrow \overset{+3}{Cr^{+3}} + \overset{0}{Cl_2}$

Reduction

$(n = 3 \times 2 = 6)$

$+\ \overset{-1}{Cl^-}$

O.A.

Oxidation

$(n = 1)$

(R.A.)

(2) $\overset{+7}{Mn}O_4^- + \overset{+3}{C_2}O_4^{-2} \longrightarrow \overset{+4}{Mn}O_2 + \overset{+4}{C}O_2$

$(n = 3)$

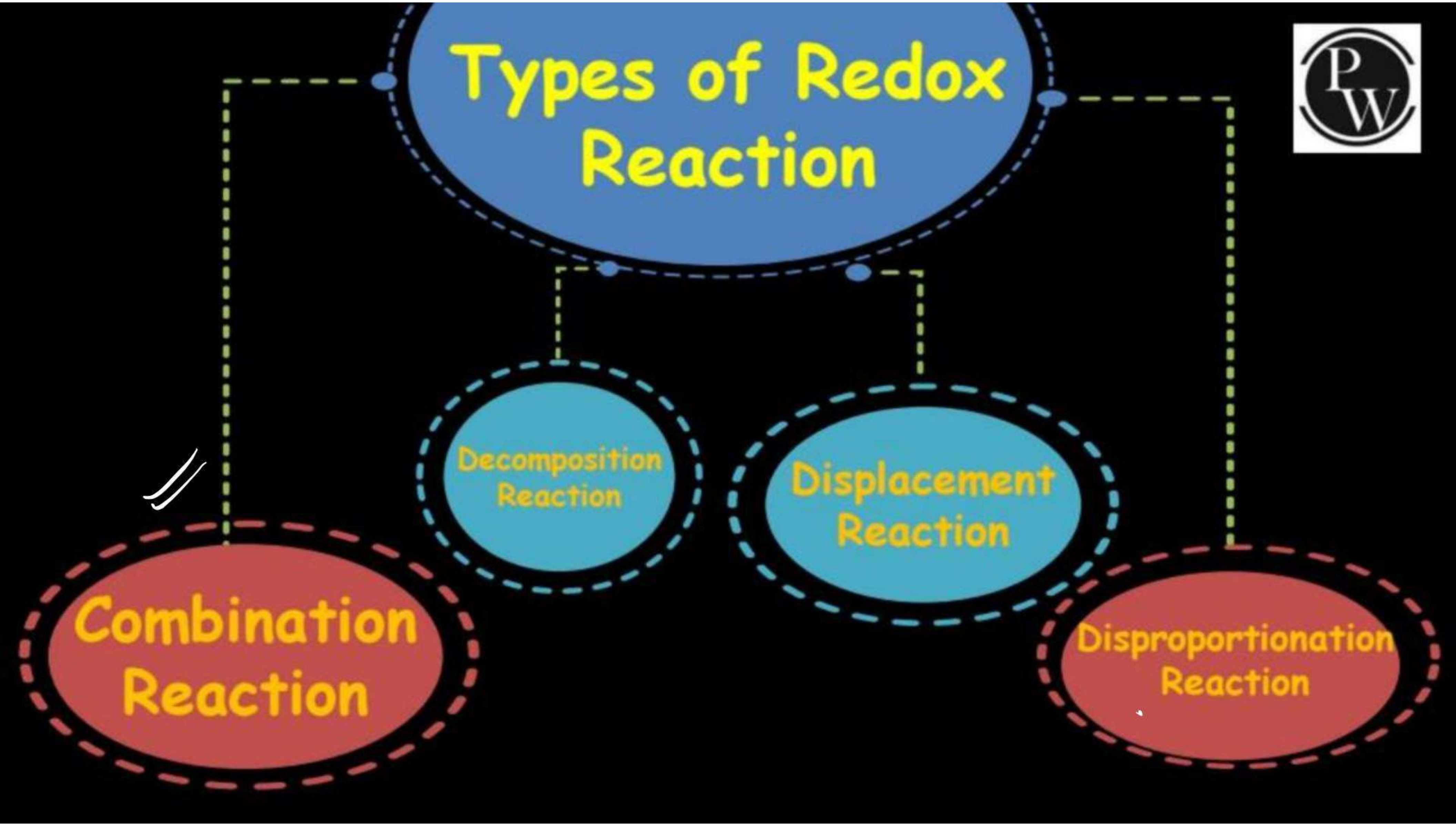
Reduction

$(n_1 = 2)$

Oxidation

O.A.

R.A.



Types of Redox Reaction
Combination Reaction
Decomposition Reaction
Displacement Reaction
Disproportionation Reaction

Combination Reaction

Red.

$$\Rightarrow \overset{(0)}{C} + \underset{(0)}{O_2} \longrightarrow \overset{+4}{C}\underset{-2}{O_2}$$

Oxi.

Decomposition Reaction

Red.

$$\overset{+5}{KClO_3} \xrightarrow{\Delta} \overset{-1}{KCl} + O_2$$

$$\text{O: } -2 \xrightarrow{\text{Oxid}} 0$$

$$\overset{+2}{Ca}\overset{+4}{C}\overset{-2}{O_3} \xrightarrow{\Delta} \overset{+2}{Ca}\overset{-2}{O} + \overset{+4}{C}\overset{-2}{O_2}$$

$\longrightarrow$ Not all Decomposition $Rx^{n}s$ are Redox

Displacement Reaction

Oxi

$$\Rightarrow \overset{(0)}{Zn} + \overset{+1}{H_2}SO_4 \longrightarrow \overset{(+2)}{Zn}SO_4 + \overset{0}{H_2}$$

Red.

Red

$$\Rightarrow \overset{(0)}{Zn} + \overset{+2}{Cu}SO_4 \longrightarrow \overset{+2}{Zn}SO_4 + \overset{0}{Cu}$$

Oxid.

Disproportionation Reaction

Red $(n_1 = 1 \times 2 = 2)$

$$\overset{0}{Cl_2} \xrightarrow{OH^-} \overset{-1}{Cl^-} + \overset{+5}{ClO_3^-}$$

Oxid $(n_2 = 5 \times 2 = 10)$

$$n_f = \frac{n_1 \times n_2}{n_1 + n_2}$$

$$\Rightarrow \frac{2 \times 10}{2 + 10} \Rightarrow \frac{20}{12} \Rightarrow 5/3$$

Identify Disproportionation Reaction and also calculate n factor:

$n_1 = 1 \times 2 = 2$

$$\text{(1)}\ \overset{0}{I_2} + OH^- \longrightarrow \overset{-1}{I^-} + \overset{+5}{IO_3^-}$$

$n_2 = 5 \times 2 = 10$

$$n_f = \frac{2 \times 10}{2 + 10} = \frac{20}{12}.$$

$$\text{(2)}\ Cl_2 + NaOH \longrightarrow NaCl + NaOCl$$

(3) $\overset{0}{F_2} + Na\overset{-2}{O}H \longrightarrow NaF + \boxed{\overset{+2}{O}F_2}$ → Disp → ✗

→ Redox

(4) $Cl_2 + NaOH \longrightarrow NaCl + NaClO_3$

BALANCING OF REDOX REACTION

1) OXIDATION NO. METHOD :-

Step 1 → Calculate the change in Oxidation state and cross multiply to reactant side only.

Step-2 :→ Balance all the atoms other than 'H' and 'O'

Step-3 :→ For Balancing 'O' add required no. of H_2O molecules to the deficient side.

Step-4 For balancing 'H' add required no. of H^+ ions to the deficient side in acidic medium.

Balancing the following Reaction.

(1) $Cr_2O_7^{-2} + Fe^{+2} \longrightarrow Cr^{+3} + Fe^{+3}$

(2) $MnO_4^- + C_2O_4^- \longrightarrow Mn^{+2} + CO_2$

5

$\overset{+7}{2MnO_4^-} + \overset{+3}{5C_2O_4^{-2}} \rightarrow \overset{+2}{2Mn^{+2}} + \overset{+4}{10CO_2}$

$+16H^+$ $+8H_2O$

Basic medi

$16OH^-$ $16OH^-$

$\rightarrow 16H_2O$ B

$\Rightarrow 2MnO_4^- + 5C_2O_4^{-2} \rightarrow 2Mn^{+2} + 10CO_2$

$+8H_2O$ $+16OH^-$

$n_1 = 2$ $\qquad$ $n_2 = 5 \times 2.$

③ $\overset{0}{Cl_2} \xrightarrow{OH^-} \overset{-1}{Cl^-} + \overset{+5}{ClO_3^-}$ $\qquad$ Basic med.

$$5\,Cl_2 \longrightarrow 10Cl^-$$

$$+$$

$$1\,Cl_2 \longrightarrow 2ClO_3^-$$

$$6Cl_2 \rightarrow 10Cl^- + 2ClO_3^-$$

$$+6H_2O \qquad +12H^+$$

$$12OH^- \qquad 12OH^-$$

$$\Rightarrow 6Cl_2 + 12OH^- \longrightarrow 10Cl^- + 2ClO_3^- + 6H_2O$$

n_1

$$A \rightarrow B + C$$

n_2

$$n_2 A \xrightarrow{n_1} B$$

$$+$$

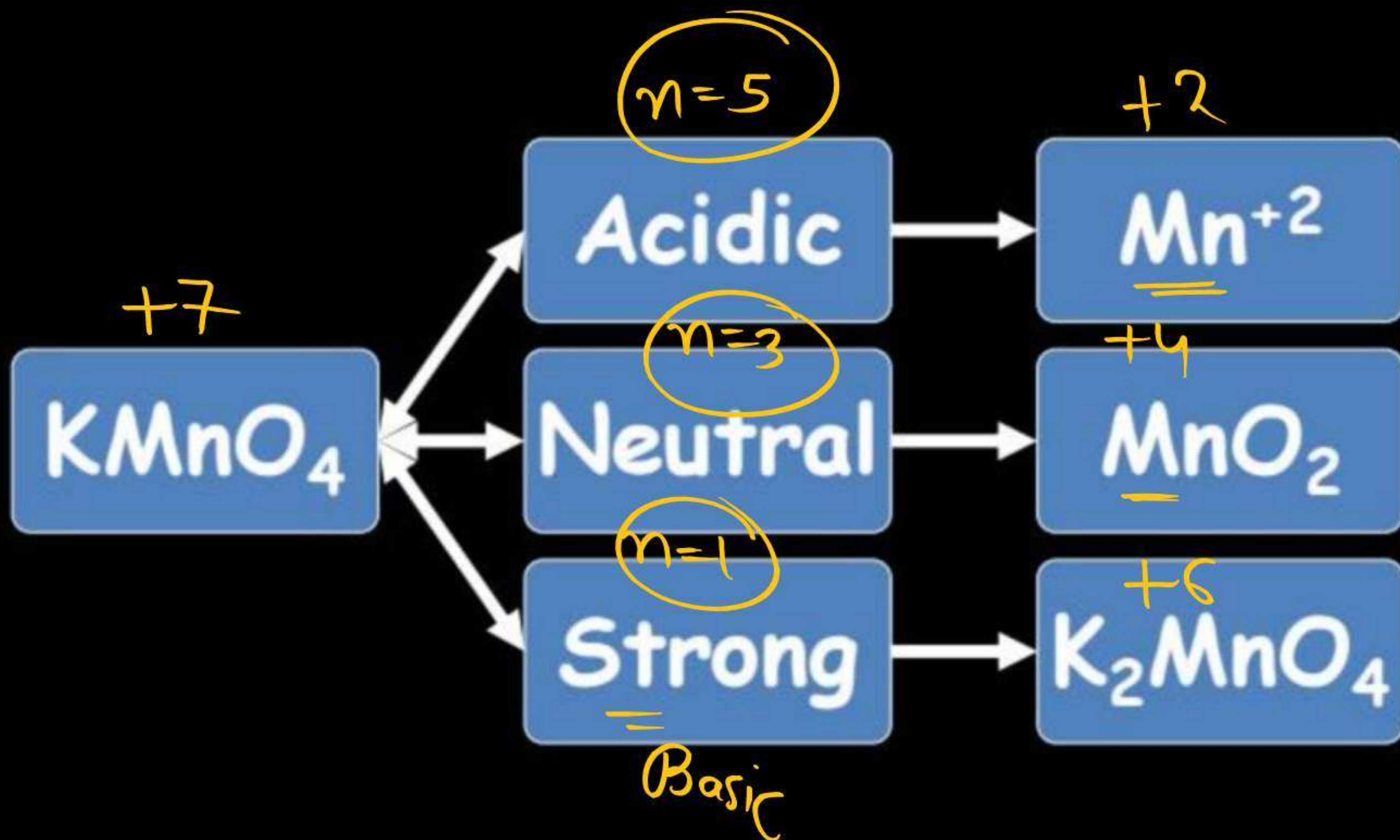
$$n_1 A \xrightarrow{n_2} C$$

REDOX TITRATION

(1) $KMnO_4$ (Potassium Permanganate)

❖ Strong oxidizing agent used in estimation of many reducing agents.

❖ No indicator is used because $KMnO_4$ it self is deeply coloured. (act as self indicator)


+7
KMnO4
n=5
Acidic
n=3
Neutral
n=1
Strong
Basic
+2
Mn+2
+4
MnO2
+6
K2MnO4

(2) $K_2Cr_2O_7$ (Potassium Dichromate)

- $K_2Cr_2O_7$ act as oxidising agent in redox titration.
- Weaken oxidizing agent as compared to $KMnO_4$.
- It does not act as self indicator because no dramatic auto-colour change occurs in its titrations.

$[K_3(Fe(CN)_6)]$

- Generally diphenylamine, potassium ferricyanide are used as indicators.

Both $K_2Cr_2O_7$ and $KMnO_4$ oxidises as follows:-

n=2

(1) $\overset{+3}{C_2O_4^{-2}} \longrightarrow \overset{+4}{CO_2}$

Oxalate

n=2

(2) $\overset{+3}{NO_2^-} \longrightarrow \overset{+5}{NO_3^-}$

Nitrite Nitrate

(3) $\underset{\text{Ferrous}}{Fe^{2+}} \xrightarrow{n=1} \underset{\text{Ferric}}{Fe^{+3}}$

(4) $\underbrace{\overset{+4}{SO_2} \longrightarrow \overset{+6}{SO_4^{2-}}}_{n=2}$

(5) $\overset{+4}{S}O_3^{-2} \xrightarrow{\quad n=2 \quad} \overset{+6}{S}O_4^{-2}$

Sulphite → Sulphate

(6) $\overset{+4}{AS}O_3^{-2} \longrightarrow \overset{+6}{AS}O_4^{-2}$

Arsenite → Arsenate

(7) $\overset{-1}{I^-} \xrightarrow{n=1} \overset{0}{I_2}$

(8) $\overset{-1}{HCl} \xrightarrow{} \overset{0}{Cl_2}$ $n=1$

(3) Iodine (I_2)

- Act as strong oxidizing agent

$\Rightarrow$ $I_2 + 2e^- \longrightarrow 2I^-$

- Iodine can also be used for Titrating strong reducing agents like sodium thiosulphate.

$\Rightarrow$ $I_2(aq) + Na_2S_2O_3(aq) \longrightarrow 2NaI(aq) + Na_2S_4O_6$

- Those Titration in which iodine is directly Titrated against a reducing agent are called **Iodimetric titrations.**

- There is another method in which iodine is liberated from potassium Iodide by some oxidizing agent and liberated iodine is titrated against standard sodium thiosulphate solution. These are called **Iodometric titations**.

- Cu^{2+} ion is estimated by oxidizing I^- ions (from KI) to liberate I_2, which is litrated against $Na_2S_2O_3$.

  $2Cu^{2+}\,(aq.) + 4I^-\,(aq.) \rightarrow Cu_2I_2\,(s) + I_2\,(aq.)$

  $2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$

- In these Iodimetric Titration, end point can be detected by adding freshly prepared starch solution.

- It is reacts with I_2 to form intensely blue-coloured complex. Appearance & disappearance of iodine can be identified accurately by this method.

Application:-

In redox reaction:

gm equivalent of oxidizing agent = gm equivalent of reducing agent.

$$\text{Normality} = \frac{\text{No. of gm Equivalents}}{\text{Volume of sol}^n\text{ (L)}} \Rightarrow \boxed{\frac{\frac{w}{MM} \times n\text{-}f}{V(L)}}$$

No. of gm Equivalent $\Rightarrow \dfrac{\text{given mass}}{\text{Equivalent mass}} \Rightarrow \dfrac{w}{EM}$

$\Rightarrow \dfrac{w}{MM} \times$ n-factor

$\Rightarrow$ no. of mole $\times$ n-factor.

$\Rightarrow N \times V(L)$

$\Rightarrow M \times$ n-factor $\times V(L)$

Find no. of moles of KMnO$_4$ which oxidises

(i) One mole of ferrous sulphate is acidic medium.

~~(ii)~~ 1 mole of sodium oxalate.

~~(iii)~~ 1 mole of ferrous oxalate.

(i) $KMnO_4 = FeSO_4$

$\eta_{moles} \times n\text{-}f = \eta_{moles} \times n\text{-}f$

$\eta_{moles} \times 5 = 1 \times 1$

$$\boxed{\eta_{moles} = 1/5}$$

Ratio of moles of $K_2Cr_2O_7$ & $KMnO_4$ Required to oxidic 0.3 mole Sn^{+2} in acidic medium.

No. of gm eq. of $KMnO_4$ = No. of gm eq. of Sn^{+2}

— " — $K_2Cr_2O_7$ = — " —

$$\frac{n \times 5}{n \times 6} = \frac{\cancel{0.3} \times 2}{\cancel{0.3} \times 2}$$

$$\boxed{\frac{n_{KMnO_4}}{n_{K_2Cr_2O_7}} = \frac{6}{5}}$$

Find moles of $KMnO_4$ which reacts completely with 100ml 10 volume strength H_2O_2.

$KMnO_4 = H_2O_2$

$n_{moles} = ?$ 100 ml

10 V.S.

$N = \frac{10}{5.6}$

$n_{KMnO_4} \times 5 = N \times V(L)$

$n_{KMnO_4} \times 5 = \frac{10}{5.6} \times \frac{100}{1000}$

$n_{KMnO_4} = ?$

H_2O_2

(1) **Percentage Strength:-**

$\Rightarrow$ 3% H_2O_2 solution – 3 gm H_2O_2 in 100 ml solution.

(2) **Volume Strength:-**

$H_2O_2 \rightarrow H_2O_2 + O_2$

1L solution give 10L O_2 at STP

1L solution give 20L O_2 at STP

1L solution give 30L O_2 at STP

(1) $\boxed{\text{Volume Strength} = 5.6 \times \text{normality}}$

$N = \frac{V.S.}{5.6}$

(2) Volume Strength = 5.6 × % strength/17 × 10

$$\boxed{N = \frac{\text{Volume strength}}{5.6}}$$

MnO_4^- is good oxidizing agent in different medium changing to-

$\underset{+7}{MnO_4^-} \longrightarrow Mn^{2+}$ $n = 5$

$\longrightarrow \overset{+6}{MnO_4^{-2}}$ $n = 1$

$\longrightarrow \overset{+4}{MnO_2}$ - $n = 3$

$\longrightarrow \overset{+3}{Mn_2O_3}$ $n = 4$

Changes in oxidation number respectively are – [AIEEE -02]

(A) 1,3,4,5 (B) 5,4,3,2

(C) 5,1,3,4 (D) 2,6,4,3

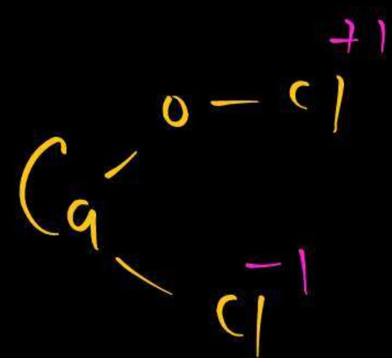
Oxidation number of Cl in $CaOCl_2$ (bleaching powder is) [AIEEE -02]

(A) Zero, since it contain Cl_2

(B) –1 , since it contains Cl^-

(C) + 1, since it contains ClO^-

(D) + 1 and –1, since contains ClO^- and Cl^-



Which of the following is a redox [AIEEE -02]

(A) $2Na\overset{+1}{Ag}(CN)_2 + \overset{0}{Zn} \rightarrow Na_2\overset{+2}{Zn}(CN)_4 + 2\overset{0}{Ag}$ oxi

(B) $BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$

(C) $N_2O_5 + H_2O \rightarrow 2HNO_3$

(D) $AgNO3 + Kl \rightarrow Agl + KNO_3$

In the coordination compound, $\boxed{K_4[Ni(CN)_6]}$, the oxidation state of nickel is

[AIEEE -03]

(A) + 1

~~(B)~~ + 2

(C) – 1

(D) 0

$\downarrow$

$x + 4 - 6 = 0$

$x = +2$

The oxidation state of Cr in $[Cr(NH_3)_4Cl_2]^+$ is - [AIEEE -05]

(A) + 2

(B) + 3

(C) 0

(D) + 1

$x + 0 - 2 = +1$

$x = +1 + 2$

$+3$

The oxidation state of chromium in the final product formed by the reaction between Kl and acidified potassium dichromate solution is –

[AIEEE -05]

(A) + 6

(B) + 4

(C) + 3

(D) + 2

$$\overset{+6}{Cr_2}O_7^{-2} + \overset{-1}{I^-} \longrightarrow \overset{+3}{\underline{\underline{Cr}}} + \overset{0}{I_2}.$$

Consider4 the following reaction :

$xMnO_4^- + yC_2O_4^- + zH^+ \rightarrow xMn^{2+} + 2yCO_2 + z/2\, H_2O$

The value of x, y, and z in the reaction are respectively :-

[JEE (Main)-2013]

(A) 5,2, and 16

(B) 2, 5 and 8

(C) 2, 5 and 16

(D) 5 , 2 and 8

Oxid.

Consider the reaction Red

$$\underset{\text{R.A.}}{H_2\overset{+4}{S}O_{3(aq)}} + \underset{\text{O.A.}}{Sn^{4+}_{(aq)}} + H_2O_{(l)} \rightarrow Sn^{2+}_{(aq)} + H\overset{+6}{S}O^{-}_{4(aq)} + 3H^{+}_{(aq)}$$

How of the following statements is correct? [JEE (Main-online)-2014]

(A) H_2SO_3 is the reducing agent because it undergoes oxidation.

(B) H_2SO_3 is the reducing agent because it undergoes reduction.

(C) Sn^{4+} is the reducing agent because it undergoes oxidation.

(D) Sn^{4+} is the oxidizing agent because it undergoes oxidation.