



REDOX & EQUIVALENT CONCEPTS (STOCHIOMETRY-II)

□ OXIDATION & REDUCTION

Let us do a comparative study of oxidation and Reduction ;

Oxidation	Reduction
(1) Addition of oxygen	(i) Removal of oxygen
e.g. $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$	e.g. $\text{CuO} + \text{C} \rightarrow \text{Cu} + \text{CO}$
(2) Removal of Hydrogen	(ii) Addition of Hydrogen
e.g. $\text{H}_2\text{S} + \text{Cl}_2 \rightarrow 2\text{HCl} + \text{S}$	e.g. $\text{S} + \text{H}_2 \rightarrow \text{H}_2\text{S}$
(3) Increase in positive charge	(iii) Decrease in positive charge
e.g. $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$	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. $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$

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 arbitrary set of rules.
- ◆ It is a relative charge in a particular bonded state.

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 :

- (i) peroxide (e.g. H_2O_2 , Na_2O_2) is -1
- (ii) super oxide (e.g. KO_2) is $-\frac{1}{2}$
- (iii) ozonide (KO_3) is -1_3
- (iv) 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. KClO_3 HIO_3 HClO_4 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. $\text{O}_2, \text{S}_8, \text{P}_4, \text{O}_3$

◆ 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 ($\text{NH}_3, \text{NO}, \text{N}_2\text{O}_3, \text{NO}_2, \text{N}_2\text{O}_5$)

Calculation of average oxidation number :

Solved Examples :

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

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

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 $\underline{\text{Na}}_2\underline{\text{S}}_2\text{O}_3$ have two S-atom and there are four S-atom in $\underline{\text{Na}}_2\underline{\text{S}}_4\text{O}_6$ 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.

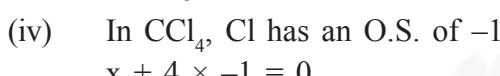


Ex. Calculate the O.S. of all the atoms in the following species :

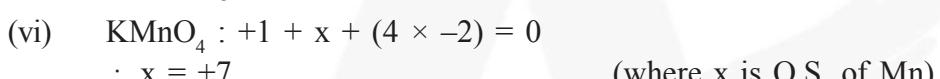
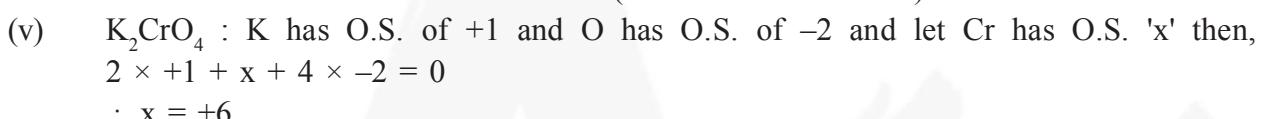


Sol. (i) In ClO^- , the net charge on the species is -1 and therefore the sum of the oxidation states of Cl and O must be equal to -1 . Oxygen will have an O.S. of -2 and if the O.S. of Cl is assumed to be ' x ' then $x - 2$ should be equal to -1 .

x is $+1$

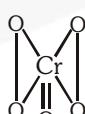


$\therefore x = +4$ (where ' x ' is O.S. of C)



□ 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 :

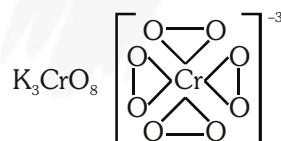
- The structure of CrO_5 is
 

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 .

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

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

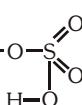


From the structure it is evident that in CrO_8^{-3} there are four peroxide linkages.

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

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

\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.

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

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

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

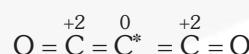
$$\text{or } x = 6$$

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

□ PARADOX OF FRACTIONAL OXIDATION NUMBER

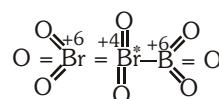
Fractional oxidation state is the average oxidation state of the element under examination and the structural parameters reveal that the element for whom fractional oxidation state is realised is actually present in different oxidation states. Structure of the species C_3O_2 , Br_3O_8 and $\text{S}_4\text{O}_6^{2-}$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



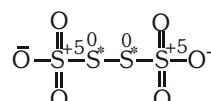
Structure of C_3O_2
(Carbon suboxide)

- 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)

□ OXIDISING AND REDUCING AGENT

- ◆ **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.

- ◆ **Reducing agent or Reductant :**

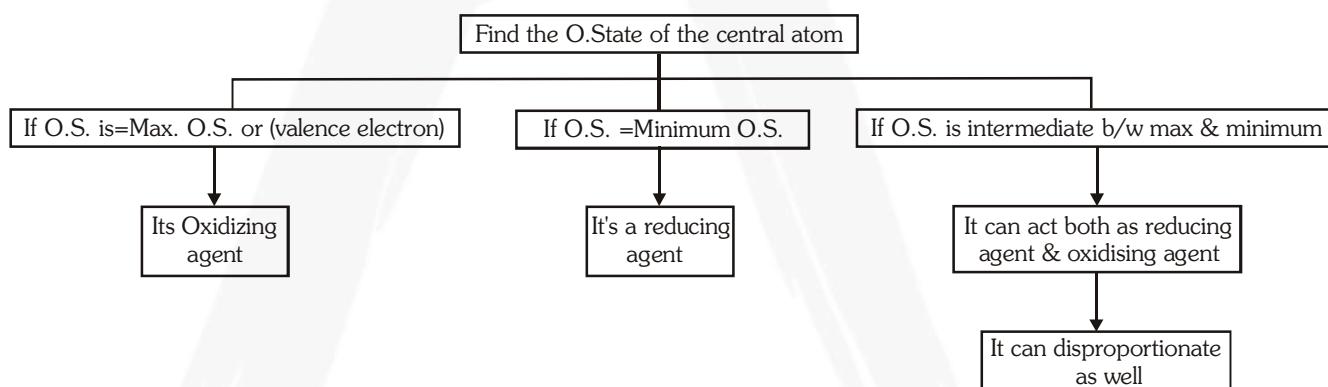
Reducing agents are those compound which can reduce others and oxidise itself during the chemical reaction. Those reagents whose O.N. increase or which loses electrons in a redox reaction are termed as reductants.

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^-

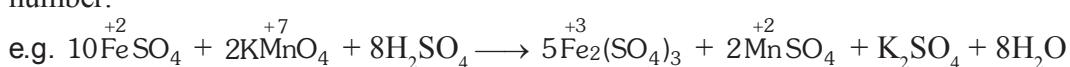
□ HOW TO IDENTIFY WHETHER A PARTICULAR SUBSTANCE IS AN OXIDISING OR REDUCING AGENT



□ 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.



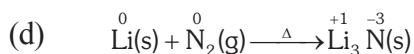
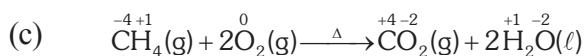
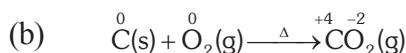
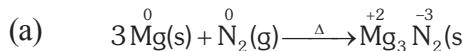
□ TYPE OF REACTION

- ◆ **Combination Reactions :**

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

For example

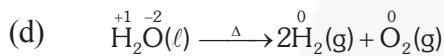
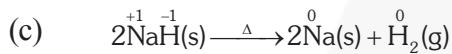
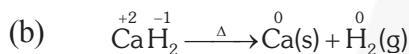
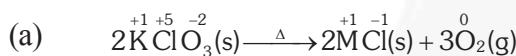




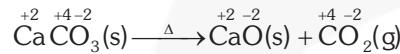
In reaction (c), there is no change in the oxidation number of hydrogen.

◆ **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 :



◆ **Displacement Reactions :**

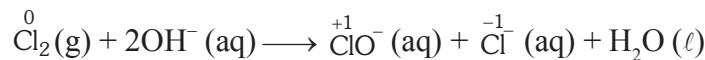
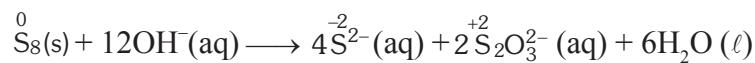
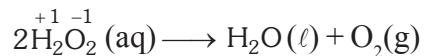
A reaction in which an atom or iron in a compound is replaced by an atom or ion of another element is called a displacement reaction. It may be denoted as :



◆ **Disproportionations reactions :**

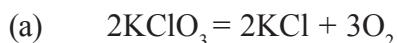
A redox reaction in which a same element present in a particular compound in a definite oxidation state is oxidized as well as reduced simultaneously is a disproportionation reactions.

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.

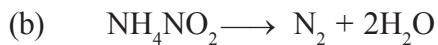




◆ Consider following reactions :



KClO_3 plays a role of oxidant and reductant both. Because same element is not oxidised and reduced. Here, Cl present in KClO_3 is reduced and O present in KClO_3 is oxidized. So **its not a disproportion reaction** although it looks like one.

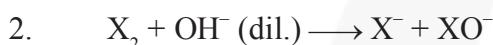
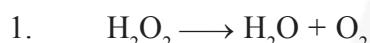


Nitrogen in this compound has -3 and $+3$ oxidation number so it is not a definite value, so its not a disproportion reaction. Its a example of **comproportionation reaction** which is a class of redox reaction in which a element from two different oxidation state gets converted into a single oxidation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



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

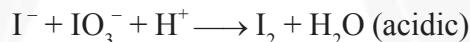
◆ List of some important disproportionation reaction :



F₂ 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.



□ 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 :**

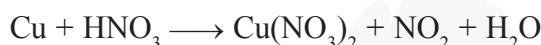
This method was given by Jonson. In a balanced redox reaction, total increase in oxidation number must be equal to total decreases in oxidation number. This equivalence provides the basis for balancing redox reactions.



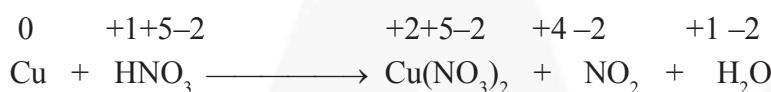
The general procedure involves the following steps :

- (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. Balance the following reaction by the oxidation number method :



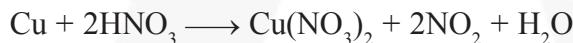
Sol. Write the oxidation number of all the atoms.



There is change in oxidation number of Cu and N.



To make increase and decrease equal, eq. (2) is multiplied by 2.



Balancing nitrates ions, hydrogen and oxygen, the following equation is obtained.



This is the balanced equation.

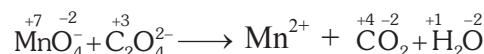
Ex. Write the skeleton equation for each of the following processes and balance them by ion electron method :

- (i) Permagnet ion oxidizes oxalate ions in acidic medium to carbon dioxide and gets reduced itself to Mn^{2+} ions.
- (ii) Bromine and hydrogen peroxide react to give bromate ions and water.
- (iii) 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 :

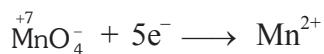
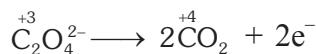




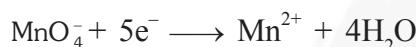
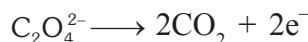
- ◆ **Step (2) :** Writing oxidation and reduction half reaction :



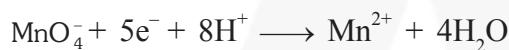
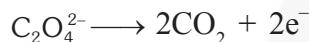
- ◆ **Step (3) :** Adding electrons to make the difference in O.N.



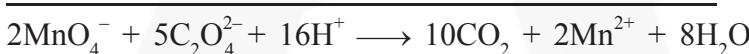
- ◆ **Step (4) :** Balancing 'O' atom by adding H_2O molecules



- ◆ **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 is



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

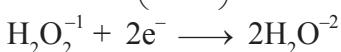
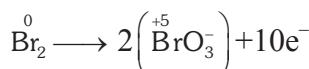


Thus, Br and O changes their oxidation numbers.

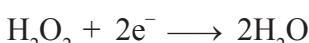
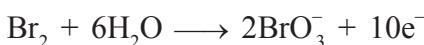
- ◆ **Step (2) :** Write the oxidation and reduction half reaction.



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

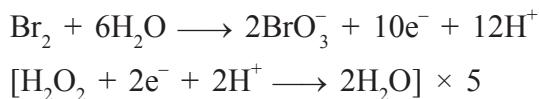


- ◆ **Step (4) :** Balance 'O' atoms by adding H_2O molecules





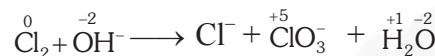
- ◆ **Step (5) :** Equalize the electrons by multiplying the reduction half with 5 and add the two half reactions



- (iii) The skeleton equation for the given process :



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

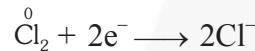


Thus, chlorine is the only element which undergoes the change in oxidation number. It decreases its oxidation number from 0 to 1 and also increases its oxidation number from 0 to 5.

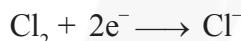
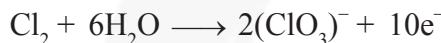
- ◆ **Step (2) :** Write the oxidation and reduction half reactions



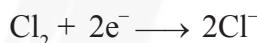
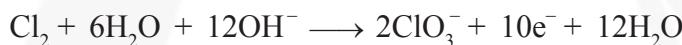
- ◆ **Step (3) :** Add electrons to make up for the difference in O.N.



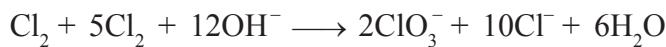
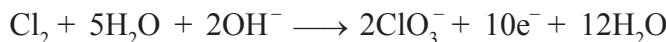
- ◆ **Step (4) :** Balance O atoms by adding H_2O molecules



- ◆ **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.



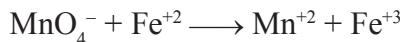
- ◆ **Step (6) :** Multiply the reduction half reaction by 5 and add two half reactions.



or, $6\text{Cl}_2 + 12\text{OH}^- \longrightarrow 2\text{ClO}_3^- + 10\text{Cl}^- + 6\text{H}_2\text{O}$

or, $3\text{Cl}_2 + 6\text{OH}^- \longrightarrow \text{ClO}_3^- + 5\text{Cl}^- + 3\text{H}_2\text{O}$

Ex : Balance the following reaction by the oxidation number method :





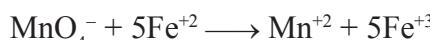
Sol : Write the oxidation number of all the atoms.



change in oxidation number has occurred in Mn and Fe.



To make increase and decrease equal, eq. (2) is multiplied by 5.



To balance oxygen, $4\text{H}_2\text{O}$ are added to R.H.S. and to balance hydrogen, 8H^+ are added to L.H.S.

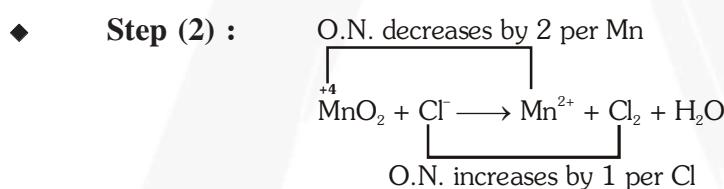
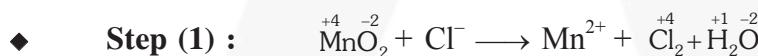


This is the balanced equation.

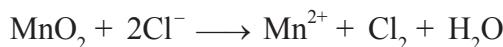
Ex. Balance the following chemical reaction by oxidation number method and write their skeleton equation :

- (i) Chloride ions reduce manganese dioxide to manganese (II) ions in acidic medium and get itself oxidized to chlorine gas.
- (ii) 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

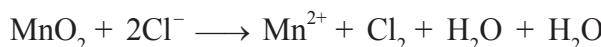


◆ **Step (3) :** Equalize the increase/decrease in O.N. by multiplying



◆ **Step (4) :** Balance other atoms except H and O. Here they are all balanced.

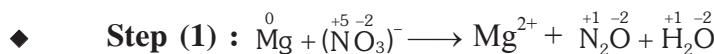
◆ **Step (5) :** Balance O atoms by adding H_2O molecules to the side falling short of O atoms.



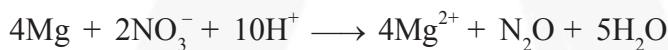
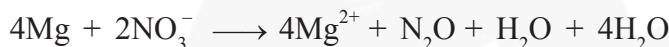
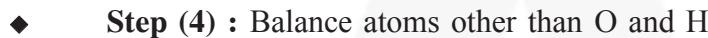
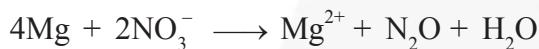
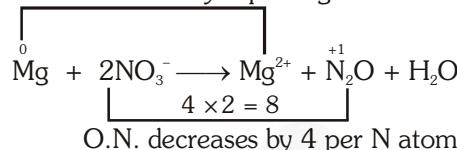
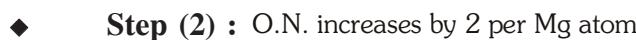
◆ **Step (6) :** Balance H atoms by adding H^+ ions to the side falling short of H atoms.



- (ii) The skeleton equation for the given process is



Multiply NO_3^- by 2 to equalize N atoms



(b) Ion electron method or half cell method :

By this method redox equation are balanced in two different medium

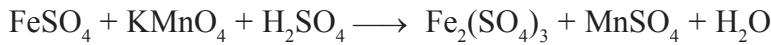
- (a) Acidic medium (b) Basic medium

◆ Balancing in acidic medium

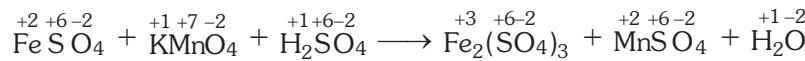
Students are advised to follow the following steps to balance the redox reactions by ion electron method in acidic medium.

Solved Examples :

Ex : Balance the following redox reaction.



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

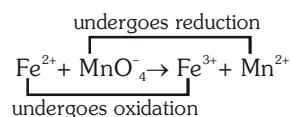


Step-II Now convert the reaction in ionic form by eliminating the elements or species which are not going either oxidation or reduction





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

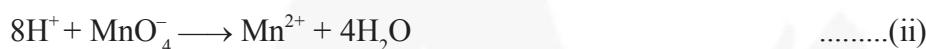


Step-V Balance the atom other than oxygen and hydrogen atom in both half reactions

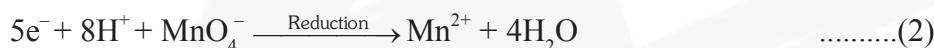


Fe & Mn atom are balanced in both side.

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.

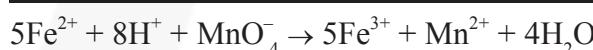
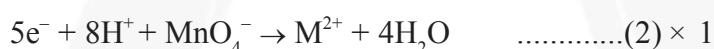


Step VII Now see equation (i) & (ii) is balanced atomwise. Now balance both equations chargewise to balance the charge add electrons to the electrically positive side.



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.

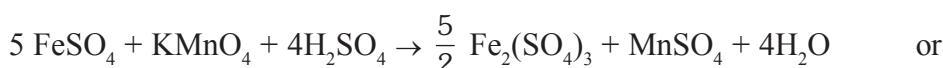
Here we multiply equation (i) by 5 and (ii) by one



(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



◆ **Balancing in basic medium :**

In this case except step VI all the steps are same. We can understand it by following example balance the redox reaction in basic medium



$$\text{Eq.wt.} \rightarrow \frac{M}{1} \quad \frac{M}{2} \quad \frac{M}{3} \quad \frac{M}{2}$$

Self practice problems :

1. Find the valence factor for following acids

- (i) CH_3COOH
- (ii) NaH_2PO_4
- (iii) H_3BO_3

Answers :

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

◆ **For Base :**

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

Solved Examples :

Ex : NaOH , KOH

Sol : v.f. \rightarrow 1 1

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

Self practice problems :

1. Find the valence factor for following bases

- (i) $\text{Ca}(\text{OH})_2$
- (ii) CsOH
- (iii) $\text{Al}(\text{OH})_3$

Answers :

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

Solved Examples :

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

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

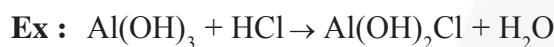


Base Acid

Sol : valence factor of acid = 2

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

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



Base Acid

Sol : valence factor of base = 1

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

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

◆ **For Salts :**

(a) In non reacting condition

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

Solved Examples :



Sol : V.f. 2 $2 \times 3 = 6$ 2

$$\text{E.} \quad \frac{\text{M}}{2} \quad \frac{\text{M}}{6} \quad \frac{\text{M}}{2}$$

(b) **Salt in reacting condition :**

Solved Examples :



Base Acid

Sol : It is a acid base reaction therefore v.f. for Na_2CO_3 is one while in non reaction condition it will be two.

Note :- In neutral condition if salt is not given take valency factor as for complete neutralization.

(c) **Eq. wt. of oxidising / reducing agents in redox reaction :**

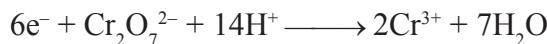
The equivalent weight of an oxidising agent is that weight which accepts one mole electron in a chemical reaction.



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

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

Ex : In acidic medium



$$\text{Eq. wt. of } K_2Cr_2O_7 = \frac{\text{Mol. wt of } K_2Cr_2O_7}{6} = \frac{\text{Mol. wt.}}{6}$$

Note : [6 in denominator indicates that 6 electrons were gained by $Cr_2O_7^{2-}$ 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: In acidic medium, $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$

$$\text{Here, Total electrons lost} = 2 \quad \text{So, eq. wt.} = \frac{\text{Mol. wt.}}{2}$$

(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 : (i) $MnO_4^- \longrightarrow Mn^{2+}$ (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) $MnO_4^- \longrightarrow Mn^{+4}$ (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) $MnO_4^- \longrightarrow MnO_4^{-2}$ (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 : $2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$

(Reducing agent)

$$\text{equivalent weight of } S_2O_3^{2-} = \frac{2M}{2} = M$$



◆ Questions based on Equivalent weight :

1. 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.

2. Equivalent wt. of H_3PO_4 in each of the reaction will be respectively :



- (A) 98, 49, 32.67
- (B) 49, 98, 32.67
- (C) 98, 32.67, 49
- (D) 32.67, 49, 98

3. 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

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 $\frac{W \times 1000}{E \times \text{VmL}}$
- ◆ **Normality (N) = $\frac{W \times 1000}{E \times \text{VmL}}$**
- ◆ **Normality (N) = Molarity × Valence factor**

$$\text{Normality (N)} = \text{molarity} \times \text{Valence factor (n)}$$

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

$$\text{or milli equivalents} = \text{millimoles} \times n$$

Solved Examples :



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

Sol : Normality (N) = $\frac{W \times 1000}{E \times V_m}$.

where $W = 15.8 \text{ g}$, $V = 50 \text{ mL}$

$$E = \frac{\text{molar mass of KMnO}_4}{\text{Valence factor}} = 158/5 = 31.6$$

So, N = 10

Ex : Calculate the normality of a solution containing 50 mL of 5 M solution $\text{K}_2\text{Cr}_2\text{O}_7$ in acidic medium.

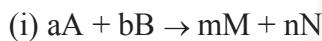
Sol : Normality (N) = Molarity × Valence factor

$$= 5 \times 6 = 30 \text{ N}$$

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 milli equivalent of reactants react in equal amount to give same no. of equivalent or milli equivalents of products separately.

According :

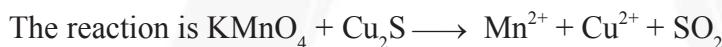


m.eq of A = m.eq of B = m.eq of M = m.eq of N



m.eq of $M_x N_y$ = m.eq of M = m.eq of N

Solved Examples :



Sol : From law of equivalence

equivalents of Cu_2S = equivalents of KMnO_4

$$\text{moles of Cu}_2\text{S} \times v.f = \text{moles of KMnO}_4 \times v.f.$$

$$\text{moles of Cu}_2\text{S} \times 8 = 1 \times 5 \Rightarrow \text{moles of Cu}_2\text{S} = 5/8$$

Ex : 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^-

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

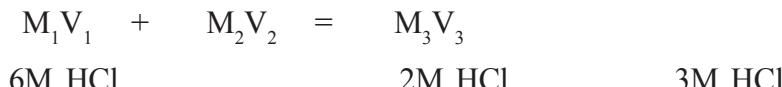
$$x = \frac{5}{2}$$



Ex. 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

∴ Volume of 2 M HCl required = $(2 - x)$ L



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

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

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

Hence, volume of 6 M HCl required = 0.5 L

Volume of 2M HCl required = 1.5 L

Ex. 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. 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 H_2SO_4 = 45.6×0.235

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

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

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

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

$$\begin{aligned} \therefore \text{For } 0.5679 \text{ g of pure } \text{Na}_2\text{CO}_3, \text{ weighed sample} &= \frac{100}{85} \times 0.5679 \\ &= 0.6681 \text{ g} \end{aligned}$$

Drawbacks of Equivalent concept :

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



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



$$\therefore \text{Eq. wt. of } MnO_4^- = \frac{MnO_4^-}{3}$$

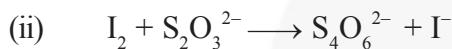
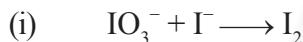
Thus the no. of equivalents of MnO_4^- will be different in the above two cases but no. of moles will be same.

- ◆ **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 = $0.1 \times 5 = 0.5 N$. This same sample of $KMnO_4$, if employed in a reaction giving MnO_2 as product (Mn in +4 state) will have normality $0.1 \times 3 = 0.3 N$.

- ◆ **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



$$\text{meq of hypo} = \text{meq of } I_2 = \text{meq of } IO_3^- + \text{meq of } I^-$$

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

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

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 is sequence. In this type of case students are advised to use mole concept.

Solved Example :

Ex : How many milliliters of 0.02000 M $KMnO_4$ solution would be required to exactly titrate 25.00 mL of 0.2000 M $Fe(NO_3)_2$ solution.

Sol : Method - 1 : Mole concept method

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

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

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

$$\text{Millimoles of } MnO_4^- = V (0.02000)$$

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 MnO_4^- = $5 \times$ moles of MnO_4^-

Normality MnO_4^- = $5 \times$ molarity of MnO_4^-

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

At the equivalence point,

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

or $V_{\text{MnO}_4^-} \times$ Normality of MnO_4^-

= $V_{\text{Fe}^{2+}} \times$ Normality of Fe^{2+}

For 0.02000 M MnO_4^- solution

Normality of MnO_4^- = $(5)(0.02000) = 0.1 \text{ N}$ and for 0.2000 M Fe^{2+} solution

Normality of Fe^{2+} = 0.2000 N

$$V_{\text{MnO}_4^-} = (25.00 \text{ mL}) \left(\frac{0.2000}{0.1000} \right) = 50.00 \text{ mL}$$

□ 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).

□ 'n' FACTOR : FACTOR RELATING MOLECULAR WEIGHT AND EQUIVALENT WEIGHT

$$\text{n-factor} = \frac{M}{E}$$

$$E = \frac{M}{\text{n-factor}}$$

□ n-FACTOR IN VARIOUS CASES

In Non Redox Change

- ◆ **n-factor for element :** Valency of the element

- ◆ **For acids :** Acids will be treated as species which furnish H^+ ions when dissolved in a solvent.

The n-factor of an acid is the no. of acidic H^+ ions that a molecule of the acid would give when dissolved in a solvent (Basicity).

For example, for HCl ($n = 1$), HNO_3 ($n = 1$), H_2SO_4 ($n = 2$), H_3PO_4 ($n = 3$) and H_3PO_3 ($n = 2$)



- ◆ **For bases :** Bases will be treated as species which furnish OH^- ions when dissolved in a solvent. The n-factor of a base is the no. of OH^- ions that a molecule of the base would give when dissolved in a solvent (**Acidity**).

For example, NaOH ($n = 1$), Ba(OH)_2 ($n = 2$), Al(OH)_3 ($n = 3$), etc.

- ◆ **For salts :** A salt reacting such that no atom of the salt undergoes any change in oxidation state.

For example, $2\text{AgNO}_3 + \text{MgCl}_2 \rightarrow \text{Mg}(\text{NO}_3)_2 + 2\text{AgCl}$

In this reaction, it can be seen that the oxidation state of Ag, N, O, Mg and Cl remains the same even in the product. The n-factor for such a salt is the total **charge on cation or anion**.

In Redox Change

For oxidizing agent or reducing agent n-factor is the **change in oxidation number per mole of the substance**.

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

Species	Changed to	Reaction	Electrons exchanged or change in O.N.	Eq. wt.
MnO_4^- (O.A.)	Mn^{+2} in acidic medium	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	5	$E = \frac{M}{5}$
MnO_4^- (O.A.)	MnO_2 in neutral medium	$\text{MnO}_4^- + 3\text{e}^- + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 + 4\text{OH}^-$	3	$E = \frac{M}{3}$
MnO_4^- (O.A.)	MnO_4^{2-} in basic medium	$\text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-}$	1	$E = \frac{M}{1}$
$\text{Cr}_2\text{O}_7^{2-}$ (O.A.)	Cr^{3+} in acidic medium	$\text{CrO}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	6	$E = \frac{M}{6}$
MnO_2 (O.A.)	Mn^{2+} in acidic medium	$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	2	$E = \frac{M}{2}$
Cl_2 (O.A.) in bleaching powder	Cl^-	$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	2	$E = \frac{M}{2}$
CuSO_4 (O.A.) in iodometric titration	Cu^+	$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	1	$E = \frac{M}{1}$
$\text{S}_2\text{O}_3^{2-}$ (R.A.)	$\text{S}_4\text{O}_6^{2-}$	$2\text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{e}^-$	2	$E = \frac{2M}{2} = M$
(for two molecules)				
H_2O_2 (O.A.)	H_2O	$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	2	$E = \frac{M}{2}$
H_2O_2 (R.A.)	O_2	$\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$ (O.N. of oxygen in H_2O_2 is -1 per atom)	2	$E = \frac{M}{2}$
Fe^{2+} (R.A.)	Fe^{3+}	$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$	1	$E = \frac{M}{1}$



Ex. 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.

$$n = |2 \times (+3) - 2 \times (+4)| = 2$$

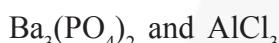
(vi) In this reaction, ferrous ions get oxidized to ferric ions.

$$n = |1 \times (+2) - 1 \times (+3)| = 1$$

(vi) In this reaction, ferric ions are getting reduced to ferrous ions.

$$n = |2 \times (+3) - 2 \times (+2)| = 2$$

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



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

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

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

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

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



□ APPLICATIONS OF THE LAW OF EQUIVALENCE

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.

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

From this we can calculate the value of N_2 .

Ex. 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 ?

Sol. $0.4 \times 5 \times V = 0.05 \times 50$

$$V = 1.25 \text{ mL}$$

Ex. 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 $\text{Na}_2\text{CO}_3 = x \text{ g}$

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

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

For neutralization reaction of 100 mL

$$\text{Meq. of } \text{Na}_2\text{CO}_3 + \text{Meq. of } \text{K}_2\text{CO}_3 = \text{Meq. of HCl}$$

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

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

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

$$(\text{Meq. of } \text{Na}_2\text{CO}_3 + \text{Meq. of } \text{K}_2\text{CO}_3) \text{ in 20 mL} = \text{Meq. of } \text{BaCO}_3$$

$$\Rightarrow \text{Meq. of HCl for 20 mL mixture} = \text{Meq. of } \text{BaCO}_3$$

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



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

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

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

□ 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 gs 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 = $N_1 V_1$.

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

$$\text{gm. equivalents of B used in the second titration} = N_1 V_2$$

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

$$\text{gm. equivalents of A that reacted with C} = N_1 V_1 - N_1 V_2$$

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

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

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



□ SOME REDOX TITRATIONS (EXCLUDING IODOMETRIC / IODIMETRIC)

Estimation of	By titrating with	Reactions	Relation between O.A. and R.A.
Fe ²⁺	MnO ₄ ⁻	Fe ²⁺ → Fe ³⁺ + e ⁻ MnO ₄ ⁻ + 8H ⁺ + 5e ⁻ → Mn ²⁺ + 4H ₂ O	5Fe ²⁺ ≡ MnO ₄ ⁻ Eq. wt. Fe ²⁺ = M/1 Eq. wt. MnO ₄ ⁻ = M/5
Fe ²⁺	Cr ₂ O ₇ ²⁻	Fe ²⁺ → Fe ³⁺ + e ⁻ Cr ₂ O ₇ ²⁻ + 14H ⁺ + 6e ⁻ → 2Cr ³⁺ + 7H ₂ O	6Fe ²⁺ ≡ Cr ₂ O ₇ ²⁻ Eq. wt. Cr ₂ O ₇ ²⁻ = M/6
C ₂ O ₄ ²⁻	MnO ₄ ⁻	C ₂ O ₄ ²⁻ → 2CO ₂ + 2e ⁻ MnO ₄ ⁻ + 8H ⁺ + 5e ⁻ → Mn ²⁺ + 4H ₂ O	5C ₂ O ₄ ²⁻ ≡ 2MnO ₄ ⁻ Eq. wt. C ₂ O ₄ ²⁻ = M/2 Eq. wt. MnO ₄ ⁻ = M/5
H ₂ O ₂	MnO ₄ ⁻	H ₂ O ₂ → 2H ⁺ + O ₂ + 2e ⁻ MnO ₄ ⁻ + 8H ⁺ + 5e ⁻ → Mn ²⁺ + 4H ₂ O	5H ₂ O ₂ ≡ 2MnO ₄ ⁻ Eq. wt. H ₂ O ₂ = M/2 Eq. wt. MnO ₄ ⁻ = M/5
As ₂ O ₃ AsO ₃ ³⁻	MnO ₄ ⁻ BrO ₃ ⁻	As ₂ O ₃ + 5H ₂ O → 2AsO ₄ ³⁻ + 10H ⁺ + 4e ⁻ AsO ₃ ³⁻ + H ₂ O → AsO ₄ ³⁻ + 2H ⁺ + 2e ⁻ BrO ₃ ⁻ + 6H ⁺ + 6e ⁻ → Br ⁻ + 3H ₂ O	Eq. wt. As ₂ O ₃ = M/4 Eq. wt. AsO ₃ ³⁻ = M/2 Eq. wt. BrO ₃ ⁻ = M/6

Ex. 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 0.2 N NaOH. The volume of NaOH used was 20 cc. Calculate the percentage of Ba(OH)₂ in the sample.

Sol. Milli eq. of HCl initially = $10 \times 0.5 = 5$

Milli eq. of NaOH consumed = Milli eq. of HCl in excess = $10 \times 0.2 = 2$

∴ Milli eq. of HCl consumed = Milli eq. of Ba(OH)₂ = $5 - 2 = 3$

∴ Eq. of Ba(OH)₂ = $3/1000 = 3 \times 10^{-3}$

Mass of Ba(OH)₂ = $3 \times 10^{-3} \times (171/2) = 0.2565$ g

% Ba(OH)₂ = $(0.2565 / 20) \times 100 = 1.28\%$

Ex. 3.2 g of pyrolusite 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 KMnO₄ required 32 mL of the solution : Find the % of MnO₂ in the sample and also the percentage of available oxygen.

Sol. Redox changes are C₂O₄²⁻ → 2CO₂ (n-factor = 2)
 MnO₄⁻ → Mn²⁺ (n-factor = 5)
 MnO₂ → Mn²⁺ (n-factor = 2)

Meq. of MnO₂ = Meq. of oxalic acid taken - Meq. of oxalic acid left



$$= 50 \times 0.5 \times 2 - 32 \times 0.02 \times 5 \times 10 \text{ (in } 250 \text{ mL)} = 18$$

$$\frac{W_{\text{MnO}_2}}{M_{\text{MnO}_2}} \times 2 \times 1000 = 18 \Rightarrow \frac{W_{\text{MnO}_2}}{87} \times 2 \times 1000 = 18,$$

$$\therefore W_{\text{MnO}_2} = 0.7821 \text{ g}$$

$$\therefore \% \text{ of MnO}_2 = \frac{0.7821}{3.2} \times 100 = 24.44 \%$$

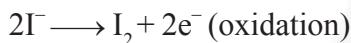
Meq. of MnO_2 = Meq. of O_2

$$\frac{W_{\text{O}_2}}{16} \times 2 \times 1000 = 18, \therefore W_{\text{O}_2} = 0.144 \text{ g}$$

$$\% \text{ of available O}_2 = \frac{0.144}{3.2} \times 100 = 4.5$$

Iodometric and Iodimetric Titration :

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



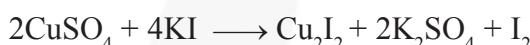
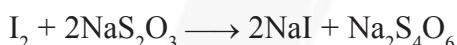
These are divided into two types :

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.



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.

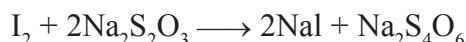
In iodimetric and iodometric titration, starch solution is used as an indicator. Starch solution gives blue or violet colour with free iodine. At the end point, the blue or violet colour disappears when iodine is completely changed to iodide.

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

Estimation of

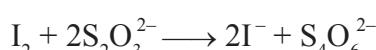
Reaction

Relation between O.A. and R.A.

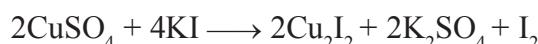
 I_2 

$$\text{I}_2 = 2\text{I} \equiv 2\text{Na}_2\text{S}_2\text{O}_3$$

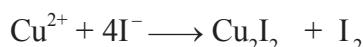
or



$$\text{Eq. wt. of } \text{Na}_2\text{S}_2\text{O}_3 = M/1$$

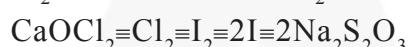
 CuSO_4 

$$2\text{CuSO}_4 \equiv \text{I}_2 \equiv 2\text{I} \equiv 2\text{Na}_2\text{S}_2\text{O}_3$$



$$\text{Eq. wt. of } \text{CuSO}_4 = M/1$$

(White ppt.)

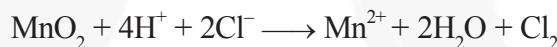
 CaOCl_2 

$$\text{Eq. wt. of } \text{CaOCl}_2 = M/2$$

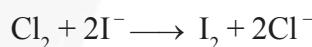
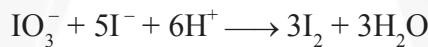
 MnO_2

or

$$\text{MnO}_2 \equiv \text{Cl}_2 \equiv \text{I}_2 \equiv 2\text{I} \equiv 2\text{Na}_2\text{S}_2\text{O}_3$$



$$\text{Eq. wt. of } \text{MnO}_2 = M/2$$

 IO_3^- 

$$\text{IO}_3^- \equiv 3\text{I}_2 \equiv 6\text{I} \equiv 6\text{Na}_2\text{S}_2\text{O}_3$$

$$\text{Eq. wt. of } \text{IO}_3^- = M/6$$

 H_2O_2 

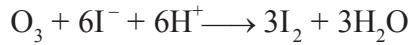
$$\text{H}_2\text{O}_2 \equiv \text{I}_2 \equiv 2\text{I} \equiv 2\text{Na}_2\text{S}_2\text{O}_3$$

$$\text{Eq. wt. of } \text{H}_2\text{O}_2 = M/2$$

 Cl_2 

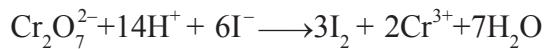
$$\text{Cl}_2 \equiv \text{I}_2 \equiv 2\text{I} \equiv 2\text{Na}_2\text{S}_2\text{O}_3$$

$$\text{Eq. wt. of } \text{Cl}_2 = M/2$$

 O_3 

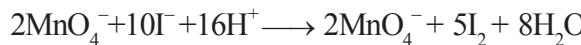
$$\text{O}_3 \equiv 3\text{I}_2 \equiv 6\text{I} \equiv 6\text{Na}_2\text{S}_2\text{O}_3$$

$$\text{Eq. wt. of } \text{O}_3 = M/6$$

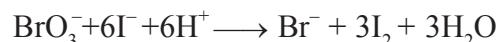
 $\text{Cr}_2\text{O}_7^{2-}$ 

$$\text{Cr}_2\text{O}_7^{2-} \equiv 3\text{I}_2 \equiv 6\text{I}$$

$$\text{Eq. wt. of } \text{Cr}_2\text{O}_7^{2-}$$

 MnO_4^- 

$$2\text{MnO}_4^- \equiv 5\text{I}_2 \equiv 10\text{I}$$

Eq. wt. of $\text{MnO}_4^- = M/5$ $\text{BrO}_3^- \equiv 3\text{I}_2 \equiv \text{I}_2$ Eq. wt. of $\text{BrO}_3^- = M/6$  $\text{H}_3\text{AsO}_4 \equiv \text{I}_2 \equiv 2\text{I}$ Eq. wt. of $\text{H}_3\text{AsO}_4 = M/2$

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

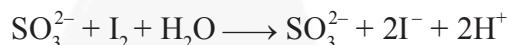
Estimation of

Reaction

Relation between O.A. and R.A.

 $\text{H}_2\text{S} \equiv \text{I}_2 \equiv 2\text{I}$

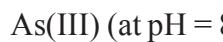
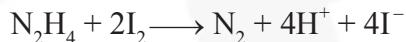
(in acidic medium)

Eq. wt. of $\text{H}_2\text{S} = M/2$  $\text{SO}_3^{2-} \equiv \text{I}_2 \equiv 2\text{I}$

(in acidic medium)

Eq. wt. of $\text{SO}_3^{2-} = M/2$  $\text{Sn}^{2+} \equiv \text{I}_2 \equiv 2\text{I}$

(in acidic medium)

Eq. wt. of $\text{Sn}^{2+} = M/2$  $\text{H}_2\text{AsO}_3^- \equiv \text{I}_2 \equiv 2\text{I}$ Eq. wt. of $\text{H}_2\text{AsO}_3^- = M/2$  $\text{N}_2\text{H}_4 \equiv 2\text{I}_2 \equiv 4\text{I}$ Eq. wt. of $\text{N}_2\text{H}_4 = M/4$

□ SUMMARY

$$1. \quad \text{Number of moles of molecules} = \frac{\text{wt. in g}}{\text{Mol. wt.}}$$

$$\text{Number of moles of atoms} = \frac{\text{wt. in g}}{\text{Atomic mass}}$$

$$\text{Number of moles of gases} = \frac{\text{Volume at STP}}{\text{Standard molar volume}}$$

$$\text{Number of moles of particles, e.g. atoms, molecular ions etc.} = \frac{\text{Number of particles}}{\text{Avogadro No.}}$$

$$\text{Moles of solute in solution} = M \times V(L)$$



2. Equivalent wt. of element = $\frac{\text{Atomic wt.}}{\text{Valence}}$

Equivalent wt. of compound = $\frac{\text{Mol. wt.}}{\text{Total charge on cation or anion}}$

Equivalent wt. of acid = $\frac{\text{Mol wt.}}{\text{Basicity}}$

Equivalent wt. of base = $\frac{\text{Mol wt.}}{\text{Acidity}}$

Equivalent wt. of an ion = $\frac{\text{Formula wt.}}{\text{Charge on ion}}$

Equivalent wt. of acid salt = $\frac{\text{Molecular wt.}}{\text{Replaceable H atom in acid salt}}$

Equivalent wt. of oxidizing or reducing agent = $\frac{\text{Mol. wt.}}{\text{Change in oxidation number per mole}}$

No. of equivalent = $N \times V(L) = \frac{\text{wt. in g}}{\text{Eq. wt.}}$

3. Molarity (M) = $\frac{W_s \times 1000}{M_s \times V} = \frac{x \times d \times 10}{M_s}$

where

W_s = wt. of solute in g

M_s = Mol. wt. of solute

x = % by mass of solute

d = density of solution in g/ml

V = volume of solution in ml

4. Normality (N) = $\frac{W_s \times 1000}{E_s \times V} = \frac{x \times d \times 1000}{E_s}$

W_s = wt. of solute in g.

E_s = eqv. wt. of solute

V = volume of solution in ml

x = % by mass of solute

d = density of solution in g/ml

5. Moles = $M \times V(L) = \frac{\text{wt. of solute}}{\text{Mol. wt.}}$

Millimoles = $M \times V(\text{ml}) = \frac{\text{wt. of solute}}{\text{Mol. wt.}} \times 1000$

Equivalents of solute = $N \times V(L)$

Meq. of solute $\frac{\text{wt.}}{\text{Eq. wt.}} \times 1000$

6. Molarity equation :



If a solution having molarity M_1 and volume V_1 is diluted to volume V_2 so that new molarity is M_2 then total number of moles remains the same.

$$M_1 V_1 = M_2 V_2$$

For a balanced equation involving n_1 moles of reactant 1 and n_2 moles of reactant 2.

$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

Normality equation : According to the law of equivalence, the substances combine together

$$\text{in the ratio of their equivalent masses } \frac{\text{wt. of A}}{\text{wt. of B}} = \frac{\text{Eq. wt. of A}}{\text{Eq. wt. of B}}$$

$$\Rightarrow \frac{\text{wt. of A}}{\text{Eq. wt. of A}} = \frac{\text{wt. of B}}{\text{Eq. wt. of B}}$$

Number of gram equivalents of A = Number of gram equivalents of B

$$\text{Number of gram equivalents of A} = \frac{N_A \times V_A}{1000}$$

$$\text{Number of gram equivalents of B} = \frac{N_B \times V_B}{1000}$$

$$\Rightarrow \frac{N_A V_A}{1000} = \frac{N_B V_B}{1000}$$

$$\Rightarrow N_A \times V_A = N_B \times V_B$$

The above equation is called normality equation.

$$7. \quad \text{Normality (N)} = \text{Molarity (M)} \times n$$

(where n = n-factor)

For acid-base (neutralization reaction or redox reaction)

$$N_1 V_1 = N_2 V_2 \text{ always true}$$

$$\text{But } M_1 V_1 = M_2 V_2 \text{ (may or may not be true)}$$

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

$$8. \quad \text{Molality (m)} = \frac{\text{Moles of solute}}{\text{wt. of solvent (in kg)}}$$

$$9. \quad \text{Strength of solution (S)} = N \times \text{Eq. wt.}$$

$$= M \times \text{mol. wt.}$$

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.