REDOX REACTION

Oxidation & Reduction

Let us do a comparative study of oxidation and reduction :

Oxidation

1. Addition of Oxygen e.g. $2Mg + O_2 \rightarrow 2MgO$

2. Removal of Hydrogen e.g. $H_2S + Cl_2 \rightarrow 2HCl + S$

3. Increase in positive charge e.g. $Fe^{2+} \rightarrow Fe^{3+} + e^-$

4. Increase in oxidation number

   $\quad$ (+2) $\qquad$ (+4)

   e.g. $SnCl_2 \rightarrow SnCl_4$

5. Removal of electron e.g. $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$

Reduction

1. Removal of Oxygen e.g. $CuO + C \rightarrow Cu + CO$

2. Addition of Hydrogen e.g. $S + H_2 \rightarrow H_2S$

3. Decrease in positive charge e.g. $Fe^{3+} + e^- \rightarrow Fe^{2+}$

4. Decrease in oxidation number

   $\quad$ (+7) $\qquad$ (+2)

   e.g. $MnO_4^- \rightarrow Mn^{2+}$

5. Addition of electron e.g. $Fe^{3+} + e^- \rightarrow Fe^{2+}$

Oxidation Number

❑ It is an imaginary or apparent charge developed over atom of an element when it goes from its elemental free state to combined state in molecules.

❑ It is calculated on basis of an arbitrary set of rules.

❑ It is a relative charge in a particular bonded state.

❑ In order to keep track of electron-shifts in chemical reactions involving formation of compounds, a more practical method of using oxidation number has been developed.

❑ In this method, it is always assumed that there is a complete transfer of electron from a less electronegative atom to a more electronegative atom.

Rules governing oxidation number

The following rules are helpful in calculating oxidation number of the elements in their different compounds. it is to be remembered that the basis of these rule is the electronegativity of the element.

❑ **Fluorine atom :**

Fluorine is most electronegative atom (known). It always has oxidation number 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

(i) peroxide (e.g. H_2O_2, Na_2O_2) is –1,

(ii) super oxide (e.g. KO_2) is –1/2

(iii) ozonide (e.g. KO_3) is –1/3

(iv) in 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 atoms (Cl, Br, I) have oxidation number equal to –1.

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

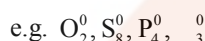e.g. $\overset{+5}{K\,Cl}O_3$, $\overset{+5}{HIO_3}$, $\overset{+7}{HClO_4}$, $\overset{+5}{KBrO_3}$
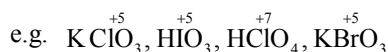
○ **Metals :**

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

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

    (c) Aluminium always has +3 oxidation number

Note : Metal may have negative or zero oxidation number

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

e.g. O_2^0, S_8^0, P_4^0, $\overset{0}{3}$

○ Sum of the oxidation numbers of atoms of all elements in a molecule is zero.

○ Sum of the oxidation numbers of atoms of all elements in an ion is equal to the charge on the ion.

○ If the group number of an element in modern periodic table is n, then its oxidation number may vary from

    (n – 10) to (n – 18) (but it is mainly applicable for p-block elements)

    e.g. N-atom belongs to 15th group in the periodic table, therefore as per rule, its oxidation number may vary from
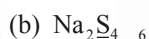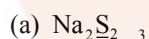
-3 to $+5$ $\left(\overset{-3}{NH_3}, \overset{+2}{NO}, \overset{+3}{N_2}\,_3, \overset{+4}{NO_2}, \overset{+5}{N_2}\,_5 \right)$
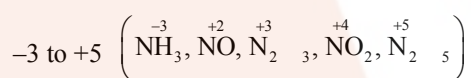
○ The maximum possible oxidation number of any element in a compound is never more than the number of electrons in valence shell. (but it is mainly applicable for p-block elements)

Calculation of average oxidation number :

Solved Examples

Example-1 :

    Calculate oxidation number of underlined element :

    (a) $Na_2\underline{S}_2\,_3$ (b) $Na_2\underline{S}_4\,_6$

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

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

        $x = +2$

    (b) Let oxidation number of S-atom is x

        $\therefore (+1) \times 2 + (x) \times 4 + (-2) \times 6 = 0$

        $x = +2.5$

○ It is important to note here that $Na_2S_2O_3$ have two S-atoms and there are four S-atom in $Na_2S_4O_6$. However none of the sulphur atoms in both the compounds have +2 or + 2.5 oxidation number, it is the average of oxidation number, which reside on each sulphur atom. Therefore, we should work to calculate the individual oxidation number of each sulphur atom in these compounds.

Calculation of individual oxidation number

It is important to note that to calculate individual oxidation number of the element in its compound one should know the structure of the compound and use the following guidelines.
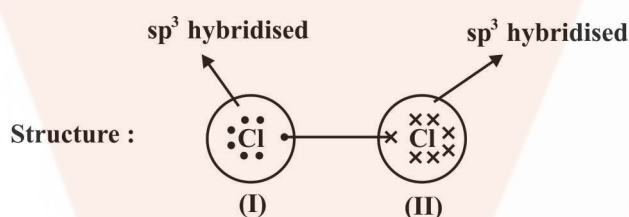
Formula :

Oxidation Number = Number of electrons in the valence shell - Number of electrons taken up after bonding

Guidelines : It is based on electronegativity of elements.

1. If there is a bond between similar type of atom and each atom has same type of hybridisation, then bonded pair electrons are equally shared by each element.

Example :

Calculate oxidation number of each Cl-atom in Cl_2 molecule

I : Number of electrons in the valence shell = 7

Number of electrons taken up after bonding = 7.

∴ oxidation number = 7 – 7 = 0.

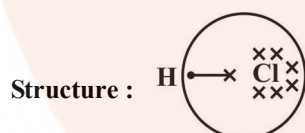II : similarly, oxidation number = 7 – 7 = 0

2. If there is a bond between different type of atoms :

e.g. A – B (if B is more electronegative than A)

Then after bonding, bonded pair of electrons are counted with B-atom

Example :

Calculate oxidation number of each atom in HCl molecule

Note : Electron of H-atom is now counted with Cl-atom, because Cl-atom is more electronegative than H-atom

H : Number of electrons in the valence shell = 1

Number of electrons taken up after bonding = 0

Oxidation number of H = 1 – 0 = + 1

Cl : Number of electrons in the valence shell = 7
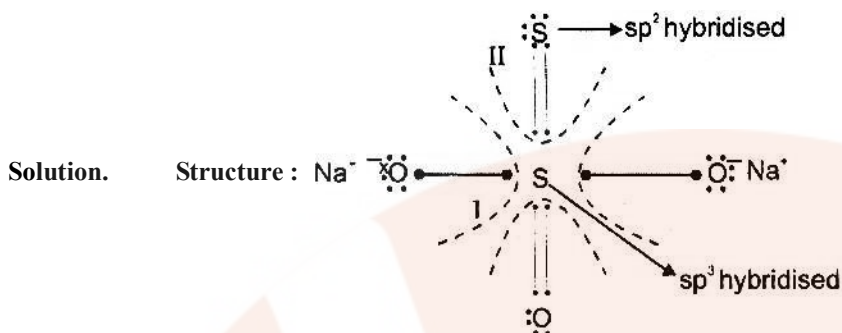
Number of electrons taken up after bonding = 8

Oxidation number of Cl = 7 – 8 = –1

Solved Examples

Example - 2

Calculate individual oxidation number of each S-atom in $Na_2S_2O_3$ (sodium thiosulphate) with the help of its structure.

Solution. **Structure :**

Note : I (central S-atom) is sp^3 hybridised (25% s-character) and II (terminal S-atom) is sp^2 hybridised (33% s-character). Therefore, terminal sulphur atom is more electronegative than central sulphur atom. Now, the shared pair of electrons are counted with terminal S-atom.

∴   I, S-atom : Number of electrons in the valence shell = 6

Number of electrons left after bonding = 0

Oxidation number of central S-atom = 6 – 0 = +6

II, S-atom : Number of electrons in the valence shell = 6

Number of electrons left after bonding = 8

Oxidation number of terminal S-atom = 6 – 8 = – 2

Now, you can also calculate Average Oxidation number of $S = \dfrac{6 + (-2)}{2} = +2$ (as we have calculated before)

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 oxidation number of Cr is x.

∴ x + (–2) 2 + (–2) = 0 or x = 6

∴ Oxidation number of Cr = +6 **Ans.**

❍   The structure of H_2SO_5 is
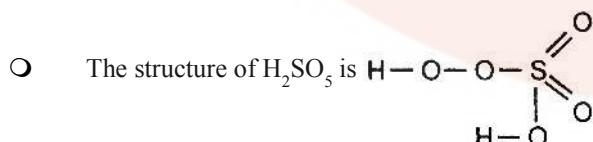
From the structure, it is evident that in H_2SO_5, there is one peroxide linkage, two sulphur-oxygen double bonds and one OH group. Let the oxidation number of S = x.

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

or $x + 2 - 8$ or $x - 6 = 0$ or $x = 6$

$\therefore$ Oxidation number of S in H_2SO_5 is $+ 6$ Ans.

Paradox of fractional oxidation number

Fractional oxidation number is the average of oxidation state of all atoms of element under examination and the structural parameters reveal that the atoms of element for whom fractional oxidation state is realised a actually present in different oxidation states. Structure of the species C_3O_2, Br_3O_8 and $S_4O_6^{2-}$ reveal the following bonding situations :

❍ The element marked with asterisk (*) in each species is exhibiting different 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.

$$O = \overset{+2}{C} = \overset{0}{C*} = \overset{+2}{C} = O$$
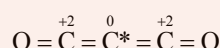
Structure of C_3O_2 (Carbon suboxide)

❍ 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.
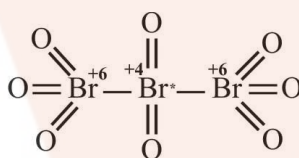
Structure of Br_3O_8 (Tribromooctaoxide)

❍ In the same fashion, in the species $S_4O_6^{2-}$, average oxidation number of S is + 2.5, whereas the reality being + 5, 0*, 0* and +5 oxidation number respectively for respective sulphur atoms.
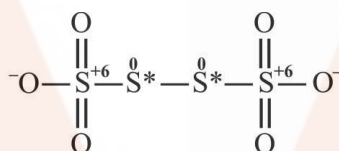
Structure of $S_4O_6^{2-}$, (tetrathionate ion)

In general, the conclusion is that the idea of fractional oxidation state should be taken with care and the reality is revealed by the structures only.

Oxidising and reducing agent

❍ **Oxidising agent or Oxidant :**

Oxidising agents are those compounds which can oxidise others and reduce itself during the chemical reaction. Those reagents in which for an element, oxidation number decreases or which undergoes gain of electrons in a redox reaction are termed as oxidants.

e.g. $KMnO_4$, $K_2Cr_2O_7$, HNO_3, conc. H_2SO_4 etc are powerful oxidising agents.

❍ **Reducing agent or Reductant :**

Reducing agents are those compounds which can reduce other and oxidise itself during the chemical reaction. Those reagents in which for an element, oxidation number increases or which undergoes loss of electrons in a redox reaction are termed as reductants.

e.g. KI, $Na_2S_2O_3$ etc are the powerful reducing agents.

Note : There are some compounds also which can work both as oxidising agent and reducing agent
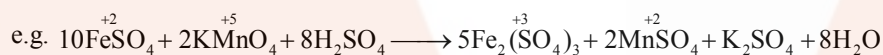
e.g. H_2O_2, NO_2^-

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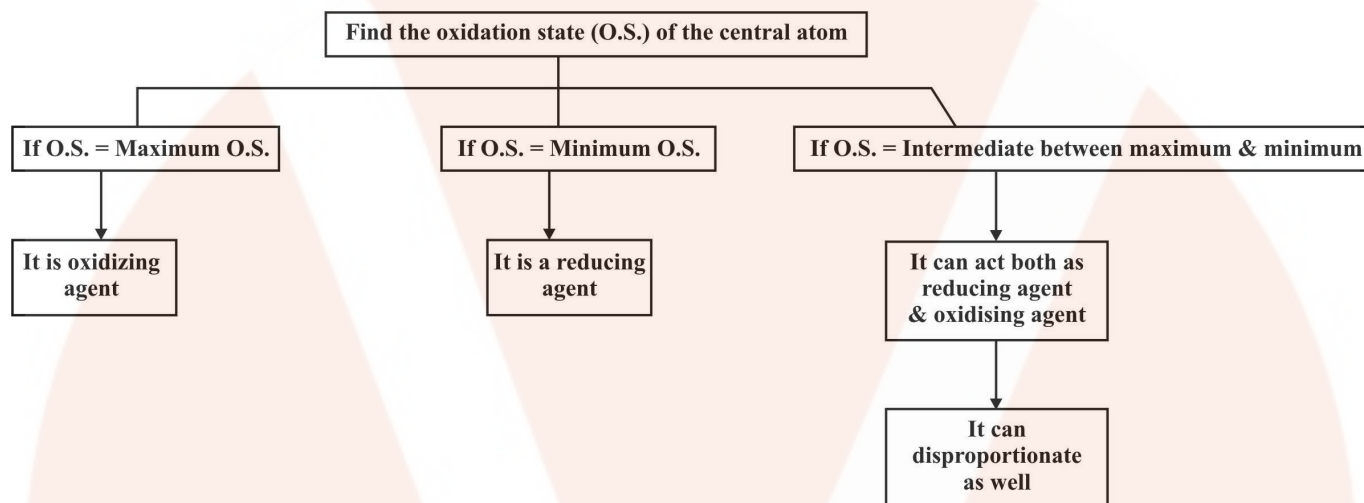
Redox reaction

A reaction in which oxidation and reduction simultaneously take place is called a redox reaction
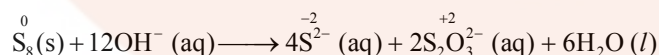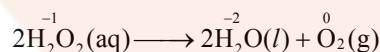
In all redox reactions, the total increase in oxidation number must be equal to the total decrease in oxidation number.

e.g. $$10\overset{+2}{Fe}SO_4 + 2K\overset{+5}{Mn}O_4 + 8H_2SO_4 \longrightarrow 5\overset{+3}{Fe_2}(SO_4)_3 + 2\overset{+2}{Mn}SO_4 + K_2SO_4 + 8H_2O$$
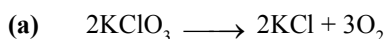
Disproportionation Reaction :

A redox reaction in which same element present in a particular compound in a definite oxidation state is oxidized as well as reduced simultaneously is a disproportionation reaction.
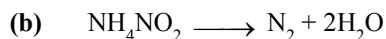
Disproportionation reactions are a special type of redox reactions. One of the reactants in a disproportionation reaction always contains **an element that can exist in at least three oxidation states.** The element in the form of reacting substance is in the intermediate oxidation state and both higher and lower oxidation states of that element are formed in the reaction. For example :

$$2\overset{-1}{H_2}O_2(aq) \longrightarrow 2\overset{-2}{H_2}O(l) + \overset{0}{O_2}(g)$$

$$\overset{0}{S_8}(s) + 12OH^-(aq) \longrightarrow 4\overset{-2}{S^{2-}}(aq) + 2\overset{+2}{S_2}O_3^{2-}(aq) + 6H_2O(l)$$

$$\overset{0}{Cl_2}(g) + 2OH^-(aq) \longrightarrow \overset{+1}{Cl}O^-(aq) + \overset{-1}{Cl}^-(aq) + H_2O(l)$$

Consider the following reations :

(a) $2KClO_3 \longrightarrow 2KCl + 3O_2$

$KClO_3$ plays a role of oxidant and reductant both. Here, Cl present in $KClO_3$ is reduced and O present in $KClO_3$ is oxidized. Since same element is not oxidized and reduced, so it is not a disproportionation reaction, although it looks like one.

(b) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

Nirogen in this compound has -3 and +3 oxidation number, which is not a definite value. So it is not a disporportionation reaction. It is an example of comproportionation reaction, which is a class of redox reaction in which an element from two different oxidation state gets converted into a single oxidation state.
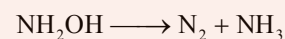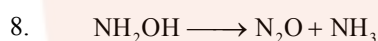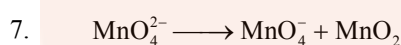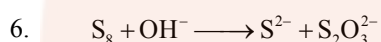
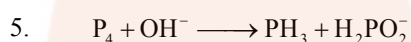**(c)** $4K\overset{+5}{Cl}O_3 \longrightarrow 3K\overset{+7}{Cl}O_4 + K\overset{-1}{Cl}$
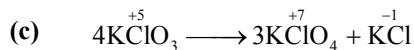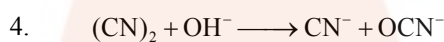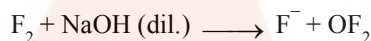
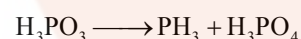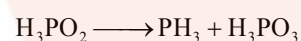It is a case of disproportionation reaction and Cl atom is disproportionating.

List of some important disproportionation reactions

1. $H_2O_2 \longrightarrow H_2O + O_2$

2. $X_2 + OH^- \text{(dil.)} \longrightarrow X^- + XO^- \text{ (X = Cl, Br, I)}$

3. $X_2 + OH^- \text{(conc.)} \longrightarrow X^- + XO_3^-$

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

$F_2 + NaOH \text{(dil.)} \longrightarrow F^- + OF_2$

$F_2 + NaOH \text{(conc.)} \longrightarrow F^- + O_2$

4. $(CN)_2 + OH^- \longrightarrow CN^- + OCN^-$

5. $P_4 + OH^- \longrightarrow PH_3 + H_2PO_2^-$

6. $S_8 + OH^- \longrightarrow S^{2-} + S_2O_3^{2-}$

7. $MnO_4^{2-} \longrightarrow MnO_4^- + MnO_2$

8. $NH_2OH \longrightarrow N_2O + NH_3$

$NH_2OH \longrightarrow N_2 + NH_3$

9. Oxyacids of Phosphorus (+1, +3 oxidation number)

$H_3PO_2 \longrightarrow PH_3 + H_3PO_3$

$H_3PO_3 \longrightarrow PH_3 + H_3PO_4$

10. Oxyacids of Chlorine (Halogens) (+1, +3, +5 Oxidation number)

$ClO^- \longrightarrow Cl^- + ClO_2^-$

$ClO_2^- \longrightarrow Cl^- + ClO_3^-$

$ClO_3^- \longrightarrow NO + HNO_3$

11. $HNO_2 \longrightarrow NO + HNO_3$
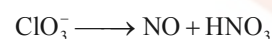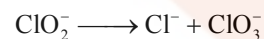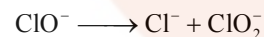
❍ Reverse of disproportionation is called Comproportionation. In some of the disproportionation reactions, by changing the medium (from acidic to basic or reverse), the reaction goes in backward direction and can be taken as an example of Comproportionation reaction.

$I^- + IO_3^- + H^+ \longrightarrow I_2 + H_2O$
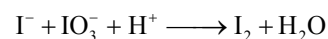
REDOX REACTION

Balancing of redox reactions

All balanced equations must satisfy two criteria.

1. **Atom balance (mass balance) :**

    There should be the same number of atoms of each kind on reactant and product side.

2. **Charge balance :**

    The sum of actual charges on both sides of the equation must be equal.

    There are two methods for balancing the redox equations :

    1. Oxidation – number change method

    2. Ion electron method or half cell method

❍   Since First method is not very much fruitful for the balancing of redox reactions, students are advised to use second method (Ion electron method) to balance the redox reactions

Ion electron method :

By this method redox equations are balanced in two different medium.

(a) Acidic medium   (b) Basic medium
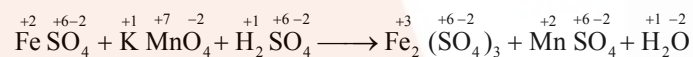
❍   **Balancing in acidic medium**

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

Solved Examples

Example - 3 :

Balance the following redox reaction :

$$FeSO_4 + KMnO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + MnSO_4 + H_2O + K_2SO_4$$

Sol.   **Step-I** Assign the oxidation number to each element present in the reaction

$$\overset{+2}{Fe}\overset{+6-2}{SO_4} + \overset{+1}{K}\overset{+7}{Mn}\overset{-2}{O_4} + \overset{+1}{H_2}\overset{+6-2}{SO_4} \longrightarrow \overset{+3}{Fe_2}\overset{+6-2}{(SO_4)_3} + \overset{+2}{Mn}\overset{+6-2}{SO_4} + \overset{+1-2}{H_2O}$$

Step II :

Now convert the reaction in Ionic form by eliminating the elements or species, which are not undergoing either oxidation or reduction.

$$Fe^{2+} + \overset{+7}{Mn}O_4^- \longrightarrow Fe^{3+} + Mn^{2+}$$
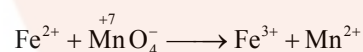
Step III :

Now identify the oxidation/reduction occuring in the reaction
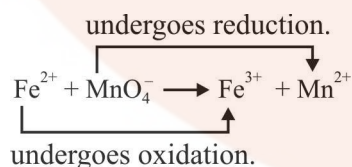
Step IV :

Spilt 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

$$Fe^{2+} \longrightarrow Fe^{3+} \quad | \quad MnO_4^- \longrightarrow Mn^{2+}$$

Fe & Mn atoms are balanced on both side.
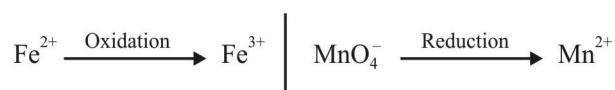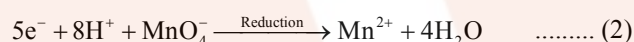
Step VI :

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.

$$Fe^{2+} \longrightarrow Fe^{3+} \quad \text{(no oxygen atom)} \quad \text{............... (i)}$$

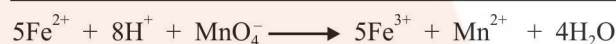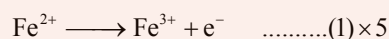$$8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O \quad \text{................ (ii)}$$

Step VII :

Equation (i) & (ii) are balanced atomwise. Now balance both equations chargewise. To balance the charge, add electrons to the electrically positive side.

$$Fe^{2+} \xrightarrow{\text{oxidation}} Fe^{3+} + e^- \quad \text{........ (1)}$$

$$5e^- + 8H^+ + MnO_4^- \xrightarrow{\text{Reduction}} Mn^{2+} + 4H_2O \quad \text{......... (2)}$$

Step VIII :

The number of electrons gained and lost in each half-reaction are equalised by multiplying both the half reactions with a suitable factor and finally the half reactions are added to give the overall balanced reaction.

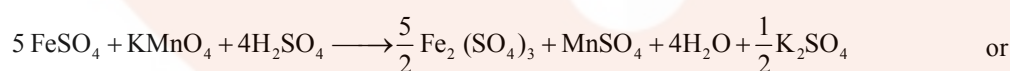Here, we multiply equation (1) by 5 and (2) by 1 and add them :

$$Fe^{2+} \longrightarrow Fe^{3+} + e^- \quad \text{..........(1)} \times 5$$

$$\underline{5e^- + 8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O \quad \text{............(2)} \times 1}$$

$$5Fe^{2+} + 8H^+ + MnO_4^- \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

(Here, at his stage, you will get balanced redox reaction in Ionic form)

Step IX :

Now convert the ionic reaction into molecular form by adding the elements or species, which are removed in step (2).

Now, by some manipulation, you will get :

$$5\, FeSO_4 + KMnO_4 + 4H_2SO_4 \longrightarrow \frac{5}{2} Fe_2(SO_4)_3 + MnSO_4 + 4H_2O + \frac{1}{2}K_2SO_4 \qquad \text{or}$$

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow 5\, Fe_2(SO_4)_3 + 2MnSO_4 + 8H_2O + K_2SO_4.$$

❍ **Balancing in basic medium :**
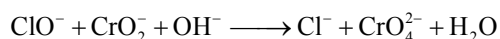
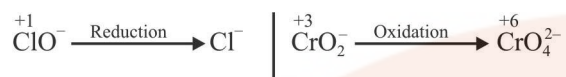In this case, except step VI, all the steps are same. We can understand it by the following example :

Solved Examples

Example - 4 :

Balance the following redox reaction in basic medium :

$$ClO^- + CrO_2^- + OH^- \longrightarrow Cl^- + CrO_4^{2-} + H_2O$$

Sol. By using upto step V, we will get :

$$\overset{+1}{Cl}O^- \xrightarrow{\text{Reduction}} Cl^- \quad \Big| \quad \overset{+3}{Cr}O_2^- \xrightarrow{\text{Oxidation}} \overset{+6}{Cr}O_4^{2-}$$

Now, students are advised to follow step VI to balance 'O' and 'H' atom.

$$2H^+ + ClO^- \longrightarrow Cl^- + H_2O \quad | \quad 2H_2O + CrO_2^- + 4H^+$$

◯ Now, since we are balancing in basic medium, therefore add as many as OH^- on both side of equation as there are H^+ ions in the equation.
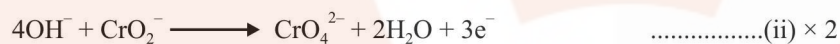
$$2OH^- + 2H^+ + ClO^- \longrightarrow Cl^- + H_2O + 2OH^- \qquad 4OH^- + 2H_2O + CrO_2^- \longrightarrow CrO_4^{2-} + 4H^+ + 4OH^-$$

Finally you will get   Finally you will get

$$H_2O + ClO^- \longrightarrow Cl^- + 2OH^- \quad \text{.............. (i)} \qquad 4OH^- + CrO_2^- \longrightarrow CrO_4^{2-} + 2H_2O \quad \text{............. (ii)}$$
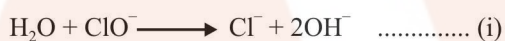
Now see equation (i) and (ii) in which O and H atoms are balanced by OH^- and H_2O

Now from step VIII

$$2e^- + H_2O + ClO^- \longrightarrow Cl^- + 2OH^- \qquad\qquad \text{................ (i)} \times 3$$

$$\underline{4OH^- + CrO_2^- \longrightarrow CrO_4^{2-} + 2H_2O + 3e^- \qquad\qquad \text{................(ii)} \times 2}$$

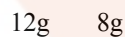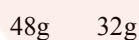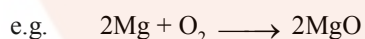Adding : $3ClO^- + 2CrO_2^- + 2OH^- \longrightarrow 3Cl^- + 2CrO_4^{2-} + H_2O$

Concept of equivalents

Equivalent mass of element

Number of parts by mass of an element which reacts or displaces from a compound 1.008 parts by mass of hydrogen, 8 parts by mass of oxygen and 35.5 parts by mass of chlorine, is known as the equivalent weight of the element.
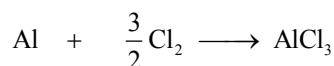
e.g. $2Mg + O_2 \longrightarrow 2MgO$

           48g   32g

           12g   8g

∵   32g of O_2 reacts with 48 g of Mg

∴   8 g of $O_2 = \dfrac{48 \times 8}{32} = 12g$

∴   Equivalent weight of Mg $= 12$

Similarly, $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

           65.5 g   32.75

$\therefore$ Equivalent weight of Zn = $\dfrac{65.5}{2} = 32.75g$

$$Al \quad + \quad \dfrac{3}{2}Cl_2 \longrightarrow AlCl_3$$

27 g $\dfrac{3}{2} \times 71$ g

$\because$ 111.5 g chlorine reacts with 27 g of Al.

$\therefore$ 35.5 chlorine reacts with $\dfrac{27 \times 35.5}{111.5} = 9.0$ g of Al

$\therefore$ Equivalent weight of aluminium = $\dfrac{27}{3} = 9.0$

As we can see from the above examples that equivalent weight is the ratio of atomic weight and a factor (say n-factor or valency factor) which is in above three cases is their respective valencies.

Equivalent weight (E) :

In general, Eq. wt. (E) = $\dfrac{\text{Atomic weight or molecular weight}}{\text{valency factor (v.f)}} = \dfrac{\text{Mol. wt.}}{\text{n} - \text{factor}} = \dfrac{\text{M}}{\text{x}}$

Number of Equivalents = $\dfrac{\text{mass of species}}{\text{eq. wt. of that species}}$

For a solution, Number of equivalents = N_1V_1, where N is the normality and V is the volume in litres

❍ Equivalent mass is a pure number which, when expressed in gram, is called gram equivalent mass.

❍ The equivalent mass of substance may have different values under different conditions.

❍ There is no hard and fast rule that equivalent weight will be always less than the molecular mass.

Valency factor calculation :

❍   **For Elements :**

Valency factor = valency of the element.

❍   **For Acids :**

Valency factor = number of replaceable H^+ ions per acid molecule

Solved Examples

Example - 5 :   NaOH,   KOH

Sol.   v.f. →   1   1

          Eq. wt. $\dfrac{M}{1}$ $\dfrac{M}{1}$

❍ Bases may be defined as the substances in which OH group is/are directly attached with group I elements (Li, Na, K, Rb, Cs), group II elements (Be, Mg, Ca, Ba) or group III elements (Al, Ga, ln, Tl), transition metals, non-metallic cations like PH_4^+, NH_4^+ etc.

❍   **Acid - base reation :**

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 replaceble H^+ or OH^- than actually replaced in reaction.

❍   **v. f.** for base is the number of H^+ ion from the acid replaced by each molecule of the base

Solved Examples

Example - 6 :

$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$$
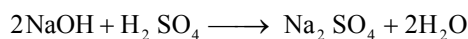
$\qquad$ Base $\qquad$ Acid

Sol. Valency factor of base $= 1$

Here, two molecule of NaOH replaced $2H^+$ ion from the H_2SO_4. Therefore, each molecule of NaOH replaced only one H^+ ion of acid, so v.f. $= 1$.

❍ **v. f.** for acid is the number of OH^- replaced from the base by each molecule of acid

Solved Examples

Example - 7 :

$$NaOH + H_2SO_4 \longrightarrow NaHSO_4 + H_2O$$

$\quad$ Base $\qquad$ Acid

Sol. Valency factor of acid $= 1$

Here, one of molecule of H_2SO_4 replaced one OH^- from NaOH. Therefore, valency factor for H_2SO_4 is one

∴ $\qquad$ Eq. wt. of $H_2SO_4 = \dfrac{\text{Mol. wt}}{1}$

❍ **Salts :**

$\quad$ **(a) In non-reacting condition**

❍ **Valency factor** = Total number of positive charge or negative charge present in the compound.

Solved Examples

Example - 8 :

		Na_2CO_3,	$Fe_2(SO_4)_3$	$FeSO_4.7H_2O$
Sol.	v.f.	2	$2 \times 3 = 6$	2
	Eq. wt.	$\dfrac{M}{2}$	$\dfrac{M}{6}$	$\dfrac{M}{2}$

(b) $\quad$ **In reacting condition**

Solved Examples

Example - 9 :

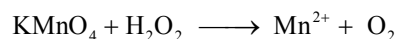$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$

$\qquad$ Base $\qquad$ Acid

Sol. It is an acid base reaction, therefore valency factor for Na_2CO_3 is one while in non-reacting condition, it will be two.

(c) $\quad$ **Equivalent weight of oxidising / reducing agents in a redox reaction**

In case of redox change, **v.f.** = Total change in oxidation number per molecule.

Solved Examples

Example - 10 :

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

Sol. Mn in $KMnO_4$ is going from +7 to +2, so change in oxidation number per molecule of $KMnO_4$ is 5. So the valency factor of

$KMnO_4$ is 5 and equivalent weight is $\dfrac{M}{5}$.

Normality :

Normality of a solution is defined as the number of equivalents of solute present in one litre (1000 mL) solution.

Let V mL of a solution is prepared by dissolving W g of solute of equivalent weight E in water.

○   Number of equivalents of solute = $\dfrac{W}{E}$

VmL of solution contain $\dfrac{W}{E}$ equivalents of solute

∴   1000 mL solution will contain $\dfrac{W \times 1000}{E \times V}$ equivalents of solute.

○   **Normality (N) =** $\dfrac{W \times 1000}{E \times V}$

○   **Normality (N) = Molarity × Valency factor**

N × V (in mL) = M × V (in mL) × n

     or

○   milliequivalents = millimoles × n

Solved Examples

Example 11 :

Calculate the normality of a solution containing 15.8 g of $KMnO_4$ in 50 mL acidic solution.

Sol :   **Normality (N) =** $\dfrac{W \times 1000}{E \times V}$

Here   W = 15.8 g,   V = 50 mL $E = \dfrac{\text{molar mass of } KMnO_4}{\text{Valency factor}} = 158/5 = 31.6$

So, normality = 10 N

Example 12 :

Calculate the normality of a solution containing 50 mL of 5 M solution of $K_2Cr_2O_7$ in acidic medium.

**Sol :**   Normality (N) Molarity × valency factor = 5 × 6 = 30 N

REDOX REACTION

Law of Equivalence

The law states that one equivalent of an element combine with one equivalent of the other. In a chemical reaction, equivalents and milli equivalents of reactants react in equal amount to give same number of equivalents or milli equivalents of products separately.

Accordingly

(i) $aA + bB \rightarrow mM + nN$
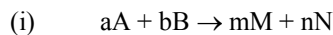
meq of A = meq of B = meq of M = m.eq. of N

(ii) In a compound M_xN_y
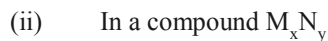
meq of M_xN_y = meq of M = meq of N

Solved Examples

Example 13 :

Find the number of moles of $KMnO_4$ needed to oxidise one mole Cu_2S in acidic medium.

The reaction is $KMnO_4 + Cu_2S \longrightarrow Mn^{2+} + Cu^{2+} + SO_2$
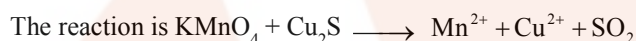
Sol. From law of equivalence,

equivalents of Cu_2S = equivalents of $KMnO_4$

moles of Cu_2S × v.f. = moles of $kMnO_4$ × v.f.

1×8 = moles of $KMnO_4 \times 5$ $\Rightarrow$ moles of $KMnO_4 = 8/5$

($\therefore$ v.f. of $Cu_2S = 2(2-1) + 1(4 - (-2)) = 8$ and v.f. of $KMnO_4 = 1(7-2) = 5$)

Example 14 :

The number of moles of oxalate ions oxidized by one mole of MnO_4^- ion in acidic medium are :

(a) $\dfrac{5}{2}$ (b) $\dfrac{2}{5}$ (c) $\dfrac{3}{5}$ (d) $\dfrac{5}{3}$

Sol. Equivalents of $C_2O_4^{2-}$ = equivalents of MnO_4^-

x (mole) × 2 = 1 × 5

($\therefore$ v.f. of $C_2O_4^{2-} = 2(4-3) = 2$ and v.f. of $MnO_4^- = 1(7-2) = 5$.

$x = \dfrac{5}{2}$ mole of $C_2O_4^{2-}$ ions.

Solved Examples

Example : 15

How many millilitres of 0.02 M $KMnO_4$ solution would be required to exactly titrate 25 mL of 0.2 M $Fe(NO_3)_2$ solution in acidic medium ?

Sol. **Method -1 : Mole concept method**

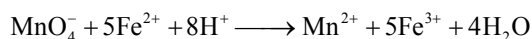Starting with 25 mL of 0.2 M Fe^{2+}, we can write :

Millimoles of Fe^{2+} = 25 × 0.2 .... (1)

and in volume V (in milliliters) of the $KMnO_4$,

Millimoles of MnO_4^- = V (0.02) .... (2)

The balanced reaction is :

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

This requires that at the equivalent point,

$$\frac{\text{m.moles of } MnO_4^-}{1} = \frac{\text{m.moles of } Fe^{2+}}{5}$$

$\therefore \quad \dfrac{V(0.02)}{1} = \dfrac{(25)\,(0.2)}{5}$ (from (1) & (2))

$\therefore \quad$ V = 50 mL.

Method -2 : Equivalent Method :

At the equivalence point,

milliequivalents of MnO_4^- = milliequivalents of Fe^{2+}

$M_1 \times vf_1 \times V_1 = M_2 \times vf_2 \times V_2$

$0.02 \times 5 \times V_1 = 0.2 \times 1 \times 25 \qquad \because MnO_4^- \rightarrow Mn^{2+}; \text{v.f.} = 5, \ Fe^{2+} \rightarrow Fe^{3+}; \text{v.f.} = 1)$

$\therefore \qquad V_1 = 50$ mL.

Titrations

Titration is procedure for determining the concentration of a solution by allowing a carefully measured volume to react with a standard solution of another substance, whose concentration is known.

Standard solution - It is a solution whose concentration is known and is taken in burette. It is also called **Titrant.**

There are two type of **titrants :**

○ **Primary titrants/standard -** These reagents can be accurately weighed and their solutions are not to be standardised before use.

Ex : Oxalic acid, $K_2Cr_2O_7$, $AgNO_3$, $CuSO_4$, ferrous ammonium sulphate, hypo etc.

○ **Secondardy titrants/standard :** These reagents cannot be accurately weighed and their solutions are to be standardised before use.

Ex : NaOH, KOH, HCl, H_2SO_4, I_2, $KMnO_4$, etc.

Titrate : Solution consisting of substance to be estimated, generally taken in a beaker.

Equivalence point : It is the point when number of equivalents of titrant added becomes equal to number of equivalents of titrate.

At equivalence point :

$$n_1 V_1 M_1 = n_2 V_2 M_2$$

Indicator : An auxiliary substance added for physical detection of completion of titration at equivalence point. It generally show colour change on completion of titration.

Types of Titrations :

○ Acid-base titrations (to be studied in Ionic equilibrium)

❍ **Redox Titrations**

Some Common Redox Titrations

Table of Redox Titrations : (Excluding lodometric/Iodimetric titrations)

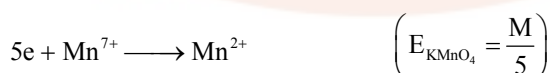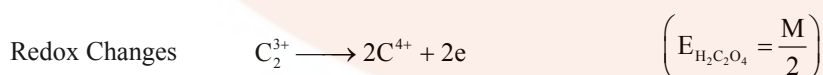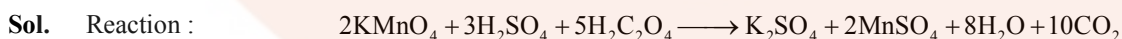|	Estimation of	By titrating with	Reactions	Relation *between OA and RA
1.	Fe^{2+}	MnO_4^-	$Fe^{2+} \rightarrow Fe^{3+} + e^-$ $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	$5Fe^{2+} \equiv MnO_4^-$ Eq. wt. of $Fe^{2+} = M/1$
2.	Fe^{2+}	$Cr_2O_7^{2-}$	$Fe^{2+} \rightarrow Fe^{3+} + e^-$ $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	$6Fe^{2+} \equiv Cr_2O_7^{2-}$ Eq. wt. of $Cr_2O_7^{2-} = M/6$
3.	$C_2O_4^{2-}$	MnO_4^-	$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$ $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	$5C_2O_4^{2-} \equiv 2MnO_4^-$ Eq. wt. of $C_2O_4^{2-} = M/2$
4.	H_2O_2	MnO_4^-	$H_2O_2 \rightarrow 2H^+ + O_2 + 2e^-$ $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	$5H_2O_2 \equiv 2MnO_4^-$ Eq. wt. of $H_2O_2 = M/2$
5.	As_2O_3	MnO_4^-	$As_2O_3 + 5H_2O \rightarrow 2AsO_4^{3-} + 10H^+ + 4e^-$ $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	Eq. wt of $As_2O_3 = M/4$
6.	AsO_3^{3-}	BrO_3^-	$AsO_3^{3-} + H_2O \rightarrow AsO_4^{3-} + 2H^+ + 2e^-$ $BrO_3^- + 6H^+ + 6e^- \rightarrow Br^- + 3H_2O$	Eq. wt. of $AsO_3^{3-} = M/2$ Eq. wt. of $BrO_3^- = M/6$

Permanganate Titrations :

❍ $KMnO_4$ is generally used as oxidising agent in acidic medium, generally provided by dilute H_2SO_4.

❍ $KMnO_4$ works as self indicator persistent pink color is indication of end point.

❍ Mainly used for estimation of Fe^{2+}, oxalic acid, oxalates, H_2O_2 etc.
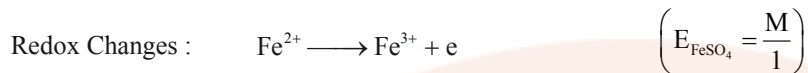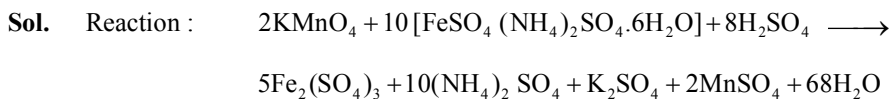
Solved Examples

Example 16 :

Write the balanced reaction of titration of $KMnO_4$ Vs oxalic acid in presence of H_2SO_4.

Sol. Reaction : $\qquad 2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$

Redox Changes $\qquad C_2^{3+} \longrightarrow 2C^{4+} + 2e \qquad \left(E_{H_2C_2O_4} = \dfrac{M}{2} \right)$

$\qquad\qquad\qquad\qquad 5e + Mn^{7+} \longrightarrow Mn^{2+} \qquad \left(E_{KMnO_4} = \dfrac{M}{5} \right)$

Indicator : $\qquad KMnO_4$ acts as self indicator.

Example : 17

Write the balanced reaction of titration of $KMnO_4$ Vs ferrous ammonium sulphate in presence of H_2SO_4.
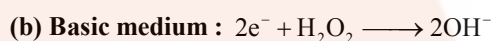
Sol.   Reaction : $2KMnO_4 + 10\,[FeSO_4\,(NH_4)_2SO_4.6H_2O] + 8H_2SO_4 \longrightarrow$

$5Fe_2(SO_4)_3 + 10(NH_4)_2\,SO_4 + K_2SO_4 + 2MnSO_4 + 68H_2O$

Redox Changes : $Fe^{2+} \longrightarrow Fe^{3+} + e$ $\left(E_{FeSO_4} = \dfrac{M}{1} \right)$

$Mn^{7+} + 5e \longrightarrow Mn^{2+}$ $\left(E_{KMnO_4} = \dfrac{M}{5} \right)$

Indicator : $KMnO_4$ acts as self indicator.

Hydrogen peroxide (H_2O_2)

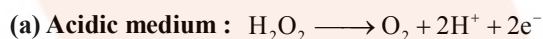H_2O_2 can behave both like oxidising and reducing agent in both the mediums (acidic and basic).
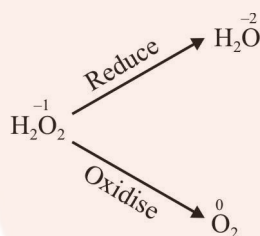
○   **Oxidising agent :** $(H_2O_2 \rightarrow H_2O)$

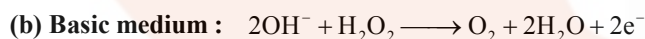**(a) Acidic medium :** $2e^- + 2H^+ + H_2O_2 \longrightarrow 2H_2O$

$v.f = 2$

(b) Basic medium : $2e^- + H_2O_2 \longrightarrow 2OH^-$
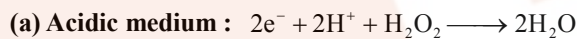
$v.f = 2$

○   **Reducing agent :** $(H_2O_2 \rightarrow O_2)$

(a) Acidic medium : $H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$

$v.f = 2$

(b) Basic medium : $2OH^- + H_2O_2 \longrightarrow O_2 + 2H_2O + 2e^-$
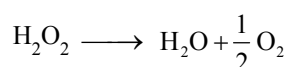
$v.f = 2$

Note : Valency factor of H_2O_2 is always equal to 2.

Volume strength of H_2O_2 : Strength of H_2O_2 is represented as 10V, 20V, 30V etc.

20VH_2O_2 means **one litre** of this sample of H_2O_2 on decomposition gives **20L of O_2 gas of STP.**

Decomposition of H_2O_2 is given as :

$H_2O_2 \longrightarrow H_2O + \dfrac{1}{2} O_2$

1 mole $\quad \frac{1}{2} \times 22.4$ L O_2 at STP

$= 34$g $\quad = 11.2$ L O_2 at STP

To obtain 11.2 litre O_2 at STP, at least 34 g H_2O_2 must be decomposed.

For 20 L O_2, we should decompose atleast $\frac{34}{11.2} \times 20$ g H_2O_2

$\therefore \quad$ 1L solution of H_2O_2 contains $\frac{34}{11.2} \times 20$ g H_2O_2

$\therefore \quad$ 1L solution of H_2O_2 contains $\frac{34}{11.2} \times \frac{20}{17}$ equivalents of H_2O_2 $\qquad (E_{H_2O_2} = \frac{M}{2} = \frac{34}{2} = 17)$

Nomality of $H_2O_2 = \frac{34}{11.2} \times \frac{20}{17} = \frac{20}{5.6}$

$\bigcirc$ **Normality of H_2O_2 (N)** $= \dfrac{\text{Volume strength of } H_2O_2}{5.6}$

$\because \qquad M_{H_2O_2} = \dfrac{N_{H_2O_2}}{\text{v.f.}} = \dfrac{N_{H_2O_2}}{2}$

$\bigcirc$ **Molarity of H_2O_2 (M)** $= \dfrac{\text{Volume strength of } H_2O_2}{11.2}$

Strength (in g/L) : Denoted by S

Strength = Molarity × Mol. wt = Molarity × 34

Strength = Normality × Eq. weight = Normality × 17

Solved Examples

Example 18 :

20 mL of H_2O_2 after acidification with dilute H_2SO_4 required 30 mL of $\dfrac{N}{12}$ $KMnO_4$ for complete oxidation. Final the strength of H_2O_2 solution. [Molar mass of $H_2O_2 = 34$]

Sol. meq. of $KMnO_4$ = meq. of H_2O_2

$30 \times \dfrac{1}{12} = 20 \times N'$

$N' = \dfrac{30}{12 \times 20} = \dfrac{1}{8}N$

$\therefore \quad$ strength $= N' \times$ equivalent mass $= \dfrac{1}{8} \times 17 = 2.12$ g / L.

Hardness of water (Hard water does not give lather with soap)

Temporary hardness - due to bicarbonates of Ca & Mg

Permanent hardness - due to chlorides & sulphates of Ca & Mg. There are some method by which we can soften the water sample.

(a) By boiling : $2HCO_3^- \longrightarrow H_2O + CO_2 + CO_3^{2-}$ or

By Slaked lime : $Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow CaCO_3 + 2H_2O$

$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3$

(b) By Washing Soda : $CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$

(c) By ion exchange resins : $Na_2R + Ca^{2+} \longrightarrow CaR + 2Na^+$

(d) By adding chelating agents like $(PO_3^-)_3$ etc.

Parts Per Million (ppm)

When the solute is present in very less amount, then this concentration term is used. It is defined as the number of parts of the solute present in every 1 million parts of the solution. ppm can both be in terms of mass or in terms of moles. If nothing has been specified, we take ppm to be in terms of mass. Hence, a 100 ppm solution means that 100 g of solute is present in every 1000000g of solution.

$$ppm_A = \frac{\text{mass of A}}{\text{Total mass}} \times 10^6 = \text{mass fraction} \times 10^6$$

Measurement of Hardness :

Hardness is measured in terms of ppm (parts per million) of $CaCO_3$ or equivalent to it.

$$\text{Hardness in ppm} = \frac{\text{mass of } CaCO_3}{\text{Total mass of solution}} \times 10^6$$

Solved Examples

Example 19 :

0.00012% $MgSO_4$ and 0.000111% $CaCl_2$ is present in water. What is the measured hardness of water and millimoles of washing soda required to purify water 1000 L water ?

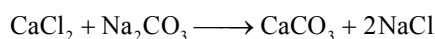**Sol.** Basis of calculation = 100 g hard water

$$MgSO_4 = 0.00012g = \frac{0.00012}{120} \text{ mole}$$
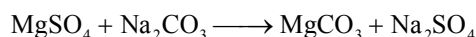
$$CaCl_2 = 0.000111g = \frac{0.000111}{111} \text{ mole}$$

∴ equivalent moles of $CaCO_3 = \left(\frac{0.00012}{120} + \frac{0.000111}{111} \right) \text{mole}$

∴ mass of $CaCO_3 = \left(\frac{0.00012}{120} + \frac{0.000111}{111} \right) \times 100 = 2 \times 10^{-4} \text{ g}$

Hardness (in terms of ppm of $CaCO_3$) $= \frac{2 \times 10^{-4}}{100} \times 10^6 = 2 \text{ ppm}$

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$$

$$MgSO_4 + Na_2CO_3 \longrightarrow MgCO_3 + Na_2SO_4$$

∴ Required Na_2CO_3 for 100g of water = $\left(\dfrac{0.00012}{120} + \dfrac{0.000111}{111}\right)$ mole
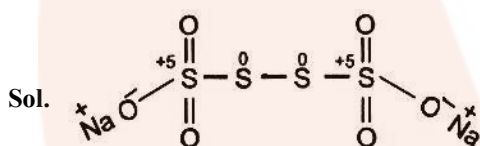
$$= 2 \times 10^{-6} \text{ mole}$$

∴ Required Na_2CO_3 for 1000 litre water = $\dfrac{2 \times 10^{-6}}{100} \times 10^6 = \dfrac{2}{100}$ mole   (∵ d = 1g/mL)

$$= \dfrac{20}{1000} \text{ mole} = 20 \text{ m mole}$$

SOLVED EXAMPLES

Example – 1

Calculate individual oxidation number of each S-atom in $Na_2S_4O_6$ (sodium tetrathionate) with the help of its structure.

Sol.

Example – 2

Find the average and individual oxidation number of Fe & Pb in Fe_3O_4 & Pb_3O_4, which are mixed oxides.

Sol. (i) Fe_3O_4 is mixture of FeO & Fe_2O_3 in 1 : 1 ratio

so, individual oxidation number of Fe = +2 & +3

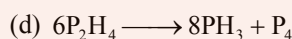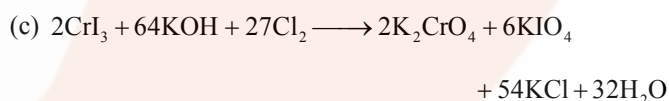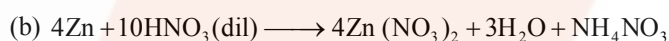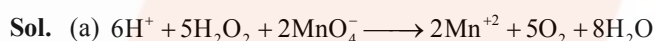& average oxidation number = $\dfrac{1(+2) + 2(+3)}{3} = 8/3$

(ii) Pb_3O_4 is a mixture of PbO & PbO_2 in 2 : 1 molar ratio

so, individual oxidation number of Pb are +2 & +4

& average oxidation number of Pb = $\dfrac{2(+2) + 1(+4)}{3} = 8/3$

Example – 3

Balance the following equations :

(a) $H_2O_2 + MnO_4^- \longrightarrow Mn^{+2} + O_2$ (acidic medium)

(b) $Zn + HNO_3 \text{ (dil)} \longrightarrow Zn(NO_3)_2 + H_2O + NH_4NO_3$

(c) $CrI_3 + KOH + Cl_2 \longrightarrow K_2CrO_4 + KIO_4 + KCl + H_2O$

(d) $P_2H_4 \longrightarrow PH_3 + P_4$

(e) $Ca_3(PO_4)_2 + SiO_2 + C \longrightarrow CaSiO_3 + P_4 + CO$

Sol. (a) $6H^+ + 5H_2O_2 + 2MnO_4^- \longrightarrow 2Mn^{+2} + 5O_2 + 8H_2O$

(b) $4Zn + 10HNO_3(dil) \longrightarrow 4Zn(NO_3)_2 + 3H_2O + NH_4NO_3$

(c) $2CrI_3 + 64KOH + 27Cl_2 \longrightarrow 2K_2CrO_4 + 6KIO_4$
$$+ 54KCl + 32H_2O$$

(d) $6P_2H_4 \longrightarrow 8PH_3 + P_4$

(e) $2Ca_3(PO_4)_2 + 6SiO_2 + 10C \longrightarrow 6CaSiO_3 + P_4 + 10CO$

Example – 4

Calculate the normality of a solution obtained by mixing 50 mL of 5M solution of $K_2Cr_2O_7$ and 50 mL of 2 M $K_2Cr_2O_7$ in acidic medium.

Sol. v.f. of $K_2Cr_2O_7 = 6$

so $N_f = \dfrac{N_1V_1 + N_2V_2}{V_1 + V_2}$

$= \dfrac{5 \times 6 \times 50 + 2 \times 6 \times 50}{50 + 50} = 21\,N$

Example – 5

Calculate the normality of a solution containing 13.4 g of sodium oxalate in 100 mL Sol.

Sol. Normality $= \dfrac{\text{wt. in g} / \text{eq. wt}}{\text{vol of solution in litre}}$

Here, eq. wt. of $Na_2C_2O_4 = 134/2 = 67$

so $N = \dfrac{13.4/67}{100/1000} = 2N$

Example – 6

The number of moles of ferrous oxalate oxidised by one mole of $KMnO_4$ in acidic medium is :

(a) $\dfrac{5}{2}$ (b) $\dfrac{2}{5}$

(c) $\dfrac{3}{5}$ (d) $\dfrac{5}{3}$

Sol. Eq. of $FeC_2O_4 =$ Eq. of $KMnO_4$
moles of $FeC_2O_4 \times 3 =$ moles of $KMnO_4 \times 5$
so, moles of $FeC_2O_4 = 5/3$ **Ans. (d)**

Example – 7

How many moles of $KMnO_4$ are needed to oxidise a mixture of 1 mole of each $FeSO_4$ & FeC_2O_4 in acidic medium ?

(a) $\dfrac{4}{5}$ (b) $\dfrac{5}{4}$

(c) $\dfrac{3}{4}$ (d) $\dfrac{5}{3}$

Sol. Eq. of $KMnO_4 =$ Eq. of $FeSO_4 +$ Eq. of FeC_2O_4
moles of $KMnO_4 \times 5 =$ moles of $FeSO_4 \times 1 +$ moles of $FeC_2O_4 \times 3$
∴ moles of $KMnO_4 = 4/5$ **Ans. (a)**

Example – 8

A fresh H_2O_2 solution is labelled 11.2 V. This solution has the same concentration as a solution which is :
(a) 3.4 % (w/w)   (b) 3.4% (v/v)
(c) 3.4% (w/v)   (d) None of these

Sol. Molarity of $H_2O_2 = \dfrac{\text{vol. strength}}{11.2} = \dfrac{11.2}{11.2} = 1$

Now, % (w/v) $= \dfrac{\text{wt. of solute in g}}{\text{wt. of solution in mL}} \times 100$

$=$ Molarity × Mol. wt. of solute × $\dfrac{1}{10}$

$= 1 \times 34 \times \dfrac{1}{10} = 3.4\%$ **Ans. (c)**

Example – 9

100 mL each of 1N H_2O_2 and 11.2 V H_2O_2 solution are mixed, then the final solution is equivalent to :
(a) 3 M H_2O_2 solution   (b) 0.5 N H_2O_2 solution
(c) 25.5 g/L H_2O_2 solution
(d) 2.55 g/L H_2O_2 Sol.

Sol. $N_{final} = \dfrac{N_1V_1 + N_2V_2}{V_1 + V_2} = \dfrac{1 \times 100 + \left(\dfrac{11.2}{5.6}\right) \times 100}{100 + 100} = 3/2 = 1.5N$

So, Molarity $= \dfrac{\text{Normality}}{\text{v.f.}} = \dfrac{1.5}{2} = 0.75\,M$

Strength of solution in g/L $=$ Molarity × Mol. wt. $= 0.75 \times 34 = 25.5$ g/L **Ans. (c)**