Redox Reaction (Equivalent Concept & Titration)

Oxidation & Reduction

Let us do a comparative study of oxidation and reduction :

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

Oxidation Number

- It is an imaginary or apparent charge developed over atom of an element when it goes from its elemental free state to combined state in molecules.
- It is calculated on basis of an arbitrary set of rules.
- It is a relative charge in a particular bonded state.
- In order to keep track of electron-shifts in chemical reactions involving formation of compounds, a more practical method of using oxidation number has been developed.
- In this method, it is always assumed that there is a complete transfer of electron from a less electronegative atom to a more electronegative atom.

Rules governing oxidation number

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

- **Fluorine atom :**
  Fluorine is most electronegative atom (known). It always has oxidation number equal to –1 in all its compounds
- **Oxygen atom :**
  In general and as well as in its oxides , oxygen atom has oxidation number equal to –2.

In case of

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

(ii) super oxide (e.g. KO_2) is –1/2

(iii) ozonide (e.g. KO_3) is –1/3

(iv) in OF_2 is + 2 & in O_2F_2 is +1

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

In general, all halogen atoms (Cl, Br , I) have oxidation number equal to –1. But if halogen atom is attached with a more electronegative atom than halogen atom, then it will show positive oxidation numbers.

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

- **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
  e.g. $\overset{0}{O}_2$, $\overset{0}{S}_8$, $\overset{0}{P}_4$,$\overset{0}{O}_3$
- 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)
  e.g. N- atom belongs to 15th group in the periodic table, therefore as per rule, its oxidation number may vary from
  –3 to +5 ($\overset{-3}{N}H_3$,$\overset{+2}{N}O$, $\overset{+3}{N_2}O_3$, $\overset{+4}{N}O_2$, $\overset{+5}{N_2}O_5$)
- 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 :

Solved Examples

Example-1 ***Calculate oxidation number of underlined element*** **:**

(a) $Na_2\underline{S}_2O_3$ **(b) $Na_2\underline{S}_4O_6$**

Solution. (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

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

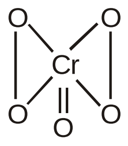
$x = +2.5$

❍ 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.

Miscellaneous Examples :

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

- The structure of CrO_5 is

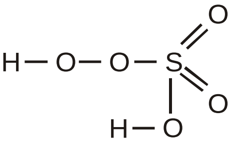


From the structure, it is evident that in CrO_5 there are two peroxide linkages and one double bond. The contribution of each peroxide linkage is –2. Let the oxidation number of Cr is x.

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

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

- The structure of H_2SO_5 is



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

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

or x + 2 – 8 = 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 :

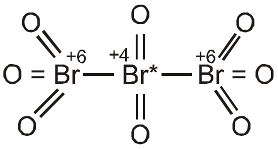
- ○ The element marked with asterisk (*) in each species is exhibiting different oxidation number from rest of the atoms of the same element in each of the species. This reveals that in C_3O_2, two carbon atoms are present in +2 oxidation state each whereas the third one is present in zero oxidation 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

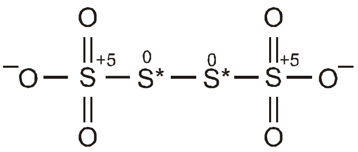
(Carbon suboxide)

- ○ 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.

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

- **Reducing agent or Reductant :**

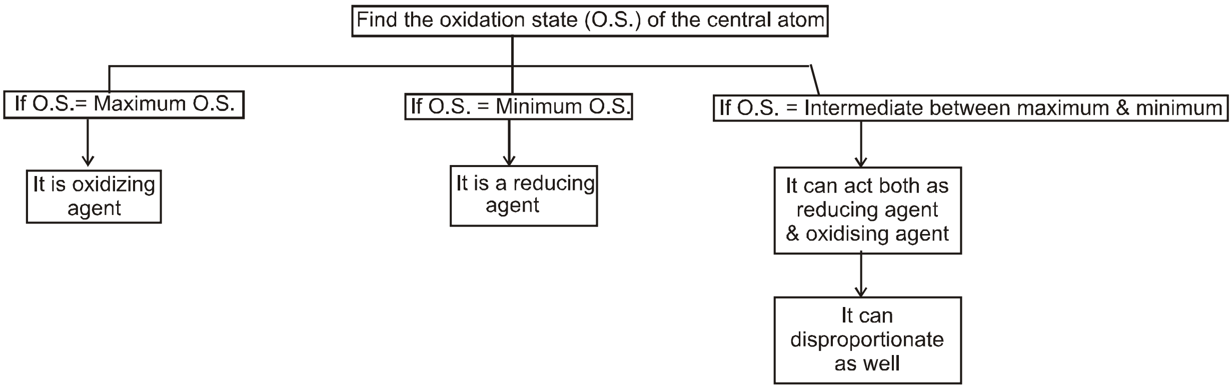
  Reducing agents are those compounds which can reduce other and oxidise itself during the chemical reaction. Those reagents in which for an element, oxidation number increases or which undergoes loss of electrons in a redox reaction are termed as reductants.

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

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

  e.g. H_2O_2, NO_2^-

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



Redox reaction

A reaction in which oxidation and reduction simultaneously take place is called a redox reaction

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

e.g. $10\overset{+2}{Fe}SO_4 + 2K\overset{+5}{Mn}O_4 + 8H_2SO_4 \longrightarrow 5\overset{+3}{Fe}_2(SO_4)_3 + 2\overset{+2}{Mn}SO_4 + K_2SO_4 + 8H_2O$

Disproportionation Reaction :

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

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

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

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

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

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. $X_2 + OH^-(\text{dil.}) \longrightarrow X^- + XO^-$ (X = Cl, Br, I)
3. $X_2 + OH^-(\text{conc.}) \longrightarrow X^- + XO_3^-$

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

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

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

4. $(CN)_2 + OH^- \longrightarrow CN^- + OCN^-$
5. $P_4 + OH^- \longrightarrow PH_3 + H_2PO_2^-$
6. $S_8 + OH^- \longrightarrow S^{2-} + S_2O_3^{2-}$
7. $MnO_4^{2-} \longrightarrow MnO_4^- + MnO_2$
8. Oxyacids of Phosphorus (+1, +3 oxidation number)

   $H_3PO_2 \longrightarrow PH_3 + H_3PO_3$

   $H_3PO_3 \longrightarrow PH_3 + H_3PO_4$
9. Oxyacids of Chlorine(Halogens)(+1, +3, +5 Oxidation number)

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

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

   $ClO_3^- \longrightarrow Cl^- + ClO_4^-$
10. $HNO_2 \longrightarrow NO + HNO_3$

- 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 reactions

All balanced equations must satisfy two criteria.

1. Atom balance (mass balance) :

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

2. Charge balance :

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

There are two methods for balancing the redox equations :

1. Oxidation - number change method
2. Ion electron method or half cell method

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

Ion electron method :

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

(a) Acidic medium (b) Basic medium

- **Balancing in acidic medium**

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

Solved Examples

Example-2 Balance the following redox reaction :

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

Solution. **Step–I** Assign the oxidation number to each element 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 undergoing either oxidation or reduction.

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

Step III :

Now identify the oxidation / reduction occuring in the reaction

undergoes reduction.

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

undergoes oxidation.

Step IV : Spilt 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

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

Fe & Mn atoms are balanced on both side.

Step VI :

Now balance O & H atom by H_2O & H^+ respectively by the following way : For one excess oxygen atom, add one H_2O on the other side and two H^+ on the same side.

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

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

Step VII :

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

$Fe^{2+} \xrightarrow{\text{oxidation}} Fe^{3+} + e^-$ ....(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 multiplying both the half reactions with a suitable factor and finally the half reactions are added to give the overall balanced reaction.

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

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

$$\begin{array}{l} 5e^- + 8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O \quad ....(2)\ \times 1 \\ \hline 5Fe^{2+} + 8H^+ + MnO_4^- \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O \end{array}$$

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

Step IX :

Now convert the Ionic reaction into molecular form by adding the elements or species, which are removed in step (2).
Now, by some manipulation, you will get :

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

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

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

Solved Examples

Example-3 Balance the following redox reaction in basic medium :

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

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

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

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

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

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

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

Finally you will get Finally you will get

$H_2O + ClO^- \longrightarrow Cl^- + 2OH^-$ ....(i) $4OH^- + CrO_2^- \longrightarrow CrO_4^{2-} + 2H_2O$ .... (ii)

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

Now from step VIII

$2e^- + H_2O + ClO^- \longrightarrow Cl^- + 2OH^-$ .... (i) ×3

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

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

Concept of equivalents

Equivalent mass of element

Number of parts by mass of an element which reacts or displaces from a compound 1.008 parts by mass of hydrogen, 8 parts by mass of oxygen and 35.5 parts by mass of chlorine, is known as the equivalent weight of that element.

e.g. $2Mg + O_2 \longrightarrow 2MgO$
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, $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$
65.5 g 32.75

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

$$Al + \frac{3}{2}Cl_2 \longrightarrow AlCl_3$$

27 g $\quad \frac{3}{2} \times 71$ g

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

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

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.

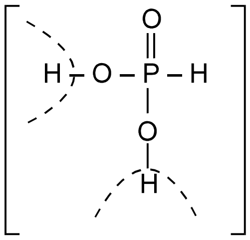
Valency factor calculation :

- **For Elements :**
  Valency factor = valency of the element.
- **For Acids :**
  Valency factor = number of replaceable H^+ ions per acid molecule

Solved Examples

Example-4

	HCl ,	H_2SO_4	H_3PO_4	H_3PO_3
Solution. Valency factor →	1	2	3	2
Eq. wt. (E) →	$\frac{M}{1}$	$\frac{M}{2}$	$\frac{M}{3}$	$\frac{M}{2}$



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

(assume 100% dissicoiation)

○ 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.

Solved Examples

Example-5

	NaOH,	KOH
Solution. 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

Solved Examples

Example-6 $2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$

Base Acid

Solution. Valency factor of base = 1

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

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

Solved Examples

Example-7 $NaOH + H_2SO_4 \longrightarrow NaHSO_4 + H_2O$

Base Acid

Solution. 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.

Solved Examples

Example-8 Na_2CO_3, $Fe_2(SO_4)_3$ $FeSO_4.7H_2O$

		Na_2CO_3	$Fe_2(SO_4)_3$	$FeSO_4.7H_2O$
Solution.	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

Solved Examples

Example-9 $Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$

Base Acid

Solution. 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 .

Solved Examples

Example-10 $KMnO_4 + H_2O_2 \longrightarrow Mn^{2+} + O_2$

Solution. 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 × V (in mL) = M × V (in mL) × n

or

- **milliequivalents = millimoles × n**

Solved Examples

Example-11 Calculate the normality of a solution containing 15.8 g of $KMnO_4$ in 50 mL acidic solution.

Solution. **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

Example-12 Calculate the normality of a solution containing 50 mL of 5 M solution of $K_2Cr_2O_7$ in acidic medium.

Solution. 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

Solved Examples

Example-13 Find the number of moles of $KMnO_4$ needed to oxidise one mole Cu_2S in acidic medium.

The reaction is $KMnO_4 + Cu_2S \longrightarrow Mn^{2+} + Cu^{2+} + SO_2$

Solution. From law of equivalence,
equivalents of Cu_2S = equivalents of $KMnO_4$
moles of Cu_2S × v.f. = moles of $kMnO_4$ × v.f.
1×8 = moles of $KMnO_4 \times 5$ $\Rightarrow$ moles of $KMnO_4$ **= 8/5**
($\therefore$ v.f. of $Cu_2S = 2\,(2 - 1) + 1\,(4 - (-2))) = 8$ and v.f. of $KMnO_4 = 1\,(7 - 2) = 5$)

Example-14 The number of moles of oxalate ions oxidized by one mole of MnO_4^- ion in acidic medium are :

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

Solution. 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.

Solved Examples

Example-15 How many millilitres of 0.02 M $KMnO_4$ solution would be required to exactly titrate 25 mL of 0.2 M $Fe(NO_3)_2$ solution in acidic medium ?

Solution. **Method -1 : Mole concept method**
Starting with 25 mL of 0.2 M Fe^{2+}, we can write :
Millimoles of Fe^{2+} = 25 x 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+}

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

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

$\therefore$ V_1 = 50 mL.

Titrations

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

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

There are two type of titrants :

- **Primary titrants/standard** - These reagents can be accurately weighed and their solutions are not to be standardised before use.
  Ex : Oxalic acid, $K_2Cr_2O_7$, $AgNO_3$, $CuSO_4$, ferrous ammonium sulphate, hypo etc.
- **Secondary titrants/standard** : These reagents cannot be accurately weighed and their solutions are to be standardised before use.
  Ex : NaOH, KOH, HCl, H_2SO_4, I_2, $KMnO_4$ etc.

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

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

At equivalence point :

$n_1V_1M_1 = n_2V_2M_2$

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

Type of Titrations :

- Acid-base titrations (to be studided in Ionic equilibrium)
- **Redox Titrations**

Some Common Redox Titrations

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

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

Permanganate Titrations :

- $KMnO_4$ is generally used as oxidising agent in acidic medium, generally provided by dilute H_2SO_4 .
- $KMnO_4$ works as self indicator persistent pink color is indication of end point.
- Mainly used for estimation of Fe^{2+} , oxalic acid ,oxalates, H_2O_2 etc.

Solved Examples

Example-16 Write the balanced reaction of titration of $KMnO_4$ Vs oxalic acid in presence of H_2SO_4.

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

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

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

Indicator : $KMnO_4$ acts as self indicator.

Example-17 Write the balanced reaction of titration of $KMnO_4$ Vs ferrous ammonium sulphate in presence of H_2SO_4.

Solution. Reaction : $2KMnO_4 + 10[FeSO_4(NH_4)_2SO_4.\ 6H_2O] + 8H_2SO_4 \longrightarrow$
$5Fe_2(SO_4)_3 + 10(NH_4)_2SO_4 + K_2SO_4 + 2MnSO_4 + 68H_2O$

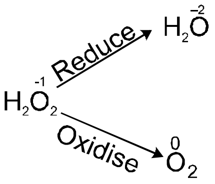
Redox Changes : $Fe^{2+} \longrightarrow Fe^{3+} + e \qquad \left(E_{FeSO_4} = \frac{M}{1}\right)$

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

Indicator : $KMnO_4$ acts as self indicator

Hydrogen peroxide (H_2O_2)

H_2O_2 can behave both like oxidising and reducing agent in both the mediums (acidic and basic).



- **Oxidising agent : ($H_2O_2 \rightarrow H_2O$)**

  Acidic medium : $2e^- + 2H^+ + H_2O_2 \longrightarrow 2H_2O$

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

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

  v.f = 2

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

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

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

$$\therefore \qquad M_{H_2O_2} = \frac{N_{H_2O_2}}{v.f.} = \frac{N_{H_2O_2}}{2}$$

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

  Strength (in g/L) : Denoted by S

  Strength = Molarity × Mol. wt = Molarity × 34

  Strength = Normality × Eq. weight = Normality × 17

Solved Examples

Example-18 20 mL of H_2O_2 after acidification with dilute H_2SO_4 required 30 mL of $\frac{N}{12}$ $KMnO_4$ for complete oxidation. Final the strength of H_2O_2 solution. [Molar mass of H_2O_2 = 34]

Solution. meq. of $KMnO_4$ = meq. of H_2O_2

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

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

$\therefore$ strength = $N' \times$ 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 chlorides & sulphates of Ca & Mg. There are some method by which we can soften the water sample.

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

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

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

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

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

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

Parts Per Million (ppm)

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

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

Solved Examples

Example-19 0.00012% $MgSO_4$ and 0.000111% $CaCl_2$ is present in water. What is the measured hardness of water and millimoles of washing soda required to purify water 1000 L water ?

Solution. Basis of calculation = 100 g hard water

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

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

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

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

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

$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$

$NaSO_4 + Na_2CO_3 \longrightarrow MgCO_3 + Na_2SO_4$

$\therefore$ Required Na_2CO_3 for 100g of water = $\left(\frac{0.00012}{120}+\frac{0.000111}{111}\right)$ mole

$= 2\times 10^{-6}$ mole

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

$= \frac{20}{1000}$ mole = 20 m mole