

REDOX & EQUIVALENT CONCEPTS (STOICHIOMETRY-II)

1. OXIDATION & REDUCTION

Let us do a comparative study of oxidation and Reduction ;

Oxidation	Reduction
(1) Addition of oxygen e.g. $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$	(i) Removal of oxygen e.g. $\text{CuO} + \text{C} \rightarrow \text{Cu} + \text{CO}$
(2) Removal of Hydrogen e.g. $\text{H}_2\text{S} + \text{Cl}_2 \rightarrow 2\text{HCl} + \text{S}$	(ii) Addition of Hydrogen e.g. $\text{S} + \text{H}_2 \rightarrow \text{H}_2\text{S}$
(3) Increase in positive charge e.g. $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$	(iii) Decrease in positive charge e.g. $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$
(4) Increase in oxidation number (+2) (+4) $\text{SnCl}_2 \rightarrow \text{SnCl}_4$	(iv) Decrease in oxidation number (+7) (+2) $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$
(5) Removal of electron e.g. $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2\text{e}^-$	(v) Addition of electron e.g. $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$

2. Oxidation Number :

- It is an imaginary or apparent charge gained by an element when it goes from its elemental free state to combined state in molecules.
- It is calculated on basis of a arbitrary set of rules.
- It is a relative charge in a particular bonded state.

2.1 Rules governing oxidation number :

The following rules are helpful in calculating oxidation number of the elements in their different compounds. It is remember that the basis of these rule is the electronegativity of the element.

◆ Fluorine atom :

Fluorine is most electronegativity atom (known). It always has oxidation no. equal to -1 in all its compounds.

◆ Oxygen atom :

In general and as well as in its oxides, oxygen atom has oxidation number equal to -2 .

In case of :

- peroxide (e.g. H_2O_2 , Na_2O_2) is -1
- super oxide (e.g. KO_2) is $-\frac{1}{2}$
- ozonide (KO_3) is $-\frac{1}{3}$
- oxygen fluoride OF_2 is $+2$ & in O_2F_2 is $+1$

♦ **Hydrogen atom :**

In general, H atom has oxidation number equal to +1. But in metallic hydrides (e.g. NaH, KH) it is -1.

♦ **Halogen atom :**

In general, all halogen atom (Cl, Br, I) has oxidation number equal to -1.

But if halogen atom is attached with an more electronegative atom than halogen atom then it will show positive oxidation numbers.

e.g. $\overset{+5}{\text{KClO}_3}$ $\overset{+5}{\text{HIO}_3}$ $\overset{+7}{\text{HClO}_4}$ $\overset{+5}{\text{KBrO}_3}$

♦ **Metals :**

(a) Alkali metal (Li, Na, K, Rb,) always have oxidation number +1.

(b) Alkaline earth metal (Be, Mg, Ca) always have oxidation number +2.

Note : Metal may have positive or zero oxidation number.

(c) Aluminium always have +3 oxidation number

♦ Oxidation number of an element in free state or in allotropic forms is always zero.

e.g. $\overset{0}{\text{O}_2}$, $\overset{0}{\text{S}_8}$, $\overset{0}{\text{P}_4}$, $\overset{0}{\text{O}_3}$

♦ Sum of the charges of elements in a molecule is zero.

♦ Sum of the charges of all elements in an ions is equal to the charge on the ion.

♦ If the group no. of an element in periodic table is n then its oxidation number may vary from n to n - 8 (but it is mainly applicable in p-block elements)

e.g. N-atom belongs to v group in the periodic table therefore as per rule its oxidation number may vary from

-3 to +5 ($\overset{-3}{\text{NH}_3}$, $\overset{+2}{\text{NO}}$, $\overset{+3}{\text{N}_2\text{O}_3}$, $\overset{+4}{\text{NO}_2}$, $\overset{+5}{\text{N}_2\text{O}_5}$)

Ex.1 Calculate oxidation number of underlined element $\text{Na}_2\underline{\text{S}_2}\text{O}_3$:

Sol. Let oxidation number of S-atom is x. Now work accordingly with the rules given before.

$$(+1) \times 2 + (x) \times 2 + (-2) \times 3 = 0$$

$$x = +2$$

Ex.2 $\text{Na}_2\underline{\text{S}_4}\text{O}_6$:

Sol. Let oxidation number of S-atom is x

$$(+1) \times 2 + (x) \times 2 + (-2) \times 6 = 0$$

$$x = +2.5$$

♦ It's important to note here that $\text{Na}_2\underline{\text{S}_2}\text{O}_3$ have two S-atom and there are four S-atom in $\text{Na}_2\underline{\text{S}_4}\text{O}_6$ but sulphur atom in both the compound have +2 or +2.5 oxidation number, it is the average charge (O. No.) Which reside on each sulphur atom therefore we should work to calculate the individual oxidation number of each sulphur atom in these compound.

Ex.3 Calculate the O.S. of all the atoms in the following species :

(i) ClO^- , (ii) NO_2^- , (iii) NO_3^- (iv) CCl_4 (v) K_2CrO_4 and (vi) KMnO_4

Sol. (i) In ClO^- , the net charge on the species is -1 and therefore the sum of the oxidation states of Cl and O must be equal to -1 . Oxygen will have an O.S. of -2 and if the O.S. of Cl is assumed to be 'x' then $x - 2$ should be equal to -1 .

x is $+1$

(ii) NO_2^- : $(2 \times -2) + x = -1$ (where 'x' is O.S. of N)

$\therefore x = +3$

(iii) NO_3^- : $x + (3 \times -2) = -1$ (where 'x' is O.S. of N)

$x = +5$

(iv) In CCl_4 , Cl has an O.S. of -1

$x + 4 \times -1 = 0$

$\therefore x = +4$

(where 'x' is O.S. of C)

(v) K_2CrO_4 : K has O.S. of $+1$ and O has O.S. of -2 and let Cr has O.S. 'x' then,
 $2 \times +1 + x + 4 \times -2 = 0$

$\therefore x = +6$

(vi) KMnO_4 : $+1 + x + (4 \times -2) = 0$

$\therefore x = +7$

(where x is O.S. of Mn).

2.2 MISCELLANEOUS EXAMPLES

In order to determine the exact or individual oxidation number we need to take help from the structures of the molecules. Some special cases are discussed as follows :

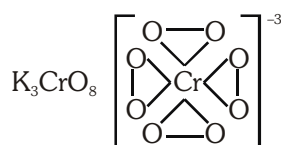
♦ The structure of CrO_5 is

From the structure it is evident that in CrO_5 there are two peroxide linkages and one double bond.

The contribution of each peroxide linkage is -2 . Let the O.N. of Cr is x.

$\therefore x + (-2)2 + (-2) = 0$ or $x = 6$

\therefore O.N. of Cr = $+6$ **Ans.**



From the structure it is evident that in CrO_8^{-3} there are four peroxide linkages.

The contribution of each peroxide linkage is -2 . Let the O.N. of Cr is x.

$\therefore x + (-2)4 = -3$ or $x = +5$

\therefore O.N. of Cr = $+5$ **Ans.**

♦ The structure of H_2SO_5 is

From the structure, it is evident that in H_2SO_5 , there are one peroxide linkage, two sulphur - oxygen double bond and one OH group. Let the O.N. of S = x.

$$\therefore +1 - 2 + x + (-2) \cdot 2 + (-2) + 1 = 0$$

$$\text{or } x + 2 - 8 = 0$$

$$\text{or } x - 6 = 0$$

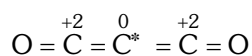
$$\text{or } x = 6$$

$$\therefore \text{O.N. of S in } \text{H}_2\text{SO}_5 \text{ is } +6 \text{ Ans}$$

2.3 PARADOX OF FRACTIONAL OXIDATION NUMBER

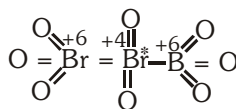
Fractional oxidation state is the average oxidation state of the element under examination and the structural parameters reveal that the element for whom fractional oxidation state is realised is actually present in different oxidation states. Structure of the species C_3O_2 , Br_3O_8 and $\text{S}_4\text{O}_6^{2-}$ reveal the following bonding situations.

- The element marked with asterisk in each species is exhibiting the different oxidation state (oxidation number) from rest of the atoms of the same element in each of the species. This reveals that in C_3O_2 , two carbon atoms are present in +2 oxidation state each whereas the third one is present in zero oxidation state and the average is $4/3$. However the realistic picture is +2 for two terminal carbons and zero for the middle carbon.



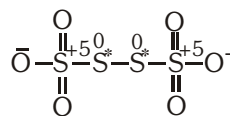
Structure of C_3O_2
(Carbon suboxide)

- Likewise in Br_3O_8 , each of the two terminal bromine atoms are present in +6 oxidation state and the middle bromine is present in +4 oxidation state. Once again the average, that is different from reality is $16/3$.



Structure of Br_3O_8 (tribromooctaoxide)

- In the same fashion, in the species $\text{S}_4\text{O}_6^{2-}$, is 2.5, whereas the reality being +5, 0, 0 and +5 oxidation number respectively for each sulphur.



Structure of $\text{S}_4\text{O}_6^{2-}$ (tetrathionate ion)

3.1 OXIDISING AND REDUCING AGENT

3.1 Oxidising agent or Oxidant :

Oxidising agents are those compound which can oxidise others and reduced itself during the chemical reaction. Those reagents whose O.N. decrease or which gain electrons in a redox reaction are termed as oxidants

e.g. KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, HNO_3 , conc. H_2SO_4 etc, are powerful oxidising agents.

3.1 Reducing agent or Reductant :

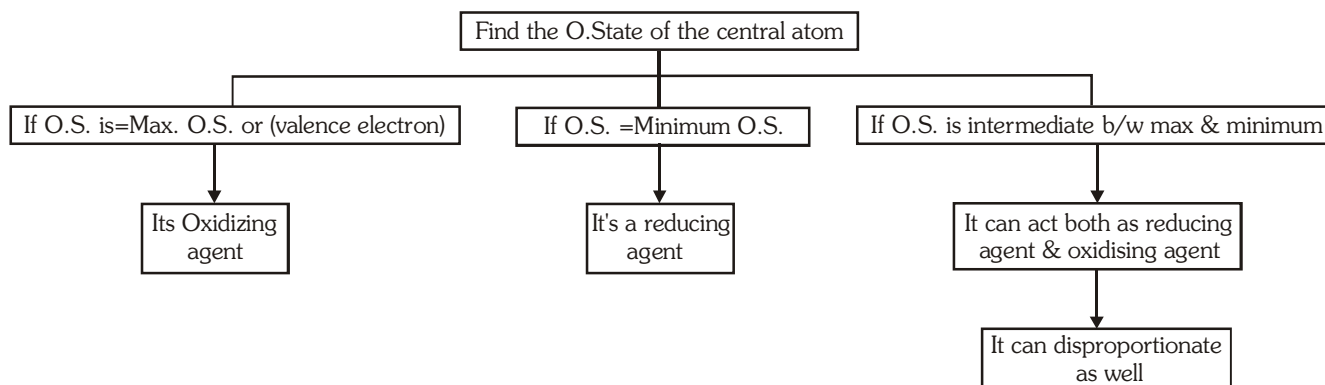
Reducing agents are those compound which can reduce others and oxidise itself during the chemical reaction. Those reagents whose O.N. increase or which loses electrons in a redox reaction are termed as reductants.

e.g. KI , $\text{Na}_2\text{S}_2\text{O}_3$ are powerful reducing agents.

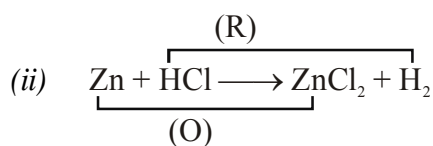
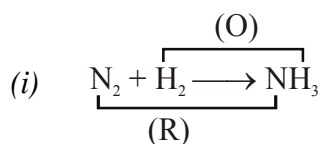
Note : There are some compounds also which can work both oxidising agent and reducing agent.

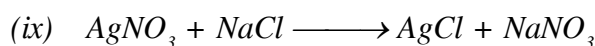
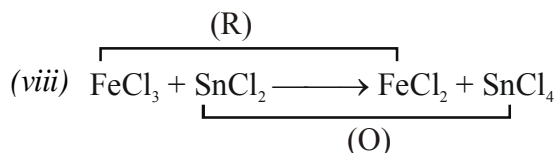
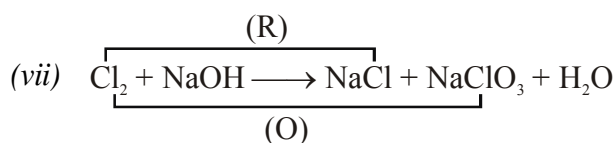
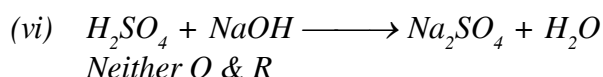
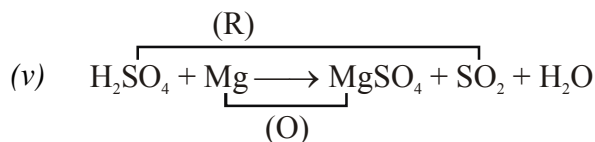
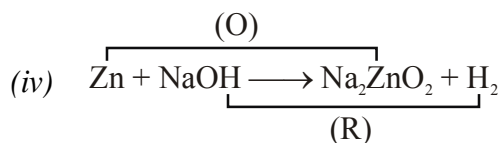
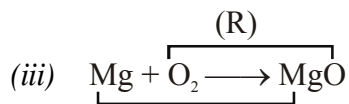
e.g. H_2O_2 , NO_2^-

3.3 HOW TO IDENTIFY WHETHER A PARTICULAR SUBSTANCE IS AN OXIDISING OR REDUCING AGENT



Ex.4. Identify the species undergoing oxidation and reduction



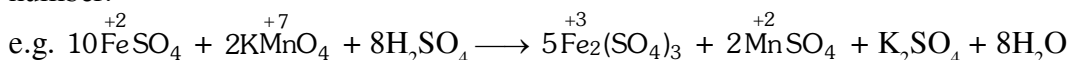


No oxidation and no reduction.

4 REDOX REACTION

A reaction in which oxidation and reduction simultaneously take place.

In all redox reactions the total increase in oxidation number must equal the total decrease in oxidation number.

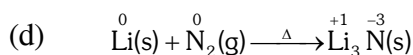
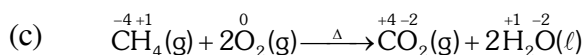
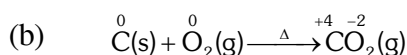
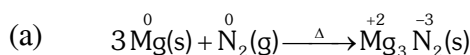
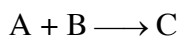


5. TYPE OF REACTION

5.1 Combination Reactions :

When two or more element combine to form compound then such reaction are redox reaction.

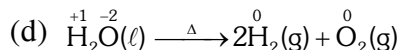
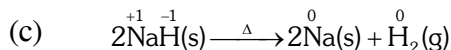
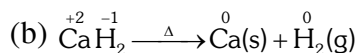
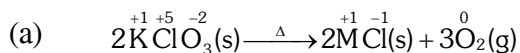
For example



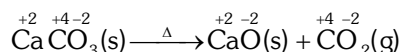
In reaction (c), there is no change in the oxidation number of hydrogen.

5.2 Decomposition Reactions :

Decomposition reactions are opposite of combination. Decomposition reactions are those in which when a molecule breaks down to form two or more components, at least one of them must be in the elemental state. For example :

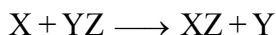


Exception :



5.3 Displacement Reactions :

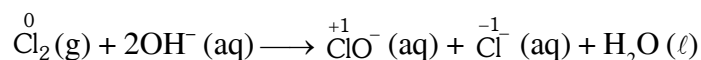
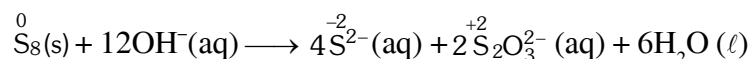
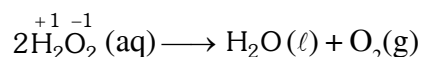
A reaction in which an atom or ion in a compound is replaced by an atom or ion of another element is called a displacement reaction. It may be denoted as :



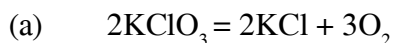
5.4 Disproportionation reactions :

A redox reaction in which a same element present in a particular compound in a definite oxidation state is oxidized as well as reduced simultaneously is a disproportionation reactions.

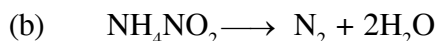
Disproportionation reactions are a special type of redox reactions. One of the reactants in a disproportionation reaction always contains **an element that can exist in at least three oxidation states**. The element in the form of reacting substance is in the intermediate oxidation state and both higher and lower oxidation states of that element are formed in the reaction.



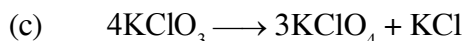
◆ Consider following reactions :



KClO₃ plays a role of oxidant and reductant both. Because same element is not oxidised and reduced. Here, Cl present in KClO₃ is reduced and O present in KClO₃ is oxidized. So **its not a disproportion reaction** although it looks like one.



Nitrogen in this compound has -3 and +3 oxidation number so it is not a definite value, so its not a disproportion reaction. Its a example of **comproportionation reaction** which is a class of redox reaction in which a element from two different oxidation state gets converted into a single oxidation state.

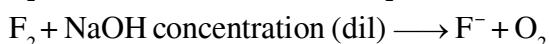
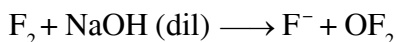


Its a case of disproportionation reaction in which Cl is the atom disproportionating.

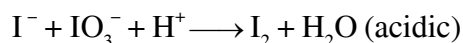
◆ **List of some important disproportionation reaction :**

1. $\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{O}_2$
2. $\text{X}_2 + \text{OH}^- (\text{dil.}) \longrightarrow \text{X}^- + \text{XO}^-$
3. $\text{X}_2 + \text{OH}^- (\text{conc.}) \longrightarrow \text{X}^- + \text{XO}_3^-$

F_2 does not (can not) undergo disproportionation as it is the most electronegative element.



- ◆ Reverse of disproportionation is called Comproportionation. In some of the disproportionation reactions by changing the medium (from acidic to basic or reverse) the reaction goes in backward direction and can be taken as an example of Comproportionation.



6. BALANCING OF REDOX REACTION

All balanced equations must satisfy two criteria

1. Atom balance (mass balance) :

That is there should be the same number of atoms of each kind in reactant and products side.

2. Charge balance :

That is the sum of actual charges on both side of the equation must be equal

There are two methods for balancing the redox equations

- (a) Oxidation - number change method
- (b) Ion electron method or half cell method
- (a) **Oxidation number change method :**

This method was given by Jonson. In a balanced redox reaction, total increase in oxidation number must be equal to total decreases in oxidation number. This equivalence provides the basis for balancing redox reactions.

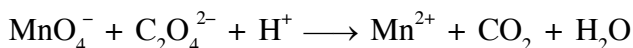
The general procedure involves the following steps :

- (i) Select the atom in oxidising agent whose oxidation number decreases and indicate the gain of electrons.
- (ii) Select the atom in reducing agent whose oxidation number increases and write the loss of electrons.
- (iii) Now cross multiply i.e. multiply oxidising agent by the number of loss of electrons and reducing agent by number of gain of electrons.
- (iv) Balance the number of atoms on both sides whose oxidation numbers change in the reaction.
- (v) In order to balance oxygen atoms, add H_2O molecules to the side deficient in oxygen. Then balance the number of H atoms by adding H^+ ions in the hydrogen.

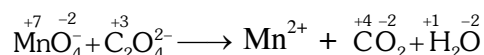
Ex.5 Write the skeleton equation for each of the following processes and balance them by ion electron method :

- (i) *Permagnet ion oxidizes oxalate ions in acidic medium to carbon dioxide and gets reduced itself to Mn^{2+} ions.*
- (ii) *Chlorine reacts with base to form chlorate ion, chloride ion and water in acidic medium.*

Sol. (i) The skeleton equation for the process :



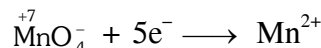
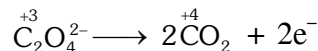
◆ **Step (1)** : Indicating oxidation number :



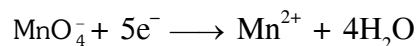
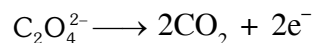
◆ **Step (2)** : Writing oxidation and reduction half reaction :



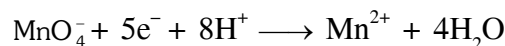
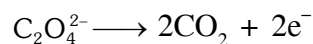
◆ **Step (3)** : Adding electrons to make the difference in O.N.



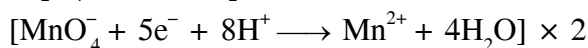
◆ **Step (4)** : Balancing 'O' atom by adding H_2O molecules



◆ **Step (5)** : Balancing H atom by adding H^+ ions



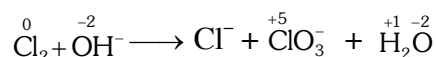
◆ **Step (6)** : Multiply the oxidation half reaction by 2 and reduction half reaction by 5 to equalize the electrons lost and gained and add the two half reactions.



(ii) The skeleton equation for the given process :



◆ **Step (1)** : Indicate the oxidation number of each atom

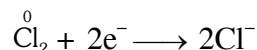


Thus, chlorine is the only element which undergoes the change in oxidation number. It decreases its oxidation number from 0 to 1 and also increases its oxidation number from 0 to 5.

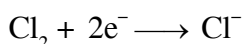
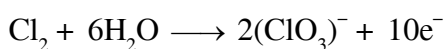
- ◆ **Step (2) :** Write the oxidation and reduction half reactions



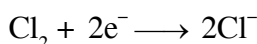
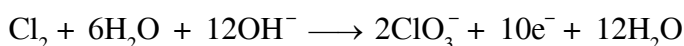
- ◆ **Step (3) :** Add electrons to make up for the difference in O.N.



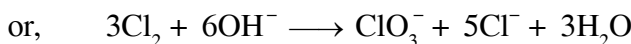
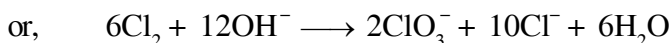
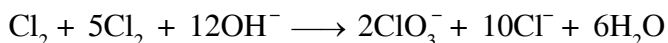
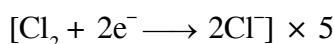
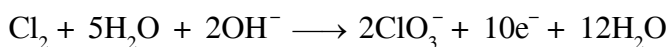
- ◆ **Step (4) :** Balance O atoms by adding H_2O molecules



- ◆ **Step (5) :** Since medium is basic, balance H atoms by adding H_2O molecules to the side falling short of H atoms and equal number of OH^- ions to the other side.



- ◆ **Step (6) :** Multiply the reduction half reaction by 5 and add two half reactions.



Ex.6 Balance the following chemical reaction by oxidation number method and write their skeleton equation :

- (i) *The nitrate ions in acidic medium oxidize magnesium to Mg^{2+} ions but itself gets reduced to nitrous oxide.*

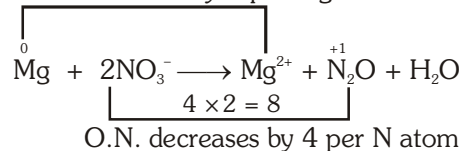
Sol. (i) The skeleton equation for the given process is



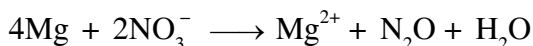
- ◆ **Step (1) :** $\overset{0}{\text{Mg}} + (\overset{+5}{\text{N}}\overset{-2}{\text{O}_3})^- \longrightarrow \text{Mg}^{2+} + \overset{+1}{\text{N}}\overset{-2}{\text{O}_2} + \overset{+1}{\text{H}}\overset{-2}{\text{O}}$

Multiply NO_3^- by 2 to equalize N atoms

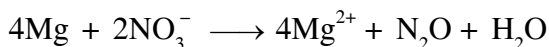
- ◆ **Step (2) :** O.N. increases by 2 per Mg atom



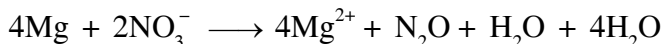
- ◆ **Step (3) :** Equalize increase/decrease in O.N. by multiplying Mg by 4 and 2NO_3^- by 1.



- ◆ **Step (4) :** Balance atoms other than O and H



- ◆ **Step (5) :** Balance O atoms



- ◆ **Step (6) :** Balance H atoms as is done in acidic medium.



- (b) **Ion electron method or half cell method :**

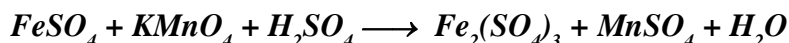
By this method redox equation are balanced in two different medium

- (a) Acidic medium (b) Basic medium

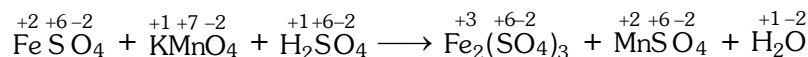
- ◆ **Balancing in acidic medium**

Students are advised to follow the following steps to balance the redox reactions by ion electron method in acidic medium.

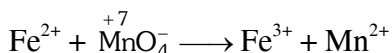
Ex.7 Balance the following redox reaction.



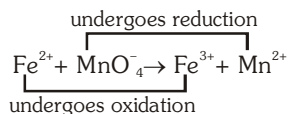
Sol : Step-I assign the oxidation No. to each elements present in the reaction.



Step-II Now convert the reaction in ionic form by eliminating the elements or species which are not going either oxidation or reduction



Step-III Now identify the oxidation / reduction occurring into the reaction.



Step-IV Split the ionic reaction in two half one for oxidation and other for reduction



Step-V Balance the atom other than oxygen and hydrogen atom in both half reactions

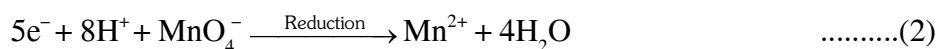


Fe & Mn atom are balanced in both side.

Step-VI Now balance O & H atom by H_2O & H^+ respectively by the following way for one excess oxygen atom add one H_2O on the other side and two H^+ on the same side.

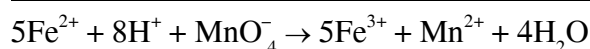
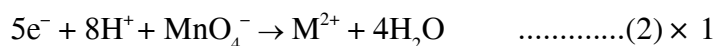


Step VII Now see equation (i) & (ii) is balanced atomwise. Now balance both equations chargewise to balance the charge add electrons to the electrically positive side.



Step VIII The number of electrons gained and lost in each half-reaction are equalised by multiply suitable factor in both the half reaction and finally the half reactions are added to give the over all balanced reaction.

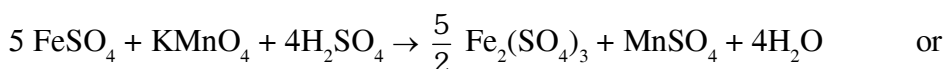
Here we multiply equation (i) by 5 and (ii) by one



(Here at this stage you will get balanced redox reaction in ionic form)

Step IX Now convert the ionic reaction in to molecular form by adding the elements or species which are removed instep (II).

Now by some manipulation you will get



7. Equivalent weight (E) :

$$\text{Eq. wt (E)} = \frac{\text{Molecular weight}}{\text{valency factor (v.f)}} = \frac{\text{Mol. wt.}}{n - \text{factor}}$$

$$\text{no of Equivalents} = \frac{\text{mass of a sample}}{\text{eq. wt. of that species}}$$

- ◆ Equivalent mass is a pure number when expressed in gram, it is called gram equivalent mass.
- ◆ The equivalent mass of substance may have different values under different conditions.

8. Valency factor calculation :

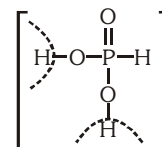
◆ For Acids :

valence factor = number of replaceable H^+ ions

Solved Examples :



{ see there are only two replaceable H^+ ions }



Self practice problems :

1. Find the valence factor for following acids



Answers :

1. (i) 1 (ii) 2 (iii) 1

8.2 For Base :

v.f. = number of replicable OH^- ions

Solved Examples :

Ex : NaOH KOH

Sol : v.f. \rightarrow 1 1

E. \rightarrow $\frac{M}{1}$ $\frac{M}{1}$

Self practice problems :

1. Find the valence factor for following bases



Answers :

1. (i) 2 (ii) 1 (iii) 3

8.3 Acid - base reaction :

In case of acid base reaction, the valence factor is the actual number of H^+ or OH^- replaced in the reaction. The acid or base may contain more number of replaceable H^+ or OH^- than actually replaced in reaction.

v.f. for base is the number of H^+ ion form the acid replaced by per molecule of the base.



Base Acid

Sol : valency factor of base = 1

valency factor of acid = 2

Here two molecule of NaOH replaced 2H^+ ion from the H_2SO_4 therefore per molecule of NaOH replaced only one H^+ ion of acid so v.f. = 1

♦ v.f. for acid is number of OH^- replaced for the base by per molecule of acid



Base Acid

Sol : valence factor of acid = 1

here one of molecule of H_3PO_4 replaced one OH^- from NaOH therefore v.f. for H_3PO_4 is = 1

$$E = \frac{\text{mol. wt. of } \text{H}_3\text{PO}_4}{1}$$

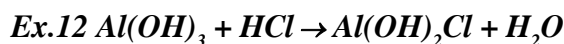


Base Acid

Sol : valence factor of acid = 2

here one of molecule of H_3PO_4 replaced two OH^- from NaOH therefore v.f. for H_3PO_4 is = 2

$$E = \frac{\text{mol. wt. of } \text{H}_3\text{PO}_4}{2}$$



Base Acid

Sol : valence factor of base = 1

here one of molecule of $\text{Al}(\text{OH})_3$ replaced one H^+ from HCl therefore v.f. for $\text{Al}(\text{OH})_3$ is = 1

$$E = \frac{\text{mol. wt. of } \text{Al}(\text{OH})_3}{1}$$

8.4 For Salts :

v.f. = Total number of positive charge or negative charge present into the compound.

Solved Examples :

Ex.13	Na_2CO_3	$\text{Fe}_2(\text{SO}_4)_3 (2\text{Fe}^{3+} + 3\text{SO}_4^{2-})$	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Sol : V.f.	2	$2 \times 3 = 6$	2
E.	$\frac{M}{2}$	$\frac{M}{6}$	$\frac{M}{2}$

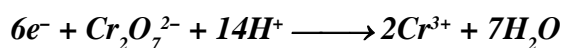
8.5 Eq. wt. of oxidising / reducing agents in redox reaction :

The equivalent weight of an oxidising agent is that weight which accepts one mole electron in a chemical reaction.

(a) Equivalent wt. of an oxidant (get reduced)

$$= \frac{\text{Mol. wt.}}{\text{No. of electrons gained by one mole}}$$

Ex.14 In acidic medium



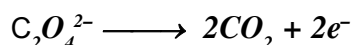
$$\text{Eq. wt. of } \text{K}_2\text{Cr}_2\text{O}_7 = \frac{\text{Mol. wt of } \text{K}_2\text{Cr}_2\text{O}_7}{6} = \frac{\text{Mol. wt.}}{6}$$

Note : [6 in denominator indicates that 6 electrons were gained by $\text{Cr}_2\text{O}_7^{2-}$ as it is clear from the given balanced equation]

(b) Similarly equivalent wt. of a reductant (gets oxidised)

$$= \frac{\text{Mol. wt.}}{\text{No. of electrons lost by one mole}}$$

Ex.15 In acidic medium,



Here, Total electrons lost = 2

$$\text{So, eq. wt.} = \frac{\text{Mol. wt.}}{2}$$

(c) In different condition a compound may have different equivalent weights. Because, it depends upon the number of electrons gained or lost by that compound in that reaction.

Ex.15 (i) $\text{MnO}_4^- \longrightarrow \text{Mn}^{2+}$ (acidic medium)
(+7) (+2)

$$\text{Here 5 electrons are taken so eq. wt.} = \frac{\text{Mol. wt. of KMnO}_4}{5} = \frac{158}{5} = 31.6$$

(ii) $\text{MnO}_4^- \longrightarrow \text{Mn}^{+4}$ (neutral medium)
(+7) (+4)

$$\text{Here, only 3 electrons are gained, so eq. wt.} = \frac{\text{Mol. wt. of KMnO}_4}{3} = \frac{158}{3} = 52.7$$

(iii) $\text{MnO}_4^- \longrightarrow \text{MnO}_4^{2-}$ (alkaline medium)
(+7) (+6)

$$\text{Here, only one electron is gained, so eq. wt.} = \frac{\text{Mol. wt. of KMnO}_4}{1} = 158$$

Note : It is important to note that KMnO_4 acts as an oxidant in every medium although with different strength which follows the order.

acidic medium > neutral medium > alkaline medium

Ex.16 $2\text{S}_2\text{O}_3^{--} \longrightarrow \text{S}_4\text{O}_6^{--} + 2e^-$
(Reducing agent)

$$\text{equivalent weight of } \text{S}_2\text{O}_3^{--} = \frac{2M}{2} = M$$

◆ **Questions based on Equivalent weight :**

- Molecular weight of KMnO_4 in acidic medium and neutral medium will be respectively :
(A) $7 \times$ equivalent wt. and $2 \times$ equivalent wt. (B) $5 \times$ equivalent wt. and $3 \times$ equivalent wt.
(C) $4 \times$ equivalent wt. and $5 \times$ equivalent wt. (D) $2 \times$ equivalent wt. and $4 \times$ equivalent wt.
- In acidic medium, equivalent weight of $\text{K}_2\text{Cr}_2\text{O}_7$ (Mol. wt. = M) is –
(A) $M/3$ (B) $M/4$ (C) $M/6$ (D) $M/2$

Answers :

- (1) B (2) A (3) C

9. NORMALITY

Normality of solution is defined as the number of equivalent of solute present in one litre (1000 mL) solutions. Let a solution is prepared by dissolving W g of solute of eq. wt. E in V mL water.

- ◆ No. of equivalent of solute = $\frac{W}{E}$
- ◆ V mL of solution have $\frac{W}{E}$ equivalent of solute
- ◆ 1000 mL solution have $\frac{W \times 1000}{E \times V_{\text{mL}}}$
- ◆ **Normality (N) = $\frac{W \times 1000}{E \times V_{\text{mL}}}$**
- ◆ **Normality (N) = Molarity \times Valence factor**

Normality (N) = molarity \times Valence factor (n)

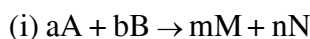
or $N \times V$ (in mL) = $M \times V$ (in mL) \times n

or milli equivalents = millimoles \times n

10. LAW OF EQUIVALENCE

The law states that one equivalent of an element combine with one equivalent of the other, and in a chemical reaction equivalent and mill equivalent of reactants react in equal amount to give same no. of equivalent or milli equivalents of products separately.

According :



$$\text{m.eq of A} = \text{m.eq of B} = \text{m.eq of M} = \text{m.eq of N}$$



$$\text{m.eq of } M_xN_y = \text{m.eq of M} = \text{m.eq of N}$$

Ex.17 The number of moles of oxalate ions oxidized by one mole of MnO_4^- ion in acidic medium.

(A) $\frac{5}{2}$

(B) $\frac{2}{5}$

(C) $\frac{3}{5}$

(D) $\frac{5}{3}$

Sol : Equivalents of $\text{C}_2\text{O}_4^{2-}$ = equivalents of MnO_4^-

$$x (\text{mole}) \times 2 = 1 \times 5$$

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

Ex.18 What volume of 6 M HCl and 2 M HCl should be mixed to get two litre of 3 M HCl ?

Sol. Let, the volume of 6 M HCl required to obtain 2 L of 3M HCl = x L

\therefore Volume of 2 M HCl required = (2 - x) L

$$\begin{array}{ccc} M_1V_1 & + & M_2V_2 & = & M_3V_3 \\ 6\text{M HCl} & & 2\text{M HCl} & & 3\text{M HCl} \end{array}$$

$$6 \times (x) + 2 \times (2 - x) = 3 \times 2$$

$$\Rightarrow 6x + 4 - 2x = 6 \Rightarrow 4x = 2$$

$$\therefore x = 0.5 \text{ L}$$

Hence, volume of 6 M HCl required = 0.5 L

Volume of 2M HCl required = 1.5 L

Ex.19 In a reaction vessel, 1.184 g of NaOH is required to be added for completing the reaction. How many millilitre of 0.15 M NaOH should be added for this requirement ?

Sol. Amount of NaOH present in 1000 mL of 0.15 M NaOH = $0.15 \times 40 = 6 \text{ g}$

$$\therefore 1 \text{ mL of this solution contain NaOH} = \frac{6}{1000} \times 10^{-3} \text{ g}$$

$$\therefore 1.184 \text{ g of NaOH will be present in} = \frac{1}{6 \times 10^{-3}} \times 1.184 = 197.33 \text{ mL}$$

Ex.20 What weight of Na_2CO_3 of 85% purity would be required to prepare 45.6 mL of 0.235N H_2SO_4

Sol. Meq. of Na_2CO_3 = Meq. of $\text{H}_2\text{SO}_4 = 45.6 \times 0.235$

$$\therefore \frac{W_{\text{Na}_2\text{CO}_3}}{E_{\text{Na}_2\text{CO}_3}} \times 1000 = 45.6 \times 0.235$$

$$\Rightarrow \frac{W_{\text{Na}_2\text{CO}_3}}{106/2} \times 1000 = 45.6 \times 0.235$$

$$\therefore W_{\text{Na}_2\text{CO}_3} = 0.5679 \text{ g}$$

For 85 g of pure Na_2CO_3 , weighed sample = 100 g

$$\therefore \text{For } 0.5679 \text{ g of pure } \text{Na}_2\text{CO}_3, \text{ weighed sample} = \frac{100}{85} \times 0.5679$$

$$= 0.6681 \text{ g}$$

10.1 Drawbacks of Equivalent concept :

- (i) Since equivalent weight of a substance for example oxidising or reducing agent may be variable hence it is better to use mole concept.



$$\therefore \text{Eq. wt of } \text{MnO}_4^- = \frac{\text{MnO}_4^-(\text{mol.wt.})}{5}$$



$$\therefore \text{Eq. wt. of } \text{MnO}_4^- = \frac{\text{MnO}_4^-}{3}$$

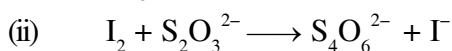
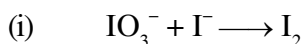
Thus the no. of equivalents of MnO_4^- will be different in the above two cases but no. of moles will be same.

- (ii) **Normality of any solution depends on reaction while molarity does not.**

For example.

Consider 0.1 mol KMnO_4 dissolved in water to make 1L solution. Molarity of this solution is 0.1 M. However, its normality is not fixed. It will depend upon the reaction in which KMnO_4 participates, e.g. If KMnO_4 forms Mn^{2+} , normality = $0.1 \times 5 = 0.5 \text{ N}$. This same sample of KMnO_4 , if employed in a reaction giving MnO_2 as product (Mn in +4 state) will have normality $0.1 \times 3 = 0.3 \text{ N}$.

- (iii) **The concept of equivalents is handy, but it should be used with care.** One must never equate equivalents in a sequence which involves same element in more than two oxidation states. Consider an example KIO_3 reacts with KI to liberate iodine and liberated iodine is titrated with standard hypo solution, The reaction are



meq of hypo = meq of I_2 = meq of IO_3^- + meq of I^-

$\therefore \text{IO}_3^-$ react with $\text{I}^- \Rightarrow$ meq of IO_3^- = meq of I^-

◆ meq of hypo = $2 \times$ meq of IO_3^-

This is wrong. Note that I_2 formed by (i) have v.f. = 5/3 & reacted in equation (ii) have v.f. = 2.

\therefore v.f. of I_2 in both the equation are different therefore we cannot equate m.eq in sequence. In this type of case students are advised to use mole concept.

Ex.21 How many milliliters of 0.02000 M KMnO_4 solution would be required to exactly titrate 25.00 mL of 0.2000 M $\text{Fe}(\text{NO}_3)_2$ solution.

Sol : Method - 1 : Mole concept method

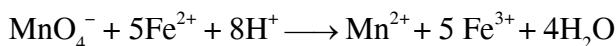
Starting with 25.00 mL of 0.2000M Fe^{2+} , we can write.

Millimoles of $\text{Fe}^{2+} = 25.00 \times 0.2000$

and in volume V (in milliliters of the MnO_4^-)

Millimoles of $\text{MnO}_4^- = V (0.02000)$

The balanced reaction is :



This requires that at the equivalent point,

$$\frac{V(0.02000)}{1} = \frac{(25.00)(0.2000)}{5} \quad V = 50.00 \text{ mL}$$

Method - 2 : Equivalent Method :

Equivalents of $\text{MnO}_4^- = 5 \times$ moles of MnO_4^-

Normality $\text{MnO}_4^- = 5 \times$ molarity of MnO_4^-

For Fe^{2+} , moles and equivalents are equal,

At the equivalence point,

Equivalents of $\text{MnO}_4^- = \text{Equivalents of Fe}^{2+}$

$$\begin{aligned} \text{or } V_{\text{MnO}_4^-} \times \text{Normality of MnO}_4^- \\ = V_{\text{Fe}^{2+}} \times \text{Normality of Fe}^{2+} \end{aligned}$$

For 0.02000 M MnO_4^- solution

Normality of $\text{MnO}_4^- = (5) (0.02000) = 0.1 \text{ N}$ and for 0.2000 M Fe^{2+} solution

$$\text{Normality of Fe}^{2+} = 0.2000 \text{ N} \quad V_{\text{MnO}_4^-} = (25.00 \text{ mL}) \left(\frac{0.2000}{0.1000} \right) = 50.00 \text{ mL}$$

10.2 FOR ACID-BASE (NEUTRALIZATION REACTION) OR REDOX REACTION

$N_1 V_1 = N_2 V_2$ is always true.

But $M_1 V_1 = M_2 V_2$ (may or may not be true)

But $M_1 \times n_1 \times V_1 = M_2 \times n_2 \times V_2$ (always true where n terms represent n-factor).

10.3 SOME OXIDIZING AGENTS/REDUCING AGENTS WITH EQ. WT.

Species	Changed to	Reaction	Electrons exchanged or change in O.N.	Eq. wt.
$\text{MnO}_4^- (\text{O.A.})$	Mn^{+2} in acidic medium	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	5	$E = \frac{M}{5}$
$\text{MnO}_4^- (\text{O.A.})$	MnO_2 in neutral medium	$\text{MnO}_4^- + 3\text{e}^- + 2\text{H}_2\text{O} \longrightarrow \text{MnO}_2 + 4\text{OH}^-$	3	$E = \frac{M}{3}$
$\text{MnO}_4^- (\text{O.A.})$	MnO_4^{2-} in basic medium	$\text{MnO}_4^- + \text{e}^- \longrightarrow \text{MnO}_4^{2-}$	1	$E = \frac{M}{1}$
$\text{Cr}_2\text{O}_7^{2-} (\text{O.A.})$	Cr^{3+} in acidic medium	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	6	$E = \frac{M}{6}$
$\text{MnO}_2 (\text{O.A.})$	Mn^{2+} in acidic medium	$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \longrightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	2	$E = \frac{M}{2}$
$\text{Cl}_2 (\text{O.A.})$ in bleaching powder	Cl^-	$\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Cl}^-$	2	$E = \frac{M}{2}$
$\text{CuSO}_4 (\text{O.A.})$ in iodometric titration	Cu^+	$\text{Cu}^{2+} + \text{e}^- \longrightarrow \text{Cu}^+$	1	$E = \frac{M}{1}$
$\text{S}_2\text{O}_3^{2-} (\text{R.A.})$	$\text{S}_4\text{O}_6^{2-}$	$2\text{S}_2\text{O}_3^{2-} \longrightarrow \text{S}_4\text{O}_6^{2-} + 2\text{e}^-$ (for two molecules)	2	$E = \frac{2M}{2} = M$
$\text{H}_2\text{O}_2 (\text{O.A.})$	H_2O	$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \longrightarrow 2\text{H}_2\text{O}$	2	$E = \frac{M}{2}$
$\text{H}_2\text{O}_2 (\text{R.A.})$	O_2	$\text{H}_2\text{O}_2 \longrightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$ (O.N. of oxygen in H_2O_2 is -1 per atom)	2	$E = \frac{M}{2}$
$\text{Fe}^{2+} (\text{R.A.})$	Fe^{3+}	$\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{e}^-$	1	$E = \frac{M}{1}$

Ex.22 To find the *n*-factor in the following chemical changes.

- (i) $\text{KMnO}_4 \xrightarrow{\text{H}^+} \text{Mn}^{2+}$ (ii) $\text{KMnO}_4 \xrightarrow{\text{H}_2\text{O}} \text{Mn}^{4+}$
 (iii) $\text{KMnO}_4 \xrightarrow{\text{OH}^-} \text{Mn}^{6+}$ (iv) $\text{K}_2\text{Cr}_2\text{O}_7 \xrightarrow{\text{H}^+} \text{Cr}^{3+}$
 (v) $\text{C}_2\text{O}_4^{2-} \rightarrow \text{CO}_2$ (vi) $\text{FeSO}_4 \rightarrow \text{Fe}_2\text{O}_3$
 (vii) $\text{Fe}_2\text{O}_3 \rightarrow \text{FeSO}_4$

- Sol.** (i) In this reaction, KMnO_4 which is an oxidizing agent, itself gets reduced to Mn^{2+} under acidic conditions.
 $n = |1 \times (+7) - 1 \times (+2)| = 5$
 (ii) In this reaction, KMnO_4 gets reduced to Mn^{4+} under neutral or slightly (weakly) basic conditions.
 $n = |1 \times (+7) - 1 \times (+4)| = 3$
 (iii) In this reaction, KMnO_4 gets reduced to Mn^{6+} under basic conditions.
 $n = |1 \times (+7) - 1 \times (+6)| = 1$
 (iv) In this reaction, $\text{K}_2\text{Cr}_2\text{O}_7$ which acts as an oxidizing agent reduced to Cr^{3+} under acidic conditions. (It does not react under basic conditions.)
 $n = |2 \times (+6) - 2 \times (+3)| = 6$
 (v) In this reaction, $\text{C}_2\text{O}_4^{2-}$ (oxalate ion) gets oxidized to CO_2 when it is reacted with an oxidizing agent.
 $n = |2 \times (+3) - 2 \times (+4)| = 2$
 (vi) In this reaction, ferrous ions get oxidized to ferric ions.
 $n = |1 \times (+2) - 1 \times (+3)| = 1$
 (vi) In this reaction, ferric ions are getting reduced to ferrous ions.
 $n = |2 \times (+3) - 2 \times (+2)| = 2$

Ex.23 Calculate the molar ratio in which the following two substances would react ?

$\text{Ba}_3(\text{PO}_4)_2$ and AlCl_3

Sol. *n*-factor of $\text{Ba}_3(\text{PO}_4)_2 = 3 \times (+2) = 6 = n_1$

While *n*-factor of $\text{AlCl}_3 = 1 \times (+3) = 3 = n_2$

$$\frac{n_1}{n_2} = \frac{6}{3} \quad \text{If} \quad \frac{n_1}{n_2} = \frac{x}{y}$$

Molar ratio = $\frac{y}{x}$ (inverse of equivalent ratio)

\therefore Molar ratio in which $\text{Ba}_3(\text{PO}_4)_2$ and AlCl_3 will react = $3 : 6 = 1 : 2$

10.4 APPLICATIONS OF THE LAW OF EQUIVALENCE

10.4.1 Simple Titration

In this, we can find the concentration of unknown solution by reacting it with solution of known concentration (standard solution).

For example, let there be a solution of substance A of unknown concentration. We are given solution of another substance B whose concentration is known (N_1). We take a certain known volume of A in a flask (V_2) and then we add B to A slowly till all the A is consumed by B (this can be known with the help of indicators). Let us, assume that the volume of B consumed is V_1 . According to the law of equivalence, the number of g equivalents of B at the end point.

$\therefore N_1 V_1 = N_2 V_2$, where N_2 is the conc. of A.

From this we can calculate the value of N_2 .

Ex.24 1.20 g sample of Na_2CO_3 and K_2CO_3 was dissolved in water to form 100 mL of a Solution. 20 mL of this solution required 40 mL of 0.1 N HCl for complete neutralization. Calculate the weight of Na_2CO_3 in the mixture. If another 20 mL of this solution is treated with excess of BaCl_2 what will be the weight of the precipitate ?

Sol. Let, weight of $\text{Na}_2\text{CO}_3 = x$ g

Weight of $\text{K}_2\text{CO}_3 = y$ g

$$\therefore x + y = 1.20 \text{ g} \quad \text{.....(i)}$$

For neutralization reaction of 100 mL

Meq. of Na_2CO_3 + Meq. of K_2CO_3 = Meq. of HCl

$$\Rightarrow \frac{x}{106} \times 2 \times 1000 + \frac{y}{138} \times 2 \times 1000 = \frac{40 \times 0.1 \times 100}{20}$$

$$\therefore 69x + 53y = 73.14 \quad \text{.....(ii)}$$

From Eqs. (i) and (ii), we get

$$x = 0.5962 \text{ g}$$

$$y = 0.604 \text{ g}$$

Solution of Na_2CO_3 and K_2CO_3 gives ppt. of BaCO_3 with BaCl_2

(Meq. of Na_2CO_3 + Meq. of K_2CO_3) in 20 mL = Meq. of BaCO_3

\Rightarrow Meq. of HCl for 20 mL mixture = Meq. of BaCO_3

\Rightarrow Meq. of $\text{BaCO}_3 = 40 \times 0.1 = 4$

$$\frac{W_{\text{BaCO}_3}}{M_{\text{BaCO}_3}} \times 1000 = 40 \times 0.1 = 4$$

$$\frac{W_{\text{BaCO}_3}}{197} \times 2 \times 1000 = 4$$

$$\therefore W_{\text{BaCO}_3} = 0.394 \text{ g}$$

10.4.2 BACK TITRATION

Back titration is used to calculate % purity of a sample. Let us assume that we are given an impure solid substance C weighing w g and we are asked to calculate the percentage of pure C in the sample. We will assume that the impurities are inert. We are provided with two solutions A and B, where the concentration of B is known (N_1) and that of A is not known. This type of titration will work only if the following condition is satisfied, i.e. the nature of compounds A, B and C should be such that A and B can react with each other. A and C can react with each other but the product of A and C should not react with B.

Now, we take a certain volume of A in a flask (the g equivalents of A taken should be \geq g equivalents of C in the sample and this can be done by taking A in excess). Now, we perform a simple titration using B. Let us assume that the volume of B used is V_1 . In another beaker, we again take the solution of A in the same volume as taken earlier. Now, C is added to this and after the reaction is completed, the solution is being titrated with B. Let us assume that the volume of B used up is V_2 . Gram equivalents of B used in the first titration = $N_1 V_1$.

\therefore gm. equivalents of A initially = $N_1 V_1$

gm. equivalents of B used in the second titration = $N_1 V_2$

\therefore gm. equivalents of A left in excess after reacting with C = $N_1 V_2$

gm. equivalents of A that reacted with C = $N_1 V_1 - N_1 V_2$

If the n-factor of C is x, then the moles of pure C = $\frac{N_1 V_1 - N_1 V_2}{x}$

\therefore The weight of C = $\frac{N_1 V_1 - N_1 V_2}{x} \times \text{Molecular weight of C}$

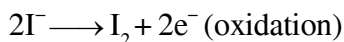
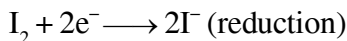
\therefore Percentage of C = $\frac{N_1 V_1 - N_1 V_2}{x} \times \frac{\text{Molecular wt. of C}}{w} \times 100$

□ SOME REDOX TITRATIONS (EXCLUDING IODOMETRIC / IODIMETRIC)

Estimation of	By titrating with	Reactions	Relation between O.A. and R.A.
Fe^{2+}	MnO_4^-	$\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^-$ $\text{MnO}_4^- + 8\text{H}^+ + 5e^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	$5\text{Fe}^{2+} \equiv \text{MnO}_4^-$ Eq. wt. $\text{Fe}^{2+} = M/1$ Eq. wt. $\text{MnO}_4^- = M/5$
Fe^{2+}	$\text{Cr}_2\text{O}_7^{2-}$	$\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^-$ $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	$6\text{Fe}^{2+} \equiv \text{Cr}_2\text{O}_7^{2-}$ Eq. wt. $\text{Cr}_2\text{O}_7^{2-} = M/6$
$\text{C}_2\text{O}_4^{2-}$	MnO_4^-	$\text{C}_2\text{O}_4^{2-} \longrightarrow 2\text{CO}_2 + 2e^-$ $\text{MnO}_4^- + 8\text{H}^+ + 5e^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	$5\text{C}_2\text{O}_4^{2-} \equiv 2\text{MnO}_4^-$ Eq. wt. $\text{C}_2\text{O}_4^{2-} = M/2$ Eq. wt. $\text{MnO}_4^- = M/5$
H_2O_2	MnO_4^-	$\text{H}_2\text{O}_2 \longrightarrow 2\text{H}^+ + \text{O}_2 + 2e^-$ $\text{MnO}_4^- + 8\text{H}^+ + 5e^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	$5\text{H}_2\text{O}_2 \equiv 2\text{MnO}_4^-$ Eq. wt. $\text{H}_2\text{O}_2 = M/2$ Eq. wt. $\text{MnO}_4^- = M/5$
As_2O_3	MnO_4^-	$\text{As}_2\text{O}_3 + 5\text{H}_2\text{O} \longrightarrow 2\text{AsO}_4^{3-} + 10\text{H}^+ + 4e^-$	Eq. wt. $\text{As}_2\text{O}_3 = M/4$
AsO_3^{3-}	BrO_3^-	$\text{AsO}_3^{3-} + \text{H}_2\text{O} \longrightarrow \text{AsO}_4^{3-} + 2\text{H}^+ + 2e^-$ $\text{BrO}_3^- + 6\text{H}^+ + 6e^- \longrightarrow \text{Br}^- + 3\text{H}_2\text{O}$	Eq. wt. $\text{AsO}_3^{3-} = M/2$ Eq. wt. $\text{BrO}_3^- = M/6$

10.4.3 Iodometric and Iodimetric Titration :

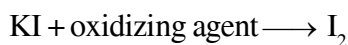
The reduction of free iodine to iodide ions and oxidation of iodide ions to free iodine occurs in these titrations.



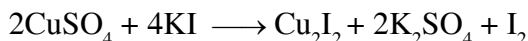
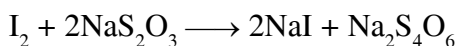
These are divided into two types :

(i) Iodometric Titration :

In iodometric titrations, an oxidizing agent is allowed to react in neutral medium or in acidic medium with excess of potassium iodide to liberate free iodine.



Free iodine is titrated against a standard reducing agent usually with sodium thiosulphate. Halogen, dichromates, cupric ion, peroxides etc., can be estimated by this method.



(ii) Iodimetric Titration

These are the titrations in which free iodine is used as it is difficult to prepare the solution of iodine (volatile and less soluble in water), it is dissolved in KI solution :



This solution is first standardized before using with the standard solution of substance such as sulphite, thiosulphate, arsenite etc, are estimated.

In iodimetric and iodometric titration, starch solution is used as an indicator. Starch solution gives blue or violet colour with free iodine. At the end point, the blue or violet colour disappears when iodine is completely changed to iodide.

□ SOME IODOMETRIC TITRATIONS (TITRATING SOLUTIONS IS $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$)

Estimation of	Reaction	Relation between O.A. and R.A.
I_2	$\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$ or $\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \longrightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$	$\text{I}_2 = 2\text{I} = 2\text{Na}_2\text{S}_2\text{O}_3$ Eq. wt. of $\text{Na}_2\text{S}_2\text{O}_3 = \text{M}/1$
CuSO_4	$2\text{CuSO}_4 + 4\text{KI} \longrightarrow 2\text{Cu}_2\text{I}_2 + 2\text{K}_2\text{SO}_4 + \text{I}_2$ $\text{Cu}^{2+} + 4\text{I}^- \longrightarrow \text{Cu}_2\text{I}_2 + \text{I}_2$ (White ppt.)	$2\text{CuSO}_4 = \text{I}_2 = 2\text{I} = 2\text{Na}_2\text{S}_2\text{O}_3$ Eq. wt. of $\text{CuSO}_4 = \text{M}/1$
CaOCl_2	$\text{CaOCl}_2 + \text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2 + \text{Cl}_2$ $\text{Cl}_2 + 2\text{KI} \longrightarrow 2\text{KCl} + \text{I}_2$ $\text{CaOCl}_2 = \text{Cl}_2 = \text{I}_2 = 2\text{I} = 2\text{Na}_2\text{S}_2\text{O}_3$ $\text{Cl}_2 + 2\text{I}^- \longrightarrow 2\text{Cl}^- + \text{I}_2$	Eq. wt. of $\text{CaOCl}_2 = \text{M}/2$
MnO_2	$\text{MnO}_2 + 4\text{HCl}(\text{conc}) \xrightarrow{\Delta} \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$ $\text{Cl}_2 + 2\text{KI} \longrightarrow 2\text{KCl} + \text{I}_2$ or $\text{MnO}_2 + 4\text{H}^+ + 2\text{Cl}^- \longrightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} + \text{Cl}_2$ $\text{Cl}_2 + 2\text{I}^- \longrightarrow \text{I}_2 + 2\text{Cl}^-$	$\text{MnO}_2 = \text{Cl}_2 = \text{I}_2 = 2\text{I} = 2\text{Na}_2\text{S}_2\text{O}_3$ Eq. wt. of $\text{MnO}_2 = \text{M}/2$
IO_3^-	$\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \longrightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$	$\text{IO}_3^- = 3\text{I}_2 = 6\text{I} = 6\text{Na}_2\text{S}_2\text{O}_3$ Eq. wt. of $\text{IO}_3^- = \text{M}/6$
H_2O_2	$\text{H}_2\text{O}_2 + 2\text{I}^- + 2\text{H}^+ \longrightarrow \text{I}_2 + 2\text{H}_2\text{O}$	$\text{H}_2\text{O}_2 = \text{I}_2 = 2\text{I} = 2\text{Na}_2\text{S}_2\text{O}_3$ Eq. wt. of $\text{H}_2\text{O}_2 = \text{M}/2$
Cl_2	$\text{Cl}_2 + 2\text{I}^- \longrightarrow 2\text{Cl}^- + \text{I}_2$	$\text{Cl}_2 = \text{I}_2 = 2\text{I} = 2\text{Na}_2\text{S}_2\text{O}_3$ Eq. wt. of $\text{Cl}_2 = \text{M}/2$
O_3	$\text{O}_3 + 6\text{I}^- + 6\text{H}^+ \longrightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$	$\text{O}_3 = 3\text{I}_2 = 6\text{I} = 6\text{Na}_2\text{S}_2\text{O}_3$ Eq. wt. of $\text{O}_3 = \text{M}/6$
$\text{Cr}_2\text{O}_7^{2-}$	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{I}^- \longrightarrow 3\text{I}_2 + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	$\text{Cr}_2\text{O}_7^{2-} = 3\text{I}_2 = 6\text{I}$ Eq. wt. of $\text{Cr}_2\text{O}_7^{2-}$
MnO_4^-	$2\text{MnO}_4^- + 10\text{I}^- + 16\text{H}^+ \longrightarrow 2\text{MnO}_4^- + 5\text{I}_2 + 8\text{H}_2\text{O}$	$2\text{MnO}_4^- = 5\text{I}_2 = 10\text{I}$ Eq. wt. of $\text{MnO}_4^- = \text{M}/5$
BrO_3^-	$\text{BrO}_3^- + 6\text{I}^- + 6\text{H}^+ \longrightarrow \text{Br}^- + 3\text{I}_2 + 3\text{H}_2\text{O}$	$\text{BrO}_3^- = 3\text{I}_2 = 6\text{I}$ Eq. wt. of $\text{BrO}_3^- = \text{M}/6$
As(V)	$\text{H}_3\text{AsO}_4 + 2\text{I}^- + 2\text{H}^+ \longrightarrow \text{H}_3\text{AsO}_3 + \text{H}_2\text{O} + \text{I}_2$	$\text{H}_3\text{AsO}_4 = \text{I}_2 = 2\text{I}$ Eq. wt. of $\text{H}_3\text{AsO}_4 = \text{M}/2$

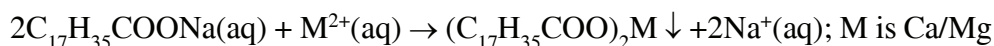
□ SOME IODIMETRIC TITRATION (TITRATING SOLUTIONS IS I_2 IN KI)

Estimation of	Reaction	Relation between O.A. and R.A.
H_2S (in acidic medium)	$H_2S + I_2 \longrightarrow S + 2I^- + 2H^+$	$H_2S \equiv I_2 \equiv 2I$ Eq. wt. of $H_2S = M/2$
SO_3^{2-} (in acidic medium)	$SO_3^{2-} + I_2 + H_2O \longrightarrow SO_4^{2-} + 2I^- + 2H^+$	$SO_3^{2-} \equiv I_2 \equiv 2I$ Eq. wt. of $SO_3^{2-} = M/2$
Sn^{2+} (in acidic medium)	$Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^-$	$Sn^{2+} \equiv I_2 \equiv 2I$ Eq. wt. of $Sn^{2+} = M/2$
As(III) (at pH = 8)	$H_2AsO_3^- + I_2 + H_2O \longrightarrow$ $HAsO_4^{2-} + 2I^- + 2H^+$	$H_2AsO_3^- \equiv I_2 \equiv 2I$ Eq. wt. of $H_2AsO_3^- = M/2$
N_2H_4	$N_2H_4 + 2I_2 \longrightarrow N_2 + 4H^+ + 4I^-$	$N_2H_4 \equiv 2I_2 \equiv 4I$ Eq. wt. of $N_2H_4 = M/4$

11. Hardness of water :

Hard water does not give lather with soap. Water free from soluble salts of calcium and magnesium is called **Soft water**. It gives lather with soap easily.

Hard water forms scum/precipitate with soap. Soap containing sodium stearate ($C_{17}H_{35}COONa$) reacts with hard water to precipitate out Ca/Mg stearate.



Hardness of water is of two types

(a) Temporary Hardness

(b) Permanent Hardness

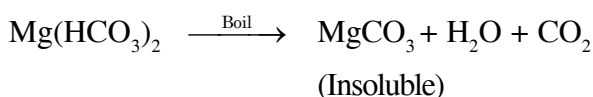
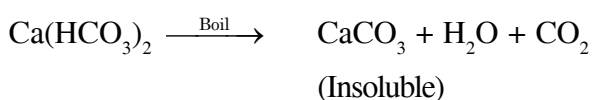
Temporary Hardness :-

This is due to presence of bicarbonate of calcium and magnesium. Rain water dissolves a small quantities of CO_2 from the atmosphere forming a very dilute solution of carbonic acid.

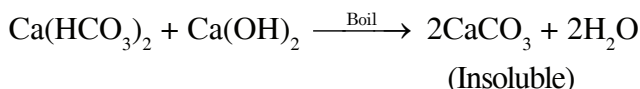
This water attacks Ca and Mg carbonate in any rock



Temporary hardness in water is easily removed by boiling, as the bicarbonates decomposes readily and the insoluble carbonates are precipitated.

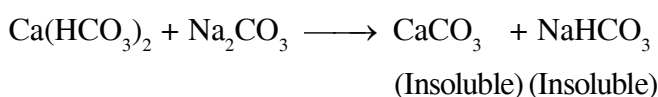
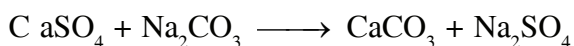
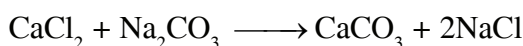


Temporarily hardness can also be removed by Clark's process which involves the addition of slaked lime Ca(OH)_2



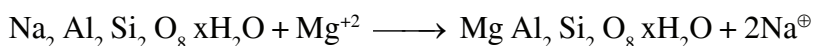
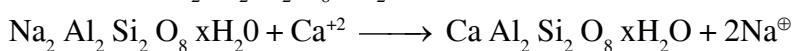
Permanent Hardness :- Permanent hardness is due to presence of sulphates and chlorides of both calcium and magnesium. This type of hardness cannot be removed by boiling or by Ca(OH)_2 . Substance used to remove the hardness of water are known as water softener. These various water softeners are -

- (i) **Washing soda :-** It removes both the temporary and permanent hardness by converting soluble Ca and Mg compounds into insoluble carbonates.

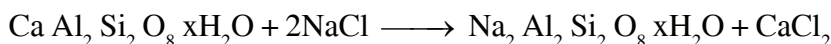


- (ii) **Permutit:** Permutit is technical name given to certain hydrated silicates of aluminium and sodium or sodium aluminium orthosilicate or sodium zeolite.

Example : $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot x\text{H}_2\text{O}$.

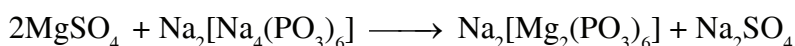
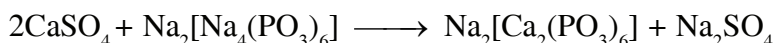


These ions can be re-exchanged by treating it with brine (NaCl) solution.

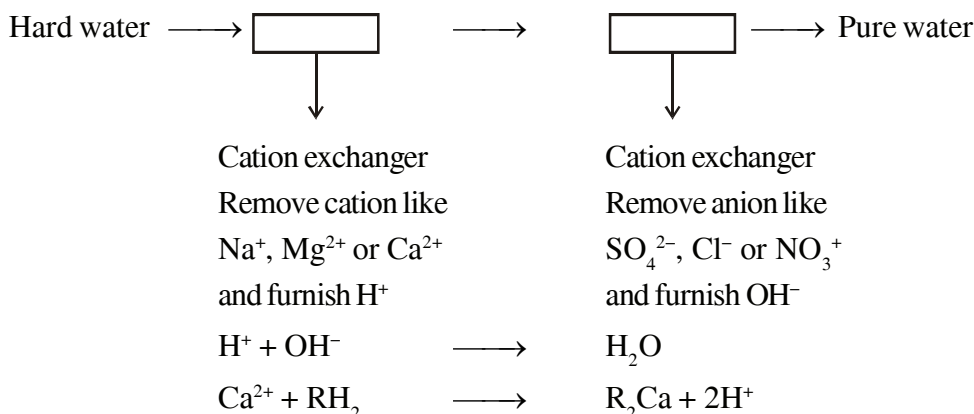


This method is useful for the removal of both temporary and permanent hardness of water.

- (iii) **CALGON:** The complex salt of metaphosphoric acid, sodium hexametaphosphate ($\text{Na}_4(\text{PO}_3)_6$) is called Calgon. It is represented as $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$.

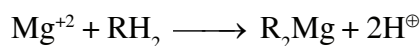
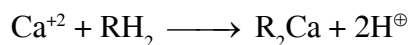


- (iv) **Ion exchange Resins:-** Ion exchange resins are the most popular water softener these days. These resins are synthetic substance. The cation exchanger consists of granular insoluble organic acid resins having giant molecules with $-\text{SO}_3\text{H}$ or $-\text{COOH}$ groups while the anion exchanger contains giant organic molecules with basic groups derived from amine. Ion exchange resins remove all soluble mineral from water.

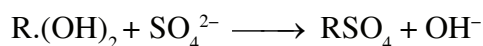
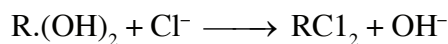


The water coming from cation exchanger is acidic due to H^+ . This water is then passed through another bed containing anion exchanger. This exchanger removes anion like Cl^- , SO_4^{2-} , NO_3^- by exchanging with OH^- ions.

Reaction at Cation exchanger :



Reaction at Anion exchanger :



NOTE : Degree of Hardness of water is measured in terms of ppm of $CaCO_3$ which is defined as number of parts of $CaCO_3$ by mass present in one million parts by mass of water whose equivalent is equal to the gram equivalent of various calcium & magnesium salts.

For **example** consider the sample of hard water which is found to contain 36 mg of $MgSO_4$ per kg of water.

gm equivalent of $CaCO_3$ = gm eq. of $MgSO_4$

$$\frac{W_{CaCO_3}}{100} \times 2 = \frac{36 \times 10^{-3}}{120} \times 2$$

$$W_{CaCO_3} = 3 \times 10^{-2} \text{ gm}$$

$$\text{degree of hardness} = \text{ppm of } CaCO_3 = \frac{3 \times 10^{-2}}{1000} \times 10^6 = 30$$

12. GLOSSARY

Aliquot. A portion of the whole, usually a simple fraction. A portion of a sample withdraw from a volumetric flask with a pipet is called an aliquot.

Analytical concentration. The total number of moles per litre of a solute regardless of any reactions that might occur when the solute dissolves. Used synonymously with formality.

Equivalent. The amount of a substance which furnishes or reacts with 1 mol of H^+ (acid-base), 1 mol of electrons (redox), or 1 mol of a univalent cation (precipitation and complex formation).

Equivalent weight. The weight in grams of one equivalent of a substance.

Equivalence point. The point in a titration where the number of equivalents of titrant is the same as the number of equivalents of analyte.

End point. The point in a titration where an indicator changes color.

Formula weight. The number of formula weights of all the atoms in the chemical formula of a substance.

Formality. The number of formula weights of solute per litre of solution; synonymous with analytical concentration.

Indicator. A chemical substance which exhibits different colors in the presence of excess analyte or titrant.

Normality. The number of equivalents of solute per litre of solution.

Primary standard. A substance available in a pure form or state of known purity which is used in standardizing a solution.

Standardization. The process by which the concentration of a solution is accurately ascertained.

Standard solution. A solution whose concentration has been accurately determined.

Titrant. The reagent (a standard solution) which is added from a buret to react with the analyte.

SOME MORE SOLVED EXAMPLES

Ex.25 A 3.00 g sample containing Fe_3O_4 , Fe_2O_3 and an inert impure substance, is treated with excess of KI solution in presence of dilute H_2SO_4 . The entire iron is converted into Fe^{2+} along with the liberation of iodine. The resulting solution is diluted to 100 mL. A 20 mL of the diluted solution require 11 mL of 0.5 M $\text{Na}_2\text{S}_2\text{O}_3$ solution to reduce the iodine present. A 50 mL of diluted solution after complete extraction of the iodine requires 12.80 mL of 0.25 KMnO_4 solution in dilute H_2SO_4 medium for the oxidation of Fe^{2+} . Calculate the percentages of Fe_2O_3 and Fe_3O_4 in the original sample.

Sol. Let number of moles of Fe_3O_4 is 'a' and no. of moles of Fe_2O_3 is 'b' in 3 gram sample.

Now, 'a' moles Fe_3O_4 means (a moles Fe_2O_3 + a mole of FeO)

So, in sample (a + b) moles Fe_2O_3 and 'a' mole FeO present.



No. of gram equivalent of Fe_2O_3 = no. of gram equivalent of I_2

$$n_{\text{Fe}_2\text{O}_3} \times n_{f(\text{Fe}_2\text{O}_3)} = n_{\text{I}_2} \times n_{f(\text{I}_2)}$$

$$(a + b) \times 2 = n_{\text{I}_2} \times 2$$

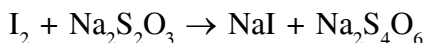
$$n_{\text{I}_2} = (a + b) \text{ moles.}$$

Now, solution is diluted to 100 ml

$$\text{So, } [\text{I}_2] = \frac{n}{V_{\text{litre}}} = \frac{(a + b)}{100/1000} = 10(a + b)$$

$$[\text{Fe}^{2+}] = \left(\frac{n(\text{Fe}^{2+})}{V_{\text{litre}}} \right) = \frac{(3a + 2b)}{100/1000} = 10(3a + 2b)$$

Now 20 ml of this solution titrated with 11 ml, 0.5 M $\text{Na}_2\text{S}_2\text{O}_3$



No. of gram equivalent of I_2 = no. of gram equivalent of $\text{Na}_2\text{S}_2\text{O}_3$

$$(N \times V)_{\text{I}_2} = (N \times V)_{\text{Na}_2\text{S}_2\text{O}_3}$$

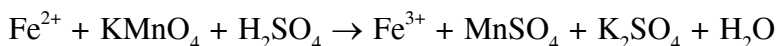
$$(M \times n_f \times V)_{\text{I}_2} = (M \times n_f \times V)_{\text{Na}_2\text{S}_2\text{O}_3}$$

$$10(a + b) \times 2 \times 20 = 0.5 \times 1 \times 11$$

$$a + b = \frac{11}{800} \quad \dots\dots (i)$$

50 ml of solution after extraction of I_2 allowed to oxidation

of Fe^{2+} by 12.80 ml, 0.25 M $KMnO_4$.



no. of gram equivalent of Fe^{2+} = no. of gram equivalent of $KMnO_4$.

$$(M \times n_f \times V)_{Fe^{2+}} = (M \times n_f \times V)_{KMnO_4}$$

$$10(3a + 2b) \times 1 \times 50 = 0.25 \times 5 \times 12.80$$

$$3a + 2b = \frac{16}{500} \dots\dots(ii)$$

By (i) & (ii)

$$a = 0.0045 \text{ moles}$$

$$b = 0.00925 \text{ moles}$$

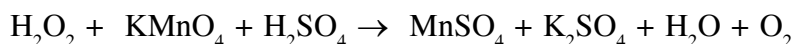
$$\text{so } \% Fe_2O_3 = \frac{Wt(Fe_2O_3)}{\text{Total wt.}} \times 100 = \frac{b \times 160}{3} \times 100 = \frac{0.00925 \times 160}{3} \times 100 = 49.33\%.$$

$$\% Fe_2O_3 = \frac{Wt(Fe_2O_3)}{\text{Total wt.}} \times 100 = \frac{a \times 232}{3} \times 100 = \frac{0.0045 \times 232}{3} \times 100 = 34.8\%$$

Ex.26 Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of $KMnO_4$ (20 mL) acidified with dilute H_2SO_4 . The same volume of $KMnO_4$ solution is just decolorized by 10 mL of $MnSO_4$ in neutral medium simultaneously forming a dark brown precipitate of hydrated MnO_2 . The brown precipitate is dissolved in 10 mL of 0.2 M sodium oxalate under boiling condition in the presence of dilute H_2SO_4 . Write the equations involved in the reactions and calculate the molarity of H_2O_2 .

Sol. Let molarity of H_2O_2 solution is M_1

20 ml, M_1 molar H_2O_2 react with 20 ml $KMnO_4$ in H_2SO_4 solution

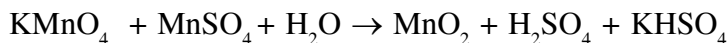


no. of gram equivalent of H_2O_2 = no. of gram equivalent of $KMnO_4$

$$(M \times n_f \times V)_{H_2O_2} = (M \times n_f \times V)_{KMnO_4}$$

$$M_1 \times 2 \times 20 = M_{KMnO_4} \times 5 \times 20 \dots\dots(i)$$

20 ml $KMnO_4$ decolourise by 10 ml $MnSO_4$ in neutral medium.

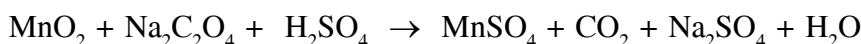


no. of gram equivalent of $KMnO_4$ = no. of gram equivalent of MnO_2

$$M_{KMnO_4} \times 3 \times 20 \text{ ml} = \text{no. of gram equivalent of } MnO_2$$

$$M_{KMnO_4} \times 3 \times 20 \times 10^{-3} = n_{MnO_2} \times 6/5 \dots\dots(ii)$$

and obtained MnO_2 dissolved in 10 ml, 0.2 M $Na_2C_2O_4$



no. of gram equivalent of MnO_2 = no. of gram equivalent of $Na_2C_2O_4$

$$n_{MnO_2} \times 2 = 0.2 \times 2 \times 10 \times 10^{-3}$$

$$n_{\text{MnO}_2} = 2 \times 10^{-3} \text{ moles} \quad \dots\dots(\text{iii})$$

From equation (ii)

$$M_{\text{KMnO}_4} \times 3 \times 20 \times 10^{-3} = 2 \times 10^{-3} \times \frac{6}{5}$$

$$M_{\text{KMnO}_4} = \frac{2}{50}$$

From equation (1)

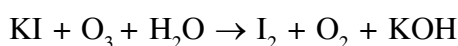
$$M_1 \times 2 \times 20 = \frac{2}{50} \times 5 \times 20$$

$$M_1 = 0.1\text{M}$$

Ex.27 One litre of a mixture of O_2 and O_3 ($\text{O}_3 \longrightarrow \text{O}_2 + \text{O}^{2-}$) at 1 atm and 273 K was allowed to react with an excess of acidified solution of KI. The iodine liberated required 40 ml of M/10 sodium thiosulphate solution for titration. What is the percent of ozone in the mixture? Ultraviolet radiation of wave length 300 nm can decompose ozone. Assuming that one photon can decompose one ozone molecule, how many photons would have been required for the complete decomposition of ozone in the original mixture?

Sol. Let in 1 litre mixture x litre is O_2 and y litre is O_3 at NTP

excess KI reduce O_3 into O_2 and O^{2-}



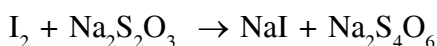
no. of gram equivalent of O_3 = no. of gram equivalent of I_2

$$(n \times n_f)_{\text{O}_3} = (n \times n_f)_{\text{I}_2}$$

$$\frac{y}{22.4} \times 2 = n_{\text{I}_2} \times 2$$

$$n_{\text{I}_2} = \frac{y}{22.4} \quad \dots\dots(1)$$

Now, released I_2 required 40 ml, $\frac{1}{10}\text{M}$ $\text{Na}_2\text{S}_2\text{O}_3$



No. of gram equivalent of I_2 = no. of gram equivalent of $\text{Na}_2\text{S}_2\text{O}_3$

$$n_{\text{I}_2} \times 2 = \frac{1}{10} \times 1 \times 40 \times 10^{-3}$$

$$n_{\text{I}_2} = 2 \times 10^{-3} \text{ moles}$$

Now from equation (1)

$$\frac{y}{22.4} = 2 \times 10^{-3}$$

$$y = (44.8 \times 10^{-3}) \text{ litre} = 0.0448 \text{ litre}$$

$$x = 1 - y = 1 - 0.0448 = 0.9552 \text{ litre}$$

$$\% \text{ (by wt)} = \frac{\text{wt}(\text{O}_3)}{\text{wt. (total)}} \times 100$$

$$= \frac{n(\text{O}_3) \times 48}{n(\text{O}_3) \times 48 + n(\text{O}_2) \times 32} \times 100$$

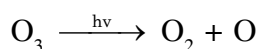
$$= \frac{\frac{y}{22.4} \times 48}{\frac{y}{22.4} \times 48 + \frac{x}{22.4} \times 32} \times 100$$

$$= \frac{3y}{3y + 2x} \times 100$$

$$= \frac{3 \times 0.0448}{3 \times 0.0448 + 2 \times 0.9552} \times 100$$

$$= \frac{0.1344}{2.0448} \times 100 = 6.57 \%$$

One photon required for breaking of one O_3 bond in to O_2 & O



So, no. of photon required = no. of O_3 bonds break

= no. of O_3 molecules

$$= n_{\text{O}_3} \times N_A = \frac{0.0448}{22.4} \times 6 \times 10^{23}$$

$$= 1.2 \times 10^{21} \text{ photons.}$$

Ex.28 A mixture of FeO and Fe_2O_3 is reacted with acidified KMnO_4 solution having a concentration of $2/5 \text{ M}$, 100 mL of which was used. The solution was then titrated with Zn dust which converted Fe^{3+} of the solution to Fe^{2+} . The Fe^{2+} required 1000 mL of $2/15 \text{ M}$ $\text{K}_2\text{Cr}_2\text{O}_7$ solution. Find the % by mol of FeO and Fe_2O_3 .

Sol. Let no. of moles of FeO is x millimoles & Fe_2O_3 is y millimoles in mixture.



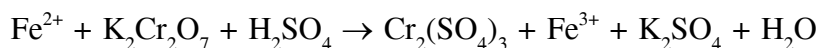
no. of milligram equivalent of FeO = no. of milli gram equivalent of KMnO_4 .

$$x \times 1 = \frac{2}{5} \times 5 \times 100$$

$$x = 200 \text{ m moles.}$$

Zn - dust convert all Fe^{3+} to Fe^{2+}

So no. of millimoles of Fe^{2+} in solution is $= (x + 2y)$.



no. of milli gram equivalent of Fe^{2+} = no. of milligram equivalent of $\text{K}_2\text{Cr}_2\text{O}_7$

$$(x + 2y) \times 1 = \frac{2}{15} \times 6 \times 1000$$

$$(200 + 2y) = \frac{2}{15} \times 1000$$

$$y = 300 \text{ millimoles.}$$

$$\% \text{ FeO (by moles)} = \frac{x}{x+y} \times 100 = \frac{200}{500} \times 100 = 40\%$$

$$\% \text{ Fe}_2\text{O}_3 \text{ (by moles)} = 60\%$$

Ex.29 A substance of crude copper is boiled in H_2SO_4 till all the copper has reacted. The impurities are inert to the acid. The SO_2 liberated in the action is passed into 100 mL of 0.4 M acidified KMnO_4 ($\text{SO}_2 \rightarrow \text{SO}_4^{2-}$). The solution of KMnO_4 after passage of SO_2 is allowed to react with oxalic acid and requires 25 mL of 1 M oxalic acid. If the purity of copper is 95.25%, what was the weight of the sample.

Sol. let given sample is w gram and no. of moles of Cu in given sample is x millimoles.



x millimoles x millimoles



no. of milligram eq. of SO_2 = no. of milli gram eq. of KMnO_4

$$x \times 2 = \text{no. of gram eq. of } \text{KMnO}_4$$

left KMnO_4 reduced by $\text{H}_2\text{C}_2\text{O}_4$



no. of milligram eq. of KMnO_4 (left)

= no. of mill gram eq. of $\text{H}_2\text{C}_2\text{O}_4$

$$= 1 \times 2 \times 25$$

So, total milligram eq. of KMnO_4 = milligram eq. of SO_2 + milligram eq. of $\text{H}_2\text{C}_2\text{O}_4$

$$0.4 \times 5 \times 100 = x \times 2 + 1 \times 2 \times 25$$

$$x = 75 \text{ millimoles}$$

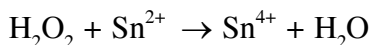
$$\text{wt}(\text{Cu}) = 95.25\% \text{ of } W$$

$$75 \times 10^{-3} \times 63.5 = \frac{95.25}{100} \times W$$

$$\Rightarrow W = 5 \text{ gram.}$$

Ex.30 H_2O_2 is reduced rapidly by Sn^{2+} , the products being Sn^{4+} and water. H_2O_2 decomposes slowly at room temperature to yield O_2 and water. Calculate the volume of O_2 produced at 273 K and 1.00 atm when 200 g of 10.0 % by mass H_2O_2 in water is treated with 88.2 mL of 1 M Sn^{2+} and then the mixture is allowed to stand until no further reaction occurs.

Sol. Let x millimoles of H_2O_2 react with 1M, 88.2 ml Sn^{2+}



no. of milligram equivalent of H_2O_2

= no. of milligram eq. of Sn^{2+}

$$x_{\text{millimole}} \times 2 = 1 \times 2 \times 88.2$$

$$x = 88.2 \text{ millimoles}$$

Total given moles of H_2O_2 is

$$n_{\text{total}} = \frac{W(\text{H}_2\text{O}_2)}{34} = \frac{10\% \text{ of } 200 \text{ gram}}{34}$$

$$= \frac{20}{34} \text{ moles}$$

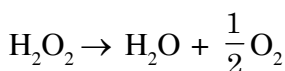
$$= 0.5882 \text{ moles}$$

$$= 588.2 \text{ millimoles.}$$

so. no. of moles of H_2O_2 that decomposed to O_2

$$= 588.2 - 88.2$$

$$= 500 \text{ millimoles}$$

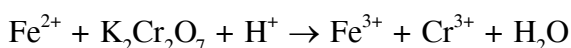


$$n(\text{O}_2) \text{ released} = \frac{1}{2} \times 500 = 250 \text{ millimoles}$$

$$V_{\text{O}_2} \text{ (at 1atm, 273 K)} = 250 \times 10^{-3} \times 22.4 = 5.6 \text{ litre.}$$

Ex.31 0.84 g iron ore containing x percent of iron was taken in a solution containing all the iron in ferrous condition. The solution required x ml of a dichromatic solution for oxidizing the iron content to ferric state. Calculate the normality of dichromatic solution.

Sol. Let Normality of $\text{K}_2\text{Cr}_2\text{O}_7$ solution is N



no. of gram eq. of Fe^{2+} = no. of gram eq. of $\text{K}_2\text{Cr}_2\text{O}_7$

$$n_{\text{Fe}^{2+}} \times 1 = N \times x \times 10^{-3}$$

$$\frac{W_{\text{Fe}^{2+}}}{56} \times 1 = N \times x \times 10^{-3}$$

$$\frac{\frac{x}{100} \times 0.84}{56} \times 1 = N \times x \times 10^{-3}$$

$$N = 0.15$$

Ex.32 5 g of pyrolusite (impure MnO_2) were heated with conc. HCl and Cl_2 evolved was passed through excess of KI solution. The iodine liberated required 40 mL of $\text{N}/10$ hypo solution. Find the % of MnO_2 in the pyrolusite.

Sol. Let moles of MnO_2 in 5 gram sample is x .



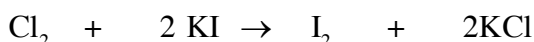
no. of gram eq. of MnO_2 = no. of gram equivalent of Cl_2

$$x \times 2 = n_{(\text{Cl}_2)} \times 2$$

$$x = n_{(\text{Cl}_2)}$$

$$\text{so } n_{\text{I}_2} = n_{\text{Cl}_2} = x$$

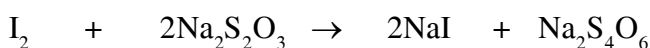
evolved Cl_2 passes through KI that released I_2



x moles

x moles

Evolved I_2 required 40 ml, $\frac{\text{N}}{10} \text{Na}_2\text{S}_2\text{O}_3$



no. of gram equivalent of I_2 = no. of gram equivalent of hypo

$$x \times 2 = \frac{1}{10} \times 40 \times 10^{-3}$$

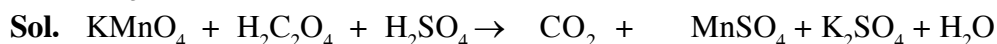
$$x = 2 \times 10^{-3} \text{ moles}$$

$$\% \text{MnO}_2 = \frac{\text{wt.}(\text{MnO}_2)}{\text{total wt.}} \times 100$$

$$= \frac{x \times 87}{5} \times 100 = \frac{2 \times 10^{-3} \times 87}{5} \times 100$$

$$= 3.48 \%$$

Ex.33 A 458 g sample containing Mn_3O_4 was dissolved and all manganese was converted to Mn^{2+} . In the presence of fluoride ion, Mn^{2+} is titrated with 3 lit of KMnO_4 solution (which was 1.25 N against oxalate in acidic medium), both reactants being converted to a complex of Mn(III) , What was the % of Mn_3O_4 in the sample?



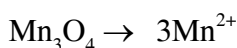
3 litre, M molar

$$\text{Normality}(\text{KMnO}_4) = \text{Molarity} \times n_f$$

$$1.25 = M \times 5$$

$$M = 0.25$$

Let x moles of Mn_3O_4 present in 458 gram sample



x mole $3x$ moles



no. of gram eq. of Mn^{2+} = no. of gram eq. KMnO_4

$$3x \times 1 = (M \times n_f \times V)_{\text{KMnO}_4}$$

$$3x \times 1 = 0.25 \times 4 \times 3$$

$$x = 1 \text{ moles}$$

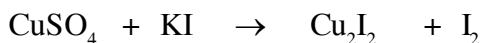
$$\begin{aligned} \% \text{ Mn}_3\text{O}_4 \text{ (by wt)} &= \frac{w(\text{Mn}_3\text{O}_4)}{w_{\text{total}}} \times 100 \\ &= \frac{1 \times 229}{458} \times 100 = 50\% \end{aligned}$$

Ex.34 80 gm of a sample of Anhydrous CuSO_4 was dissolved in water and made to 250 mL. 25 mL of this solution after taking usual precaution was treated with a little excess of KI solution. A white ppt. of Cu_2I_2 and iodine was evolved. The iodine so evolved required 40 mL of 1 M hypo solution. What is the approximate purity of CuSO_4 solution.

[Mol. wt. of CuSO_4 = 160]

Sol. Let 80 gram sample contains x moles of CuSO_4 that desolve in 250 ml solution

So 25 ml solution contain (x/10) moles CuSO_4

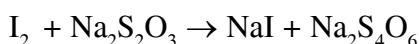


no. of gram eq. of CuSO_4 = no. of gram eq. of I_2

$$\frac{x}{10} \times 1 = n_{(\text{I}_2)} \times 2$$

$$n_{(\text{I}_2)} = \frac{x}{20}$$

Evalved I_2 required 40 ml, 1M hypo solution



no. of gram eq. of I_2 = no. of gram eq. of hypo

$$n_{(\text{I}_2)} \times 2 = 1 \times 1 \times 40 \times 10^{-3}$$

$$\frac{x}{20} \times 2 = 40 \times 10^{-3}$$

$$x = 40 \times 10^{-2} \text{ moles}$$

$$\begin{aligned} \% \text{ CuSO}_4 \text{ (by mass)} &= \frac{\text{wt}(\text{CuSO}_4)}{\text{wt total}} \times 100 \\ &= \frac{40 \times 10^{-2} \times 160}{80} \times 100 = 80\% \end{aligned}$$

EXERCISE # S-I

OXIDATION NUMBER

1. Calculate oxidation number of underlined elements in the following compounds

- (a) $\text{H}_2\underline{\text{S}}_2\text{O}_7$ (b) $\text{H}_4\underline{\text{P}}_2\text{O}_7$ (c) $\underline{\text{S}}_2\text{O}_3^{2-}$ (d) $\underline{\text{C}}\text{H}_4$
 (e) $\underline{\text{C}}\text{Cl}_4$ (f) $\text{Ca}\underline{\text{O}}_2$ (g) $\underline{\text{Zn}}\text{O}_2^{2-}$ (h) $\underline{\text{Cr}}\text{O}_2\text{Cl}_2$
 (i) $\text{Ca}(\underline{\text{ClO}}_2)_2$

RR0001

2. Classify each of the following unbalanced half-reactions as either an oxidation or a reduction :

- (a) $\text{O}_2(\text{g}) \longrightarrow \text{OH}^-(\text{aq})$ (b) $\text{H}_2\text{O}_2(\text{aq}) \longrightarrow \text{O}_2(\text{g})$
 (c) $\text{MnO}_4^-(\text{aq}) \longrightarrow \text{MnO}_4^{2-}(\text{aq})$ (d) $\text{CH}_3\text{OH}(\text{aq}) \longrightarrow \text{CH}_2\text{O}(\text{aq})$

RR0002

3. Identify the oxidant and reductant in the following reactions :

- (a) $\text{Zn}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{ZnO}(\text{s})$
 (b) $\text{Zn}(\text{s}) + 2\text{H}^+(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$
 (c) $10\text{H}^+(\text{aq}) + 4\text{Zn}(\text{s}) + \text{NO}_3^-(\text{aq}) \longrightarrow 4\text{Zn}^{2+}(\text{aq}) + \text{NH}_4^+(\text{aq}) + 3\text{H}_2\text{O}(\ell)$

RR0003

BALANCING OF REDOX

4. Balance the following redox reactions by oxidation number method :

- (i) $\text{Cu} + \text{HNO}_3 \longrightarrow \text{Cu}(\text{NO}_3)_2 + \text{NO}_2 + \text{H}_2\text{O}$ (Acidic medium) RR0004
 (ii) $\text{Br}_2 + \text{H}_2\text{O}_2 \longrightarrow \text{BrO}_3^- + \text{H}_2\text{O}$ (Acidic medium) RR0005
 (iii) $\text{MnO}_4^- + \text{Fe}^{+2} \longrightarrow \text{Mn}^{+2} + \text{Fe}^{+3}$ (Acidic medium) RR0006
 (iv) $\text{MnO}_2 + \text{Cl}^- \longrightarrow \text{Mn}^{+2} + \text{Cl}_2 + \text{H}_2\text{O}$ (Acidic medium) RR0007
 (v) $\text{ClO}^- + \text{CrO}_2^- \xrightarrow{\text{OH}^-} \text{Cl}^- + \text{CrO}_4^{2-} + \text{H}_2\text{O}$ (Basic medium) RR0008

5. Balance the following redox reactions by half-reaction method (Ion electron method):

- (i) $\text{MnO}_4^-(\text{aq}) + \text{I}^-(\text{aq}) \longrightarrow \text{MnO}_2(\text{s}) + \text{I}_2(\text{s})$ (in basic medium) RR0009
 (ii) $\text{MnO}_4^-(\text{aq}) + \text{SO}_2(\text{g}) \longrightarrow \text{Mn}^{2+}(\text{aq}) + \text{HSO}_4^-(\text{aq})$ (in acidic solution) RR0010
 (iii) $\text{H}_2\text{O}_2(\text{aq}) + \text{Fe}^{2+}(\text{aq}) \longrightarrow \text{Fe}^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$ (in acidic solution) RR0011
 (iv) $\text{Cr}_2\text{O}_7^{2-}(\text{aq.}) + \text{SO}_2(\text{g}) \longrightarrow \text{Cr}^{3+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$ (in acidic solution) RR0012

6. Find the valence factor for the following acid/bases -

- (1) CH_3COOH (2) NaH_2PO_4 (3) H_3BO_3
 (4) NaOH (5) $\text{Ca}(\text{OH})_2$ (6) CsOH

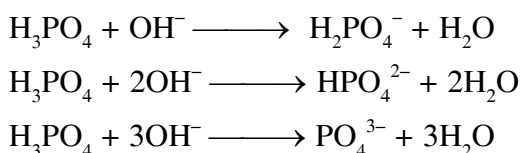
RR0013

7. Find the n-factor of underlined species in the following non redox reaction.

- (1) $\text{NaOH} + \underline{\text{H}_3\text{PO}_4} \longrightarrow \text{NaH}_2\text{PO}_4 + \text{H}_2\text{O}$
 (2) $\text{NaOH} + \underline{\text{H}_2\text{SO}_4} \longrightarrow \text{NaHSO}_4 + \text{H}_2\text{O}$
 (3) $\underline{\text{Ca}(\text{OH})_2} + \text{HCl} \longrightarrow \text{Ca}(\text{OH})\text{Cl} + \text{H}_2\text{O}$
 (4) $\underline{\text{Na}_2\text{CO}_3} + \text{HCl} \longrightarrow \text{NaHCO}_3 + \text{NaCl}$
 (5) $\underline{\text{Na}_2\text{CO}_3} + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$

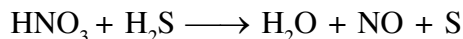
RR0014

8. What will be the equivalent wt. of H_3PO_4 in each of the reaction.



RR0015

9. What is the equivalent weight of HNO_3 in following reaction ?



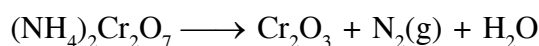
RR0016

10. Find out the equivalent weight of the underlined species in the following reaction :

- (i) $\underline{\text{ClO}_3^-} + \text{Fe}^{2+} + \text{H}^+ \longrightarrow \text{Cl}^- + \text{Fe}^{3+} + \text{H}_2\text{O}$
 (ii) $\text{CuO} + \underline{\text{NH}_3} \longrightarrow \text{Cu} + \text{N}_2 + \text{H}_2\text{O}$

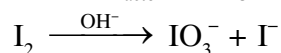
RR0017

11. Find out the n_{factor} of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ in the following decomposition reaction.



RR0018

12. Find out the n_{factor} of IO_3^- in the following disproportionation reaction.



RR0019

ACID BASE TITRATION

13. How many millilitre of 0.5 M H_2SO_4 are needed to dissolve 0.5 g of copper II carbonate ? [JEE 1999]

RR0020

14. An aqueous solution of 6.3 g of oxalic acid dihydrate is made upto 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is : [JEE 2001]
RR0021
15. Calculate volume of 1N H_3PO_4 required to react with 20 ml 2N $\text{Ca}(\text{OH})_2$ solution RR0022
16. Calculate volume of 1N H_2SO_4 required to react with 20 ml 1 M $\text{Al}(\text{OH})_3$ solution RR0023
17. Calculate volume of 0.4 M NaOH required to react with following mixture
 $\text{HCl}(1 \text{ mol}) + \text{H}_2\text{SO}_4(2 \text{ mol})$ RR0024
18. Calculate volume of 0.2 M H_2SO_4 required to react with following mixture
 $\text{NaOH}(1 \text{ mol}) + \text{Ca}(\text{OH})_2(2 \text{ mol})$ RR0025
19. How many litre of 0.1N HCl are required to react completely with 19 gm mixture of Na_2CO_3 and NaHCO_3 containing equimolar amount of two ? RR0026
20. H_3PO_4 is a tri basic acid and one of its salt is NaH_2PO_4 . What volume in ml of 1 M NaOH solution should be added to 12 g of NaH_2PO_4 to convert it into Na_3PO_4 ? RR0027

REDOX TITRATION

21. Calculate the normality of a solution containing 50 mL of 5 M solution of $\text{K}_2\text{Cr}_2\text{O}_7$ in acidic medium. RR0028
22. A 5.0 cm^3 solution of H_2O_2 liberates 0.508 g of iodine from an acidified KI solution. Calculate the strength of H_2O_2 solution in terms of volume strength at STP. [JEE' 1995]
RR0029
23. Calculate the normality of a solution containing 15.8 g of KMnO_4 in 50 mL acidic solution. RR0030
24. 20 mL of H_2O_2 after acidification with dil H_2SO_4 required 30 mL of $\frac{\text{N}}{12}$ KMnO_4 for complete oxidation. The strength of H_2O_2 solution is [Molar mass of $\text{H}_2\text{O}_2 = 34$] RR0031
25. It required 40 ml of 1 M Ce^{4+} to titrate 20 ml of 1 M Sn^{2+} to Sn^{4+} . What is the oxidation state of cerium in the product. RR0032
26. A volume of 10.0 ml of 1 M SeO_2 reacted with exactly 20 ml of 2 M CrSO_4 . In the reaction, Cr^{2+} was oxidized to Cr^{3+} . To what oxidation state was selenium converted by the reaction. RR0033

27. Potassium acid oxalate $K_2C_2O_4 \cdot 3H_2C_2O_4 \cdot 4H_2O$ can be oxidized by MnO_4^- in acid medium. Calculate the volume of 0.1 M $KMnO_4$ reacting in acid solution with 5.08 gm of the acid oxalate. **RR0034**
28. A 1 g sample of H_2O_2 solution containing x% H_2O_2 by mass requires x cm³ of a $KMnO_4$ solution for complete oxidation under acidic condition. Calculate the normality of $KMnO_4$ solution. **RR0035**
29. Metallic tin in the presence of HCl is oxidized by $K_2Cr_2O_7$ to stannic chloride, $SnCl_4$. What volume of deci-normal dichromate solution would be reduced by 11.9 gm of tin [Sn = 119] **RR0036**
30. Calculate the number of millimoles of $K_2Cr_2O_7$ which will completely react with 40 ml 0.1 MKI Solution. **RR0037**
31. Find the number of moles of $KMnO_4$ needed to oxidise one mole Cu_2S in acidic medium. The reaction is : $Cu_2S + KMnO_4 \longrightarrow Cu^{2+} + Mn^{2+} + SO_2$ **RR0038**
32. 0.4 M $KMnO_4$ solution completely reacts with 0.05 M $FeSO_4$ solution under acidic conditions. The volume of $FeSO_4$ used is 50 mL. What volume of $KMnO_4$ was used ? **RR0039**

BACK TITRATION

33. 50 gm of a sample of $Ca(OH)_2$ is dissolved in 50 ml of 0.5 N HCl solution. The excess of HCl was titrated with 0.3N – NaOH. The volume of NaOH used was 20cc. Calculate % purity of $Ca(OH)_2$ **RR0040**
34. 10 g $CaCO_3$ were dissolved in 250 ml of 1 M HCl. What volume of 2 M KOH would be required to neutralise excess HCl. **RR0041**
35. 20 g of a sample of $Ba(OH)_2$ is dissolved in 10 mL of 0.5 N HCl solution : The excess of HCl was titrated with 0.1 N NaOH. The volume of NaOH used was 20 cc. Calculate the percentage of $Ba(OH)_2$ in the sample. (Ba = 137) **RR0042**
36. To 50 L of 0.2 N NaOH, 2.5 L of 2N HCl and 15 L of 0.1 N $FeCl_3$ solutions are added. What weight of Fe_2O_3 can be obtained from the precipitate? Also report the normality of NaOH left in resultant solution : **RR0043**

Hardness of water

37. Softening of hard water by using sodium aluminium silicate (zeolite) is due to - Adsorption of andions of hard water, replacing ions **RR0044**
38. One litre of a sample of hard water contains 10 mg of $CaCl_2$ & 9.5 mg of $MgCl_2$. What is degree of hardness in terms of ppm of $CaCO_3$ **RR0045**

EXERCISE # S-II

1. Find out the oxidation number of the underlined elements in the following compounds:

- (a) $\text{Na}_2\underline{\text{S}}_4\text{O}_6$ (b) $\underline{\text{C}}_3\text{O}_2$ (c) $\text{K}\underline{\text{I}}_3$ (d) $\underline{\text{Fe}}_3\text{O}_4$
 (e) $\underline{\text{C}}\text{H}_3\underline{\text{C}}\text{H}_2\text{OH}$ (f) $\underline{\text{C}}\text{H}_3\underline{\text{C}}\text{OOH}$ (g) $\underline{\text{Br}}_3\text{O}_8$ (h) $\text{CaO}\underline{\text{Cl}}_2$
 (i) $\underline{\text{Fe}}\underline{\text{S}}_2$ (j) $\underline{\text{O}}\text{F}_2$ (k) $\text{H}\underline{\text{O}}\underline{\text{F}}$ (l) $\underline{\text{O}}_2^+$
 (m) $\underline{\text{O}}_2^-$ (n) $\text{C}_6\text{H}_5\underline{\text{C}}\text{HO}$ (o) $\text{C}_6\text{H}_5\underline{\text{N}}\text{O}_2$ (p) $\text{C}_6\text{H}_5\underline{\text{N}}\text{H}_2$
 (q) $(\underline{\text{C}}\text{N})_2$ (r) $\underline{\text{C}}\text{N}^-$ (s) $\underline{\text{C}}\text{NO}^-$

RR0046

RR0047

RR0048

RR0049

RR0050

2. Calculate oxidation number of underlines elements in the following compounds

- (a) $\text{K}[\underline{\text{Co}}(\text{C}_2\text{O}_4)_2(\text{NH}_3)_2]$ (b) $\text{K}\underline{\text{Al}}(\underline{\text{S}}\text{O}_4)_2 \cdot 12\text{H}_2\text{O}$
 (c) $[\underline{\text{Fe}}(\text{CN})_6]^{4-}$ (d) $\underline{\text{Fe}}_{0.93}\text{O}$
 (e) $\text{H}_2\underline{\text{S}}_2\text{O}_8$ (f) $\underline{\text{Cr}}\text{O}_5$
 (g) $\text{H}_2\underline{\text{S}}\text{O}_5$ (h) $\text{K}_3\underline{\text{Cr}}\text{O}_8$
 (r) $\text{Na}_2[\underline{\text{Fe}}(\text{CN})_5\text{NO}^+]$ (s) $\underline{\text{Cr}}(\text{CN})_6^{3-}$

RR0051

RR0052

RR0053

3. Balance the following redox reactions by half-reaction method

- (i) $\text{KMnO}_4(\text{aq.}) + \text{FeC}_2\text{O}_4(\text{aq.}) + \text{H}_2\text{SO}_4(\text{aq.}) \longrightarrow$
 $\text{MnSO}_4(\text{aq.}) + \text{Fe}_2(\text{SO}_4)_3(\text{aq.}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$ (Acidic medium)
 (ii) $\text{P}_4(\text{s}) + \text{OH}^-(\text{aq.}) \longrightarrow \text{PH}_3(\text{aq.}) + \text{HPO}_2^-(\text{aq.})$ (Basic medium)
 (iii) $\text{I}_2(\text{s}) + \text{NaOH}(\text{aq.}) \longrightarrow \text{NaI}(\text{aq.}) + \text{NaIO}_3(\text{aq.}) + \text{H}_2\text{O}(\text{l})$ (Basic medium)
 (iv) $\text{HNO}_2(\text{aq.}) \rightarrow \text{NO}_3^- + \text{NO}(\text{g})$ (acidic medium)
 (v) $\text{IO}_3^- + \text{I}^- + \text{H}^+ \rightarrow \text{I}_2 + \text{H}_2\text{O}$ (acidic medium)
 (vi) $\text{Cu}_2\text{S} + \text{MnO}_4^- + \text{H}^+ \rightarrow \text{Cu}^{2+} + \text{Mn}^{2+} + \text{SO}_2$ (Acidic medium)
 (vii) $\text{HCHO}(\text{l}) + 2[\text{Ag}(\text{NH}_3)_2]^+(\text{aq.}) + 3\text{OH}^-(\text{aq.}) \rightarrow 2\text{Ag}(\text{s}) + \text{HCOO}^-(\text{aq.}) + 4\text{NH}_3(\text{aq.}) + 2\text{H}_2\text{O}(\text{l})$
 (basic medium)

RR0054

RR0055

RR0056

RR0057

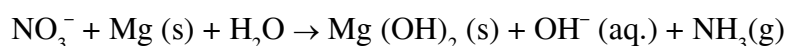
RR0058

RR0059

RR0060

4. A solution containing 4.2g of KOH and Ca(OH)_2 is neutralized by an acid. It consumes 0.1 equivalent of acid, calculate the percentage composition of the sample.
RR0061
5. Calculate volume of 0.4 M KMnO_4 required to react with following in acidic medium
 $\text{KHC}_2\text{O}_4(1 \text{ mol}) + \text{H}_2\text{C}_2\text{O}_4(2 \text{ mol})$
RR0062
6. Calculate volume of 0.4 M NaOH required to react with following mixture.
 $\text{KHC}_2\text{O}_4(1 \text{ mole}) + \text{H}_2\text{C}_2\text{O}_4(2 \text{ mol})$
RR0063
7. Calculate volume of 0.2 M KMnO_4 required to react with following mixture in acidic medium.
 $\text{KHC}_2\text{O}_4(128 \text{ gm}) + \text{H}_2\text{C}_2\text{O}_4(180 \text{ gm})$
RR0064
8. 520 gm mixture of Fe_2O_3 and FeO reacts completely with 158 gm KMnO_4 in acidic medium Calculate the mole % of Fe_2O_3 in mixture.
RR0065
9. Calculate the millimoles of Br_2 produced when 10 ml of 0.1 M BrO_3^- reacts with excess of Br^- .
RR0066
10. One gm of impure sodium carbonate is dissolved in water and the solution is made up to 250 ml. To 50 ml of this made up solution, 50 ml of 0.1N – HCl is added and the mix after shaking well required 10 ml of 0.16 N – NaOH solution for complete titration. Calculate the % purity of the sample.
RR0067
11. 100 ml sample of hard water containing only Ca^{2+} hardness is passed through a column of cation exchange resin ($\text{H}^+ - \text{resin}$). The water coming out the column require 20 ml of 0.02M NaOH for its titration. What is hardness of water as ppm of Ca^{2+}
RR0068
12. 3.55 g sample of bleaching powder suspended in H_2O was treated with enough acetic acid and KI solution. Iodine thus liberated required 80 mL of 0.2 M hypo for titration. Calculate the % of available chlorine.
RR0069
13. 3.2 g of pyrolusite (MnO_2) was treated with 50 mL of 0.5 M oxalic acid and some sulphuric acid. The oxalic acid left undecomposed was raised to 250 mL in a flask. 25 mL of this solution when treated with 0.02 M KMnO_4 required 32 mL of the solution : Find the % of MnO_2 in the sample.
RR0070

- 14.. Mg can reduce NO_3^- to NH_3 in basic medium.



A 25.0 mL sample of NO_3^- solution was treated with Mg. The NH_3 (g) was passed into 100 mL of 0.15 N HCl. The excess of HCl required 32.10 mL of 0.10 N NaOH for neutralization. What was the molarity of NO_3^- ions in the original sample ?

RR0071

15. A mixture of H_2SO_4 and $\text{H}_2\text{C}_2\text{O}_4$ (oxalic acid) and some inert impurity weighing 3.185 g was dissolved in water and the solution made up to 1 litre, 10 mL of this solution required 3 mL of 0.1 N NaOH for complete neutralization. In another experiment 100 mL of the same solution in hot condition required 4 mL of 0.02M KMnO_4 solution for complete reaction. The wt. % of H_2SO_4 in the mixture was :-

RR0072

16. An aqueous solution containing 0.10 g KIO_3 (formula wt. 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated I_2 consumed 45.0 mL of thiosulphate solution to decolourise the blue starch – iodine complex. Calculate the molarity of the sodium thiosulphate solution.

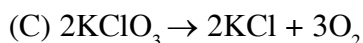
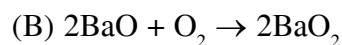
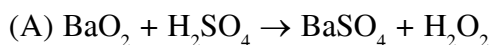
[JEE 1998]

RR0073

EXERCISE # O-I

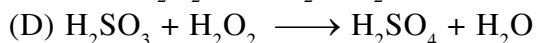
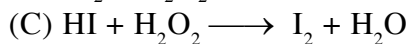
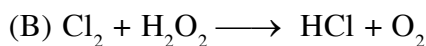
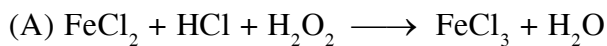
- The oxidation number of phosphorus in $\text{Ba}(\text{H}_2\text{PO}_2)_2$ is :
(A) +3 (B) +2 (C) +1 (D) -1
RR0074
- The oxidation states of the most electronegative element in the products of the reaction of BaO_2 with dilute H_2SO_4 .
(A) 0 and -1 (B) -1 and -2 (C) -2 and 0 (D) -2 and +2
RR0075
- In the coordination compound, $\text{K}_4[\text{Ni}(\text{CN})_6]$, the oxidation state of nickel is [AIEEE-03]
(A) +1 (B) +2 (C) -1 (D) 0
RR0076
- The oxidation state of Cr in $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$ is - [AIEEE-05]
(A) +2 (B) +3 (C) 0 (D) +1
RR0077
- Oxidation number of Cl in CaOCl_2 (bleaching powder is) [AIEEE-02]
(A) Zero, since it contains Cl_2 (B) -1, since it contains Cl^-
(C) +1, since it contains ClO^- (D) +1 and -1 since it contains ClO^- and Cl^-
RR0078
- The oxidation number of sulphur in S_8 , S_2F_2 and H_2S respectively are :
(A) 0, +1 and -2 (B) +2, +1 and -2
(C) 0, +1 and +2 (D) -2, +1 and -2
RR0079
- The incorrect order of decreasing oxidation number of S in compounds is :-
(A) $\text{H}_2\text{S}_2\text{O}_7 > \text{Na}_2\text{S}_4\text{O}_6 > \text{Na}_2\text{S}_2\text{O}_3 > \text{S}_8$ (B) $\text{H}_2\text{SO}_5 > \text{H}_2\text{SO}_3 > \text{SCl}_2 > \text{H}_2\text{S}$
(C) $\text{SO}_3 > \text{SO}_2 > \text{S}_8 > \text{H}_2\text{S}$ (D) $\text{H}_2\text{SO}_4 > \text{SO}_2 > \text{H}_2\text{S} > \text{H}_2\text{S}_2\text{O}_8$
RR0080
- Which of the following is a redox [AIEEE-02]
(A) $2\text{NaAg}(\text{CN})_2 + \text{Zn} \longrightarrow \text{Na}_2\text{Zn}(\text{CN})_4 + 2\text{Ag}$
(B) $\text{BaO}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + \text{H}_2\text{O}_2$
(C) $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \longrightarrow 2\text{HNO}_3$
(D) $\text{AgNO}_3 + \text{KI} \longrightarrow \text{AgI} + \text{KNO}_3$
RR0081
- Which reaction does not represent autoredox or disproportionation :-
(A) $\text{Cl}_2 + \text{OH}^- \longrightarrow \text{Cl}^- + \text{ClO}_3^- + \text{H}_2\text{O}$
(B) $2\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{O}_2$
(C) $2\text{Cu}^+ \longrightarrow \text{Cu}^{+2} + \text{Cu}$
(D) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \longrightarrow \text{N}_2 + \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O}$
RR0082

10. Which of the following is not a redox reaction?



RR0083

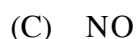
11. H_2O_2 acts as a reducing agent in:



RR0084

12. Match List-I (Compounds) with List-II (Oxidation states of nitrogen) and select answer using the codes given below the lists :-

List-I



List-II

1. +5

2. +2

3. $-1/3$

4. -1

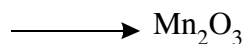
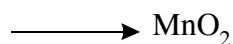
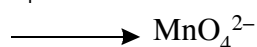
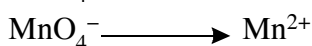
Code :

	(a)	(B)	(C)	(D)
(A)	3	4	2	1
(B)	4	3	2	1
(C)	3	4	1	2
(D)	4	3	1	2

RR0085

13. MnO_4^- is good oxidising agent in different medium changing to -

[AIEEE-02]



Changes in oxidation number respectively are -

(A) 1, 3, 4, 5

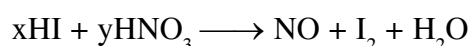
(B) 5, 4, 3, 2

(C) 5, 1, 3, 4

(D) 2, 6, 4, 3

RR0086

14. In the reaction,



(A) $x = 3, y = 2$

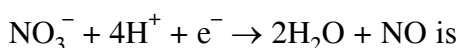
(B) $x = 2, y = 3$

(C) $x = 6, y = 2$

(D) $x = 6, y = 1$

RR0087

15. The number of electrons to balance the following equation :-



- (A) 5 (B) 4 (C) 3 (D) 2

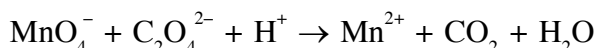
RR0088

16. Number of moles of electrons taken up when 1 mole of NO_3^- ions is reduced to 1 mole of NH_2OH is

- (A) 2 (B) 4 (C) 5 (D) 6

RR0089

17. For the redox reaction,



the correct coefficients of the reactants for the balanced reaction are :

- | MnO_4^- | $\text{C}_2\text{O}_4^{2-}$ | H^+ |
|------------------|-----------------------------|--------------|
| (A) 2 | 5 | 16 |
| (B) 16 | 5 | 2 |
| (C) 5 | 16 | 2 |
| (D) 2 | 16 | 5 |

RR0090

18. In a redox reaction, the equivalent weight of HNO_2 is found to be 23.5. The reaction products might contain

- (A) NO_2 (B) NO (C) NH_3 (D) HNO_3

RR0091

19. When N_2 is converted into NH_3 , the equivalent weight of nitrogen will be :

- (A) 1.67 (B) 2.67 (C) 3.67 (D) 4.67

RR0092

20. The equivalent mass of MnSO_4 is half its molecular mass when it is converted to : [JEE 1998]

- (A) Mn_2O_3 (B) MnO_2 (C) MnO_4^- (D) MnO_4^{2-}

RR0093

21. When KBrO_3 ion reacts with Br^- ion in acid solution Br_2 is liberated. The equivalent weight of KBrO_3 in this reaction is

- (A) $M/8$ (B) $M/3$ (C) $M/5$ (D) $M/6$

RR0094

22. In the reaction $\text{CrO}_5 + \text{H}_2\text{SO}_4 \rightarrow \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O} + \text{O}_2$ one mole of CrO_5 will liberate how many moles of O_2 :-

- (A) $5/2$ (B) $5/4$ (C) $9/2$ (D) $7/4$

RR0095

23. A solution of KMnO_4 is reduced to MnO_2 . The normality of solution is 0.6. The molarity is :

- (A) 1.8M (B) 0.6M (C) 0.1M (D) 0.2M

RR0096

24. The normality of 0.3 M phosphorus acid (H_3PO_3) is :
 (A) 0.1 (B) 0.9 (C) 0.3 (D) 0.6
RR0097
25. 0.52 g of a dibasic acid required 100 mL of 0.2 N NaOH for complete neutralization. The equivalent weight of acid is
 (A) 26 (B) 52 (C) 104 (D) 156
RR0098
26. What is the equivalent weight of H_2SO_4 in the reaction ?

$$\text{H}_2\text{SO}_4 + \text{NaI} \rightarrow \text{Na}_2\text{SO}_4 + \text{I}_2 + \text{H}_2\text{S} + \text{H}_2\text{O}$$
 (A) 12.25 (B) 49 (C) 61.25 (D) None of these
RR0099
27. 125 mL of 63% (w/v) $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ is made to react with 125 mL of a 40% (w/v) NaOH solution. The resulting solution is :-
 (A) neutral (B) acidic (C) strongly acidic (D) alkaline
RR0100
28. The mass of oxalic acid crystals ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) required to prepare 50 mL of a 0.2 N solution is :-
 (A) 4.5 g (B) 6.3 g (C) 0.63 g (D) 0.45 g
RR0101
29. If 25 mL of a H_2SO_4 solution reacts completely with 1.06 g of pure Na_2CO_3 , what is the normality of this acid solution :
 (A) 1 N (B) 0.5 N (C) 1.8 N (D) 0.8 N
RR0102
30. The number of moles of KMnO_4 that will be required to react with 2 mol of ferrous oxalate is
 (A) $\frac{6}{5}$ (B) $\frac{2}{5}$ (C) $\frac{4}{5}$ (D) 1
RR0103
31. The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is -
 (A) +6 (B) +4 (C) +3 (D) +2
[AIEEE-05]
RR0104
32. The number of mole of KMnO_4 that will need to react completely with one mole ferrous oxalate in acidic solution is :
 (A) 2/5 (B) 3/5 (C) 4/5 (D) 1
[JEE 1997]
RR0105
33. The number of mole of KMnO_4 that will be needed to react with one mole of sulphite ion in acidic solution is :
 (A) 2/5 (B) 3/5 (C) 4/5 (D) 1
[JEE 1997]
RR0106

34. What volume of 0.1 M KMnO_4 is needed to oxidize 100 mg of FeC_2O_4 in acid solution ?
 (A) 4.1 mL (B) 8.2 mL (C) 10.2 mL (D) 4.6 mL
 RR0107
35. What volume of 6 M HNO_3 is needed to oxidize 8 g of Fe^{2+} to Fe^{3+} , HNO_3 gets converted to NO?
 (A) 8 mL (B) 7.936 mL (C) 32 mL (D) 64 mL
 RR0108
36. The minimum quantity of H_2S needed to precipitate 63.5 g of Cu^{2+} will be nearly.
 (A) 63.5 g (B) 31.75 g (C) 34 g (D) 2.0 g
 RR0109
37. The volume of 1.5 M H_3PO_4 solution required to neutralize exactly 90 mL of a 0.5 M $\text{Ba}(\text{OH})_2$ solution is :-
 (A) 10 mL (B) 30 mL (C) 20 mL (D) 60 mL
 RR0110
38. Hydrogen peroxide in aqueous solution decomposes on warming to give oxygen according to the equation

$$2\text{H}_2\text{O}_2(\text{aq}) \longrightarrow 2\text{H}_2\text{O}(\ell) + \text{O}_2(\text{g})$$

 Under conditions where 1 mole of gas occupies 24 dm^3 . 100 cm^3 of XM solution of H_2O_2 produces 3 dm^3 of O_2 . Thus X is :-
 (A) 2.5 (B) 1 (C) 0.5 (D) 0.25
 RR0111
39. A mixture of NaHC_2O_4 and $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$ required equal volumes of 0.2 N KMnO_4 and 0.12 N NaOH separately. What is the molar ratio of NaHC_2O_4 and $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$ in the mixture ?
 (A) 6 : 1 (B) (C) 1 : 3 (D) none
 RR0112
40. Volume V_1 mL of 0.1 M $\text{K}_2\text{Cr}_2\text{O}_7$ is needed for complete oxidation of 0.678 g N_2H_4 in acidic medium. The volume of 0.3 M KMnO_4 needed for same oxidation in acidic medium will be :-
 (A) $\frac{2}{5} V_1$ (B) $\frac{5}{2} V_1$ (C) $113 V_1$ (D) can't say
 RR0113
41. As_2O_3 is oxidised to H_3AsO_4 by KMnO_4 in acidic medium. Volume of 0.02M KMnO_4 required for this purpose by 1mmol of As_2O_3 will be
 (A) 10 mL (B) 20 mL (C) 40 mL (D) 80 mL
 RR0114

42. When ozone is passed through dry KOH, KO_3 is obtained and O_2 is liberated. In this reaction _____ is oxidised and _____ is reduced.

(A) hydrogen, oxygen (B) potassium, oxygen
(C) oxygen, oxygen (D) oxygen, hydrogen

RR0115

43. 100 ml of 0.1M $\text{NaAl}(\text{OH})_2\text{CO}_3$ is neutralised by 0.25 N HCl to form NaCl, AlCl_3 and CO_2 . Volume of HCl required is

(A) 10 mL (B) 40 mL (C) 100mL (D) 160 mL

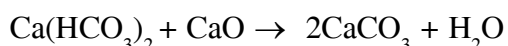
RR0116

44. x mmol of XeF_4 quantitatively oxidized KI to I_2 and liberated Xe, alongwith formation of KF. This iodine required 20 ml of decinormal hypo solution for exact titration. The value of x is

(A) 0.5 (B) 1.0 (C) 2.0 (D) 5.0

RR0117

45. Temporary hardness is due to HCO_3^- of Mg^{2+} and Ca^{2+} . It is removed by addition of CaO.



Mass of CaO required to precipitate 2 g CaCO_3 is :-

(A) 2.00 (B) 0.56 g (C) 0.28 g (D) 1.12 g

RR0118

46. 0.3 g of an oxalate salt was dissolved in 100 mL solution. The solution required 90 mL of N/20 KMnO_4 for complete oxidation. The % of oxalate ion in salt is :-

(A) 33% (B) 66% (C) 70% (D) 40%

RR0119

EXERCISE # O-II

1. If 10 g of V_2O_5 is dissolved in acid and is reduced to V^{2+} by zinc metal, how many mole I_2 could be reduced by the resulting solution if it is further oxidised to VO^{2+} ions ?

[Assume no change in state of Zn^{2+} ions] ($V = 51$, $O = 16$, $I = 127$) :

- (A) 0.11 mole of I_2 (B) 0.22 mole of I_2 (C) 0.055 mole of I_2 (D) 0.44 mole of I_2

RR0120

2. The number of moles of $Cr_2O_7^{2-}$ needed to oxidize 0.136 equivalents of $N_2H_5^+$ by the reaction $N_2H_5^+ + Cr_2O_7^{2-} \rightarrow N_2 + Cr^{3+} + H_2O$ is

- (A) 0.136 (B) 0.068 (C) 0.0227 (D) 0.272

RR0121

3. Dichloroacetic acid ($CHCl_2COOH$) is oxidized to CO_2 , H_2O and Cl_2 by 600 meq of an oxidizing agent. Same amount of acid can neutralize how many moles of ammonia to form ammonium dichloroacetate?

- (A) 0.0167 (B) 0.1 (C) 0.3 (D) 0.6

RR0122

4. HNO_3 oxidises NH_4^+ ions to nitrogen and itself gets reduced to NO_2 . The moles of HNO_3 required by 1 mol of $(NH_4)_2SO_4$ is :-

- (A) 4 (B) 5 (C) 6 (D) 2

RR0123

5. During the disproportionation of iodine to iodide and iodate ions, the ratio of iodate and iodide ions formed in alkaline medium is :-

- (A) 1 : 5 (B) 5 : 1 (C) 3 : 1 (D) 1 : 3

RR0124

6. When arsenic sulphide is boiled with $NaOH$, sodium arsenite and sodium thioarsenite are formed

$x As_2S_3 + y NaOH \longrightarrow Na_3AsO_3 + x Na_3AsS_3 + \frac{y}{2} H_2O$. What are the values of x and y ?

- (A) 1, 6 (B) 2, 8 (C) 2, 6 (D) 1, 4

RR0125

7. 35 mL sample of hydrogen peroxide gives of 500 mL of O_2 at $27^\circ C$ and 1 atm pressure. Volume strength of H_2O_2 sample will be :-

- (A) 10 volume (B) 13 volumes (C) 11 volume (D) 12 volume

RR0126

8. An element A in a compound ABD has oxidation number A^n . It is oxidised by $Cr_2O_7^{2-}$ in acid medium. In the experiment 1.68×10^{-3} moles of $K_2Cr_2O_7$ were used for 3.26×10^{-3} moles of ABD. The new oxidation number of A after oxidation is :-

- (A) 3 (B) $3 - n$ (C) $n - 3$ (D) $+n3$

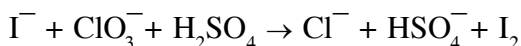
RR0127

9. 50g of pure CaCO_3 is heated to liberate CO_2 . Liberated CO_2 required 0.4 mol of moist ammonia to yield only $(\text{NH}_4)_2\text{CO}_3$. Find the volume of CO_2 liberated at STP adding excess dil. HCl to this heated residue.

(A) zero (B) 4.42 L (C) 6.81 L (D) 6.72 L

RR0128

10. For the reaction



The correct statement(s) in the balanced equation is / are :

- (A) Stoichiometric coefficient of HSO_4^- is 6
 (B) Iodide is oxidized
 (C) Sulphur is reduced
 (D) H_2O is one of the products

RR0129

11. A sample of KMnO_4 solution required 50 ml when titrated against 3 mmol of oxalic acid. The normality of same solution in reaction with alkaline H_2O_2 is

(A) 0.120 N (B) 0.060 N (C) 0.072 N (D) 0.036 N

RR0130

Assertion Reason Type

12. **Statement-1 :-** Moles of KMnO_4 required for oxidation of Fe^{2+} in acidic and basic medium will be different.

Statement-2 :- Final oxidation state to which Mn^{7+} will be reduced will be different in case of acidic and basic medium.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.

RR0131

13. **Statement-1 :-** Mass of a particular substance that combine with 8 gm of oxygen is said to be equivalent weight of substance.

Statement-2 :- x gm of metal gave y gm of its oxide, so equivalent weight of metal is $\left(\frac{x}{y-x}\right) \times 8$

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.

RR0132

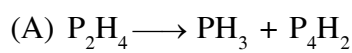
14. **Statement-1 :-** Degree of hardness of water is measured in terms of ppm of CaCO_3 .
Statement-2 :- If water contains 120 ppm of MgSO_4 , and 2ppm NaCl , its hardness in terms of CaCO_3 > 100 ppm.
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
 (C) Statement-1 is true, statement-2 is false.
 (D) Statement-1 is false, statement-2 is true.

RR0133

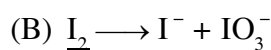
MATCH THE COLUMN

15. **Column-I**

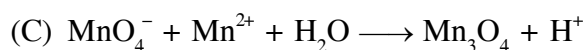
Column-II



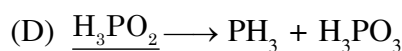
(p) $E = \frac{3M}{4}$



(q) $E = \frac{3M}{5}$



(r) $E = \frac{15M}{26}$



(s) $E = \frac{5M}{6}$

RR0134

Paragraph for Q.16 to Q.19

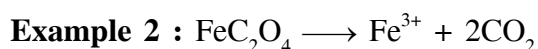
$$\text{Equivalent weight} = \frac{\text{Molecular weight} / \text{Atomic weight}}{n - \text{factor}}$$

n-factor is very important in redox as well as non-redox reactions. With the help of n-factor we can predicts the molar ratio of the reactant species taking part in reactions. The reciprocal of n-factor's ratio of the reactants is the molar ratio of the reactants.

In general n-factor of acid/base is number of moles of H^+ / OH^- furnished per mole of acid/base. n-factor of a reactant is no. of moles of electrons lost or gained per mole of reactant.

Example 1 :

- In acidic medium : KMnO_4 ($n = 5$) $\longrightarrow \text{Mn}^{2+}$
- In neutral medium : KMnO_4 ($n = 3$) $\longrightarrow \text{Mn}^{2+}$
- In basic medium : KMnO_4 ($n = 1$) $\longrightarrow \text{Mn}^{6+}$



Total no. of moles of e^- lost by 1 mole of $\text{FeC}_2\text{O}_4 = 1 + 1 \times 2 \Rightarrow 3$

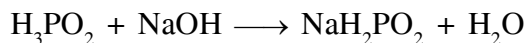
\therefore n-factor of $\text{FeC}_2\text{O}_4 = 3$

16. n-factor of $\text{Ba}(\text{MnO}_4)_2$ in acidic medium is :

- (A) 2 (B) 6 (C) 10 (D) none of these

RR0135

17. For the reaction,



What is the equivalent weight of H_3PO_2 ? (mol. wt. is M)

- (A) M (B) M/2 (C) M/3 (D) none of these

RR0136

18. For the reaction, $\text{Fe}_{0.95}\text{O}$ (molar mass : M) $\longrightarrow \text{Fe}_2\text{O}_3$. What is the eq. wt. of $\text{Fe}_{0.95}\text{O}$?

- (A) $\frac{M}{0.85}$ (B) $\frac{M}{0.95}$ (C) $\frac{M}{0.8075}$ (D) none of these

RR0137

19. In the reaction, $x\text{VO} + y\text{Fe}_2\text{O}_3 \longrightarrow \text{FeO} + \text{V}_2\text{O}_5$. What is the value of x and y respectively ?

- (A) 1, 1 (B) 2, 3 (C) 3, 2 (D) none of these

RR0138

Table type question :

Column-I

(1 mole of each oxidizing agent is taken)

- (A) KMnO_4 (acidic)
(B) KMnO_4 (neutral)

- (C) MnO_2 (acidic)
(D) K_2CrO_4 (acidic)

Column-II

(oxidation number

- (P) O.N of Mn = 4
(Q) O.N of Mn = 7
(R) O.N of Cr = 6
(S) O.N of Cr = 7

Column-III

(Reducing agents)

- (1) 3 mole of FeSO_4
(2) 0.5 mole of I_2 changes to HIO_3
(3) 1 mole of $\text{K}_2\text{C}_2\text{O}_4$
(4) 1.5 mole K_2SO_3

20. Which of the following is correct

- (A) A ; P ; 2 (B) A ; Q ; 4 (C) B ; Q ; 1 (D) B ; Q ; 3

RR0139

21. Which of the following is correct

- (A) A ; Q ; 3 (B) C ; P ; 3 (C) C ; P ; 4 (D) C ; Q ; 1

RR0139

22. Which of the following is correct

- (A) D ; R ; 1 (B) D ; R ; 2 (C) D ; S ; 1 (D) D ; R ; 4

RR0139

EXERCISE # J-MAINS

- Given : [JEE(Main-online)-2013]

$$X \text{ Na}_2 \text{ HAsO}_3 + Y \text{ NaBrO}_3 + Z \text{ HCl} \rightarrow \text{NaBr} + \text{H}_3 \text{AsO}_4 + \text{NaCl}$$

The values of X, Y and Z in the above redox reaction are respectively :

(1) 2, 1, 3 (2) 3, 1, 6 (3) 2, 1, 2 (4) 3, 1, 4

RR0140
- Consider the following reaction : [JEE(Main)-2013]

$$x \text{ MnO}_4^- + y \text{ C}_2\text{O}_4^{2-} + z \text{ H}^+ \rightarrow x \text{ Mn}^{2+} + 2y \text{ CO}_2 + \frac{z}{2} \text{ H}_2\text{O}$$

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

(1) 5, 2 and 16 (2) 2, 5 and 8 (3) 2, 5 and 16 (4) 5, 2 and 8

RR0141
- How many electrons are involved in the following redox reaction ? [JEE(Main-online)-2014]

$$\text{Cr}_2\text{O}_7^{2-} + \text{Fe}^{2+} + \text{C}_2\text{O}_4^{2-} \rightarrow \text{Cr}^{3+} + \text{Fe}^{3+} + \text{CO}_2 \text{ (Unbalanced)}$$

(1) 3 (2) 4 (3) 5 (4) 6

RR0142
- Consider the reaction [JEE(Main-online)-2014]

$$\text{H}_2\text{SO}_3(\text{aq}) + \text{Sn}^{4+}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightarrow \text{Sn}^{2+}_{(\text{aq})} + \text{HSO}_4^{-}_{(\text{aq})} + 3\text{H}^{+}_{(\text{aq})}$$

Which of the following statements is correct?

(1) H_2SO_3 is the reducing agent because it undergoes oxidation
 (2) H_2SO_3 is the reducing agent because it undergoes reduction
 (3) Sn^{4+} is the reducing agent because it undergoes oxidation
 (4) Sn^{4+} is the oxidizing agent because it undergoes oxidation

RR0143
- In which of the following reaction H_2O_2 acts as a reducing agent ? [JEE(Main)-2014]

(a) $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$ (b) $\text{H}_2\text{O}_2 - 2\text{e}^- \rightarrow \text{O}_2 + 2\text{H}^+$
 (c) $\text{H}_2\text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^-$ (d) $\text{H}_2\text{O}_2 + 2\text{OH}^- - 2\text{e}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O}$
 (1) (a), (c) (2) (b), (d) (3) (a), (b) (4) (c), (d)

RR0144
- The molecular formula of a commercial resin used for exchanging ions in water softening is $\text{C}_8\text{H}_7\text{SO}_3\text{Na}$ (Mol. w.t 206). What would be the maximum uptake of Ca^{2+} ions by the resin when expressed in mole per gram resin ? [JEE(Main)-2015]

(1) $\frac{2}{309}$ (2) $\frac{1}{412}$ (3) $\frac{1}{103}$ (4) $\frac{1}{206}$

RR0145

7. The volume of 0.1N dibasic acid sufficient to neutralize 1 g of a base that furnishes 0.04 mole of OH^- in aqueous solution is : [JEE(Main)-OnLine-2016]
 (1) 400 mL (2) 200 mL (3) 600 mL (4) 800 mL
RR0146
8. Which of the following reactions is an example of a redox reaction ? [JEE(Main)-2017]
 (1) $\text{XeF}_4 + \text{O}_2\text{F}_2 \rightarrow \text{XeF}_6 + \text{O}_2$ (2) $\text{XeF}_2 + \text{PF}_5 \rightarrow [\text{XeF}]^+\text{PF}_6^-$
 (3) $\text{XeF}_6 + \text{H}_2\text{O} \rightarrow \text{XeOF}_4 + 2\text{HF}$ (4) $\text{XeF}_6 + 2\text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + 4\text{HF}$
RR0147
9. In which of the following reaction, hydrogen peroxide acts as an oxidizing agent ? [JEE(Main)-OnLine-2017]
 (1) $\text{I}_2 + \text{H}_2\text{O}_2 + 2\text{OH}^- \rightarrow 2\text{I}^- + 2\text{H}_2\text{O} + \text{O}_2$
 (2) $\text{HOCl} + \text{H}_2\text{O}_2 \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^- + \text{O}_2$
 (3) $\text{PbS} + 4\text{H}_2\text{O}_2 \rightarrow \text{PbSO}_4 + 4\text{H}_2\text{O}$
 (4) $2\text{MnO}_4^- + 3\text{H}_2\text{O}_2 \rightarrow 2\text{MnO}_2 + 3\text{O}_2 + 2\text{H}_2\text{O} + 2\text{OH}^-$
RR0148
10. In KO_2 , the nature of oxygen species and the oxidation state of oxygen atom are, respectively [JEE(Main)-OnLine-2018]
 (1) Superoxide and $-1/2$ (2) Oxide and -2
 (3) Peroxide and $-1/2$ (4) Superoxide and -1
RR0150
11. In the reaction of oxalate with permanganate in acidic medium, the number of electrons involved in producing one molecule of CO_2 is : [JEE(Main)-(Jan.)-2019]
 (1) 10 (2) 2 (3) 1 (4) 5
RR0151
12. The chemical nature of hydrogen peroxide is :- [JEE(Main)-(Jan.)-2019]
 (1) Oxidising and reducing agent in acidic medium, but not in basic medium.
 (2) Oxidising and reducing agent in both acidic and basic medium
 (3) Reducing agent in basic medium, but not in acidic medium
 (4) Oxidising agent in acidic medium, but not in basic medium.
RR0152
13. The hardness of a water sample (in terms of equivalents of CaCO_3) containing 10^{-3} M CaSO_4 is : [JEE(Main)-(Jan.)-2019]
 (molar mass of $\text{CaSO}_4 = 136 \text{ g mol}^{-1}$)
 (1) 100 ppm (2) 50 ppm (3) 10 ppm (4) 90 ppm
RR0153

14. 50 mL of 0.5 M oxalic acid is needed to neutralize 25 mL of sodium hydroxide solution. The amount of NaOH in 50 mL of the given sodium hydroxide solution is : [JEE(Main)-(Jan.)-2019]
 (1) 4 g (2) 2 g (3) 8 g (4) 1 g
 RR0154
15. In order to oxidise a mixture one mole of each of FeC_2O_4 , $\text{Fe}_2(\text{C}_2\text{O}_4)_3$, FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ in acidic medium, the number of moles of KMnO_4 required is - [JEE(Main)-(April)-2019]
 (1) 3 (2) 2 (3) 1 (4) 1.5
 RR0155
16. The correct order of the oxidation states of nitrogen in NO , N_2O , NO_2 and N_2O_3 is :
 (1) $\text{NO}_2 < \text{N}_2\text{O}_3 < \text{NO} < \text{N}_2\text{O}$
 (2) $\text{NO}_2 < \text{NO} < \text{N}_2\text{O}_3 < \text{N}_2\text{O}$
 (3) $\text{N}_2\text{O} < \text{N}_2\text{O}_3 < \text{NO} < \text{NO}_2$
 (4) $\text{N}_2\text{O} < \text{NO} < \text{N}_2\text{O}_3 < \text{NO}_2$ [JEE(Main)-(April)-2019]
 RR0156
17. An example of a disproportionation reaction is : [JEE(Main)-(April)-2019]
 (1) $2\text{KMnO}_4 \rightarrow \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$ (2) $2\text{MnO}_4^- + 10\text{I}^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{I}_2 + 8\text{H}_2\text{O}$
 (3) $2\text{CuBr} \rightarrow \text{CuBr}_2 + \text{Cu}$ (4) $2\text{NaBr} + \text{Cl}_2 \rightarrow 2\text{NaCl} + \text{Br}_2$
 RR0158
18. 100 mL of a water sample contains 0.81 g of calcium bicarbonate and 0.73 of magnesium bicarbonate. The hardness of this water sample expressed in terms of equivalents of CaCO_3 is:
 (molar mass of calcium bicarbonate is 162 g mol^{-1} and magnesium bicarbonate is 146 g mol^{-1})
 (1) 1,000 ppm (2) 10,000 ppm [JEE(Main)-(April)-2019]
 (3) 100 ppm (4) 5,000 ppm
 RR0159
19. 25 ml of the given HCl solution requires 30 mL of 0.1 M sodium carbonate solution. What is the volume of this HCl solution required to titrate 30 mL of 0.2 M aqueous NaOH solution? [JEE(Main)-(Jan)-2019]
 (1) 25 mL (2) 50 mL (3) 12.5 mL (4) 75 mL
 RR0160
20. Oxidation number of potassium in K_2O , K_2O_2 and KO_2 , respectively, is : [JEE(Main)-(Jan)-2020]
 (1) +1, +4 and +2 (2) +1, +2 and +4
 (3) +1, +1 and +1 (4) +2, +1 and $+\frac{1}{2}$

RR0167

21. The compound that cannot act both as oxidising and reducing agent is :[JEE(Main)-(Jan)-2020]
(1) H_2O_2 (2) H_2SO_3 (3) HNO_2 (4) H_3PO_4

RR0168

22. The hardness of a water sample containing 10^{-3} M MgSO_4 expressed as CaCO_3 equivalents (in ppm) is _____. [JEE(Main)-(Jan)-2020]

(molar mass of MgSO_4 is 120.37 g/mol)

RR0169

EXERCISE # J-ADVANCED

- Reduction of the metal centre in aqueous permanganate ion involves - [JEE-2011]
 (A) 3 electrons in neutral medium (B) 5 electrons in neutral medium
 (C) 3 electrons in alkaline medium (D) 5 electrons in acidic medium
RR0161
- Reaction of Br_2 with Na_2CO_3 in aqueous solution gives sodium bromide and sodium bromate with evolution of CO_2 gas. The number of sodium bromide molecules involved in the balanced chemical equation is. [JEE- 2011]
RR0162
- Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen-
 (A) HNO_3 , NO , NH_4Cl , N_2 (B) HNO_3 , NO , N_2 , NH_4Cl
 (C) HNO_3 , NH_4Cl , NO , N_2 (D) NO , HNO_3 , NH_4Cl , N_2 [JEE- 2012]
RR0163
- 25 mL of household bleach solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4 N acetic acid. In the titration of the liberated iodine, 48 mL of 0.25 N $\text{Na}_2\text{S}_2\text{O}_3$ was used to reach the end point. The molarity of the household bleach solution is [JEE- 2012]
 (A) 0.48 M (B) 0.96 M (C) 0.24 M (D) 0.024 M
RR0164
- In neutral or faintly alkaline solution, 8 moles permanganate anion quantitatively oxidize thiosulphate anions to produce X moles of a sulphur containing product. the magnitude of X is [JEE- 2016]
RR0165
- To measure the quantity of MnCl_2 dissolved in an aqueous solution, it was completely converted to KMnO_4 using the reaction, [JEE- 2018]

$$\text{MnCl}_2 + \text{K}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} \rightarrow \text{KMnO}_4 + \text{H}_2\text{SO}_4 + \text{HCl}$$
 (equation not balanced).
 Few drops of concentrated HCl were added to this solution and gently warmed. Further, oxalic acid (225 g) was added in portions till the colour of the permanganate ion disappeared. The quantity of MnCl_2 (in mg) present in the initial solution is _____.
 (Atomic weights in g mol^{-1} : Mn = 55, Cl = 35.5)
RR0166

ANSWER-KEY

EXERCISE # S-I

1. (a) +6 (b) +5 (c) +2 (d) -4
(e) +4 (f) -1 (g) +2 (h) +6
(i) +3
2. (a) Reduction (b) Oxidation
(c) Reduction (d) Oxidation
3. (a) Oxidant : O_2 ; Reductant : Zn
(b) Oxidant : H^+ ; Reductant : Zn
(c) Oxidant : NO_3^- ; Reductant : Zn
4. (i) $Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$
(ii) $Br_2 + 5H_2O_2 \longrightarrow 2BrO_3^- + 4H_2O + 2H^+$
(iii) $MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$
(iv) $MnO_2 + 2Cl^- + 4H^+ \longrightarrow Mn^{2+} + Cl_2 + 2H_2O$
(v) $3ClO^- + 2CrO_2^- + 2OH^- \longrightarrow 3Cl^- + 2CrO_4^{2-} + H_2O$
5. (i) $2MnO_4^- + 6I^- + 4H_2O \longrightarrow 2MnO_2 + 3I_2 + 8OH^-$
(ii) $H^+ + 2MnO_4^- + 5SO_2 + 2H_2O \longrightarrow 2Mn^{2+} + 5HSO_4^-$
(iii) $2Fe^{2+} + H_2O_2 + 2H^+ \longrightarrow 2Fe^{3+} + 2H_2O$
(iv) $Cr_2O_7^{2-} + 3SO_2 + 2H^+ \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$
6. Ans. (1) 1 (2) 2, 1 (3) 1
(4) 1 (5) 2 (6) 1
7. (1) 1 (2) 1 (3) 1 (4) 1 (5) 2
8. 98, 49, 32.67 9. Ans. 21 10. Ans. (i) $\frac{83.5}{6}$; (ii) $\frac{17}{3}$
11. Ans. 6 12. Ans. 5 13. Ans. (8.097 mL)
14. Ans. (40) 15. Ans. 40 ml 16. Ans. 60 ml 17. Ans. 12.5 L
18. Ans. 12.5 L 19. Ans. $V = 3$ lit. 20. Ans. 200 mL 21. Ans. 30 N
22. Ans. (4.48) 23. Ans. 10 N 24. Ans. 2.12 g/L 25. Ans. + 3
26. Ans. Zero 27. Ans. $V = 160$ ml 28. Ans. 0.588 N 29. Ans. 4 lit.
30. Ans. $\frac{2}{3}$ 31. Ans. 8/5 32. Ans. 1.25 mL 33. Ans. 1.406 %
34. Ans. $V = 25$ mL 35. Ans. 1.28 % 36. Ans. 40 g, 0.0518 N
37. Ans. (Ca^{2+} , Mg^{2+} , Na^+)
38. Ans. (19.09)

EXERCISE # S-II

1. (a) +2.5 (b) +4/3 (c) -1/3 (d) +8/3
 (e) -3, -1 (f) -2, +2 (g) +16/3 (h) 0
 (i) +2, -1 (j) +2 (k) 0 (l) +1/2
 (m) -1/2 (n) +1 (o) +3 (p) -3
 (q) +3 (r) +2 (s) +4
2. (a) +3 (b) +3, +6 (c) +2 (d) $+\frac{200}{93}$
 (e) +6 (f) +6 (g) +6 (h) +5
 (r) +2 (s) +3
3. (i) $6\text{KMnO}_4(\text{aq.}) + 10\text{FeC}_2\text{O}_4(\text{aq.}) + 24\text{H}_2\text{SO}_4(\text{aq.}) \longrightarrow$
 $6\text{MnSO}_4(\text{aq.}) + 5\text{Fe}_2(\text{SO}_4)_3(\text{aq.}) + 20\text{CO}_2(\text{g}) + 3\text{K}_2\text{SO}_4 + 24\text{H}_2\text{O}(\text{l})$
 (ii) $5\text{P}_4(\text{s}) + 12\text{OH}^-(\text{aq.}) + 12\text{H}_2\text{O} \longrightarrow 8\text{PH}_3(\text{aq.}) + 12\text{HPO}_2^-(\text{aq.})$
 (iii) $3\text{I}_2(\text{s}) + 6\text{NaOH}(\text{aq.}) \longrightarrow 5\text{NaI}(\text{aq.}) + \text{NaIO}_3(\text{aq.}) + 3\text{H}_2\text{O}(\text{l})$
 (iv) $3\text{HNO}_2(\text{aq.}) \rightarrow \text{NO}_3^- + \text{H}^+ + 2\text{NO}(\text{g}) + \text{H}_2\text{O}$
 (v) $\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$
 (vi) $5\text{Cu}_2\text{S} + 8\text{MnO}_4^- + 44\text{H}^+ \rightarrow 10\text{Cu}^{2+} + 5\text{O}_2 + 8\text{Mn}^{2+} + 22\text{H}_2\text{O}$
 (vii) $\text{HCHO}(\text{l}) + [\text{Ag}(\text{NH}_3)_2]^+(\text{aq.}) + 2\text{OH}^-(\text{aq.}) \rightarrow \text{Ag}(\text{s}) + 2\text{NH}_3(\text{aq.}) + \text{HCOO}^-(\text{aq.}) + \text{H}_2\text{O}(\text{l})$
4. $\text{KOH} = 35\%$, $\text{Ca}(\text{OH})_2 = 65\%$
5. Ans. 3 l
6. Ans. 12.5 l
7. Ans. 6 l
8. Ans. 16.66 %
9. Ans. 3
10. Ans. 90.1 %
11. Ans. (80)
12. Ans. 16 %
13. Ans. 24.46 %
14. Ans. 0.47
15. Ans. (40)
16. Ans. (0.0626 M)

EXERCISE # O-I

- | | | | |
|--------------|--------------|--------------|--------------|
| 1. Ans. (C) | 2. Ans. (B) | 3. Ans. (B) | 4. Ans. (B) |
| 5. Ans. (D) | 6. Ans. (A) | 7. Ans. (D) | 8. Ans. (A) |
| 9. Ans. (D) | 10. Ans. (A) | 11. Ans. (B) | 12. Ans. (A) |
| 13. Ans. (C) | 14. Ans. (C) | 15. Ans. (C) | 16. Ans. (D) |
| 17. Ans. (A) | 18. Ans. (D) | 19. Ans. (D) | 20. Ans. (B) |
| 21. Ans. (C) | 22. Ans. (D) | 23. Ans. (D) | 24. Ans. (D) |
| 25. Ans. (A) | 26. Ans. (C) | 27. Ans. (D) | 28. Ans. (C) |
| 29. Ans. (D) | 30. Ans. (A) | 31. Ans. (C) | 32. Ans. (B) |
| 33. Ans. (A) | 34. Ans. (A) | 35. Ans. (B) | 36. Ans. (C) |
| 37. Ans. (C) | 38. Ans. (A) | 39. Ans. (D) | 40. Ans. (A) |
| 41. Ans. (C) | 42. Ans. (C) | 43. Ans. (D) | 44. Ans. (A) |
| 45. Ans. (B) | 46. Ans. (B) | | |

EXERCISE # O-II

- | | | | |
|--------------|------------------|---|--------------|
| 1. Ans. (A) | 2. Ans. (C) | 3. Ans. (B) | 4. Ans. (C) |
| 5. Ans. (A) | 6. Ans. (A) | 7. Ans. (B) | 8. Ans. (B) |
| 9. Ans. (C) | 10. Ans. (A,B,D) | 11. Ans. (C) | 12. Ans. (A) |
| 13. Ans. (B) | 14. Ans. (C) | 15. (A) \rightarrow s ; (B) \rightarrow q ; (C) \rightarrow r ; (D) \rightarrow p | |
| 16. Ans. (C) | 17. Ans. (A) | 18. Ans. (A) | 19. Ans. (B) |
| 20. Ans. (C) | 21. Ans. (B) | 22. Ans. (A,D) | |

EXERCISE # J-MAINS

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|--------------|----------------|--------------|--------------|
| 1. Ans. (2) | 2. Ans. (3) | 3. Ans. (4) | 4. Ans. (1) |
| 5. Ans. (2) | 6. Ans. (2) | 7. Ans. (1) | 8. Ans. (1) |
| 9. Ans. (3) | 10. Ans. (1) | 11. Ans. (3) | 12. Ans. (2) |
| 13. Ans. (1) | 14. Ans. (1) | 15. Ans. (2) | 16. Ans. (4) |
| 17. Ans. (3) | 18. Ans. (2) | 19. Ans. (1) | 20. Ans. (3) |
| 21. Ans. (4) | 22. Ans. (100) | | |

EXERCISE # J-ADVANCED

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|-----------------|---------------|-------------|-------------|
| 1. Ans. (A,C,D) | 2. Ans. (5) | 3. Ans. (B) | 4. Ans. (C) |
| 5. Ans. (6) | 6. Ans. (126) | | |