REDOX REACTION AND EQUIVALENT CONCEPT

Oxidation & Reduction

Let us do a comparative study of oxidation and reduction :

Oxidation	Reduction
1. Addition of Oxygen Ex. $2Mg + O_2 \rightarrow 2MgO$	1. Removal of Oxygen Ex. $CuO + C \rightarrow Cu + CO$
2. Removal of Hydrogen Ex. $H_2S + Cl_2 \rightarrow 2HCl + S$	2. Addition of Hydrogen Ex. $S + H_2 \rightarrow H_2S$
3. Increase in positive charge Ex. $Fe^{2+} \rightarrow Fe^{3+} + e^-$	3. Decrease in positive charge Ex. $Fe^{3+} + e^- \rightarrow Fe^{2+}$
4. Increase in oxidation number Ex. $\overset{(+2)}{SnCl_2} \rightarrow \overset{(+4)}{SnCl_4}$	4. Decrease in oxidation number Ex. $\overset{(+7)}{MnO_4^-} \rightarrow \overset{(+2)}{Mn^{2+}}$
5. Removal of electron Ex. $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$	5. Addition of electron Ex. $Fe^{3+} + e^- \rightarrow Fe^{2+}$

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.

Ex. $K\overset{+5}{Cl}O_3$, $H\overset{+5}{I}O_3$, $H\overset{+7}{Cl}O_4$, $K\overset{+5}{Br}O_3$

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

Ex. $\overset{0}{O_2}$, $\overset{0}{S_8}$, $\overset{0}{P_4}$, $\overset{0}{O_3}$

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)

Ex. N- atom belongs to 15th group in the periodic table, therefore as per rule, its oxidation number may vary from

–3 to +5 ($\overset{-3}{N}H_3$, $\overset{+2}{N}O$, $\overset{+3}{N_2}O_3$, $\overset{+4}{N}O_2$, $\overset{+5}{N_2}O_5$)

– 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

Ex. Calculate oxidation number of underlined element :

(a) $Na_2\,S_2O_3$ **(b) $Na_2\,S\,4O_6$**

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

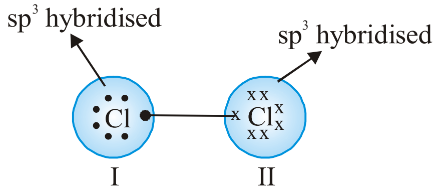
Oxidation Number = Number of electrons in the valence shell – Number of electrons taken up after bonding

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.

Ex. Calculate oxidation number of each Cl-atom in Cl_2 molecule

Structure :



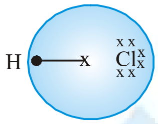
I : Number of electrons in the valence shell = 7.
Number of electrons taken up after bonding = 7.
∴ oxidation number = 7 – 7 = 0.

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

2. If there is a bond between different type of atoms :
Ex. A – B (if B is more electronegative than A)
Then after bonding, bonded pair of electrons are counted with B - atom .

Ex. Calculate oxidation number of each atom in HCl molecule

Structure :

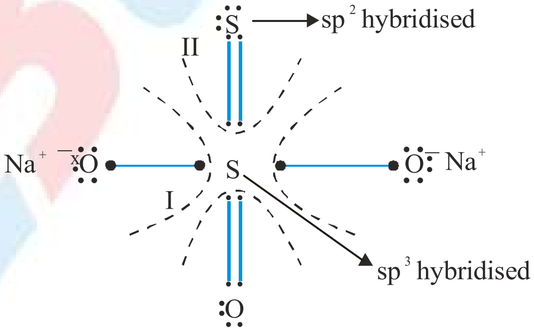


Note : Electron of H-atom is now counted with Cl-atom, because Cl-atom is more electronegative than H-atom

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

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

Sol. **Structure :**



Note : **I (central S-atom) is sp^3 hybridised (25% s-character) and II (terminal S-atom) is sp^2 hydbridised (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

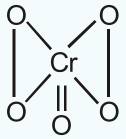
Now, you can also calculate Average Oxidation number of S = $\frac{6+(-2)}{2}$ = + 2 (as we have calculated before)

ETOOS KEY POINTS

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:

(I) The structure of CrO_5 is

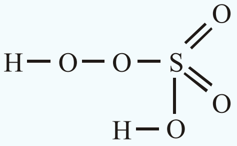


From the structure, it is evident that in CrO_5 there are two peroxide linkages and one double bond. The contribution of each peroxide linkage is –2. Let the oxidation number of Cr is x.

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

$\therefore$ Oxidation number of Cr = + 6 **Ans**

(II) 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.

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

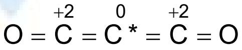
or $x + 2 - 8 = 0$ or $x - 6 = 0$ or $x = 6$

$\therefore$ 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 :

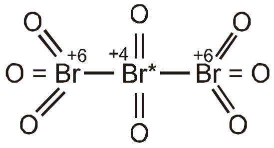
The element marked with asterisk (*) in each species is exhibiting different oxidation number from rest of the atoms of the same element in each of the species. This reveals that in C_3O_2, two carbon atoms are present in +2 oxidation state each whereas the third one is present in zero oxidation state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



$$O = \overset{+2}{C} = \overset{0}{C}{}^{*} = \overset{+2}{C} = O$$

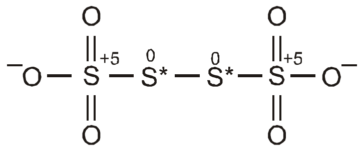
Structure of C_3O_2
(Carbon suboxide)

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.

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

Reducing agent or Reductant

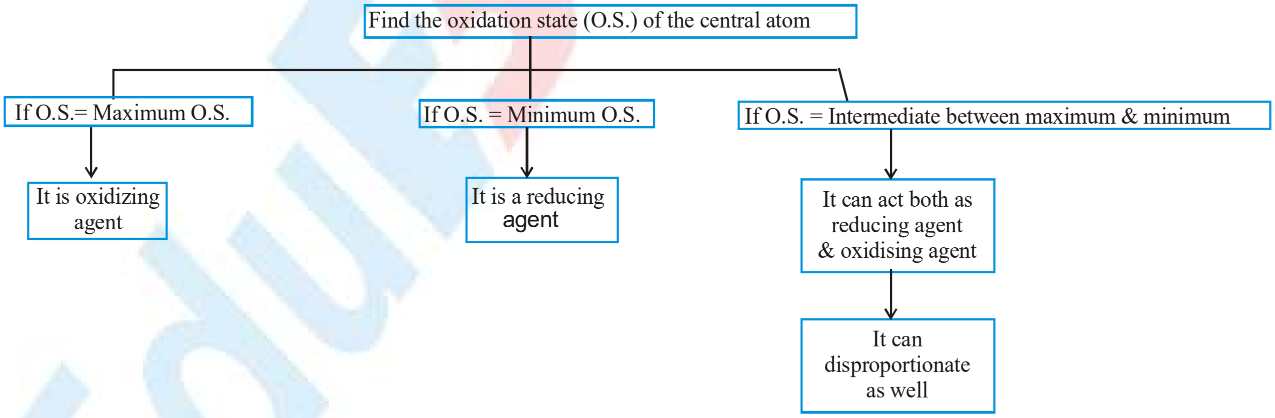
Reducing agents are those compounds which can reduce other and oxidise itself during the chemical reaction. Those reagents in which for an element, oxidation number increases or which undergoes loss of electrons in a redox reaction are termed as reductants.

Ex. 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

Ex. 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 :

$$2H_2\overset{-1}{O}_2\,(aq) \longrightarrow 2H_2\overset{-2}{O}\,(l) + \overset{0}{O}_2\,(g)$$

$$\overset{0}{S}_8\,(s) + 12OH^-(aq) \longrightarrow 4\overset{-2}{S}{}^{2-}\,(aq) + 2\overset{+2}{S}_2O_3^{2-}\,(aq) + 6H_2O\,(\bullet)$$

$$\overset{0}{Cl}_2\,(g) + 2OH^-(aq) \longrightarrow \overset{+1}{Cl}O^-\,(aq) + \overset{-1}{Cl}{}^-\,(aq) + H_2O\,(\bullet)$$

Consider the following reactions

(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) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

Nitrogen in this compound has -3 and +3 oxidation number, which is not a definite value. So it is not a disproportionation 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. $X_2 + OH^-(dil.) \longrightarrow X^- + XO^-$ $(X = Cl, Br, I)$
3. $X_2 + OH^-(conc.) \longrightarrow X^- + XO_3^-$

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

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

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

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)

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

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

$ClO_3^- \longrightarrow Cl^- + ClO_4^-$

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.**

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

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 oxidaton number method :

$$Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$$

Sol. Write the oxidation number of all the atoms.

$$\overset{0}{Cu} + \overset{+1+5-2}{HNO_3} \longrightarrow \overset{+2+5-2}{Cu(NO_3)_2} + \overset{+4\ -2}{NO_2} + \overset{+1\ -2}{H_2O}$$

There is change in oxidation number of Cu and N.

$$\overset{0}{Cu} \longrightarrow \overset{+2}{Cu(NO_3)_2} \quad ....(1) \qquad \text{(Oxidation no. is increased by 2)}$$

$$\overset{+5}{HNO_3} \longrightarrow \overset{+4}{NO_2} \quad .....(2) \qquad \text{(Oxidation no. is decreased by 1)}$$

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

$$Cu + 2HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$$

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

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

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 :

$$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$$

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

$$\overset{+7}{Mn}\overset{-2}{O_4^-} + \overset{+3}{C_2}O_4^{2-} \longrightarrow Mn^{2+} + \overset{+4}{C}\overset{-2}{O_2} + \overset{+1}{H_2}\overset{-2}{O}$$

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

$$\overset{+3}{C_2}O_4^{2-} \longrightarrow 2\overset{+4}{C}O_2 \qquad \text{(Oxidation half)}$$

$$\overset{+7}{Mn}O_4^- \longrightarrow Mn^{2+} \qquad \text{(Reduction half)}$$

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

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

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

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

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

$$MnO_4^- + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

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

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

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

– **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.

$[C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \times 5$

$[MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O] \times 2$

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

(II) The skeleton equation for the given process is

$Br_2 + H_2O_2 \longrightarrow BrO_3^- + H_2O$ (in acidic medium)

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

$$\overset{0}{Br_2} + \overset{+1}{H_2}\overset{-2}{O_2} \longrightarrow \overset{+6}{Br}\overset{-2}{O_3^-} + \overset{+1}{H_2}\overset{-2}{O}$$

Thus, Br and O changes their oxidation numbers.

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

$\overset{0}{Br_2} \longrightarrow 2\left(\overset{+5}{Br}O_3^-\right)$ (Oxidation half)

$H_2\overset{-1}{O_2} \longrightarrow 2H_2\overset{-2}{O}$ (Reduction half)

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

$\overset{0}{Br_2} \longrightarrow 2\left(\overset{+5}{Br}O_3^-\right) + 10e^-$

$H_2O_2^{-1} + 2e^- \longrightarrow 2H_2O^{-2}$

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

$Br_2 + 6H_2O \longrightarrow 2BrO_3^- + 10e^-$

$H_2O_2 + 2e^- \longrightarrow 2H_2O$

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

$Br_2 + 6H_2O \longrightarrow 2BrO_3^- + 10e^- + 12H^+$

$[H_2O_2 + 2e^- + 2H^+ \longrightarrow 2H_2O] \times 5$

$Br_2 + 5H_2O_2 \longrightarrow 2BrO_3^- + 4H_2O + 2H^+$

(III) The skeleton equation for the given process :

$Cl_2 + OH^- \longrightarrow Cl^- + ClO_3^- + H_2O$

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

$$\overset{0}{Cl_2} + \overset{+2}{OH^-} \longrightarrow Cl^- + \overset{+5}{Cl}O_3^- + \overset{+1}{H_2}\overset{-2}{O}$$

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

$\overset{0}{Cl_2} \longrightarrow 2\,\overset{+5}{Cl}O_3^-$ (Oxidation half)

$\overset{0}{Cl_2} \longrightarrow 2Cl^-$ (Reduction half)

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

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

$$\overset{0}{Cl_2} + 2e^- \longrightarrow 2Cl^-$$

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

$$Cl_2 + 6H_2O \longrightarrow 2(ClO_3)^- + 10e^-$$

$$Cl_2 + 2e^- \longrightarrow Cl^-$$

– **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.

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

$$Cl_2 + 2e^- \longrightarrow 2Cl^-$$

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

$$Cl_2 + 5H_2O + 2OH^- \longrightarrow 2ClO_3^- + 10e^- + 12H_2O$$

$$[Cl_2 + 2e^- \longrightarrow 2Cl^-] \times 5$$

$$Cl_2 + 5Cl_2 + 12OH^- \longrightarrow 2ClO_3^- + 10Cl^- + 6H_2O$$

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

or, $3Cl_2 + 6OH^- \longrightarrow ClO_3^- + 5Cl^- + 3H_2O$

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

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

Sol : Write the oxidation number of all the atoms.

$$\overset{+7\ -2}{MnO_4^-} \quad + \quad Fe^{+2} \xrightarrow{\qquad\qquad} Mn^{+2} + Fe^{+3}$$

change in oxidation number has occurred in Mn and Fe.

$$\overset{+7}{MnO_4^-} \longrightarrow \overset{+2}{Mn} \qquad ......(1) \qquad \text{(Decrement in oxidation no. by 5)}$$

$$Fe^{+2} \longrightarrow Fe^{+3} \qquad ......(2) \qquad \text{(Increment in oxidation no. by 1)}$$

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

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

To balance oxygen, $4H_2O$ are added to R.H.S. and to balance hydrogen, $8H^+$ are added to L.H.S.

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

This is the balanced equation.

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

(I) Chloride ions reduce maganese 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

$$MnO_2 + Cl^- \longrightarrow Mn^{2+} + Cl_2 + H_2O$$

– **Step (1) :** $\overset{+4}{Mn}\overset{-2}{O_2} + Cl^- \longrightarrow Mn^{2+} + \overset{+4}{Cl_2} + \overset{+1}{H_2}\overset{-2}{O}$

– **Step (2) :**

O.N. decreases by 2 per Mn

$\overset{+4}{Mn}O_2 + Cl^- \longrightarrow Mn^{2+} + Cl_2 + H_2O$

O.N. increases by 1 per Cl

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

MnO_2 by 1 and Cl^- by 2

$MnO_2 + 2Cl^- \longrightarrow Mn^{2+} + Cl_2 + H_2O$

– **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.

$MnO_2 + 2Cl^- \longrightarrow Mn^{2+} + Cl_2 + H_2O + H_2O$

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

$MnO_2 + 2Cl^- + 4H^+ \longrightarrow Mn^{2+} + Cl_2 + 2H_2O$

(II) The skeleton equation for the given process is

$Mg + NO_3^- \longrightarrow Mg^{2+} + N_2O + H_2O$

– **Step (1) :** $\overset{0}{Mg} + (\overset{+5}{N}\overset{-2}{O_3})^- \longrightarrow Mg^{2+} + \overset{+1}{N_2}\overset{-2}{O} + \overset{+1}{H_2}\overset{-2}{O}$

Multiply NO_3^- by 2 to equalize N atoms

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

$\overset{0}{Mg} + 2NO_3^- \qquad Mg^{2+} + \overset{+1}{N_2}O + H_2O$

$4 \times 2 = 8$

O.N. decreases by 4 per N atom

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

$4Mg + 2NO_3^- \longrightarrow Mg^{2+} + N_2O + H_2O$

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

$4Mg + 2NO_3^- \longrightarrow 4Mg^{2+} + N_2O + H_2O$

– **Step (5) :** Balance O atoms

$4Mg + 2NO_3^- \longrightarrow 4Mg^{2+} + N_2O + H_2O + 4H_2O$

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

$4Mg + 2NO_3^- + 10H^+ \longrightarrow 4Mg^{2+} + N_2O + 5H_2O$

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

By this method redox equation are balanced in two different medium

(a) Acidic medium (b) Basic medium

– **Balancing in acidic medium**

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

Ex : Balance the following redox reaction.

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

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

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

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

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

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

undergoes reduction

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

undergoes oxidation

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

$$Fe^{2+} \xrightarrow{\text{oxidation}} Fe^{3+} \quad \Big| \quad MnO_4^- \xrightarrow{\text{Reduction}} Mn^{2+}$$

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

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

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.

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

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

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.

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

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

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

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

$5e^- + 8H^+ + MnO_4^- \rightarrow M^{2+} + 4H_2O$ ....(2) × 1

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

(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

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

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

Balancing in basic medium

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

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

Sol : By using up to step V we will get

$$\overset{+1}{ClO^-} \xrightarrow{\text{Reuction}} Cl^- \quad \Big| \quad \overset{+3}{CrO_2^-} \xrightarrow{\text{Oxidation}} \overset{+6}{CrO}{}_4^{2-}$$

Now student are advised to follow step VI to balance 'O' and 'H' atom

$$2H^+ + ClO^- \longrightarrow Cl^- + H_2O \quad \Big| \quad 2H_2O + CrO_2^- \longrightarrow CrO_4^{2-} + 4H^+$$

- Now since we are doing balancing in basic medium therefore add as many as OH^- on both side of equation as there are H^+ ions in the equation.

$$2OH^- + 2H^+ + ClO^- \longrightarrow Cl^- + H_2O + 2OH^- \quad \Big| \quad 4OH^- + 2H_2O + CrO_2^- \rightarrow CrO_4^{2-} + 4H^+ + 4OH^-$$

Finally you will get | Finally you will get

$$H_2O + ClO^- \longrightarrow Cl^- + 2OH^- \;........\text{(I)} \qquad 4OH^- + CrO_2^- \rightarrow CrO_4^{2-} + 2H_2O\;.........\text{(II)}$$

Now see equation (I) and (II) in which O and H atoms are balanced by OH^- and H_2O

Now from step VIII

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

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

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

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 that element.

Ex. $2Mg + O_2 \longrightarrow 2MgO$

48g 32g

12g 8g

✈ 32 g of O_2 reacts with 48 g of Mg

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

$\therefore$ Equivalent weight of Mg = 12

Similarly, $\underset{65.5\text{ g}}{Zn} + H_2SO_4 \longrightarrow \underset{32.75}{ZnSO_4} + H_2$

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

$$\underset{27\text{ g}}{Al} + \underset{\frac{3}{2}\times 71\text{ g}}{\frac{3}{2}Cl_2} \longrightarrow AlCl_3$$

✈ 111.5 g chlorine reacts with 27 g of Al.

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

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

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) $= \frac{\text{Atomic weight or Molecular weight}}{\text{valency factor(v.f)}} = \frac{\text{Mol.wt.}}{\text{n}-\text{factor}} = \frac{M}{x}$

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

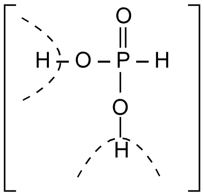
For a solution, Number of equivalents = N_1V_1, where N is the normality and V is the volume in litres

- 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 in 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

Ex. HCl , H_2SO_4 H_3PO_4 H_3PO_3



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

Sol. Valency factor → 1 2 3 2

(assume 100% dissicoiation)

Eq. wt. (E) → $\frac{M}{1}$ $\frac{M}{2}$ $\frac{M}{3}$ $\frac{M}{2}$

- Replaceable hydrogen atoms are those hydrogen atoms which are attached with the atoms of group VI and group VII i.e. O,S,Se,Te, & F, Cl ,Br ,I.

- **For Bases**

  Valency factor = number of replacable OH^- ions per base molecule.

Ex.		NaOH,	KOH
Sol.	v .f. →	1	1
	Eq. wt. →	$\frac{M}{1}$	$\frac{M}{1}$

– 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,In,Tl), transition metals, non-metallic cations like PH_4^+, NH_4^+ etc.

- **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 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

Ex. $$\underset{\text{Base}}{2NaOH} + H_2SO_4 \longrightarrow \underset{\text{Acid}}{Na_2SO_4} + 2H_2O$$

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

Ex. $$\underset{\text{Base}}{NaOH} + H_2SO_4 \longrightarrow \underset{\text{Acid}}{NaHSO_4} + H_2O$$

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

$$\therefore \quad \text{Eq. wt. of } H_2SO_4 = \frac{\text{Mol.wt}}{1}$$

- **Salts**

(a) In non-reacting condition

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

Ex.		Na_2CO_3,	$Fe_2(SO_4)_3$	$FeSO_4.7H_2O$
Sol.	V.f.	2	2×3 = 6	2
	Eq.wt.	$\frac{M}{2}$	$\frac{M}{6}$	$\frac{M}{2}$

Note : In case of hydrated salt, positive/negative charge of water molecule is not counted.

(b) In reacting condition

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

Base 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) Equivalent weight of oxidising / reducing agents in a redox reaction

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

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

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 $\frac{M}{5}$.

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 = $\frac{W}{E}$

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

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

- **Normality (N)** = $\frac{W \times 1000}{E \times V}$
- **Normality (N) = Molarity x Valency factor**

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

or

- milliequivalents = millimoles × n

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

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

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

So, normality = 10 N

Ex. 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 x 6 = 30 N

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

Ex. 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 $KMnO_4 \times 5$ ⇒ moles of $KMnO_4$ **= 8/5**

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

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

(A) $\frac{5}{2}$ (B) $\frac{2}{5}$ (C) $\frac{3}{5}$ (D) $\frac{5}{3}$

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 $MnO_4^- = 1\,(7-2) = 5$).

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

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.

  Ex. $5e^- + 8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 2H_2O$

  $$\therefore \quad \text{Eq.wt of } MnO_4^- = \frac{\text{Mol.wt.of } MnO_4^-}{5}$$

  Ex. $3e^- + 2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^-$

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

  Thus, the number of equivalents of MnO_4^- will be different in the above two cases but number of moles will be same.

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

  For example

  Consider 0.1mol $KMnO_4$ 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 x 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 × 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 reactions are :

  (I) $IO_3^- + I^- \longrightarrow I_2$ (II) $I_2 + S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + I^-$

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

  $\therefore$ meq of hypo = meq of IO_3^-.

  This is wrong. Note that I_2 formed by equation (I) has v.f. = 5/3 & in equation (II) has v.f. = 2.

  ✈ v.f. of I_2 in both the equation are different, therefore we cannot equate milli equivalents in sequence. In this type of case, students are advised to use mole concept.

Ex. 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 $Fe^{2+} = 25 \times 0.2$ ....(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,

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

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

$\therefore$ V = 50 mL.

Method -2 : Equivalent Method

At the equivalence point,

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

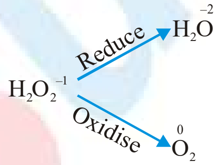
$$M_1 \times vf_1 \times V_1 = M_2 \times vf_2 \times V_2$$

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

$\therefore$ $V_1 = 50$ mL.

HYDROGEN PEROXIDE (H_2O_2)

H_2O_2 can behave both like oxidising and reducing agents in both the medium (acidic and basic).



EDUBULL KEY POINTS

(I) Oxidising agent : (H_2O_2)

(a) Acidic medium :

$$2e^- + 2H^+ + H_2O_2 \xrightarrow{\frac{3}{4}(R)} 2H_2O$$

v.f. = 2

(b) Basic medium :

$$2e^- + H_2O_2 \longrightarrow 2OH^-$$

v.f. = 2

(II) Reducing agent : (H_2O_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 10 V, 20 V, 30 V etc.
20V H_2O_2 means one litre of this sample of H_2O_2 on decomposition gives 20 L of O_2 gas at S.T.P.

$$\text{Normality of } H_2O_2 \text{ (N)} = \frac{\text{Volume, strength of } H_2O_2}{5.6}$$

✈ $$M_{H_2O_2} = \frac{N_{H_2O_2}}{\text{v.f}} = \frac{N_{H_2O_2}}{2}$$

- $$\text{Molarity of } H_2O_2 \text{ (M)} = \frac{\text{Volume, strength of } H_2O_2}{11.2}$$

Strength (in g/L) : Denoted by S

Strength = molarity × mol. wt.
= molarity × 34
Strength = Normality × Eq. weight.
= Normality × 17

Ex : 20 mL of H_2O_2 after acidification with dil H_2SO_4 required 30 mL of $\frac{N}{12}$ $KMnO_4$ for complete oxidation. The strength of H_2O_2 solution is [Molar mass of H_2O_2 = 34]

Sol : $30 \times \frac{1}{12} = 20 \times N'$

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

∴ strength = N' × equivalent mass = $\frac{1}{8} \times 17 = 2.12$ 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 chloride & sulphates of Ca & Mg. There are some method by which we can softening the water

(a) by boiling : $2HCO_3^- \rightarrow H_2O + CO_2 + CO_3^{2-}$ **or**
by slaked lime : $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O$
$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$
(b) By Washing Soda : $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$
(c) By ion exchange resins : $Na_2R + Ca^{2+} \rightarrow CaR + 2Na^+$

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 are present in every 1000000 g 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.

Ex. 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 requires to purify 1000 litre water.

Sol. 0.00012% $MgSO_4$ = 1 mg $CaCO_3$ 1 L water

0.000111% $CaCl_2$ = 1 mg $CaCO_3$ 1 L water

hardness = 2 ppm and mm of Na_2CO_3 require is 20

- **Strength of Oleum**

Oleum is SO_3 dissolved in 100% H_2SO_4. Sometimes, oleum is reported as more than 100% by weight, say y% (where y > 100). This means that (y – 100) grams of water, when added to 100 g of given oleum sample, will combine with all the free SO_3 in the oleum to give 100% sulphuric acid. Hence weight % of free SO_3 in oleum = 80(y – 100)/18

CALCULATION OF AVAILABLE CHLORINE FROM A SAMPLE OF BLEACHING POWDER

The weight % of available Cl_2 from the given sample of bleaching powder on reaction with dil acids or CO_2 is called available chlorine.

$$CaOCl_2 + H_2SO_4 \rightarrow CaSO_4 + H_2O + Cl_2$$

$$CaOCl_2 + 2HCl \rightarrow CaCl_2 + H_2O + Cl_2$$

$$CaOCl_2 + 2H_3CCOOH \rightarrow Ca(CH_3COO)_2 + H_2O + Cl_2$$

$$CaOCl_2 + CO_2 \rightarrow CaCO_3 + Cl_2$$

- **Method of determination**

$$\text{Bleaching powder} + CH_3COOH + KI \xrightarrow{\text{or } KI_3} KI_3 \ \frac{\text{starch}}{\text{Hypo}} \ \text{end point (Blue} \rightarrow \text{colourless)}$$

$$\% \text{ of } Cl_2 = \frac{3.55 \times x \times V(mL)}{W(g)}$$

where x = molarity of hypo solution

v = mL of hypo solution used in titration.

Ex : 3.55 g sample of bleaching powder suspended in H_2O was treated with enough acetic acid and KI solution. Iodine thus liberated requires 80 mL of 0.2 M hypo for titration. Calculate the % of available chlorine.

[Available Chlorine = mass of chlorine liberated / mass of bleaching powder × 100]

Sol : moles of iodine = moles of chlorine = $\frac{80 \times 0.2}{2} \times 10^{-3} = 8 \times 10^{-3}$

so required % = $\frac{8 \times 71 \times 10^{-3}}{3.55} \times 100\% = 16\%$

FOR ACID-BASE (NEUTRALIZATION REACTION) OR REDOX REACTION

$N_1V_1 = N_2V_2$ is always true.

But $M_1V_1 = M_2V_2$ (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

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

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

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, $2AgNO_3 + MgCl_2 \rightarrow Mg(NO_3)_2 + 2AgCl$

  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	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	5	$E = \frac{M}{5}$
MnO_4^-(O.A.)	MnO_2 in neutral medium	$MnO_4^- + 3e^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$	3	$E = \frac{M}{3}$
MnO_4^-(O.A.)	MnO_4^{2-} in basic medium	$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$	1	$E = \frac{M}{1}$
$Cr_2O_7^{2-}$(O.A.)	Cr^{3+} in acidic medium	$CrO_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	6	$E = \frac{M}{6}$
MnO_2(O.A.)	Mn^{2+} in acidic medium	$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	2	$E = \frac{M}{2}$
Cl_2 (O.A.) in bleaching powder	Cl^-	$Cl_2 + 2e^- \longrightarrow 2Cl^-$	2	$E = \frac{M}{2}$
$CuSO_4$ (O.A.) in iodometric titration	Cu^+	$Cu^{2+} + e^- \longrightarrow Cu^+$	1	$E = \frac{M}{1}$
$S_2O_3^{2-}$ (R.A.)	$S_4O_6^{2-}$	$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$	2 (for two molecules)	$E = \frac{2M}{2} = M$

H_2O_2(O.A.)	H_2O	$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	2	$E = \frac{M}{2}$
H_2O_2(R.A.)	O_2	$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$ (O.N. of oxygen in H_2O_2 is –1 per atom)	2	$E = \frac{M}{2}$
Fe^{2+}(R.A.)	Fe^{3+}	$Fe^{2+} \longrightarrow Fe^{3+} + e^-$	1	$E = \frac{M}{1}$

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

(I) $KMnO_4 \xrightarrow{H^+} Mn^{2+}$ (II) $KMnO_4 \xrightarrow{H_2O} Mn^{4+}$

(III) $KMnO_4 \xrightarrow{OH^-} Mn^{6+}$ (IV) $K_2Cr_2O_7 \xrightarrow{H^+} Cr^{3+}$

(V) $C_2O_4^{2-} \rightarrow CO_2$ (VI) $FeSO_4 \rightarrow Fe_2O_3$

(VII) $Fe_2O_3 \rightarrow FeSO_4$

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, $K_2Cr_2O_7$ 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, $C_2O_4^{2-}$ (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 ?

$Ba_3(PO_4)_2$ and $AlCl_3$

Sol. n-factor of $Ba_3(PO_4)_2 = 3 \times (+2) = 6 = n_1$

While n-factor of $AlCl_3 = 1 \times (+3) = 3 = n_2$

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

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

$\therefore$ Molar ratio in which $Ba_3(PO_4)_2$ 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.

$\therefore$ $N_1V_1 = N_2V_2$, where N_2 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. $0.4 \times 5 \times V = 0.05 \times 50$

$V = 1.25$ 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 Na_2CO_3 = x g

Weight of K_2CO_3 = y g

$\therefore$ $x + y = 1.20$ g ....(I)

For neutralization reaction of 100 mL

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

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

$\therefore$ $69x + 53y = 73.14$ ....(II)

From Eqs. (I) and (II), we get

$x = 0.5962$ g

$y = 0.604$ g

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

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

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

$\Rightarrow$ Meq. of $BaCO_3 = 40 \times 0.1 = 4$

$$\frac{W_{BaCO_3}}{M_{BaCO_3}} \times 1000 = 40 \times 0.1 = 4$$

$$\frac{W_{BaCO_3}}{197} \times 2 \times 1000 = 4$$

$$\therefore W_{BaCO_3} = 0.394 \text{ g}$$

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 ≥ 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_1V_1.

$\therefore$ gm. equivalents of A initially $= N_1V_1$

gm. equivalents of B used in the second titration $= N_1V_2$

$\therefore$ gm. equivalents of A left in excess after reacting with C $= N_1V_2$

gm. equivalents of A that reacted with C $= N_1V_1 - N_1V_2$

If the n-factor of C is x, then the moles of pure C $= \dfrac{N_1V_1 - N_1V_2}{x}$

$\therefore$ The weight of C $= \dfrac{N_1V_1 - N_1V_2}{x} \times$ Molecular weight of C

$\therefore$ Percentage of C $= \dfrac{N_1V_1 - N_1V_2}{x} \times \dfrac{\text{Molecular wt. of C}}{w} \times 100$

SOME REDOX TITRATIONS (EXCLUDING IODOMETRIC / IODIMETRIC)

Estimation of	By titrating with	Reactions	Relation *between O.A. and R.A.
Fe^{2+}	MnO_4^-	$Fe^{2+} \longrightarrow Fe^{3+} + e^-$ $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	$5Fe^{2+} \equiv MnO_4^-$ Eq. wt. $Fe^{2+} = M/1$ Eq. wt. $MnO_4^- = M/5$
Fe^{2+}	$Cr_2O_7^{2-}$	$Fe^{2+} \longrightarrow Fe^{3+} + e^-$ $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	$6Fe^{2+} \equiv Cr_2O_7^{2-}$ Eq. wt. $Cr_2O_7^{2-} = M/6$
$C_2O_4^{2-}$	MnO_4^-	$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$ $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O$	$5C_2O_4^{2-} \equiv 2MnO_4^-$ Eq. wt. $C_2O_4^{2-} = M/2$ Eq. wt. $MnO_4^- = M/5$
H_2O_2	MnO_4^-	$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$ $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	$5H_2O_2 \equiv 2MnO_4^-$ Eq. wt. $H_2O_2 = M/2$ Eq. wt. $MnO_4^- = M/5$
As_2O_3	MnO_4^-	$As_2O_3 + 5H_2O \rightarrow 2AsO_4^{3-} + 10H^+ + 4e^-$	Eq. wt. $As_2O_3 = M/4$
AsO_3^{3-}	BrO_3^-	$AsO_3^{3-} + H_2O \longrightarrow AsO_4^{3-} + 2H^+ + 2e^-$ $BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O$	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 × 0.5 = 5

Milli eq. of NaOH consumed = Milli eq. of HCl in excess = 10 × 0.2 = 2

$\therefore$ Milli eq. of HCl consumed = Milli eq. of $Ba(OH)_2$ = 5 – 2 = 3

$\therefore$ 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 $KMnO_4$ required 32 mL of the solution : Find the % of MnO_2 in the sample and also the percentage of available oxygen.

Sol. Redox changes are

$$C_2O_4^{2-} \longrightarrow 2CO_2 \qquad \text{(n-factor = 2)}$$
$$MnO_4^{-} \longrightarrow Mn^{2+} \qquad \text{(n-factor = 5)}$$
$$MnO_2 \longrightarrow Mn^{2+} \qquad \text{(n-factor = 2)}$$

Meq. of MnO_2 = Meq. of oxalic acid taken - Meq. of oxalic acid left

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

$$\frac{W_{MnO_2}}{M_{MnO_2}} \times 2 \times 1000 = 18 \Rightarrow \frac{W_{MnO_2}}{87} \times 2 \times 1000 = 18,$$

$\therefore \quad W_{MnO_2} = 0.7821$ g

$\therefore \quad \% \text{ of } MnO_2 = \frac{0.7821}{3.2} \times 100 = 24.44$ %

Meq. of MnO_2 = Meq. of O_2

$$\frac{W_{O_2}}{16} \times 2 \times 1000 = 18, \therefore \; W_{O_2} = 0.144 \text{ g}$$

$$\% \text{ of available } O_2 = \frac{0.144}{3.2} \times 100 = 4.5$$

Double titration

The method involves two indicators (Indicators are substances that change their colour when a reaction is complete) phenolphthalein and methyl orange. This is a titration of specific compounds. Let us consider a solid mixture of NaOH, Na_2CO_3 and inert impurities weighing w g. You are asked to find out the % composition of mixture. You are also given a reagent that can react with the sample say, HCl along with its concentration (M_1)

We first dissolve the mixture in water to make a solution and then we add two indicators in it, namely, phenolphthalein and methyl orange, Now, we titrate this solution with HCl.

NaOH is a strong base while Na_2CO_3 is a weak base. So, it is safe to assume that NaOH reacts completely and only then Na_2CO_3 reacts.

$NaOH + HCl \rightarrow NaCl + H_2O$

Once NaOH has reacted, it is the turn of Na_2CO_3 to react. It reacts with HCl in two steps :

$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$ and then,

$NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$

As can be seen, when we go on adding more and more of HCl, the pH of the solution keeps on falling. When Na_2CO_3 is converted to $NaHCO_3$, completely, the solution is weakly basic due to presence of $NaHCO_3$ (which is a weaker base as compared to Na_2CO_3). At this instant phenolphthalein changes colour since it requires this weakly basic solution to change its colour. Therefore, remember that phenolphthalein changes colour only when the weakly basic $NaHCO_3$ is present. As we keep adding HCl, the pH again falls and when all the $NaHCO_3$ reacts to form NaCl, CO_2 and H_2O, the solution becomes weakly acidic due to the presence of the weak acid H_2CO_3 ($CO_2 + H_2O$). At this instance, methyl orange changes colour since it requires this weakly acidic solution to do so. Therefore, remember methyl orange changes colour only when H_2CO_3 is present.

Now, let us assume that the volume of HCl used up for the first and the second reaction, i.e., $NaOH + HCl \rightarrow NaCl + H_2O$ and $Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$ be V_1 (this is the volume of HCl from the begining of the titation up to the point when phenolphthalein changes colour).

Let, the volume of HCl required for the last reacton, i.e. $NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$ be V_2 (this is the volume of HCl from the point where phenolphthalein had changed colour up to the point when methyl orange changes colour). Then,

Moles of HCl used for reacting with $NaHCO_3$ = Moles of $NaHCO_3$ reacted = M_1V_2

Moles of $NaHCO_3$ produced by the $Na_2CO_3 = M_1V_2$

Moles of Na_2CO_3 that gave M_1V_2 moles of $NaHCO_3 = M_1V_2$

Mass of $Na_2CO_3 = M_1V_2 \times 106$

$$\% Na_2CO_3 = \frac{M_1V_2 \times 106}{w} \times 100$$

Moles of HCl used for the first two reactions = M_1V_1

Moles of $Na_2CO_3 = M_1V_2$

Moles of HCl used for reacting with $Na_2CO_3 = M_1V_2$

Moles of HCl used for reacting with only NaOH = $M_1V_1 - M_1V_2$

$\therefore$ Moles of NaOH = $M_1V_1 - M_1V_2$

Mass of NaOH = $(M_1V_1 - M_1V_2) \times 40$

$$\% NaOH = \frac{(M_1V_1 - M_1V_2) \times 40}{w} \times 100$$

WORKING RANGE OF FEW INDICATORS

Indicator	pH range	Behaving as
Phenolphthalein	8 – 10	Weak organic acid
Methyl orange	3 – 4.4	Weak organic base

Thus, methyl orange with lower pH range can indicate complete neutralization of all types of bases. Extent of reaction for different bases with acid (HCl) using these two indicators is summarized below :

	Phenolphthalein	Methyl orange
NaOH	100% reaction is indicated $NaOH + HCl \longrightarrow NaCl + H_2O$	100% reaction is indicated $NaOH + HCl \longrightarrow NaCl + H_2O$
Na_2CO_3	50% reaction upto $NaHCO_3$ stage is indicated $Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$	100% reaction is indicated $Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$
$NaHCO_3$	No reaction is indicated	100% reaction is indicated $NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$

Ex. 0.4 g of a mixture of NaOH and Na_2CO_3 and inert impurities was first titrated with phenolphthalein and N/10 HCl, 17.5 mL of HCl was required at the end point. After this methyl orange was added and 1.5 mL of same HCl was again required for next end point. Find out percentage of NaOH and Na_2CO_3 in the mixture.

Sol. Let W_1 g NaOH and W_2 g Na_2CO_3 was present in mixture. At phenolphthalein end point,

$$\left(\frac{W_1}{40} + \frac{1}{2} \times \frac{W_2}{53}\right) = \frac{1}{10} \times 17.5 \times 10^{-3} \qquad \text{.........(1)}$$

At second end point following reaction takes place

Eq. of $NaHCO_3$ = Eq. of HCl used (in second titration)

$$= \frac{1}{2} \text{ Eq. of } Na_2CO_3$$

$$\frac{1}{2} \times \frac{W_2}{53} = 1.5 \times \frac{1}{10} \times 10^{-3}$$

$W_2 = 0.01590$ g

Putting the value of W_2 in Eq. (1) we get

$W_1 = 0.064$ g

$$\text{Percentage of NaOH} = \frac{0.064}{0.4} \times 100 = 16\%$$

$$\text{Percentage of } Na_2CO_3 = \frac{0.01590}{0.4} \times 100 = 3.975\ \%$$

Iodometric and Iodimetric Titration

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

$I_2 + 2e^- \longrightarrow 2I^-$ (reduction)

$2I^- \longrightarrow I_2 + 2e^-$ (oxidation)

These are divided into two types :

Iodometic 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.

$KI + \text{oxidizing agent} \longrightarrow I_2$

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.

$I_2 + 2NaS_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$

$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$

$K_4Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O + 3I_2$

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 :

$KI + I_2 \longrightarrow KI_3$ (Potassium triiodide)

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 $Na_2S_2O_3.5H_2O$)

Estimation of	Reaction	Relation between O.A. and R.A.
I_2	$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$ or $I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$	$I_2 = 2I \equiv 2Na_2S_2O_3$ Eq. wt. of $Na_2S_2O_3 = M/1$
$CuSO_4$	$2CuSO_4 + 4KI \longrightarrow 2Cu_2I_2 + 2K_2SO_4 + I_2$ $Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$ (White ppt.)	$2CuSO_4 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$ Eq. wt. of $CuSO_4 = M/1$
$CaOCl_2$	$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$ $Cl_2 + 2KI \longrightarrow 2KCl + I_2$ $Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$	$CaOCl_2 \equiv Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$ Eq. wt. of $CaOCl_2 = M/2$
MnO_2	$MnO_2 + 4HCl\,(conc) \xrightarrow{\Delta} MnCl_2 + Cl_2 + 2H_2O$ $Cl_2 + 2KI \longrightarrow 2KCl + I_2$ or $MnO_2 + 4H^+ + 2Cl^- \longrightarrow Mn^{2+} + 2H_2O + Cl_2$ $Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$	$MnO_2 \equiv Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$ Eq. wt. of $MnO_2 = M/2$
IO_3^-	$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$	$IO_3^- \equiv 3I_2 \equiv 6I \equiv 6Na_2S_2O_3$ Eq. wt. of $IO_3^- = M/6$
H_2O_2	$H_2O_2 + 2I^- + 2H^+ \longrightarrow I_2 + 2H_2O$	$H_2O_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$ Eq. wt. of $H_2O_2 = M/2$
Cl_2	$Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$	$Cl_2 \equiv I_2 \equiv 2I \equiv 2Na_2S_2O_3$ Eq. wt. of $Cl_2 = M/2$
O_3	$O_3 + 6I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$	$O_3 \equiv 3I_2 \equiv 6I \equiv 6Na_2S_2O_3$ Eq. wt. of $O_3 = M/6$
$Cr_2O_7^{2-}$	$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 3I_2 + 2Cr^{3+} + 7H_2O$	$Cr_2O_7^{2-} \equiv 3I_2 \equiv 6I$ Eq. wt. of $Cr_2O_7^{2-}$
MnO_4^-	$2MnO_4^- + 10I^- + 16H^+ \longrightarrow 2MnO_4^- + 5I_2 + 8H_2O$	$2MnO_4^- \equiv 5I_2 \equiv 10I$ Eq. wt. of $MnO_4^- = M/5$
BrO_3^-	$BrO_3^- + 6I^- + 6H^+ \longrightarrow Br^- + 3I_2 + 3H_2O$	$BrO_3^- \equiv 3I_2 \equiv I_2$ Eq. wt. of $BrO_3^- = M/6$
As(V)	$H_3AsO_4 + 2I^- + 2H^+ \longrightarrow H_3AsO_3 + H_2O + I_2$	$H_3AsO_4 \equiv I_2 \equiv 2I$ Eq. wt. of $H_3AsO_4 = M/2$

SOME IODIMETRIC TITRATION (TITRATING SOLUTIONS IS I_2 IN KI)

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

Ex. The sulphur content of a steel sample is determined by converting it to H_2S gas, absorbing the H_2S in 10 mL of 0.005 M I_2 and then back titrating the excess I_2 with 0.002 M $Na_2S_2O_3$. If 10 mL $Na_2S_2O_3$ is required for the titration, how many milligrams of sulphur are contained in the sample?

Reactions :

$H_2S + I_2 \longrightarrow S + 2I^- + 2H^+$

$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$

Sol. Used millimoles of I_2 = (m.moles of I_2 taken initially) – $\dfrac{\text{m.moles of hypo used}}{2}$

$$= 0.005 \times 10 - 0.002 \times \frac{10}{2}$$

$$= 0.04 = \text{millimoles of } H_2S$$

$\therefore$ weight of sulphur $= 0.04 \times 10^{-3} \times 32 \times 10^3$ mg $= 1.28$ mg.

Calculation of Available Chlorine from a sample of Bleaching Powder

The weight of available Cl_2 released from the given sample of bleaching powder on reaction with dilute acids or CO_2 is called available chlorine.

$$CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2$$

$$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$$

$$CaOCl_2 + 2CH_3COOH \longrightarrow Ca(CH_3COO)_2 + H_2O + Cl_2$$

$$CaOCl_2 + CO_2 \longrightarrow CaCO_3 + Cl_2$$

Method of determination

$$\underset{\text{(Sample of bleaching powder)}}{CaOCl_2} + 2CH_3COOH \longrightarrow Ca(CH_3COO)_2 + H_2O + Cl_2$$

$$Cl_2 + 2KI \longrightarrow 2KCl + I_2$$

$$\underset{\text{v.f.} = 2}{I_2} + \underset{\text{v.f.} = 1}{2Na_2S_2O_3} \xrightarrow{\text{Starch as indicator}} Na_2S_4O_6 + 2NaI$$

End point is indicated by disappearance of blue colour.

Let M = Molarity of hypo ($Na_2S_2O_3$) solution

∴ millimoles of Cl_2 produced = m.moles of I_2 used by hypo

$$= \frac{M \times V}{2} \quad \text{where} \quad V = \text{vol of hypo solution used in ml.}$$

$$\text{mass of } Cl_2 \text{ produced} = \frac{M \times V \times 10^{-3}}{2} \times 71$$

$$= 35.5 \times M \times V \times 10^{-3}$$

$$\therefore \quad \text{\% of available chlorine} = \frac{35.5 \times M \times V \times 10^{-3}}{W} \times 100$$

where W = amount of belaching powder taken in g.

or $$\textbf{\% of available } \mathbf{Cl_2} = \frac{3.55 \times M \times V}{W}$$

Ex. 3.55 g sample of bleaching powder suspended in H_2O was treated with enough acetic acid and KI solution. Iodine thus liberated required 80 mL of 0.2 M hypo for titration. Calculate the % of available chlorine.

Sol. $$\% \text{ of } Cl_2 = \frac{3.55 \times 0.2 \times 80}{3.55} = 16\%$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

   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) $= \dfrac{W_s \times 1000}{E_s \times V} = \dfrac{x \times d \times 1000}{E_s}$

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

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

Equivalents of solute = N × V(L)

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

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.

$M_1V_1 = M_2V_2$

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

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

Normality equation : According to the law of equivalence, the substances combine together in the ratio of their equivalent masses $\dfrac{\text{wt. of A}}{\text{wt. of B}} = \dfrac{\text{Eq. wt. of A}}{\text{Eq. wt. of B}}$

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

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

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

Number of gram equivalents of B $= \dfrac{N_B V_B}{1000}$

$\Rightarrow \quad \dfrac{N_A V_A}{1000} = \dfrac{N_B V_B}{1000}$

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

The above equation is called normality equation.

7. Normality (N) = Molarity (M) × n

(where n = n-factor)

For acid-base (neutralization reaction or redox reaction)

$N_1V_1 = N_2V_2$ always true

But $M_1V_1 = M_2V_2$ (may or may not be true)

But $M_1n_1V_1 = M_2n_2V_2$ (always true where n-terms represent n-factor)

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

9. Strength of solution (S) = N × Eq.wt.
= M × mol. wt.