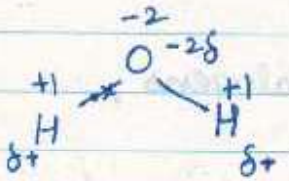
Redox & Equivalent Concept

- **Oxidation state** : Actual charge on an atom or ion if it exists in monoatomic state or it is hypothetical charge assigned to an atom if it is in combined state.
  It arises due to EN difference.

eg : $\overset{0}{H_2}$ $\overset{0}{O_2}$ $\overset{0}{N_2}$ $\overset{+1}{H}\overset{-1}{Cl}$



$Cl^- \rightarrow -1$
$O^{2-} \rightarrow -2$
$He \rightarrow 0$

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

$\overset{+2}{Ca}\overset{-1}{Cl_2}$

✱ Rules to assign O.S. :→

1. O.S. of an element in its free state is taken as zero.
   eg. $H_2 \rightarrow 0$, $N_2 \rightarrow 0$, $S_8 \rightarrow 0$, etc.

2. In combined state,

   a) Alkali metals are given O.S. +1

$\left.\begin{matrix} \overset{0}{Li}^+ \\ Na^+ \\ K^+ \\ Rb^+ \\ Cs^+ \end{matrix}\right\}$ + 1

b) Alkaline earth metals are given O.S. of +2

Be^{2+}
Mg^{2+}
Ca^{2+}
Sr^{2+}
Ba^{2+}
} +2

c) For halogens,

F → -1 (zero in F_2)

Cl
Br
I
} -1 to +7

Cl^-	ClO^-	ClO_2^-	ClO_3^-	ClO_4^-
-1	+1	+3	+5	+7

3. For some important elements

- O → oxide → -2 : CaO
- O → peroxide → -1 : H_2O_2
- O → supersonide → -1/2 : KO_2
- O → 0 : O_2
- O → +1 : O_2F_2
- O → +2 : OF_2

- H → +1 everywhere
  H → −1 {metal hydrides} LiH, CaH_2

4. d-block elements can have variable oxidation states. For eg,

Fe^{+2} Fe^{+3}
Cu^{+} Cu^{+2}
Mn^{+7} Mn^{+6} Mn^{+4}

5. O.S. can be +ve, −ve, zero or fractional

6. Maximum possible O.S. is +8 → Os & Ru

7. In case of co-ordination compounds, neutral ligands are given O.S. of zero

$K_4[Fe(CN)_6]$
central metal atom ↙ ; ligand ↘

CO, NO, NH_3, H_2O → neutral ⇒ OS = 0

except : NO can be neutral or +1

CH_3, C_6H_5 → +1

8. Algebraic sum of oxidation numbers on all atoms in a compound or ion is equal to charge on compound or ion.

Σ O.S. of each element in cpd / ion = charge on ion

eg. CO_3^{2-}

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

$\Rightarrow x = 4$

NH_4^+

$x + 4(1) = 1$

$\Rightarrow x = -3$

Q. Find O.S. on underlined atoms

1. $K_2 \underline{Cr}_2 O_7 = +6$
2. $H_2 \underline{S} O_4 = +4 / +6$
3. $\underline{Mn} O_4^- = +7$
4. $\underline{C}_6 H_{12} O_6 = 0$
5. $No_2 \underline{B}_4 O_7 = +3$
6. $C_6 H_5 \underline{N} O_2 = +3$
7. $\underline{N}_3 H = -1/3$
8. $\underline{N}H_4 \underline{N} O_3 = N_1 = +5, \; N_2 = -3$
9. $(\underline{N}O)\underline{Cl}O_4$ $N = +3$, $Cl = +7$
10. $Ca(O\underline{H})_2$ $H = +1$
11. $Ca O \underline{H}_2 \Rightarrow Ca(O\underline{H})\underline{H}$ $H = +1, -1$
12. $\underline{C}H_3 MgCl$ -4
13. $\underline{Cu}_3 P$ $+1$
14. $\underline{Fe}_{0.96} O = \frac{2}{0.96}$
15. $\underline{As}_2 S_3 = +3$
16. $Fe_2 S_3 = +3$

17. FeS_2 $+2$

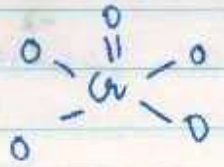
18. $Na_2\underline{S}_2$ -1

19. $\underline{Cu}\ \underline{Fe}\ S_2$ $+1, +3$

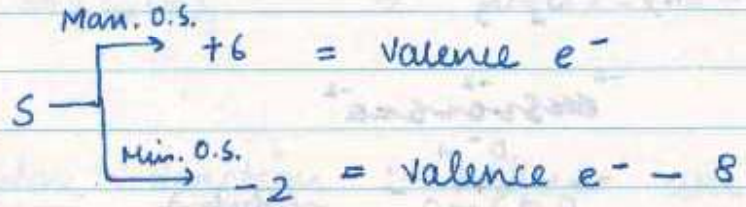
$Cu_2S \cdot Fe_2S_3$

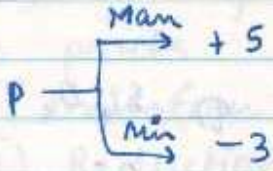
$+1$ ↙ ↘ $+3$

20. $\underline{Cr}O_5$ $+6$



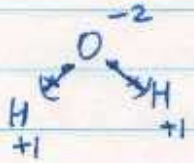
• Determination of Max. & Min. O.S.

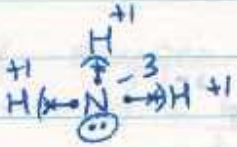




• Using Structure :→

a) $\overset{+1}{H}\leftarrow\overset{-1}{Cl}$

b) 

c) 

d) $\overset{+1}{H}-\overset{+2}{C}\equiv\overset{-3}{N}$

e) $\overset{+1}{H}-\overset{-3}{N}\equiv\overset{+2}{C}$

f) SCN^-

$S \rightleftharpoons C \equiv N:$

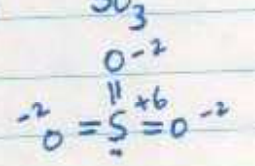
6-8 5-0 5-8

−2 5 −3

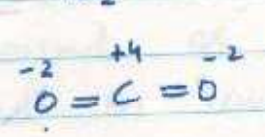
$\xrightarrow{-x}$

$\overset{-2}{S}-\overset{+4}{C}\equiv\overset{-3}{N}$

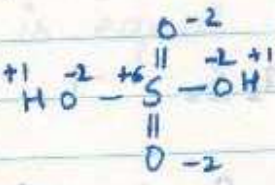
g) SO_3



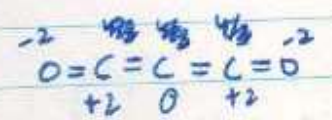
h) CO_2



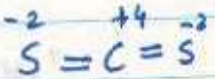
i) H_2SO_4



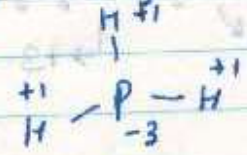
j) C_3O_2



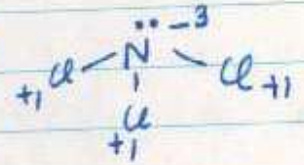
k) CS_2



l) PH_3



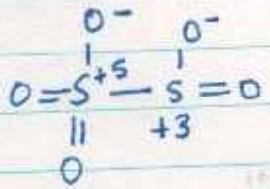
m)



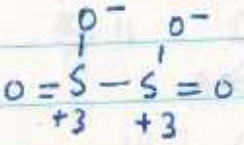
n) $S_2O_3^{2-}$

(Hyb.).

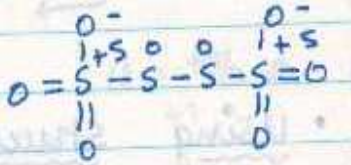
o) $S_2O_5^{2-}$



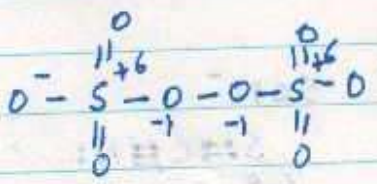
p) $S_2O_4^{2-}$



q) $S_4O_6^{2-}$



r) $S_2O_8^{2-}$



• For co-ordination compounds,

eg $[\underline{Co}(NH_3)_5 Cl]Cl_2$ $\quad x + 5\times0 - 1 - 2 = 0 \Rightarrow x = 3$

eg $K_4[\underline{Fe}(CN)_6]$ $\quad x + 4 - 6 = 0 \Rightarrow x = 2$

eg $K_3[\underline{Fe}(CN)_6]$ $\quad 3 + x + 6\times-1 = 0 \Rightarrow x = 3$

eg) $[\underline{Ni}^{\circ}(CO)_4]$ $\Rightarrow x + 4\times0 = 0 \Rightarrow x = 0$

eg $Sn(C_2O_4)_3^{4-}$ $\Rightarrow x + 3\times-2 = -4 \Rightarrow x = 2$

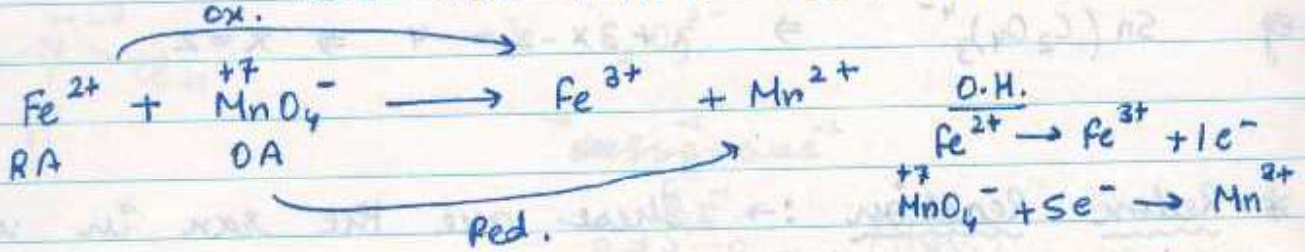
* Redox Reaction :→ These are the rxn in which exchange of e^- take place. It consists of two parts
  i) Oxidation half
  ii) Reduction half

Oxidation Half	Reduction Half
• Gain of oxygen $C + O_2 \rightarrow CO_2$	• Loss of oxygen $CO_2 \rightarrow CO + \frac{1}{2}O_2$
• Loss of hydrogen $C_2H_6 \rightarrow C_2H_4 + H_2$	• Gain of hydrogen $C_2H_2 + H_2 \rightarrow C_2H_4$
• Loss of e^- $A \rightarrow A^+ + e^-$ - increase in O.S.	• Gain of e^- $1e^- + B^{2+} \rightarrow B^+$ - decrease in O.S.

Note : Only oxidation half or only reduction half is not possible these will occur simultaneously.

Oxidising agent : Substances which oxidise others but themselves get reduced. They are also called oxidants.

Reducing agents : Substances which reduce others but themselves get oxidised. They are also called reductants.



* Balancing of Redox Reaction :→

Rule - 1 : Assign O.N. to the elements which undergo change in oxidation states

Rule - 2 : Balance only those atoms for which O.S. is changing in separate half rans.

Rule - 3 : Balance all other atoms except H & O by inspection

Rule - 4 : Now balance H & O

i) In Acidic medium :→

For one excess 'O' atom add one 'H_2O' on the other side and 2 H^+ on same side.

ii) In Alkaline medium :→

Add one H_2O on the same side & 2 OH^- on other side (for one extra 'O' atom).

Note : sometimes just by adding H_2O, rxn gets balanced so there is no need to add H^+ ion or OH^- ion.

In a balanced rxn, total no. of atoms as well as charge remains balanced.

i) $\overset{8/3}{Fe_3O_4} + \overset{+7}{MnO_4^-} \xrightarrow{OH^-} \overset{+4}{MnO_2} + \overset{+3}{Fe_2O_3}$

→ $2 Fe_3O_4 \longrightarrow 3Fe_2O_3 + 2e^-$ × 3 = 6

$MnO_4^- + 3e^- \longrightarrow MnO_2$ × 2

$2MnO_4^- + 6Fe_3O_4 \longrightarrow 9Fe_2O_3 + 2MnO_2$

$H_2O + 2MnO_4^- + 6Fe_3O_4 \longrightarrow 9Fe_2O_3 + 2MnO_2 + 2OH^-$

ii) $\overset{+6}{Cr_2O_7^{2-}} + \overset{+3}{C_2O_4^{2-}} \xrightarrow{H^+} Cr^{3+} + \overset{+4}{CO_2}\,(g)$

iii) $MnO_4^- + C_2O_4^{2-} \xrightarrow{H^+} Mn^{2+} + CO_2\,(g)$

ii)

→ $Cr_2O_7^{2-} + 6e^- = 2Cr^{3+}$

$C_2O_4^{2-} = 2CO_2 + 2e^- \quad \times 3$

$Cr_2O_7^{2-} + 3C_2O_4^{2-} = 2Cr^{3+} + 6CO_2$

$Cr_2O_7^{2-} + 3C_2O_4^{2-} + 14H^+ = 2Cr^{3+} + 6CO_2 + 7H_2O$

iii)

→ $MnO_4^- + 5e^- = Mn^{2+} \quad \times 2$

$C_2O_4^{2-} = 2CO_2 + 2e^- \quad \times 5$

$2MnO_4^- + 5C_2O_4^{2-} = 2Mn^{2+} + 10CO_2$

$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ = 2Mn^{2+} + 10CO_2 + 8H_2O$

iv) $\overset{+2}{Ba}\overset{+6}{Cr}\overset{-2}{O_4} + \overset{+1}{K}\overset{-1}{I} + \overset{+1}{H}\overset{-1}{Cl} \longrightarrow \overset{+2}{Ba}\overset{-1}{Cl_2} + \overset{+1}{K}\overset{-1}{Cl} + \overset{0}{I_2} + \overset{+3}{Cr}\overset{-3}{Cl_3} + \overset{+1}{H_2}\overset{-2}{O}\,(l)$

→ $BaCrO_4 + 3e^- = CrCl_3 \quad \times 2$

$2KI = I_2 + 2e^- \quad \times 3$

$6KI + 2BaCrO_4 = 2CrCl_3 + 3I_2$

$6KI + 2BaCrO_4 + 16HCl \longrightarrow 2CrCl_3 + 3I_2 + 2BaCl_2 + 6KCl + 8H_2O$

v) $\overset{+6}{Cr_2O_7}^{2-} + \overset{+4}{SO_3}^{2-} + H^+ \longrightarrow Cr^{3+} + \overset{+6}{SO_4}^{2-} + H_2O$

$\longrightarrow$ $Cr_2O_7^{2-} + 6e^- = 2Cr^{3+}$

$SO_3^{2-} = SO_4^{2-} + 2e^-$ $\times 3$

$Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^+ = 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$

vi) $\overset{+3\ -2}{As_2S_3} + \overset{+1\ +5\ -2}{HNO_3} \longrightarrow H_3\overset{+5}{As}O_4 + \overset{+6}{H_2SO_4} + \overset{+2\ -2}{NO}$

$\longrightarrow$ $HNO_3 + 3e^- = NO$ $\quad$ (18 e⁻)

$As_2S_3 + 4e^- - 24e^- = 2H_3AsO_4 + 3H_2SO_4$

$4H_2O + 28HNO_3 + 3As_2S_3 = 28NO + 6H_3AsO_4 + 9H_2SO_4$

vii) $\overset{+1}{Cu_3}\overset{-3}{P} + \overset{+6}{Cr_2O_7}^{2-} \longrightarrow Cu^{2+} + \overset{+5}{H_3PO_4} + Cr^{3+} + H_2O$

$\longrightarrow$ $Cr_2O_7^{2-} + 6e^- \Longrightarrow 2Cr^{3+}$

$Cu_3P - 3e^- - 8e^- = 3Cu^{2+} + H_3PO_4$

$124H^+ + 11Cr_2O_7^{2-} + 6Cu_3P = 22Cr^{3+} + 18Cu^{2+} + 6H_3PO_4 + 53H_2O$

viii) $\overset{+2}{Fe}S_2 + \overset{0}{O_2} \longrightarrow \overset{+3}{Fe_2}O_3 + \overset{+4}{S}\overset{-2}{O_2}$

$\longrightarrow Fe S_2 + 1e^- + \frac{7}{2}O_2 \longrightarrow Fe_2O_3 + 2SO_2 + 10e^-$

$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$

ix) $\overset{+2}{Cu}(\overset{+5\ -2}{NO_3})_2 \longrightarrow \overset{+2\ -2}{CuO} + \overset{+4\ -2}{NO_2} + \overset{0}{O_2}$

$\longrightarrow Cu(NO_3)_2 \longrightarrow 2NO_2 - 2e^-$

$Cu(NO_3)_2 \longrightarrow CuO + 2NO_2 + \frac{1}{2}O_2$

$\Rightarrow 2Cu(NO_3)_2 \longrightarrow 2CuO + 4NO_2 + O_2$

x) $\overset{+5\ -2}{As_2S_5} + 18\overset{+1\ +5}{HNO_3} \longrightarrow 2H_3\overset{+5}{As}O_4 + 5H_2\overset{+6}{S}O_4 + 18\overset{+4}{NO_2} + \overset{-1}{H_2}O$

$\longrightarrow As_2S_5 \longrightarrow 5H_2SO_4 + 40e^-$

$2HNO_3 \longrightarrow 2NO_2 + H_2O - 2e^- - 2e^-$

$As_2S_5 + 20HNO_3 \longrightarrow 5H_2SO_4 + 20NO_2 + 10H_2O$

• $\overset{+2}{Cu}\overset{+6}{S}O_4 + \overset{+1}{K}\overset{-1}{I} \longrightarrow \overset{+1}{Cu_2}\overset{-1}{I_2} + \overset{0}{I_2} + K_2\overset{+6}{S}O_4$

→ $2CuSO_4 \longrightarrow Cu_2I_2 + I_2 - 2e^-$

$2KI \longrightarrow I_2 + 2e^-$

$2CuSO_4 + 4KI = Cu_2I_2 + I_2 + 2K_2SO_4$

Q. $2K\overset{+7}{Mn}O_4 \longrightarrow K_2\overset{+6}{Mn}O_4 + \overset{+4}{Mn}O_2 + O_2$

→ $2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 - 1e^- - 3e^-$

$2O^{2-} - 4e^- \longrightarrow O_2$

• A redox can be balanced in more than one way.

$C_2H_5OH + I_2 \xrightarrow{\text{basic}} CHI_3 + HCO_2^- + I^-$

1 : 1

$C_2H_5OH + I_2 \longrightarrow CHI_3 + 3HCO_2^- + I^-$

1 : 3

* Types of Reactions :→

- Redox Rxn
  - Simple or intermolecular
  - Decomp. or intramolecular
  - Disproportional or con-proportional
- Non-redox Rxn
  - → Acid Base Rxn — $HCl + NaOH \rightarrow NaCl + H_2O$
  - → Precipitation — $AgNO_3 + KCl \rightarrow AgCl\downarrow + KNO_3$
  - → Decomposition — $CaCO_3 \rightarrow CaO + CO_2$
  - → Complex — $Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$

1] Simple or intermolecular Redox :→

$$Fe^{2+} + \overset{+7}{MnO_4^-} \longrightarrow Fe^{3+} + Mn^{2+}$$

It involves more than one reactant molecules in which atoms of one element are oxidised while atoms present in another molecule gets reduced.

Becoz exchange of e^- occur b/w two diff molecule that's why it is called intermolecular Redox.

2] Decomposition or intramolecular redox :→

It involves only one reactant molecule in which atoms of one element get oxidised while atoms of other element present in same molecule gets reduced becoz exchange of e^- occur within same molecule, it is also called intramolecular redox.

$$\overset{+5\ -2}{KClO_3} \longrightarrow \overset{+1\ -1}{KCl} + \overset{0}{O_2}$$

3] Disproportionation :→

$$Cl_2 \xrightarrow{\text{red.}} Cl^- + ClO_3^- \quad (\text{ox.})$$

It involves only one molecule (if other molecules r present then those will provide necessary acidic / basic med.) in which atoms of same element are oxidised as well as reduced.

$$2e^- + Cl_2 \longrightarrow 2Cl^-$$
$$Cl_2 \longrightarrow 2ClO_3^- + 10\,e^-$$

$$6Cl_2 \longrightarrow 2ClO_3^- + 10\,Cl^-$$

H.W.
DPP # 1, 2
Ex → 1

H.W.

D-block elements : $KMnO_4$, $K_2Cr_2O_7$ preparation & properties

* Law of Chemical Equivalence :→

Acc" to it, during a chemical reaction no. of equivalents of each reactant reacted will be equal to no. of equivalents of each product produced irrespective of stoichiometric coefficients of reactants & products.

$$aA + bB \longrightarrow cC + dD$$

Equivalent of A reacted = Equivalent of B reacted = Equivalent of C Produced = Equivalent of D produced

No. of equivalents $= \frac{W}{E} = \frac{W}{M} \times n_{factor} = mole \times n_{factor}$

Equivalent wt $(E) = \frac{M}{n_{factor}}$

• Normality (N) :→ No. of equivalents of solute present per litre of solution.

$$N = \frac{\text{no. of eq. of solute}}{V_s(L)}$$

$$N = \frac{n_B}{V_s(L)} \times n_{factor} = M \times n_f$$

No. of equivalents = NV [L]
No. of milli equivalents = NV (mL)

* Calculation of n factor :→

A] For Redox Reaction :→

n_f : No. of e^- lost or gained per molecule or ion of reactants or products.

$$n \text{ factor} = \frac{\text{no. of } e^- \text{ lost / gained}}{\text{stoichiometric coeff. of reactant / products}}$$

Note : Stoichiometric coeff. is obtained by balancing that atom for which O.S. is changing

- $MnO_4^- + 5e^- \longrightarrow Mn^{2+}$
  $\frac{5}{1}$ $\frac{5}{1}$
- $\overset{+6}{Cr_2O_7^{2-}} + 6e^- \longrightarrow 2Cr^{3+}$
  $\frac{\times 6}{2}$
- $3\overset{+7}{Mn}O_4^- + 13e^- \longrightarrow \overset{8/3}{Mn_3O_4}$
  $\frac{13}{3}$ 13
- $\overset{+2}{Fe}\overset{+3}{C_2}O_4 - 1e^- - 2e^- \longrightarrow Fe^{3+} + \overset{+4}{2CO_2}(g)$
  $Fe_n = 3$ 1
  $C_n = 3$ 1

- $C_2O_4^{2-} \longrightarrow 2CO_2(g) + 2e^-$
  2 1

- $\overset{+3}{Fe}(\overset{+5}{NO_3})_3 + 10e^- \longrightarrow Fe^{2+} + 3\overset{+2}{NO}$
  10 10 $\frac{10}{3}$

- $H_2\overset{-1}{O_2} + 2e^- \longrightarrow 2H_2\overset{-2}{O}$
  2 1

- $H_2\overset{-1}{O_2} \longrightarrow \overset{0}{O_2} + 2e^-$
  2 2

i) For simple redox rxn

- $Fe^{2+} + \overset{+7}{MnO_4}^- \longrightarrow Fe^{3+} + Mn^{2+}$
  $-1e^- + 5e^-$
  1 5 1 5

M-I

$Fe^{2+} \longrightarrow Fe^{3+} + 1e^-$) x 5
1 1

$MnO_4^- + 5e^- \longrightarrow Mn^{2+}$
5 5

M-II $5Fe^{2+} + MnO_4^- \longrightarrow Mn^{2+} + 5Fe^{3+}$
$\frac{5}{5} = 1$ $\frac{5}{1} = 5$ 5 1

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

$\longrightarrow$ $\overset{+7}{Mn}O_4^- + 5e^- \longrightarrow Mn^{2+}$)×2

$\overset{+3}{C_2}O_4^{2-} \longrightarrow 2\overset{+4}{C}O_2 + 2e^-$)×5

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

5 2 5 1

iii) $Cr_2O_7^{2-} + Cl_2 \longrightarrow ClO_3^- + Cr^{3+}$

$\longrightarrow$ $Cr_2O_7^{2-} + 6e^- \longrightarrow 2Cr^{3+}$ ×5

$\overset{0}{Cl_2} \longrightarrow 2\overset{+5}{Cl}O_3^- + 10e^-$ ×5

$5Cr_2O_7^{2-} + 3Cl_2 \longrightarrow 10Cr^{3+} + 6ClO_3^-$

6 10 3 5

iv) $\overset{8/3}{Fe_3}O_4 + HNO_3 \longrightarrow Fe^{3+} + NO$

$\longrightarrow$ $Fe_{3\times\frac{8}{3}}O_4 \longrightarrow 3Fe^{3+} + 1e^-$ ×3

$HN\overset{+5}{O}_3 + 3e^- \longrightarrow \overset{+2}{N}O$

$3Fe_3O_4 + HNO_3 \longrightarrow 9Fe^{3+} + NO$

1 3 1/3 3

v) $\overset{0}{I_2} + Na_2\overset{+2}{S}_2O_3 \longrightarrow Na\overset{-1}{I} + Na_2\overset{10/4}{S}_4O_6$ ×5

$\longrightarrow$ $I_2 \longrightarrow 2NaI - 2e^-$

$2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2e^-$

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

2 1 1 2

ii) For decomposition

$2\overset{+5}{K}\overset{-2}{Cl}O_3 \longrightarrow 2K\overset{-1}{Cl} + 3\overset{0}{O_2}$

$\longrightarrow KClO_3 + 6e^- \longrightarrow KCl$

$O^{2-} \longrightarrow \frac{1}{2}O_2 + 2e^-$

$KClO_3 \longrightarrow \frac{3}{2}O_2 + KCl$

1 : 3/2 : 1

$(\overset{-3}{NH_4})_2 \overset{+6}{Cr_2}O_7 \longrightarrow \overset{0}{N_2}(g) + \overset{+3}{Cr_2}O_3 + H_2O$

$\longrightarrow (NH_4)_2Cr_2O_7 + 6e^- \longrightarrow Cr_2O_3$

$N^{3-} \longrightarrow \frac{1}{2}N_2 + 6e^-$

$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$

1 : 1 : 1 : 4

iii) For disproportionation

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

M-I

$Cl_2 - 10e^- \longrightarrow 2ClO_3^-$

$Cl_2 + 2e^- \longrightarrow 2Cl^-$) ×5

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

1/6 : 10/10 : 10/2

M-II

$E = E_1 + E_2$

$E = \frac{M}{n_1} + \frac{M}{n_2} = \frac{M}{n_{eff}}$

$n_{eff} = \frac{n_1 n_2}{n_1 + n_2}$

$= \frac{2 \times 10}{12} = 5/3$

Q. 3/2

1) $\overset{+3}{H_3PO_3} \longrightarrow \overset{-3}{PH_3} + \overset{+5}{H_3PO_4}$

$H_3PO_3 + 6e^- \longrightarrow PH_3$

$H_3PO_3 - 2e^- \longrightarrow H_3PO_4$

2) $\overset{+4}{MnO_2} \longrightarrow \overset{+7}{MnO_4^-} + Mn^{2+}$

$MnO_2 + 2e^- \longrightarrow Mn^{2+}$) ×3

$MnO_2 - 3e^- \longrightarrow MnO_4^-$) ×2

$5MnO_2 \longrightarrow 3Mn^{2+} + 2MnO_4^-$

6/5 2 3

3) $Cu^+ \longrightarrow Cu^{2+} + Cu$

$Cu^+ + 1e^- \longrightarrow Cu$

$Cu^+ - 1e^- \longrightarrow Cu^{2+}$

$2Cu^+ \longrightarrow Cu + Cu^{2+}$

1/2 1 1

4) $Tl^+ \longrightarrow Tl + Tl^{3+}$

$Tl^+ + 1e^- \longrightarrow Tl$) ×2

$Tl^+ - 2e^- \longrightarrow Tl^{3+}$

$3Tl^+ \longrightarrow 2Tl + Tl^{3+}$

2/3 1 2

iv] Reactions involving molecules in which more than one element atoms either undergo oxidation / Reduction.

Eg: 1) $\overset{+3}{Cr}\overset{-1}{I_3} \longrightarrow \overset{+6}{Cr_2}O_7^{2-} + \overset{+7}{I}O_4^-$

$2CrI_3 \longrightarrow Cr_2O_7^{2-} + 6e^- \quad)\times 3$

$CrI_3 \longrightarrow 3IO_4^- + 18e^- \quad \times$

$7CrI_3 \longrightarrow 3Cr_2O_7^{2-} + 3IO_4^-$

$2CrI_3 \longrightarrow Cr_2O_7^{2-} + 6IO_4^-$

$54/2 \qquad 54 \qquad 54/6$

2) $\overset{+1}{Cu_3}\overset{-3}{P} \longrightarrow 3Cu^{2+} + H_3\overset{+5}{P}O_4$ $\quad -3e^- - 8e^-$

$1\beta \qquad 1\beta/3 \qquad 1\beta$

3) $\overset{+1}{Cu_2}\overset{-2}{S} \longrightarrow 2Cu^{2+} + \overset{+6}{S}O_3$ $\quad -2e^- - 8e^-$

$10 \qquad 5 \qquad 10$

4) $\overset{+3}{Bi_2}\overset{-2}{S_3} \longrightarrow 2Bi^{5+} + \overset{0}{3S}$ $\quad -4e^- + 6e^-$

$10 \qquad 5 \qquad 10/3$

v] Reactions in which an element undergoes either oxidation or reduction in more than one oxidation states.

1) $\overset{8}{2}Mn^{+7} \longrightarrow \underset{8}{Mn^{4+}} + \underset{8}{Mn^{2+}}$

$Mn^{7+} + 3e^- \longrightarrow Mn^{4+}$

vi) Reactions involving cmpds which are neither undergoing oxidation nor reduction.

Eg: 1) $Ba\overset{+6}{Cr}O_4 + K\overset{-1}{I} + HCl \longrightarrow BaCl_2 + KCl + \overset{0}{I_2} + \overset{+3}{Cr}Cl_3 + H_2O$

$BaCrO_4 + 3e^- \longrightarrow CrCl_3 \quad \times 2$

$2KI - 2e^- \longrightarrow I_2 \quad \times 3$

$2BaCrO_4 + 6KI + 16HCl \longrightarrow 2BaCl_2 + 3I_2 + 2CrCl_3 + 6KCl + 8H_2O$

$\frac{6}{2} \quad \frac{6}{6} \quad \frac{6}{16} \quad \frac{6}{2} \quad \frac{6}{3} \quad \frac{6}{2} \quad \frac{6}{6} \quad \frac{6}{8}$

2) $\overset{0}{Cl_2} + KOH \longrightarrow \overset{-1}{KCl} + \overset{+5}{KClO_3} + H_2O$

$\longrightarrow \quad Cl_2 \longrightarrow 2KCl - 2e^- \quad \times 5$

$Cl_2 \longrightarrow 2KClO_3 + 10e^-$

$6Cl_2 + 12KOH \longrightarrow 10KCl + 2KClO_3 + 6H_2O$

$10/6 \quad 5/6 \qquad 10/10 \quad 10/2 \quad 10/6$

B] For Non-Redox

Case I : n factor for acids / bases if Rxn is not given.

n_f : no. of replacable H^+ for Acids

n_f : no. of replacable OH^- for bases.

- $HCl \rightarrow 1$
- $H_2SO_4 \rightarrow 2$
- $H_3PO_4 \rightarrow 3$
- $H_3PO_3 \rightarrow 2$
- $H_3PO_2 \rightarrow 1$
- $Ca(OH)_2 \rightarrow 2$
- $NaOH \rightarrow 1$
- $Al(OH)_3 \rightarrow 3$

Case II : n_{factor} for acids / bases when rxn is given

n_f = no. of H^+/OH^- replaced $\times$ | charge on H^+/OH^- |

Eg: a) $\underset{1}{NaOH} + \underset{2}{H_3PO_4} \longrightarrow Na_2HPO_4 + H_2O$

b) $\underset{1}{NaOH} + \underset{3}{H_3PO_4} \longrightarrow Na_3PO_4 + H_2O$

c) $\underset{2}{H_2SO_4} + \underset{1}{NaOH} \longrightarrow Na_2SO_4 + H_2O$

d) $\underset{2}{Ca(OH)_2} + \underset{1}{H_2S} \longrightarrow Ca(HS)_2$

e) $\underset{2}{Ca(OH)_2} + \underset{2}{H_2S} \longrightarrow CaS$

f) $\underset{3}{H_3PO_3} + \underset{2}{Ca(OH)_2} \longrightarrow Ca_3(PO_4)_2$

Case III : n_f of ions

n_f = | magnitude of charge on ion |

- $Cl^- = 1$
- $SO_4^{2-} = 2$
- $PO_4^{3-} = 3$
- $NH_4^+ = 1$
- $CO_3^{2-} = 2$

Case IV : n_{factor} for salts

n_f = total +ve or total -ve charge

- $NaCl = 1$
- $CaCl_2 = 2$
- $Na_3PO_4 = 3$
- $Ca_3(PO_4)_2 = 6$
- $Al_2(SO_4)_3 = 6$

Case V : n_{factor} for Rxn involving complex cmpds

n_f = no. of ions replaced in complex × | charge on ion | = charge repla per mol

eg: • $2Zn^{2+} + K_4[Fe(CN)_6] \longrightarrow Zn_2[Fe(CN)_6] + 4K^+$
(2) (4) (4) (1)

• $K_4[Fe(CN)_6] + FeCl_3 \longrightarrow KFe[Fe(CN)_6] + 3KCl$
(3) (3) (3) (+1)

• $3Zn^{2+} + 2K_4[Fe(CN)_6] \longrightarrow Zn_3K_2[Fe(CN)_6]_2 + 6K^+$
(2) (3) (6) (1)

• $3Zn^{2+} + 2Al_4[Fe(CN)_6]_3 \longrightarrow 3ZnAl_2[Fe(CN)_6]_2 + 2Al^{3+}$
(2) (3) (2) (3)

Case VI : n_f of acidic / basic oxides is equal to n_f of acid or base obtained by dissolving that oxide in water.

$CO_2 + H_2O \longrightarrow H_2CO_3$ = 2
$SO_3 + H_2O \longrightarrow H_2SO_4$ = 2
$CaO + H_2O \longrightarrow Ca(OH)_3$ = 2
$N_2O_5 + H_2O \longrightarrow HNO_3$ = 1
$P_4O_6 + H_2O \longrightarrow H_3PO_4$ = 3

Eg. $Al(OH)_3 \longrightarrow 3$
$B(OH)_3 \rightarrow 1$
$B(OH)_3 + H_2O \longrightarrow B(OH)_4^- + H^+$

Some important oxidising agents :→

1] $KMnO_4$

$MnO_4^- \xrightarrow{\text{Acidic}} Mn^{2+}$
5

$MnO_4^- \xrightarrow[\text{neutral}]{\text{Basic}} Mn^{4+}$
3

$MnO_4^- \xrightarrow[\text{basic}]{\text{strongly}} Mn^{6+}$
1

2] $K_2Cr_2O_7$

$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$
$n_f = 6$

3] H_2O_2

(RA)

$H_2O_2 \longrightarrow O_2$

$n_f = 2$

(OA)

$H_2O_2 \longrightarrow H_2O$

$n_f = 2$

- $MnO_4^- + H_2O_2 \xrightarrow{H^+} Mn^{2+} + O_2$
- $MnO_4^- + Cu^+ \xrightarrow{H^+} Mn^{2+} + Cu^{2+}$
- $MnO_4^- + C_2O_4^{2-} \xrightarrow{OH^-} Mn^{+4} + CO_2$
- $Cr_2O_7^{2-} + Fe^{2+} \longrightarrow 2Cr^{3+} + Fe^{3+}$
- $Cr_2O_7^{2-} + SO_2 \longrightarrow 2Cr^{3+} + SO_3$

★ HNO_3 & H_2SO_4 have 'N' & 'S' in their max. O.S. So they can also act as O.A.

- Titration :→ It is process of determination of conc. of unknown sol^n with the help of known solution. We will mainly deal with the following types of titration :

a) Acid - Base Titration → HCl V/S NaOH (SA V/S SB)
→ HCl V/S NH_4OH (SA V/S WB)
→ CH_3COOH V/S NaOH (WA - SB)

b) Redox Titration
- → Titration with $KMnO_4$
- → " " $K_2Cr_2O_7$
- → Iodometric titration
- → Iodimetric titration

Q. Calculate no. of moles of $KMnO_4$ which will react with 180 g of $H_2C_2O_4$ as

$$\overset{+7}{KMnO_4} + \underset{2\text{mol}}{\overset{+3}{H_2C_2O_4}} \longrightarrow \underset{2}{\overset{+4}{2CO_2}} + \underset{3}{\overset{+2}{Mn^{2+}}} \quad +3e^-$$

Also calculate volume of CO_2 evolved at NTP.

$\longrightarrow$ $2 \rightarrow \overset{4\text{mole}^-}{-2e^-}$; $1 \rightarrow 5e^-$; $4/5$; $89.6\,L$

Q. Calculate moles of $K_2Cr_2O_7$ required to produce 254 g of I_2 from KI sol^n.

$\longrightarrow$ $K_2Cr_2O_7 + \overset{-1}{KI} \longrightarrow \overset{0}{I_2} + Cr^{3+}$

$K_2Cr_2O_7 + 6e^- \longrightarrow 2Cr^{3+}$

$2KI - 2e^- \longrightarrow I_2$ $)\times 3$

$$\underset{6}{K_2Cr_2O_7} + \underset{1}{6KI} \longrightarrow \underset{3}{2Cr^{3+}} + \underset{2}{3I_2}$$

$6 \times z = 3 \times y = 3 \times x = 2 \times 2$

$\therefore z = 4/6 = 2/3$

Q. Calculate volume of 0.05 M $KMnO_4$ which will react with 50 ml of 0.1 M H_2S in H^+ med. ($H_2S \longrightarrow SO_2$)

→ $KMnO_4 + 5e^- \longrightarrow Mn^{2+}$)×6

$H_2S - 6e^- \longrightarrow SO_2$)×5

$$\underset{5}{6KMnO_4} + \underset{6}{5H_2S} \longrightarrow \underset{5}{6Mn^{2+}} + \underset{6}{5SO_2}$$

$\Rightarrow 0.05 \times V \times 5 = 0.1 \times 50 \times 6$

$\Rightarrow V = 120$ ml

Q. Calculate mm of Fe_3O_4 that reacts completely with 25 ml of 0.3 M $K_2Cr_2O_7$

→ $K_2Cr_2O_7 + 6e^- \longrightarrow 2Cr^{3+}$

$Fe_3O_4 - 1e^- \longrightarrow 3Fe^{3+}$)×6

$$\underset{6}{K_2Cr_2O_7} + 6\underset{1}{Fe_3O_4} \longrightarrow \underset{3}{2Cr^{3+}} + \underset{1/3}{18Fe^{3+}}$$

$\Rightarrow 25 \times 0.3 \times 6 = x$

$\therefore x = 45$ mm

Q. Calculate conc. of H_2O_2 sol^n if 20 ml of H_2O_2 sol^n reacts completely with 10 ml 2M $KMnO_4$

→ $KMnO_4 + 5e^- \longrightarrow Mn^{2+}$

$H_2\overset{-1}{O}_2 - 2e^- \longrightarrow \overset{0}{O}_2$

$$\underset{5}{KMnO_4} + \underset{2}{5H_2O_2} \longrightarrow Mn^{2+} + 5O_2$$

$5 \times 10 \times 2 = x \times 20 \times 2$

$\therefore x = \frac{5}{2}$ M

Note : w.r.t. decomposition or disproportionation, N is not defined coz to find normality we need n factor which can be obtained titration.
eg. For H_2O_2, n factor is 2 whether it is oxidised or reduced, thats why we will take its n factor as 2.

Q. Calculate moles of KCl required to produce 10 mol Cl_2 by rxn with $KClO_3$.

→ $\overset{+1}{K}\overset{-1}{Cl} + K\overset{+5}{Cl}O_3 \longrightarrow Cl_2 +$

$2K\overset{-1}{Cl} \longrightarrow \overset{0}{Cl_2} + 2e^-$) × 5

$2KClO_3 \longrightarrow Cl_2 - 10e^-$

$6 \times \frac{10}{6}$; $10 \times 10/6$

$10KCl + 2KClO_3 \longrightarrow \underset{10}{6Cl_2}$

$\underline{100/6}$ moles.

Q. Calculate moles of ~~CO_2~~ $KMnO_4$ required for complete oxidation of 1.25 mol of Cu_2S

$6e^- + 2e^- + \overset{+1}{Cu_2}\overset{-2}{S} \longrightarrow 2Cu^{2+} + SO_2$

→ $8e^- \rightarrow 1$ (+5)

$1.25 \rightarrow 10e^-$ ∴ 2 mol $KMnO_4$.

Q. Calculate moles of $KMnO_4$ required to react with a mixture of

a) 1 mol of $H_2\overset{+3}{C_2}O_4$ + 2 mol of $K\overset{+3}{H}C_2O_4 \cdot H_2C_2O_4$ $\xrightarrow{10e^-}$ $10CO_2$
↳ 2 moles

b) 2 mol of $H_2C_2O_4$ + 3 mol of $KHC_2O_4 \cdot 2H_2C_2O_4$.
↳ $\frac{2}{5}$ moles.

Q. NaOH

a) → ~~8~~

b) → ~~19~~ 19.

H.W.

DPP #3

Ex 1: 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, – 23.

Q. 696 g mixture of FeO & Fe_2O_3 reacts completely with 1 mol of $KMnO_4$ in ac. md. Calculate composition by moles of FeO & Fe_2O_3.

→ $1 \times 5 = \frac{x}{72} \times 1 \Rightarrow x = \frac{360}{336}\text{g} = 5 \text{ moles} = 2.1$

Q. A min. of $\overset{0.1}{\underset{7.2g}{FeO}}$ & $\underset{0.3}{Fe_2O_3}$ is reacted with acidified $KMnO_4$ sol^n having a concentration of 0.2 M, 100 ml of which was used. The sol^n was then titrated against zinc dust which converted Fe^{3+} of sol^n to Fe^{2+}. The Fe^{2+} requires 1000 ml of 0.1M $K_2Cr_2O_7$ sol^n. find % of FeO & Fe_2O_3

→ $0.2 \times \overset{0.1}{100} \times 5 = 1 \times \frac{x}{72}$ | $1 \times 0.1 \times 6 = 1 \times \frac{x}{0.6}$ | 0.6×160 96g.

~~200g~~ 7.2g

Q. A mixture cont. equal moles of $\overset{+2}{CuS}$ & $\overset{+1}{Cu_2S}$ was treated with 100 ml of 0.15 M $K_2Cr_2O_7$. The product obt. were Cr^{3+}, Cu^{2+} & SO_2. The excess oxidant was reacted with 50 ml of 0.4 M Fe^{2+} sol^n. Calculate mw of CuS & Cu_2S. (500, 500)

$\longrightarrow$ $1 \times 0.4 \times 50 = 6 \times x \times 0.15 \Rightarrow x = \frac{200}{9}$ $\qquad \frac{700}{9}$ $\qquad \frac{x \times 2 + x \times 2 \times 2}{6x}$

$\overset{+2}{CuS} + 3\overset{+1}{Cu_2S} + K_2Cr_2O_7 \longrightarrow 2Cr^{3+} + 7Cu^{2+} + 7SO_2$

$-2x + 2 \times x$

$Cu_2S \longrightarrow 2Cu^{2+} + 2e^- \quad \times 3$

$10x$

$K_2Cr_2O_7 \longrightarrow 2Cr^{3+} + 6e^-$ $\qquad \frac{700}{9} \times 0.15 \times 6 = 2 \times x + 2 \times 2 \times 2 \times$

— x —

$CuS + K_2Cr_2O_7 \longrightarrow Cu^{2+} + SO_2$
6 $\quad$ 6 $\quad$ 6 $\quad$ 6

$7Cu_2S + 2K_2Cr_2O_7 \longrightarrow 14Cu^{2+} + 7SO_2 + 4Cr^{3+}$
8 $\quad$ 6 $\quad$ 8/2 $\quad$ 8

*

$NaCl \longrightarrow M_{NaCl} = M_{Na^+} + M_{Cl^-}$

$\hookrightarrow E_{NaCl} = \frac{M_{NaCl}}{n_f} = \frac{M_{Na^+}}{1} + \frac{M_{Cl^-}}{1} = E_{Na^+} + E_{Cl^-}$

$CaCl_2 \longrightarrow E_{CaCl_2} = \frac{M_{CaCl_2}}{2} = \frac{M_{Ca^{2+}}}{2} + \frac{2M_{Cl^-}}{2} = E_{Ca^{2+}} + E_{Cl^-}$

Q. $H_2SO_4 \rightarrow E = E_{H^+} + E_{SO_4^{2-}}$
$= 1 + 48$
$= \underline{49}$

b) $Na_2SO_4 \longrightarrow E_{Na^+} + E_{SO_4^{2-}}$

$= 23 + 48 = 71$

c) $Na_3PO_4 \longrightarrow 23 + \frac{95}{3}$

d) $E_{MgO} = E_{Mg^{2+}} + E_{O^{2-}}$

$= \frac{24}{2} + \frac{16}{2} = 20$

1 mol MgO = 2 eq. of MgO

$\frac{1}{2}$ mol MgO = 1 eq. of MgO

e) $E_{Na_2O_2} = E_{Na^{1+}} \quad E_{O^-}$

$\quad\quad\quad\quad 23 \quad\quad 16$

Q. A metal oxide contains 20% metal. Calculate eq. wt. of metal. (by mass)

$\longrightarrow$ ~~X_2O_3~~ $M_xO_y^{2-}$

eq of metal = eq of oxide

$\frac{W_{metal}}{E_{metal}} = \frac{W_{oxide}}{E_{oxide}} \Rightarrow \frac{20}{x} = \frac{80}{8}$

$\therefore E_{metal} = 2$

Q. A super oxide contains 84% by mass of metal. Calculate E_{metal}.

$\longrightarrow \quad \frac{84}{E} = \frac{16}{32} \Rightarrow E = 168$

H.W.

Ex. 1 ⇒ 1 to 36

Ex. 2 ⇒ upto 17

R. B. ⇒ 12 to 21

* Iodimetric Titration : In this titration excess of Iodine is made to react with a reducing agent & then remaining amount of Iodine is titrated against standard hypo sol". All these titrations are carried out in a solution of freshly prepared starch coz with starch Iodine forms blue coloured complex which can traced even when I_2 is present in trace amts.

$$RA + I_2 \text{ (excess)} \longrightarrow I^-$$

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

(I_2 (left): 2; Hypo: 1; 1; 2)

* Iodometric Titration : In this titration I_2 is made to evolve by reacting excess of KI with oxidising agent & then evolved Iodine is made to react with standard hypo sol".

$$OA + KI \longrightarrow I_2$$

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

Q. 50 ml of $KMnO_4$ is mixed with excess of KI. The I_2 liberated required 30 ml of 0.1 M $Na_2S_2O_3$ sol^n. Calculate molarity of $KMnO_4$.

$$\underset{5}{KMnO_4} + \underset{1}{2KI} \longrightarrow \underset{2}{I_2} + Mn^{2+} \qquad 5 \times 50 \times M = 1 \times 2 \times 30$$

$$\underset{2}{I_2} + \underset{1}{Na_2S_2O_3} \longrightarrow \underset{2}{Na_2S_4O_6} + \underset{1}{NaI}$$

$$\Rightarrow 30 \times 0.1 \times 1 = 2 \times x \qquad \Rightarrow x = 3/2$$

$$\Rightarrow M = \frac{3}{250}$$

- In this case 'n' factor of Iodine when it is formed is same as its 'n' factor when it again reacts. So no. of eq. of I_2 will be same in both rxn. We can say,

  eq. of $KMnO_4$ = eq. of hypo.

- If 'n' factor is diff. when I_2 is formed & when it again reacts then milli eq. of I_2 will be diff. So we will calculate mm in one rxn & put them in other.

3. Certain amt. of KIO_3 was mixed with KI soln. The liberated I_2 was titrated against 50 ml 0.2M $Na_2S_2O_3$ for completion. Calculate mm of KIO_3 mixed.

$$\longrightarrow \underset{5}{2K\overset{+5}{I}O_3} + \underset{1}{10K\overset{-1}{I}} \longrightarrow \underset{10/6}{6I_2}$$

$$\underset{2}{I_2} + \underset{1}{Na_2S_2O_3} \longrightarrow \underset{1}{NaI} + \underset{2}{Na_2S_4O_6}$$

$$\Rightarrow 1 \times 0.2 \times 50 = 2 \times M \times V$$

$$\Rightarrow \frac{10}{6} \times 8 = 8 \times mm$$

$\therefore$ mm of $KIO_3 = 5/3$.

- If a single reactant, reacts in more than one rxns & its n factor is same in all rxns,

$$\underset{n_1}{A} + B \longrightarrow$$
$$\underset{n_2}{A} + C \longrightarrow$$
$$\underset{n_3}{A} + D \longrightarrow$$

If, $n_1 = n_2 = n_3 = n$

Eq of A = Eq of B + Eq of C + Eq of D

If $n_1 \neq n_2 \neq n_3$

Eq of A $\neq$ eq of B + eq of C + eq of D

but still we can apply law of equivalence independently for each rxn.

Q. Calculate mm of SeO_3^{2-} in solution on the basis of following data.

20 ml of $\frac{1}{60}$ M $KBrO_3$ was added to definite volume of selenide ion (SeO_3^{2-}) solution. The Br_2 evolved was removed & excess of $KBrO_3$ require 5 ml of $\frac{1}{25}$ M solution of $NaAsO_2$ for complete destruction.

$$\rightarrow \overset{+5}{2}BrO_3^- + 5\overset{+4}{Se}O_3^{2-} \longrightarrow 5\overset{+6}{Se}O_4^{2-} + \overset{0}{Br_2}$$

(2/3 ans.)

$$\overset{+5}{BrO_3^-} + 3\overset{+3}{AsO_2^-} \longrightarrow 3\overset{+5}{AsO_4^{3-}} + \overset{-1}{Br^-}$$

$$5 \times \frac{1}{25} \times x = \frac{3}{6} \times MV = \frac{1}{15}$$

Q. 20 ml of $K_4[Fe(CN)_6]$ sol^n is divided into two equal parts. One part is completely reacted with 10 ml of $FeCl_3$ to form $KFe[Fe(CN)_6]$ & KCl. Another part of $K_4[Fe(CN)_6]$ sol^n is reacted with 20 ml of 0.5 M $FeCl_2$ sol^n to produce $K_2Fe[Fe(CN)_6]$ & KCl. Molarity of $FeCl_3$ is 1 M.

$$\rightarrow K_4[Fe(CN)_6] + \overset{+3}{Fe}Cl_3 \longrightarrow KFe[Fe(CN)_6] + 3KCl$$

$$K_4[Fe(CN)_6] + \overset{+2}{Fe}Cl_2 \longrightarrow K_2Fe[Fe(CN)_6] + 2KCl$$

* Hard Water : Presence of Ca^{2+} & Mg^{2+} salts in form of HCO_3^-, Cl^- & SO_4^{2-} makes water hard.
- Hard water does not produce lather with soap.

* Soft Water : Water free from soluble salts of Ca^{2+} & Mg^{2+}.
- It produces lather with soap solution.

Types of Hardness :→

1] Temporary hardness : It is due to presence of $Mg(HCO_3)_2$ & $Ca(HCO_3)_2$ and it can be removed by following ways,

A] Boiling, On boiling soluble hardness causing salts are converted into insoluble precipitates.

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_{3(s)} \downarrow + H_2O_{(l)} + CO_{2(g)} \uparrow$$

$$Mg(HCO_3)_2 \xrightarrow{\Delta} MgCO_{3(s)} \downarrow + H_2O_{(l)} + CO_{2(g)} \uparrow$$

B] Addition of Na_2CO_3,

$$Ca(HCO_3)_2 + Na_2CO_3 \longrightarrow CaCO_{3(s)} \downarrow + 2NaHCO_3$$

C] Clark's Method : In it calculated amt of lime is added which ppt hardness causing ions.

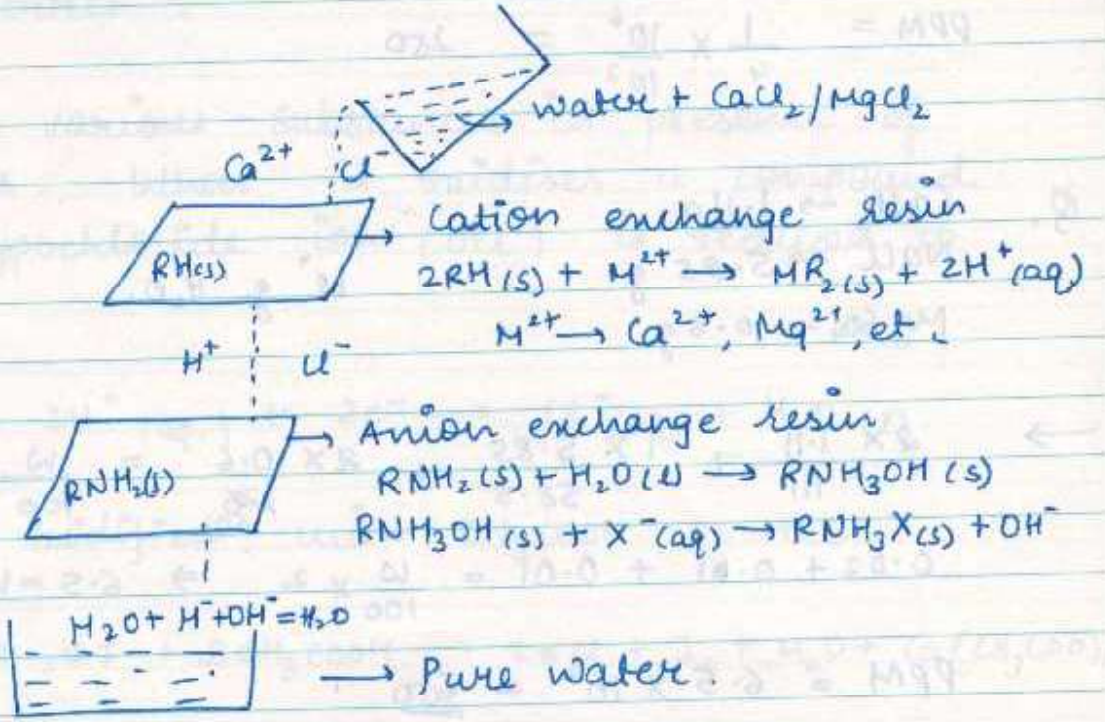
$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_{3(s)} + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_{3(s)} \downarrow + MgCO_3 \downarrow + H_2O$$

2] Permanent Hardness : due to presence of soluble salts of Ca^{2+} & Mg^{2+} in form of Cl^- & SO_4^{2-}. It cannot be simply removed by boiling.

→ To remove it, water is successively passed thru cation exchange resin where cation gets exchanged with H^+ & sol^n becomes acidic.

→ Now this acidic water is passed thru anion exchange resin where anion gets exchanged with OH^-, & now H^+ & OH^- combine to form water & it becomes neutral.



- Measurement of Hardness of Water :→

Hardness of water is measured in terms of equivalent amt. of $CaCO_3$ in PPM.

$$PPM = \frac{W_{CaCO_3}}{W_{solution}} \times 10^6$$

Q. Calculate hardness of water containing 0.3 g of $MgSO_4$ in 1000 g of water.

→ $PPM = \frac{0.3 \times 2}{1000} \times 10^6$.

Eq of $MgSO_4$ = Eq of $CaCO_3$

$2 \times \frac{0.3}{120} = \frac{W_{CaCO_3}}{100} \times 2$

$\Rightarrow W_{CaCO_3} = \frac{1}{4}$

$PPM = \frac{1}{4} \times \frac{10^6}{10^3} = 250$

- Q. $CaCl_2 \rightarrow 1.11$ g
  $NaCl \rightarrow 5.85$ g
  $MgSO_4 \rightarrow 0.6$ g
  10^4 g H_2O.

→ $2 \times \frac{1.11}{111} + 1 \times \frac{5.85}{58.5} + 2 \times \frac{0.6}{120} = \frac{W}{100} \times 2$

$0.02 + 0.01 + 0.01 = \frac{W}{100} \times 2 \Rightarrow 6.5 = W$

$PPM = 6.5 \times 10^2 = \underline{650}$.

Q. $CaCl_2 \rightarrow 1$ mm
$NaCl \rightarrow 2$ mm
$MgSO_4 \rightarrow 2$ mm

$1 + 1 + 2$
$4 \times$

→ $\frac{4 \times 10^{-3} \times 100}{10^4} \times 10^6 = \underline{40}$

* Bleaching Powder ($CaOCl_2$) :

In presence of slight amt. of dilute acids, $CaOCl_2$ loses nacent oxygen & due to this [O] it shows oxidising as well as bleaching properties.

$$CaOCl_2 + H_2SO_4 \longrightarrow CaCl_2 + CaSO_4 + 2HCl + 2[O]$$

Nascent oxygen

Oxidising Properties :

→ It oxidises various substances in presence of dilute acids. When it oxidises a compound then its hypochloride ion (OCl^-) is reduced to Cl^- ion.

$$ClO^-_{(aq.)} + 2H^+_{(aq.)} + 2e^- \longrightarrow Cl^-_{(aq)} + H_2O_{(l)}$$

→ KI solution acidified with CH_3COOH or HCl

$$Ca(OCl)Cl + KI + 2CH_3COOH \longrightarrow 2KCl + I_2 + H_2O + Ca(CH_3C$$

→ $NaAsO_3 + ClO^- \longrightarrow AsO_4^{3-} + Cl^-$

→ $PbO + CaOCl \longrightarrow PbO_2 + Cl^-$

→ $H_2S + CaOCl \rightarrow Cl^- + H_2O + S$

→ $Fe^{2+} + ClOCa \rightarrow Cl^- + Fe^{3+}$

$40 \times 0.25 = mm = l_2$

→ Action of excess of dilute acids :→

$$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$$
$$CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2$$
$$CaOCl_2 + 2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O + Cl_2$$
$$CaOCl_2 + H_2CO_3 \longrightarrow CaCO_3 + H_2O + Cl_2$$
$$CaOCl_2 + 2CH_3COOH \longrightarrow Ca(CH_3COO)_2 + H_2O + Cl_2$$

Amt. of Cl_2 liberated by action of excess of dil acids on sample of bleaching powder is called % available chlorine of that sample.

$$\% \text{ available chlorine} = \frac{W_{Cl_2}}{W_{sample}} \times 100$$

eg. $CaOCl_2 + 2H^+ \longrightarrow Ca^{2+} + H_2O_{(l)} + Cl_2$

$$\underset{2}{Cl_2} + \underset{1}{2KI} \longrightarrow \underset{1}{2KCl} + \underset{2}{I_2}$$

$$\underset{2}{I_2} + \underset{1}{2Na_2S_2O_3} \longrightarrow \underset{1}{2NaI} + Na_2S_4O_6$$

Q. 0.5 g of bleaching powder was suspended in W and excess of KI was added. On acidifying with dil. H_2SO_4, I_2 was liberated which requ 50 ml of $\frac{1}{10}$ N $Na_2S_2O_3$. Calculate % of chlorine

→ $50 \times \frac{1}{10} = 2 \times M \times V$ ⇒ moles = 2.5 mm

$$\% Cl = \frac{71 \times \frac{5}{2} \times 10^{-3}}{0.5} \times 100 = 35.5\%$$