STOICHIOMETRY

BASIC DEFINITIONS OF ATOMIC MASS

(i) **Relative Atomic Mass:** It is the ratio of the mass of 1 atom of a substance and 1/12 of mass of 1 atom of C^{12} isotope. For atoms this is done by expressing mass of one atom with respect to a fixed standard. Dalton used hydrogen as the standard (H=1). Later on oxygen (O=16) replaced hydrogen as the reference. C-12 ISOTOPE OF CARBON IS LATEST CHOSEN STANDARD SINCE 1961.
Therefore relative atomic mass is given as

$$\text{Relative atomic mass (RAM)} = \frac{\text{mass of one atom of an element}}{\frac{1}{12} \times \text{mass of one } C^{12} \text{ atom}}$$

On Hydrogen scale :

$$\text{Relative atomic mass (RAM)} = \frac{\text{mass of one atom of the element}}{\text{mass of one H atom}}$$

Oxygen scale :

$$\text{Relative atomic mass (RAM)} = \frac{\text{mass of one atom of the element}}{\frac{1}{16} \times \text{mass of one } O-16 \text{ atom}}$$

(ii) **Atomic Mass Unit (Or amu):** The atomic mass unit (amu) is equal to one twelfth $\left(\frac{1}{12}\right)$ of the mass of one atom of carbon-12 isotope.

$$\therefore \quad 1\,\text{amu} = \frac{1}{12} \times \text{mass of one } C-12 \text{ atom}$$

☐ mass of one nucleon in C–12 atom
= 1.66×10^{-24} gm or 1.66×10^{-27} kg

Today, 'amu' has been replaced by 'u' which is known as unified mass.

(iii) **Atomic Mass:** It is the mass of 1 atom of a substance it is expressed in 'u'
Atomic mass = RAM × 1 u

Note: Relative atomic mass is nothing but the number of nucleons present in the atom

(iv) **Gram Atomic Mass:** The atomic mass of an element expressed in gram is called gram atomic mass of the element.
For example : Atomic mass of 'O' atom = mass of one 'O' atom = 16 u
gram atomic mass = mass of 6.02×10^{23} 'O' atoms
   = 16 u × 6.02×10^{23}
   = 16 × 1.66×10^{-24} g × 6.02×10^{23} = 16 g

(v) **Molecules:** It is the smallest particle of matter which has free existence. Molecules can be further divided into its constituents atoms by physical and chemical process.
Element   : H_2, O_2, O_3 etc.
Compound   : H_2SO_4, SO_3 etc.

(vi) **Molecular Mass:** It is the mass of one molecule

(vii) **Gram Molecular Mass:** The molecular mass of a substance expressed in gram is called the gram-molecular mass of the substance.   **Or**
It is also defined as mass of 6.02×10^{23} molecules   **Or**
It is also defined as the mass of one mole molecules. (molar mass)
For example : Molecular mass of O_2 molecules = mass of one O_2 molecule

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$$= 2\times \text{mass of one O atom}$$
$$= 2\times16 \text{ amu}$$
$$= 32 \text{ amu}$$

gram molecular mass $\quad = \text{mass of } 6.02\times10^{23} \text{ O}_2 \text{ molecules} = 32 \text{ amu} \times 6.02\times10^{23}$
$$= 32 \times 1.66 \times10^{-24} \text{ gm} \times 6.02 \times 10^{23} = 32 \text{ gm}$$

MOLES:

In 1971, the General conference on weights and measures, adopted mole as the seventh basic SI unit of the amount of a substance.

The term 'mole' is a Latin word which means heap or pile. A mole of atom is a collection of atoms whose total weight is equal to the gram atomic weight. As equal number of moles of different elements contain equal number of atoms, it is very easy to express the amount of a substance in terms of moles. Just as a dozen means twelve objects, in the similar fashion, a mole is a collection of a 'definite number' of particles, viz., atoms, molecules, ions or electrons. This 'definite number' is called Avogadro number which is equal to 6.023×10^{23}. Thus, a mole can be defined as, "the amount of a substance containing as many atoms, molecules, ions, electrons or other elementary entities as there are carbon atoms in exactly 12 g of C-12".

Nowadays, **gram-molecules and gram-atom are termed as a mole of molecules and a mole of atoms respectively, e.g., 1 gram-molecule of chlorine and 1 gram atom of chlorine are expressed as 1 mole of Cl$_2$ and 1 mole of Cl respectively.**

The number of moles can be calculated by a number of formulae depending upon the data given:

Number of moles of molecules $\quad = \dfrac{\text{weight of the substance in g}}{\text{Molar weight of the substance}}$

Number of moles of atoms $\quad = \dfrac{\text{weight of the element in g}}{\text{Molar atomic weight of the element}}$

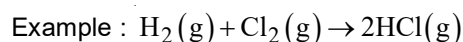Number of moles of gas $\quad = \dfrac{\text{Volume of the gas}}{\text{Molar volume at the given temperature and pressure}}$

THE LAWS OF CHEMICAL COMBINATIONS

(i)   Law of Conservation Of Mass:

In a chemical change total mass remains conserved.

i.e. mass before reaction is always equal to mass after reaction

Example : $\mathrm{H_2\left(g\right)+Cl_2\left(g\right)\rightarrow 2HCl\left(g\right)}$

Mass before reaction = 2+71 = 73 gm
Mass after reaction = 2 ×36.5 = 73

∵ mass before reaction = mass after reaction, hence it follows law of conservation of mass.

(ii)   Law of Constant or Definite Proportion:

All chemical compounds are found to have constant composition irrespective of their method of preparation or source.

For Example: In water (H$_2$O), hydrogen and oxygen combine in 2 : 1 molar ratio, this ratio remains constant whether it is tap water, river water or sea water or produced by any chemical reaction.

Illustration 1: **1.80 g of a certain metal burnt in oxygen gave 3.0 g of its oxide. 1.50 g of the same metal heated in steam gave 2.50 g of its oxide. The law shown by above data.**

(A) law of constant composition   (B) law of multiple proportion
(C) law of reciprocal proportion   (D) all

Solution :   (A)

In the first sample of oxide,
Weight of metal = 1.80 g
Weight of oxygen = (3.0–1.80) g = 1.2 g

$$\therefore \quad \frac{\text{wt of metal}}{\text{wt of oxygen}} = \frac{1.80g}{1.2g} = 1.5$$

In the second sample of the oxide,
Weight of metal = 1.50 g

Weight of oxygen = (2.50 - 1.50) g = 1 g $\qquad \therefore \quad \dfrac{\text{wt of metal}}{\text{wt of oxygen}} = \dfrac{1.50g}{1g} = 1.5$

Thus, in both samples of the oxide the proportions of the weights of the metal and oxygen a f i x e d . Hence the results follow the law of constant proportion.

(iii) Law of Multiple Proportion:

When one element combines with the other elements to form two or more different compounds, the mass of one element, which combines with a constant mass of the other, bear a simple ratio to one another.

For example, carbon and oxygen react together to form carbon monoxide and carbon dioxide. Here fixed mass of carbon (12gm) reacts with different masses of oxygen (16gm & 32gm). Hence ratio of masses of oxygen has ratio 16:32 or 1:2 which proves law of multiple proportion.

Illustration 2: Carbon is found to form two oxides, which contains 42.9% and 27.3% of carbon respectively. The law show by above data.

(A) law of constant composition   (B) law of multiple proportion
(C) law of reciprocal proportion   (D) all

Solution : (B)

I : To calculate the percentage composition of carbon and oxygen in each of the two oxides.

	First oxide	Second oxide	
Carbon	42.9%	27.3%	(Given)
Oxygen	57.1%	72.7%	

II : To calculate the masses of carbon which combine with a fixed mass i.e., one part by mass of oxygen in each of the two oxides.

In the first oxide, 57.1 parts by mass of oxygen combine with carbon = 42.9 parts.

$\therefore$ 1 part by mass of oxygen will combine with carbon $= \dfrac{42.9}{57.1} = 0.751$

In the second oxide 72.7 parts by mass of oxygen combine with carbon = 27.3 parts

$\therefore$ 1 part by mass of oxygen will combine with carbon $= \dfrac{27.3}{72.7} = 0.376$

III : To compare the masses of carbon which combine the same mass of oxygen in both the oxides. The ratio of the masses of carbon that combine with the same mass of oxygen (1 part) is 0.751 : 0.376 or 2 : 1

Since this is simple whole number ratio, so the above data illustrate the law of multiple proportions.

(iv)   Gay Lussac's Law

Gas react or formed in the simple ratio of their volume. Provided all measurement are in the same condition of temperature and pressure.

$$\underset{1\,\text{vol}}{H_2} + \underset{1\,\text{vol}}{Cl_2} \rightarrow \underset{2\,\text{vol}}{2HCl}$$
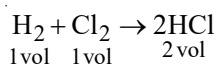
AVOGADRO'S HYPOTHESIS

Equal volume of all gases have equal number of molecules (not atoms) at same temperature and pressure conditions.

Mathematically, for ideal gases, $V \propto n$ (Constant T & P).

S.T.P. (Standard Temperature and Pressure)

At S.T.P. / N.T.P. condition: Temperature = 0°C or 273 K

Pressure = 1 atm = 760 mm of Hg

Volume of one mole of an ideal gas = 22.4 litres (experimentally determined)

DALTON'S ATOMIC THEORY

1. Matter is made up of very small indivisible particle called atoms.
2. All the atoms of a given element are identical in all respect i.e. mass, shape, size, etc.
3. Atoms cannot be created or destroyed by any chemical process.
4. Atoms of different elements are different in nature.
5. Atoms combine in a definite proportion to form molecules

PERCENTAGE COMPOSITION

Here we are going to find out the percentage of each element in the compound by knowing the molecular formula of compound.

We know that according to law of definite properties any sample of a pure compound always possess constant ratio with their combining elements.

$$\text{Percentage mass of an element} = \frac{\text{mass of that element in the compound}}{\text{molar mass of that compound}} \times 100$$

EMPIRICAL FORMULA FOR MOLECULAR FORMULA

We have just seen that known the molecular formula of the compound we can calculate percentage composition of the elements. Conversely if we know the percentage composition of the elements initially, we can calculate the relative number of atom of each element in molecules of the compound. This gives as the empirical formula of the compound. Further if the molecular mass is known then the molecular formula can easily be determined.

Thus, the empirical formula of a compound is a chemical formula showing the relative number of atoms in the simplest ratio, the molecular formula gives the actual number of atoms of each element in a molecule. The molecular formula is an integral multiple of the empirical formula.

i.e. molecular formula = empirical formula × n ; where $n = \dfrac{\text{molecular formula mass}}{\text{empirical formula mass}}$

Illustration 3: **Acetylene and benzene both have the empirical formula CH. The molecular masses of acetylene and benzene are 26 and 78 respectively. The molecular formula will be.**

(A) C_6H_6, C_2H_2　　　　(B) C_7H_7, C_2H_2　　　　(C) C_3H_6, C_4H_4　　　　(D) C_6H_6, C_6H_6

Solution : (A)

I : The empirical formula of the compounds is CH

∴　Empirical formula mass
= (1 ×10) + 1 = 13

Molecular mass = 26

II : To calculate the value of 'n'

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{26}{13} = 2$$

III : To calculate the molecular formula of the compound.

Molecular formula = n × (Empirical formula of the compound)
= 2 × CH = C_2H_2

Thus the molecular formula is C_2H_2
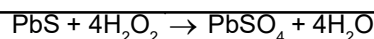
Similarly for benzene

To calculate the value of 'n'

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{78}{13} = 6$$

thus the molecular formula is 6 × CH = C_6H_6

SIGNIFICANCE OF CHEMICAL EQUATIONS

Let us consider a balanced chemical equation

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$$

This equation will provide us various quantitative informations:

(i) The molar ratio of reactants, i.e., PbS and H_2O_2 in which they react together is 1:4.

(ii) The molar ratio of the two products i.e., $PbSO_4$ and H_2O being formed in the reaction is also 1:4.

(iii) One mole of $PbSO_4$ and 4 moles of H_2O will be formed for each mole of PbS being consumed.

The stoichiometric coefficients of a balanced chemical equation is the molar ratio and not the weight ratio.

One can use the balanced chemical equation for quantitative (gravimetric or volumetric) estimation of reactants and products. But if one does not have the balanced equation, it is very difficult to calculate the amounts of reactants consumed or products being formed.

Illustration 4: **Calculate the mass of 90% pure MnO_2 to produce 35.5g of Cl_2 according to the following reaction. $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$**

    (A) 4.83 g   (B) 483g   (C) 48.3 g   (D) 0.483g

Solution: **(C)**

    $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$
     87g   71g
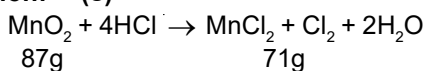
    $\because$ 71g Cl_2 is produced by 87g of MnO_2

    $\therefore$ 35.5g Cl_2 is produced = $\dfrac{87 \times 35.5}{712}$ = 43.5g

    90g pure MnO_2 is present in 100g sample

    $\therefore$ 43.5g pure MnO_2 = 48.3g

LIMITING REAGENT

The reactions in which more than one reactants are reacting and if they are not present in the same molar ratio as the balanced equation requires, then one has to find out the limiting reagent i.e., the reagent which is completely consumed in the reaction. All quantitative calculations are carried out with the help of limiting reagent only. Now, how to decide the limiting reagent of a reaction? Consider the following example.

Suppose you are given 5 moles of PbS and 18 moles of H_2O_2 and you have to calculate the maximum amount of $PbSO_4$ being produced.

The balanced equation is:
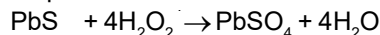
        $PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$
Initial moles 5 mol   18 mol

Now since 1 mol of PbS reacts completely with 4 moles of H_2O_2 to produce 1 mol of $PbSO_4$. Therefore, 5 moles of PbS will react with 20 moles of H_2O_2. But since moles of H_2O_2 is only 18. So, H_2O_{-2} will be the reagent, which will be consumed first, and hence H_2O_2 is the limiting reagent. If PbS had been the limiting reagent 5 mole of it would have given 5 moles of $PbSO_4$ but it is not so. As one can see from the balanced chemical equation that 1 mol of $PbSO_4$ is produced from 4 moles of H_2O_2. So 18 moles of H_2O_2 will produce 4.5 moles of $PbSO_4$.

So, one can define limiting reagent in another way,

"The reagent producing the least number of moles of products is the limiting reagent".

Illustration 5: 8 gm of methane is burnt with 4.48L of O_2 at STP. Find out the volume of CO_2 gas produced at STP and also the weight of CO_2 gas.

    (A) 22.4 L, 44 g   (B) 2.24 L, 4.4 g   (C) 1.12 L, 22 g   (D) 44.8 L, 88 g

Solution: **(B)**

The balanced chemical equation is

CH_4	+	$2O_2 \rightarrow$	CO_2	+	$2H_2O$
1 mol		2 mol	1 mol		
16 gm		2×22.4 L	22.4 L		
		44 gm			
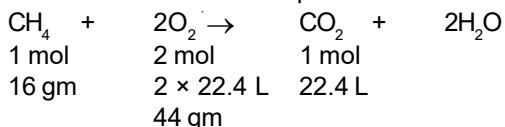
No. of moles of CH_4 = $\dfrac{8}{16} = 0.5 \, mol$

No. of moles of O_2 = $\dfrac{4.48L}{22.4L} = 0.2 mol$

Now since 1 mole of CH_4 requires 2 mol (i.e. 44.8 L) of O_2 for complete combustion. But the given moles of O_2 is only 0.2 mol. So, O_2 is the limiting reagent.

Again, since 2 moles of O_2 reacts with 1 mol of CH_4 to give 22.4 L of CO_2 at STP.

So 0.2 mole of O_2 will react with 0.1 mol of CH_4 to give 2.24 L of CO_2.

Weight of CO_2 produced = 0.1 mol × 44

= 4.4 gms of CO_2

REACTION IN SOLUTION (CONCENTRATION)

(i) Molarity (M): The no. of moles of solute present in one litre of solution is called the molarity (M).

Molarity = $\dfrac{\text{No. of moles of solute}}{\text{Volume of solution in litre}}$

or Molarity = $\dfrac{\text{weight of solute/molar mass of solute}}{\text{Volume of solution in Litre}}$

So, no. of moles of solute = Volume of solution (in litre) × Molarity of solution

Illustration 6: 149 gm of potassium chloride (KCl) is dissolved in 10 Lt of an aqueous solution. Determine the molarity of the solution (K = 39, Cl = 35.5)

(A) 0.3 M   (B) 0.1 M   (C) 0.4 M   (D) 0.2 M

Solution : (D)

Molar mass of KCl = 39+35.5 = 74.5 gm

∴ Moles of KCl $= \dfrac{149 gm / mole}{74.5 gm} = 2 mole$

∴ Molarity of the solution $= \dfrac{149 gm / mole}{74.5 gm} = 2 mole$

(ii) Molality (m): No. of moles of solute present in one kilogram of solvent is known as molality

Molality (m) = $\dfrac{\text{No. of moles of solute}}{\text{Wt. of solvent (in kg)}}$

Illustration 7: 225 gm of an aqueous solution contains 5 gm of urea. What is the concentration of the solution in terms of molality. (Mol. Weight of Urea = 60)

(A) 0.332   (B) 0.221   (C) 0.632   (D) 0.421

Solution : (A)

Mass of urea = 5 gm

Molecular mass of urea = 60

Number of moles of urea $= \dfrac{5}{60} = 0.083$

Mass of solvent = (255 – 5) = 250 gm

Molality of the solution $= \dfrac{\text{Number of moles of solute}}{\text{Mass of solvent in gram}} \times 1000 = \dfrac{0.083}{250} \times 1000 = 0.332$

(iii) Normality (N): No of equivalents of solute present in one litre of the solution is known as Normality (N).

$$\text{Normality (N)} = \frac{\text{Number of equivalents of solute}}{\text{Volume of solution in litre}}$$

$$= \frac{\text{Mass of solute/equivalent mass of solute}}{\text{Volume of solution in litre}}$$

No. of equivalent of solute = Volume of solution (in litre) × normality of solution
No. of milli equivalents of solute = Normality of solution × Volume of solution in millilitres
Equivalent weight = Molecular weight / n-factor
n-factor:
for an acid = basicity (no. of H^+ replaced)
for a base = acidity (no. of OH^- replaced)
for a redox reagent = no. of moles of electrons lost or gained per mole of compound

Illustration 8: Calculate the normality in 3.65 g of HCl in 200 ml of solution.
(A) 1 (B) 2 (C) 0.5 (D) 0.1

Solution : (C)

$$\text{Equivalent of HCl} = \frac{3.65}{36.5}$$

$$\text{Volume of solution} = 200 \text{ ml} = \frac{200}{1000} \text{ litre}$$

$$N = \frac{3.65 \times 1000}{36.5 \times 200} = 0.5$$

GRAVIMETRIC ANALYSIS

Gravimetric analysis is an analytical technique based on the measurements of mass of solid substances and/or volume of gaseous species. Gravimetric analysis is divided into three parts.
(i) Mass-Mass relationship
(ii) Mass-volume relationship
(iii) Volume-volume relationship

(i) **Mass-Mass Relationship:** It relates the mass of a species (reactant or product) with the mass of another species (reactants or product)
Let us consider a chemical reaction,

$$2NaHCO_3(s) \xrightarrow{\Delta} Na_2CO_3(s) + H_2O + CO_2(g)$$
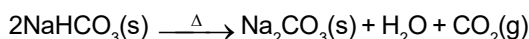
Suppose the mass of $NaHCO_3$ being heated is 'a' g and we want to calculate the weight of Na_2CO_3 being produced by heating of 'a' g of $NaHCO_3$.

$$\text{The moles of } NaHCO_3 = \frac{a}{84}$$

According to the above balanced equation 2 moles of $NaHCO_3$ upon heating gives 1 mole of Na_2CO_3. So,

$$\text{The no. of moles of } Na_2CO_3 \text{ produced} = \frac{1}{2} \times \frac{a}{84}$$

Thus, Weight of Na_2CO_3 produced = moles of Na_2CO_3 ´ Molecular weight of Na_2CO_3

$$= \frac{1}{2} \times \frac{a}{84} \times 106 = \frac{53a}{84} \text{ gms}$$

Illustration 9: By heating 10g of $CaCO_3$, 5.6g CaO is formed. What is the weight of CO_2 obtained in this reaction?
(A) 2.2 g (B) 2.3 g (C) 3.2 g (D) 4.4 g

Solution: **(D)**
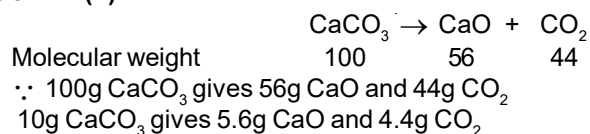
$$CaCO_3 \rightarrow CaO + CO_2$$

Molecular weight   100   56   44

∵ 100g $CaCO_3$ gives 56g CaO and 44g CO_2

10g $CaCO_3$ gives 5.6g CaO and 4.4g CO_2

(ii) **Mass-Volume Relationship:** It relates the mass of a species (reactant or product) and the volume of a gaseous species (reactant or product) involved in a chemical reaction. Suppose we are provided with 'a' gms of $NaHCO_3$ in a vessel of capacity V L and the vessel is heated, so that $NaHCO_3$ decomposes as

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$
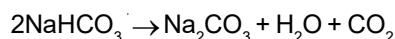
Now, we want to calculate the volume of CO_2 gas being produced.

Since 2 moles of $NaHCO_3$ gives 1 mole of CO_2 at STP. Thus

So volume of CO_2 produced = 22.4 litre at STP.

Illustration 10: Calculate the volume of hydrogen liberated at 27°C and 760 mm pressure by treating 1.2g of magnesium with excess of hydrochloric acid.

(A) 1.238 L   (B) 12.38 L   (C) 2.23 L   (D) 22.3 L

Solution: **(A)**

The balanced equation is

$Mg + 2HCl = MgCl_2 + H_2$
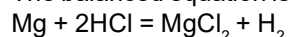
1 mole   1 mole

24g   22.4 litre at NTP

24g of Mg liberate hydrogen = 22.4 litre

1.2g of Mg will liberate hydrogen = $\dfrac{22.4}{24} \times 1.2$ = 1.12 litre

Volume of hydrogen under given condition can be calculated by applying $\dfrac{P_1 V_1}{T_1} = \dfrac{P_2 V_2}{T_2}$

P_1 = 760 mm P_2 = 760 mm

T_1 = 273 K T_2 = (27 + 273) = 300K

V_{-1} = 1.12 litres V_2 = ?

$V_2 = \dfrac{760 \times 1.12}{273} \times \dfrac{300}{760} = 1.2308 \text{litres}$

(iii) **Volume-Volume Relationship:** It relates the volume of gaseous species (reactants or products) with the volume of another gaseous species (reactant or product) involved in a chemical reaction.

Illustration 11: What volume of oxygen gas at NTP is necessary for complete combustion of 20 litre of propane measured at 0°C and 760 mm. pressure.

(A) 10L   (B) 100 L   (C) 200L   (D) 50 L

Solution: **(B)**

The balanced equation is

$CH_3 - CH_2 - CH_3 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$
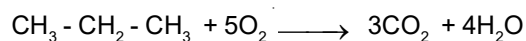
1 litre of propane requires = 5 litre of oxygen

20 litre of propane will require = 5 ×20 =100 litre of oxygen at 760 mm pressure and 0°C.

CLASSICAL IDEA OF REDOX REACTION

Oxidation and reduction can be classified according to the following :

Oxidation

(i)   Addition of oxygen is oxidation.

      e.g. $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

      $S(s) + O_2(g) \rightarrow SO_2(g)$

(ii)   Removal of hydrogen is oxidation.

$$CH_4 \text{ (g)} + 2O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)} + 2H_2O \text{ (l)}$$
$$2 H_2S(g) + O_2 \text{ (g)} \rightarrow 2 S \text{ (s)} + 2 H_2O \text{ (l)}$$
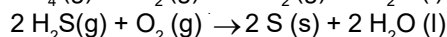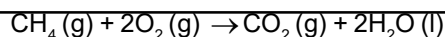
(iii) Addition of electronegative part is oxidation.

$$Mg \text{ (s)} + F_2 \text{ (g)} \rightarrow MgF_2 \text{ (s)}$$
$$Mg \text{ (s)} + Cl_2 \text{ (g)} \rightarrow MgCl_2 \text{ (s)}$$
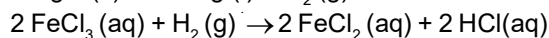$$Mg \text{ (s)} + S \text{ (s)} \rightarrow MgS \text{ (s)}$$
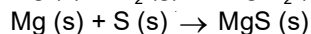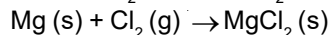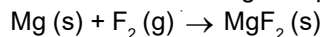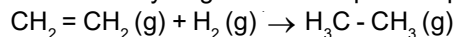
(iv) Removal of electropositive part is oxidation

$$K_4[Fe(CN)_6](aq) + H_2O_2 \text{ (aq)} \rightarrow 2K_3[Fe(CN)_6] \text{ (aq)} + 2 KOH \text{ (aq)}$$
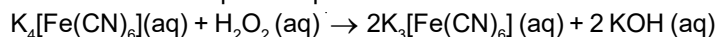
To summarize, the term **"oxidation"** is defined as the **addition of oxygen/ electronegative element to a substance or removal of hydrogen/ electropositive element from a substance.**

Reduction

(i) Removal of oxygen or electronegative part is reduction.

$$2 HgO \text{ (s)} \rightarrow 2 Hg \text{ (l)} + O_2 \text{ (g)}$$
$$2 FeCl_3 \text{ (aq)} + H_2 \text{ (g)} \rightarrow 2 FeCl_2 \text{ (aq)} + 2 HCl(aq)$$
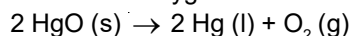
(ii) Addition of hydrogen or electropositive part is reduction

$$CH_2 = CH_2 \text{ (g)} + H_2 \text{ (g)} \rightarrow H_3C - CH_3 \text{ (g)}$$
$$2HgCl_2 \text{ (aq)} + SnCl_2 \text{ (aq)} \rightarrow Hg_2Cl_2 \text{ (s)} + SnCl_4 \text{ (aq)}$$
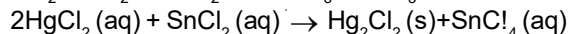
To summarize, the term **"reduction"** is defined as the **addition of hydrogen / electropositive element to a substance or removal of oxygen / electronegative element from a substance.**

MODERN CONCEPT OF OXIDATION AND REDUCTION

(ELECTRON TRANSFER)

(i) Loss of electron is oxidation where as gain of electron is reduction

(ii) Increase in positive oxidation number is oxidation whereas increase in negative oxidation number is reduction

$$4Al^0 + 3O_2^0 \rightarrow 2Al_2^{3+}O_3^{2-}$$

$$Zn^0 + Cl_2^0 \rightarrow Zn^{2+}Cl_2^{1-}$$
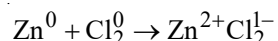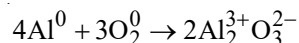
Since the positive oxidation state of Al and Zn increases i.e. they lose the electron hence they are undergo oxidation, whereas the negative oxidation state of oxygen and chlorine increases i.e. they gain electron hence undergo reduction.

Illustration 12: **In the following redox reaction, identify the element that is oxidized, the element that is reduced respectively** $\quad I_2O_5 + 5CO \rightarrow I_2 + 5CO_2$
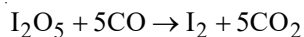
(A) I, C $\qquad\qquad$ (B) C, I $\qquad$ (C) both oxidized $\qquad$ (D) both reduced

Solution : (B)

Iodine is reduced from I^{5+} to I^0 whereas, carbon is oxidized from C^{2+} to C^{4+}

RULES FOR CALCULATION OF OXIDATION NUMBER

Following rules have been arbitrarily adopted to decide oxidation no. of elements on the basis of their periodic properties.

1. In uncombined state or free state, oxidation number of an element is zero.

2. In combined state oxidation no. of

a) F is always –1.

b) O is –2. In peroxides it is –1, in superoxides it is –1/2. However in F_2O it is +2.

c) H is +1. In ionic hydrides it is –1 (i.e., IA, IIA and IIIA metals).

d) halogens as halide is always –1.

e) sulphur as sulphide is always –2.

f) metals is always +ve.

g) alkali metals (i.e., I A group — Li, Na, K, Rb, Cs, Fr) is always +1.

h) alkaline earth metals (i.e., II A group—Be, Mg, Ca, Sr, Ba, Ra) is always +2.

3. The algebraic sum of the oxidation no. of all the atoms in a compound is equal to zero, e.g.

$KMnO_4$.

Ox. no. of K + Ox. no. of Mn + (Ox. no. of O) $\times 4 = 0$

(+1) + (+7) + 4 × (–2) = 0

4. The algebraic sum of all the oxidation no. of elements in a radical is equal to the net charge on the radical, e.g., CO_3^{-2}.

Oxidation no. of C + 3 $\times$ (Oxidation no. of O) = –2

(+4) + 3 × (–2) = –2

5. Oxidation number can be zero, +ve, –ve (integer or fraction)

6. Maximum oxidation no. of an element is = Group no.

(Except O and F)

Minimum oxidation no. of an element is = Group no. –8

(Except metals)

Redox reactions involve oxidation and reduction both. Oxidation means loss of electrons and reduction means gain of electrons. Thus redox reactions involve electron transfer and the number of electrons lost are same as the number of electrons gained during the reaction. This aspect of redox reaction can serve as the basis of a pattern for balancing redox reactions.

Illustration 13: Find the oxidation number of

S in SO_4^{2-} ion; S in HSO_3^- ion; Pt in $(PtCl_6)^{2-}$; Mn in $(MnO_4)^-$ ion

(A) 4, 6, 4, 7   (B) 4, 4, 4, 7   (C) 6, 4, 4, 7   (D) 6, 6, 4, 7

Solution: (C)

a) Let the oxidation number of S be x.
We know that Ox. no. of O = –2
So   Ox. no of S + 4 (Ox. no. O)   = –2
or   x   +   4(–2)   = –2
or   x   –   8   = –2
or   x = + 8 – 2 = + 6
The oxidation number of S in ion is +6.

b) Let the oxidation number of S be x in HSO_3^- ion.

We know that   Ox. no. of H = +1
Oxidation number of O = –2
So   Ox. no. of H + Ox. no. of S + 3 (Ox. no. O) = –1
    +1   +   x   +   3(–2)   = –1
or   +1   +   x   –   6   = –1
or   x   –   5   = –1
or   x = + 5 – 1 = +4

The oxidation number of S in HSO_3^- ion is +4.

c) Let oxidation number of Pt be x.
We know that Ox. no. of Cl = –1
So   Ox. no. Pt + 6 (Ox. no. Cl)   = –2
   x   +   6(–1)   = –2
or   x   –   6   = –2
The oxidation number of Pt in $[Pt(Cl)_6]^{2-}$ ion is +4.

d) Let oxidation number of Mn be x.
We know that Ox. no. of O = –2
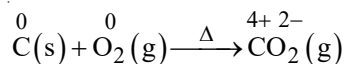So   Ox.no. Mn + 4 (Ox. no. O)   = –1
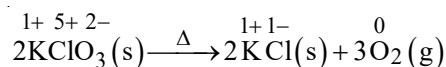   x   +   4(–2)   = –1
or   x   –   8   = –1

or   x = + 8 −1 = +7

The oxidation number of Mn in $[MnO_4]^-$ ion is +7.
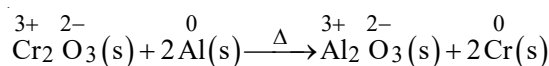
TYPE OF REDOX REACTION

(i)   Combination reactions

$$\overset{0}{C}(s)+\overset{0}{O_2}(g)\overset{\Delta}{\longrightarrow}\overset{4+\ 2-}{CO_2}(g)$$

$$3\overset{0}{Mg}(s)+\overset{0}{N_2}(g)\overset{\Delta}{\longrightarrow}\overset{2+\ 3-}{Mg_3N_2}(s)$$

(ii)   Decomposition reactions

$$2\overset{1+\ 1-}{Na\,H}(s)\overset{\Delta}{\longrightarrow}2\overset{0}{Na}(s)+\overset{0}{H_2}$$

$$2\overset{1+\ 5+\ 2-}{KClO_3}(s)\overset{\Delta}{\longrightarrow}2\overset{1+\ 1-}{K\,Cl}(s)+3\overset{0}{O_2}(g)$$
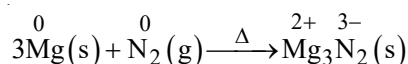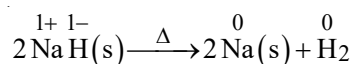
(iii)   Displacement reactions

(a) Metal displacement
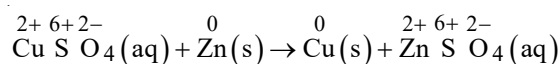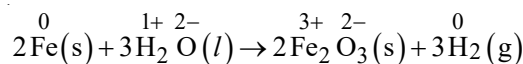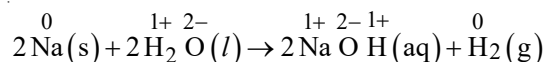
$$\overset{2+\ 6+\ 2-}{Cu\ S\ O_4}(aq)+\overset{0}{Zn}(s)\rightarrow\overset{0}{Cu}(s)+\overset{2+\ 6+\ 2-}{Zn\ S\ O_4}(aq)$$

$$\overset{3+\ 2-}{Cr_2\ O_3}(s)+2\overset{0}{Al}(s)\overset{\Delta}{\longrightarrow}\overset{3+\ 2-}{Al_2\ O_3}(s)+2\overset{0}{Cr}(s)$$

(b) Non metal displacement

$$2\overset{0}{Na}(s)+2\overset{1+\ 2-}{H_2\ O}(l)\rightarrow2\overset{1+\ 2-\ 1+}{Na\ O\ H}(aq)+\overset{0}{H_2}(g)$$

$$2\overset{0}{Fe}(s)+3\overset{1+\ 2-}{H_2\ O}(l)\rightarrow2\overset{3+\ 2-}{Fe_2\ O_3}(s)+3\overset{0}{H_2}(g)$$

(iv)   Disproportionation reactions

$$2\overset{1+\ 1-}{H_2\ O_2}(aq)\rightarrow2\overset{1+\ 2-}{H_2\ O}(l)+\overset{0}{O_2}(g)$$

$$\overset{0}{P_4}(s)+3OH^-(aq)+3\overset{}{H_2}O(l)\rightarrow\overset{3-}{P}\overset{1+}{H_3}+3H_2PO_2^-(aq)$$

$$\overset{0}{S_8}(s)+12OH^-(aq)\rightarrow4S^{2-}(aq)+2\overset{2+}{S_2}O_3^{2-}(aq)+6H_2O(l)$$

$$\overset{0}{Cl_2}(g)+2OH^-(aq)\rightarrow\overset{1+}{Cl}O^-(aq)+\ Cl^-(aq)+H_2O(l)$$
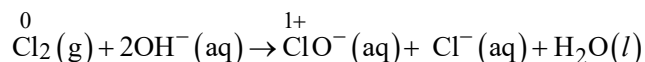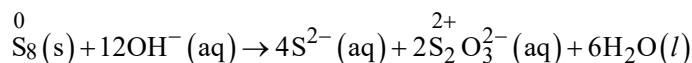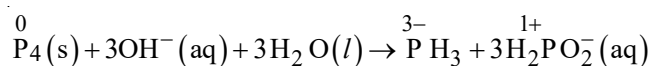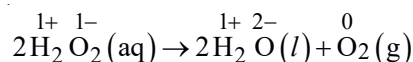
BALANCING REDOX REACTION BY OXIDATION NUMBER METHOD

For balancing a redox reaction by oxidation number method, follow the order of steps as listed below (of course, all steps may not be required for balancing some reactions).

i)   Find the oxidation numbers of the elements whose oxidation state is being changed.

ii)   Balance the number of atoms in both side of the equation of the element whose oxidation number is being changed.

iii)   Now, find the increase and decrease in oxidation no.

iv)   To equalize the change in oxidation states, multiply the species whose oxidation state is being changed, by a suitable integer.

v) If the coefficient developed are not correct, then change them by inspection (such coefficient changes is required when an element from a compound goes in 2 different compounds, one with the same oxidation state & the other with changed oxidation state).

vi) Count the charges on both sides of the equation and balance the charges in the equation by adding requisite H^+ in acidic medium or OH^- in basic medium to the required side.

vii) Balance the hydrogen and oxygen by adding the appropriate number of H_2O molecules on the required side.

Illustration 14: In the equation : $Cr_2O_7^{2-}$ + I⁻ + H⁺ ⟶ Cr³⁺ +I₂, **the stoichiometric coefficient of**

$Cr_2O_7^{2-}$, I⁻, H⁺ **are respectively**

(A) 1, 6, 14   (B) 1, 2, 14   (C) 2, 1, 14   (D) 1, 6, 12

Solution: (A)

i) Find the oxidation states of atoms undergoing redox change

$$\overset{+6\times 2}{Cr_2}O_7^{2-} + I^- \longrightarrow Cr^{3+} + \overset{0}{I_2}$$
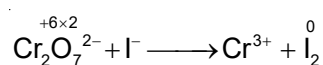
ii) Balance the number of atoms undergoing redox change.

$$\overset{(+6)\times 2}{Cr_2}O_7^{2-} + \overset{2\times(-1)}{2I^-} \longrightarrow \overset{(+3)\times 2}{2Cr^{3+}} + \overset{O\times 2}{I_2}$$
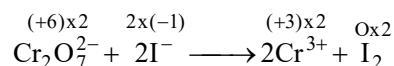
iii) Find the change in oxidation states and balance the change in oxidation states by multiplying the species with a suitable integer.

$$\overset{+12}{Cr_2}O_7^{2-} + \overset{-2}{2I^-} \longrightarrow 2\overset{+6}{C}r^{3+} + \overset{0}{I_2}$$
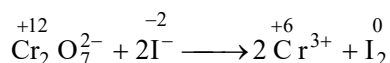
Change in ox. state = 6

As the decrease in oxidation state of chromium is 6 and increase in oxidation state of iodine is 2, so, we will have to multiply I⁻/I_2 by 3 to equalize the changes in oxidation states.

$Cr_2 + 6I^- \rightarrow 2Cr^{3+} + 3I_2$
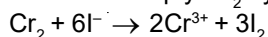
iv) Find the total charges on both the sides and also find the difference of charges.

charge on LHS = –2 + 6 × (-1) = –8

Charge on RHS = 2 × (+3) = +6.

Difference in charge = +6 –(–8) = 14

v) Now, as the reaction is taking place in acidic medium, we will have to add the H⁺ ions, to the side falling short in positive charges, so we will add 14H⁺ on LHS to equalize the charges on both sides.

$Cr_2 + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2$
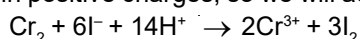
vi) To equalize the H and O atoms, add 7H_2O on RHS

$Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$
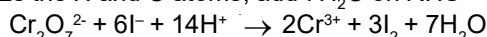
Illustration 15: In the equation Zn + NO_3^- **+** OH^- $\rightarrow$ ZnO_2^{2-} **+** NH₃ **the stoichiometry coefficient of**

Zn, NO_3^-, OH^- **are respectively**

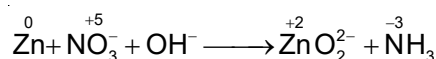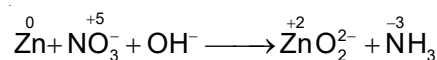(A) 4, 2, 7   (B) 4, 1, 6   (C) 4, 1, 7   (D) 1, 6, 12

Solution: (C)

i) Find the oxidation states of atoms undergoing redox changes.

$$\overset{0}{Zn} + \overset{+5}{N}O_3^- + OH^- \longrightarrow \overset{+2}{Zn}O_2^{2-} + \overset{-3}{N}H_3$$

ii) Find the changes in oxidation states and equalize the species, undergoing redox change, with a suitable integer.

$$\overset{0}{Zn} + \overset{+5}{N}O_3^- + OH^- \longrightarrow \overset{+2}{Zn}O_2^{2-} + \overset{-3}{N}H_3$$
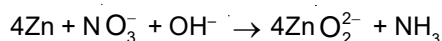
Increase in ox. state = 2 × 4

Decrease in ox. state = 8

iii) Multiply Zn by 4 to equalize the change in oxidation states.
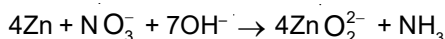
$$4Zn + NO_3^- + OH^- \rightarrow 4ZnO_2^{2-} + NH_3$$

iv) Find the total charges on both the sides and find the difference in charges.
Charge on LHS = (–1) + (–1) = –2
Charge on RHS = 4 × (–2) = –8
Difference of charges = –8 –(–2) = –6
v) Now, since reaction is taking place in alkaline medium, we will have to add 6 OH⁻ on the side falling short in –ve charges, i.e., LHS to equalize the charges on both the sides.

$$4Zn + NO_3^- + 7OH^- \rightarrow 4ZnO_2^{2-} + NH_3$$

vi) Add required no. of water molecules (i.e. $2H_2O$) on the side deficient in H and O atoms. To get the balanced equation

$$4Zn + NO_3^- + 7OH^- \rightarrow 4ZnO_2^{2-} + NH_3 + 2H_2O$$
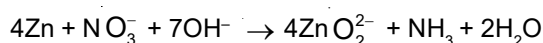
BALANCING REDOX REACTION BY ION-ELECTRON METHOD:

This method of balancing redox reaction involves following steps.
1. Separate the reactants and products into half-reactions involving the elements that changes its oxidation number. Write the skeleton equations for each half-reaction.
2. Balance each half-reaction separately involving given steps.
   i) First balance the atoms of the element undergoing oxidation or reduction.
   ii) Then balance atoms of the elements other than hydrogen and oxygen.
   iii) For balancing oxygen atoms in acidic or neutral medium, add suitable number of H_2O molecules to the side deficient in O, while in alkaline medium, add equal number of H_2O molecules as the excess of O on the side having excess of O atoms and add double the number of OH⁻ ions on the opposite side of the equation.
   iv) In order to balance the hydrogen atom in acidic or neutral medium, add required number of H⁺ to the side deficient in H, while in alkaline medium, add equal number of OH⁻ ions as the excess number of atom on the side having excess H and add equal number of H_2O molecule on the opposite side of the equation.
3. Multiply each half-reaction by suitable integer to make the number of electrons lost and gained same and add both the half-equations to get a completely balanced reaction.

Illustration 16: In the equation : $H_2C_2O_4 + KMnO_4 \rightarrow CO_2 + K_2O + MnO + H_2O$,

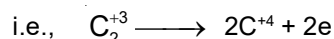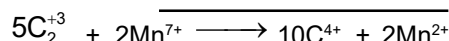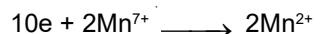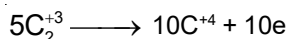(A) 10, 1, 1   (B) 10, 2, 2   (C) 4, 1, 7   (D) 10, 1, 2

Solution: **(D)**

Step 1: Select the oxidant, reductant atoms and write their half reactions, one representing oxidation and other reduction.

i.e., $C_2^{+3} \longrightarrow 2C^{+4} + 2e$

$5e + Mn^{+7} \longrightarrow Mn^{+2}$
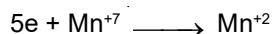
Step 2: Balance the no. of electrons and add the two equations.

$5C_2^{+3} \longrightarrow 10C^{+4} + 10e$

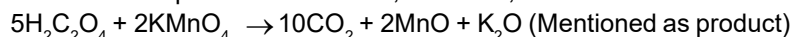$10e + 2Mn^{7+} \longrightarrow 2Mn^{2+}$

$5C_2^{+3} + 2Mn^{7+} \longrightarrow 10C^{4+} + 2Mn^{2+}$

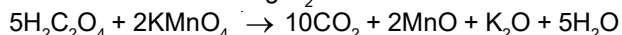**Step 3:** Write complete molecule of the reductant and oxidant from which respective redox atoms were obtained.

$$5H_2C_2O_4 + 2KMnO_4 \rightarrow 10CO_2 + 2MnO$$
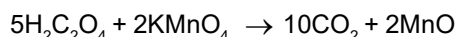
Step 4: Balance other atoms if any (except H and O).
In above example K is unbalanced, therefore,

$$5H_2C_2O_4 + 2KMnO_4 \rightarrow 10CO_2 + 2MnO + K_2O \text{ (Mentioned as product)}$$

Step 5: Balance O atom using H_2O on desired side.

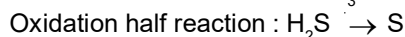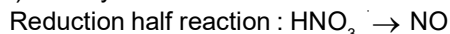$$5H_2C_2O_4 + 2KMnO_4 \rightarrow 10CO_2 + 2MnO + K_2O + 5H_2O$$

Illustration 17: The stoichiometric coefficient of the balanced redox equation,

$HNO_3 + H_2S \rightarrow NO + S$, in acidic medium will be respectively

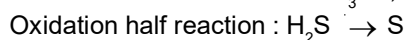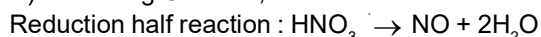(A) 2 , 4 , 3, 2   (B) 2, 2, 3, 2   (C) 2, 3, 3, 2   (D) 3, 2, 2, 3

Solution: (C)
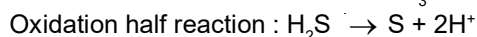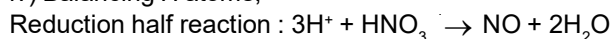
i) Identify the oxidation & reduction half reactions.

Reduction half reaction : $HNO_3 \rightarrow NO$

Oxidation half reaction : $H_2S \rightarrow S$

ii) Atoms of the element undergoing oxidation and reduction are already balanced.
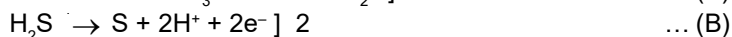
iii) Balancing O atoms,

Reduction half reaction : $HNO_3 \rightarrow NO + 2H_2O$

Oxidation half reaction : $H_2S \rightarrow S$

iv) Balancing H atoms,

Reduction half reaction : $3H^+ + HNO_3 \rightarrow NO + 2H_2O$

Oxidation half reaction : $H_2S \rightarrow S + 2H^+$

v) Balancing charge,

Reduction half reaction : $3e^- + 3H^+ + HNO_3 \rightarrow NO + 2H_2O$ … (A)

Oxidation half reaction : $H_2S \rightarrow S + 2H^+ + 2e^-$ … (B)
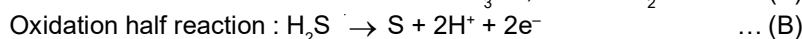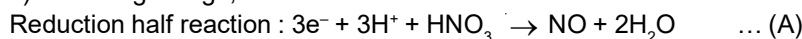
vi) Multiplying equation (A) by 2 and equation (B) by 3 and then adding them.

$3e^- + 3H^+ + HNO_3 \rightarrow NO + 2H_2O]\ 2$ … (A)

$H_2S \rightarrow S + 2H^+ + 2e^-]\ 2$ … (B)

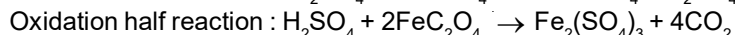$2HNO_3 + 3H_2S \rightarrow 3S + 2NO + 4H_2O$
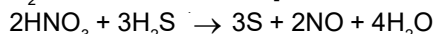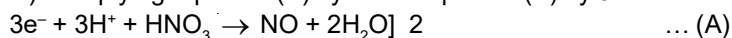
Illustration 18: The stoichiometric coefficient of FeC_2O_4, $KMnO_4$, $Fe_2(SO_4)_3$, $MnSO_4$ of the balanced redox equation:

$FeC_2O_4 + KMnO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + CO_2 + MnSO_4 + K_2SO_4$ will be respectively

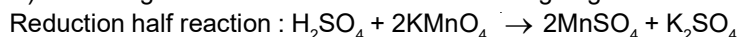(A) 10, 6, 5, 6   (B) 10, 6, 6, 5   (C) 10, 5, 6, 5   (D) 10, 5, 5, 6

Solution: (A)

i) Identify the oxidation & reduction halves.

Oxidation half reaction : $KMnO_4 \rightarrow MnSO_4$

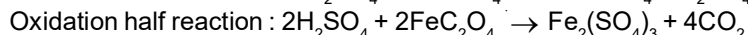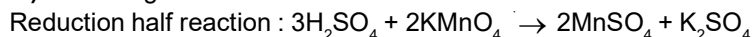Reduction half reaction : $FeC_2O_4 \rightarrow Fe_2(SO_4)_3 + CO_2$
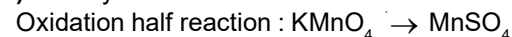
ii) In both the half-reactions, all the atoms (other than O and H) are not appearing on both sides of the reaction. So, in the oxidation half, H_2SO_4 is to be added on the reaction side, while in reduction half, H_2SO_4 and K_2SO_4 are to be added on reactant and product side respectively.

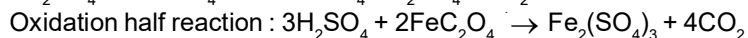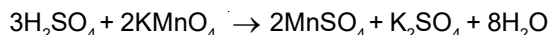**iii)** Balancing of the atoms of the element undergoing oxidation & reduction.

Reduction half reaction : $H_2SO_4 + 2KMnO_4 \rightarrow 2MnSO_4 + K_2SO_4$

Oxidation half reaction : $H_2SO_4 + 2FeC_2O_4 \rightarrow Fe_2(SO_4)_3 + 4CO_2$

iv) Balancing of the atoms of elements other than O and H

Reduction half reaction : $3H_2SO_4 + 2KMnO_4 \rightarrow 2MnSO_4 + K_2SO_4$

Oxidation half reaction : $2H_2SO_4 + 2FeC_2O_4 \rightarrow Fe_2(SO_4)_3 + 4CO_2$

v) Balancing O atoms,

Reduction half reaction:

$3H_2SO_4 + 2KMnO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O$

Oxidation half reaction : $3H_2SO_4 + 2FeC_2O_4 \rightarrow Fe_2(SO_4)_3 + 4CO_2$

vi) Balancing H atoms,

Reduction half reaction :

$10H^+ + 3H_2SO_4 + 2KMnO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O$

Oxidation half reaction:

$3H_2SO_4 + 2FeC_2O_4 \rightarrow Fe_2(SO_4)_3 + 4CO_2 + 6H^+$

vii) Balancing charge,

Reduction half reaction:

$10e^- + 10H^+ + 3H_2SO_4 + 2KMnO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O$ … (B)

Oxidation half reaction:

$3H_2SO_4 + 2FeC_2O_4 \rightarrow Fe_2(SO_4)_3 + 4CO_2 + 6H^+ + 6e^-$ … (A)
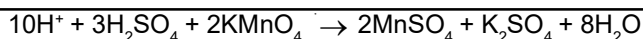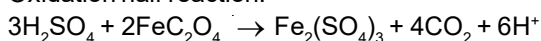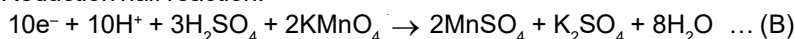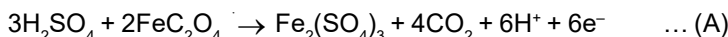
viii) Multiply equation (A) by 5 and equation (B) by 3 and then adding them,

$10e^- + 10H^+ + 3H_2SO_4 + 2KMnO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O] \ 3$

$3H_2SO_4 + 2FeC_2O_4 \rightarrow Fe_2(SO_4)_3 + 4CO_2 + 6H^+ + 6e^-] \ 5$

$10FeC_2O_4 + 6KMnO_4 + 24H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + 6MnSO_4 + 3K_2SO_4 + 20CO_2 + 24H_2O$
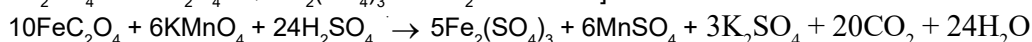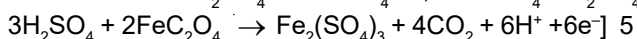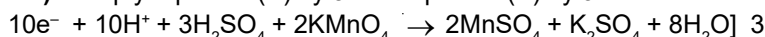
CALCULATION OF n-FACTOR

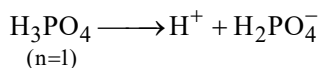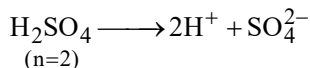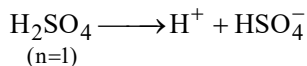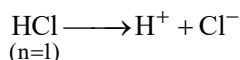For calculating the n-factor of any reactant in any reaction. One must know the kind of reaction it is, the reactions may be classified into the following three types.

1. Acid-Base Reactions/Neutralization reactions
2. Redox Reactions
3. Precipitation Reactions/Double decomposition reactions

Acid-Base Reaction: According, to the Arrhenius, an acid is a substance that furnishes H^+ ion(s) in solution, a base is a substance that furnishes OH^- ions in solution and neutralization is a reaction in which H^+ ion furnished by acid combines with OH^- ions furnished by base. The number of H^+ ion(s) furnished per molecule of the acid is its n-factor also called basicity. Similarly the number of OH^- ion(s) furnished by the base per molecule is its n-factor, also called acidity.

Some Examples

$$HCl \longrightarrow H^+ + Cl^-$$
$$(n=1)$$

$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$
$$(n=1)$$

$$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$$
$$(n=2)$$

$$H_3PO_4 \longrightarrow H^+ + H_2PO_4^-$$
$$(n=1)$$

$$H_3PO_4 \longrightarrow 3H^+ + PO_4^{3-}$$
$$(n=3)$$

$$H_3PO_3 \longrightarrow H^+ + H_2PO_3^-$$
$$(n=1)$$

$$H_3PO_3 \longrightarrow 2H^+ + HPO_3^-$$
$$(n=2)$$
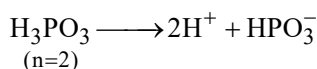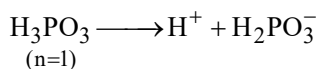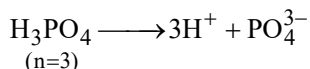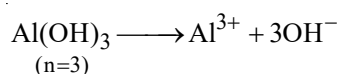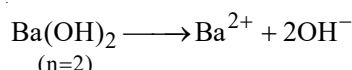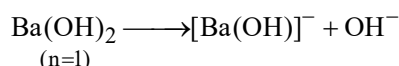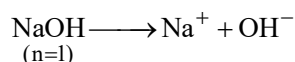
The n-factor of H_3PO_3 cannot be 3 as it has only two dissociable H^+ ions. So, its n-factor or dissociable protons is 1 or 2 as one of the H-atoms is linked with P atom directly.

$$HO-P-OH$$

with $:\ddot{O}:$ above P and H below P.

Similarly, $\underset{(n=1)}{CH_3COOH} \longrightarrow CH_3COO^- + H^+$
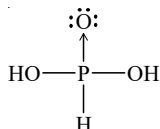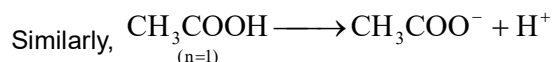
n-factor of CH_3COOH is 1, because it contains only one dissociable H^+ ion.

Now, we will consider the n-factor of some bases.

$\underset{(n=1)}{NaOH} \longrightarrow Na^+ + OH^-$

$\underset{(n=1)}{Ba(OH)_2} \longrightarrow [Ba(OH)]^- + OH^-$

$\underset{(n=2)}{Ba(OH)_2} \longrightarrow Ba^{2+} + 2OH^-$

$\underset{(n=3)}{Al(OH)_3} \longrightarrow Al^{3+} + 3OH^-$

Similarly, n-factor of $Al(OH)_3$ can also be 1 or 2 or 3, depending upon the number of OH^- released.
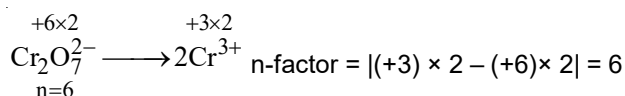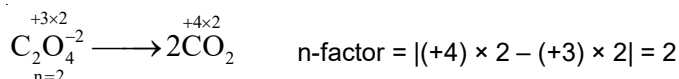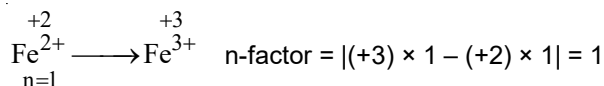
REDOX REACTIONS

Those reactions which involve the exchange of electrons are called redox reactions. For the calculation of n-factor of oxidizing agent or reducing agent, the method depends upon the change in oxidation state of the species considered. We will discuss them one by one.

i) When only one atom undergoing either reduction or oxidation e.g.

$$\underset{n=5}{\overset{+7}{MnO_4^-}} \overset{H^+}{\longrightarrow} \overset{+2}{Mn^{2+}}$$
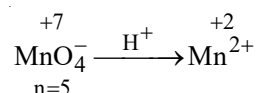
In such a case, we consider the change in oxidation state of atom undergoing oxidation or reduction change per molecule as the n-factor of the species.

n-factor = $|(+2) \times 1 - (+7) \times 1| = 5$

$\underset{n=1}{\overset{+2}{Fe^{2+}}} \longrightarrow \overset{+3}{Fe^{3+}}$ n-factor = $|(+3) \times 1 - (+2) \times 1| = 1$

$\underset{n=2}{\overset{+3\times2}{C_2O_4^{-2}}} \longrightarrow \overset{+4\times2}{2CO_2}$ n-factor = $|(+4) \times 2 - (+3) \times 2| = 2$

$\underset{n=6}{\overset{+6\times2}{Cr_2O_7^{2-}}} \longrightarrow \overset{+3\times2}{2Cr^{3+}}$ n-factor = $|(+3) \times 2 - (+6) \times 2| = 6$

ii) Salts which reacts in such a way that only one atom undergoes change in oxidation state but appears in two products with the same oxidation state:

In such a case the method of calculation of n-factor remains the same i.e., we will calculate the change in oxidation state of the atom per mole of that substance (reactant).

$$\overset{+6\times2}{Cr_2O_7^{2-}} \longrightarrow \overset{+3}{Cr^{3+}} + \overset{3+}{Cr^{3+}}$$
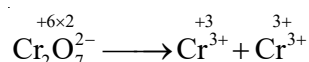
In this example, oxidation state of Cr changes from +6 to +3 in both the products. So

n-factor = $|(+6) \times 2 - (+3) \times 2| = 6$

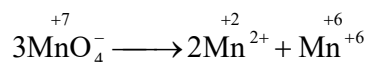iii) Salts which react in such a way that only one atom undergoes change in oxidation state but goes in two products with different oxidation state as a result of either only oxidation or only reduction.

$$3\overset{+7}{MnO_4^-} \longrightarrow 2\overset{+2}{Mn^{2+}} + \overset{+6}{Mn^{+6}}$$

In such a case, it is impossible to calculate the n-factor until and unless one knows that how much of MnO_4^- is changing to Mn^{2+} and how much to Mn^{6+} and if one knows the balanced equation then there is no need of calculation of n-factor. Nevertheless in such case the n-factor can be calculated by deducing the total change in oxidation state divided by total number of atom undergoing reduction/ oxidation change. So, for the calculation of n-factor in the above example, out of three moles of MnO_4^-, two moles are being converted to Mn^{2+} and one mole changes to Mn^{6+}. So total decrease in oxidation state of Mn.

= | [2 × (+2) – 2 × (+7)] | + | [1 × (+6) – 1 × (+7)]|

= | 4 – 14 | + | 6 – 7 | = 11

So, n-factor = $\dfrac{11}{3}$

iv) Salts which react in such a way that only one atom undergoes change in oxidation state in two product, in one product with changed oxidation state and in other product with same oxidation state as that of reactant.

In such case also one cannot calculate the n-factor without knowing the balanced chemical equation because one must know how much of atom has changed its oxidation state. For example.

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$$

Let us calculate the n-factor of HCl. Out of 14 moles of Cl^- (in HCl) only 6 moles of Cl^- are changing its oxidation state from –1 to 0 in the product Cl_2 and the oxidation state of remaining 8 Cl^- ions remains same in KCl and $CrCl_3$. So, total no. of moles of electrons lost by 14 moles of HCl is 6. So each mole of HCl takes up 6/14 i.e., 3/7 moles of electrons and hence n-factor of HCl is 3/7.

v) Salts which react in such a way that two or more atoms in the salt undergoes change in oxidation states as a result of either oxidation or reduction. Let us consider the following example,

$$FeC_2O_4 \longrightarrow Fe^{3+} + 2CO_2$$
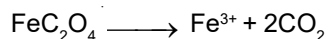
In this case, the oxidation of both Fe^{2+} and C^{3+} are changing from + 2 and +3 to +3 and +4 respectively. In such a case we will calculate the n-factor of the salt as the total increase or decrease in oxidation state per mole of the salt. As one can see that one mole of FeC_2O_4 contains one mole of Fe^{2+} and one mole of $C_2O_4^{2-}$ (i.e. 2 carbon atoms per mole of $C_2O_4^{2-}$).

Total change in oxidation state

= | 1 × (+2) – 1 × (+3) | + | 2 × (+3) – 2 × (+4) |

= 1 + 2 = 3

So, n-factor of FeC_2O_4 is 3

vi) Salts which react in such a way that two atoms undergoing change in oxidation state but one undergoing oxidation and other reduction reaction. In such a case one has to calculate the change in oxidation state of either the atom being oxidized or the atom being reduced. For example.

$$\overset{-3\times2}{(NH_4)_2}\overset{+6\times2}{Cr_2O_7} \longrightarrow \overset{0\times2}{N_2} + \overset{+3\times2}{Cr_2O_3} + 4H_2O$$
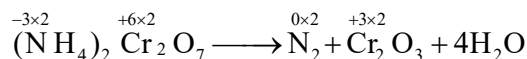
In this reaction, the oxidation state of N is increasing by 6 units and that of Cr is decreasing by 6 unit. So, we can consider either oxidation or reduction product for the calculation of n-factor and it will be the same.

n-factor of $(NH_4)_2Cr_2O_7$ considering oxidation

= |(-3) ×2 – (0) × 2| = 6
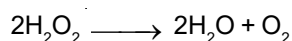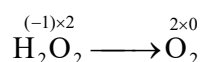
n-factor of $(NH_4)_2Cr_2O_7$ considering reduction

$= |(+6) × 2 – (+3) × 2| = 6$

vii) Species which undergoes disproportionation reaction: Those reaction in which oxidant and reductant are the same species or the same element from the species is getting oxidized as well as reduced. When the number of moles of atoms being oxidized is equal to the number of moles of atoms being reduced.

The n-factor can be calculated by knowing the balanced chemical equation and considering any of the change taking place. Say for example,

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Out of 2 moles of H_2O_2 consumed in the reaction, one mole of H_2O_2 is being oxidized

$(H_2O_2 \longrightarrow O_2)$ and one mole of H_2O_2 is being reduced $(H_2O_2 \longrightarrow 2H_2O)$. First consider the oxidation reaction

$$\overset{(-1)×2}{H_2O_2} \longrightarrow \overset{2×0}{O_2}$$

n-factor $= |2 × 0 – (–1) × 2| = 2$

Again, considering reduction reaction $\overset{(-1)×2}{H_2O_2} \longrightarrow \overset{(-2)×2}{2H_2O}$

n-factor $= |(-2) × 2 – (-1) × 2| = 2$

So, n-factor of H_2O_2 either considering oxidation or reduction reaction is same i.e. 2.

PRECIPITATION/DOUBLE DECOMPOSITION REACTIONS:

In such reaction, there is no change in oxidation state of any atom. The n-factor of the salt can be calculated by multiplying the oxidation state of the cation/anion by total no. of atoms per molecule of the salt. For example

$$\underset{n=2}{BaCl_2} + \underset{n=2}{Na_2SO_4} \longrightarrow BaSO_4 \downarrow + 2NaCl$$
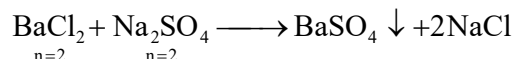
for $BaCl_2$

n-factor = Oxidation state of Ba atom in $BaCl_2$ × number of Ba atoms in 1 molecule of $BaCl_2$

$= (+2) × 1 = 2$

for Na_2SO_4

n-factor = Oxidation state of Na × number of Na-atoms in 1 molecule of Na_2SO_4

$= (+1) × 2 = 2$

TITRATION

The process of determination of concentration of a solution with the help of a solution of known concentration (standard solution) is called titration.

Titration is divided into following four categories.

i)   Simple Titration   ii)   Double Titration
iii) Back Titration   iv)   Iodimetric and Iodometric Titration

Simple Titration: A known volume of the solution of unknown concentration is taken in a flask and required reagents are added to it. The solution of known concentration is added from the burette in the solution of unknown concentration till the latter reacts completely. This process is called titration. At the end point (equivalence point) the equivalents or milliequivalent of the two reacting substances are equal.

Volume of solution (A) = V_A litres

Normality of solution (A) = N_A

Equivalents of substance (A) = $N_A V_A$

Similarly, equivalents of substance (B) = $N_B V_B$

At the equivalence point (end point) the equivalents (not the moles) of the two substance are equal.

$N_A V_A$ (litre) $= N_B × V_B$ (litre)

Illustration 19: 40 ml N/10 HCl and 60 ml N/20 KOH are mixed together. Calculate the normality of the salt formed.

    (A) 0.06   (B) 0.09   (C) 1   (D) 0.03

Solution: **(D)**

Milli equivalents of HCl = N × V (ml) $= \dfrac{1 \times 40}{10} = 4$

Milli equivalents of KOH = N × V (ml) $= \dfrac{1 \times 60}{20} = 3$

One milli equivalent of an acid neutralizes one milli equivalent of a base

        Milli equivalent of HCl left   = 4 – 3 = 1

        Total volume of the solution   = 40 + 60 = 100 ml

        Milli equivalents of HCl   = N × V (ml)

                         1 = N × 100

Normality (N) of HCl left in solution   = 0.01

               Salt formed   = Milli equivalent of acid or base neutralized

Milli equivalents of the salt formed   = N × V (ml)

                         3 = N × 100

Normality (N) of salt formed   = 0.03

Double Titration: If an aqueous solution contains a mixture of any two of the three NaOH, $NaHCO_3$ and Na_2CO_3 and it has to be titrated against an acid HCl or H_2SO_4, it will require two indicators to determine the strength of the bases present. The two indicators used are phenolphthalein and methyl orange.

Method: A given volume of the aqueous solution of the bases is taken and phenolphthalein indicator is added to it. This solution is titrated with an acid of known normality to the end point the volume of the acid used is noted. This end point is called first end point. Now in the same solution methyl orange is added and again titrated with an acid of known strength to the end point. It is called second end point. The volume of acid, used in the second end point is also noted. The normality of the bases present is then calculated.

**Principle:** In the presence of phenolphthalein indicator

i)   NaOH is completely neutralized by the acid.

ii)   Only half of the milliequivalent of Na_2CO_3 present are titrated as the phenolphthalein will show the colour change when only $NaHCO_3$ (weak base) and neutral species are left in the reaction mixture. The following reactions take place,

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

$$Na_2CO_3 + HCl \longrightarrow \underset{\text{weak base}}{NaHCO_3} + NaCl$$
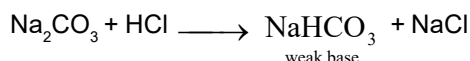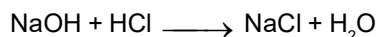
Since phenolphthalein is a weak organic acid, and it changes its colour in weakly basic medium ($NaHCO_3$), so as soon as the Na_2CO_3 is converted to $NaHCO_3$ phenolphthalein shows the colour change indicating the completion of the reaction.

In the presence of methyl orange, all the basic substances left in the mixture will be neutralized by acid and methyl orange will show the colour change when the medium is weakly acidic

$$(H_2O + CO_2 \text{ i.e. } H_2CO_3).$$
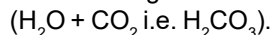
Titration of the solution containing both NaOH and Na_2CO_3:

A given volume of the aqueous solution is titrated with an acid of known normality using phenolphthalein indicator. Suppose 'a' milli equivalents of acid are used in the first end point then,

milli equivalent of NaOH + ½ milli equivalent of Na_2CO_3 = milli equivalent of acid = a   …(1)

Now in the same already titrated solution methyl orange indicator is added and again titrated to the end point. Suppose 'b' milli equivalents of the acid are used at the second end point.

½ milli equivalents of Na_2CO_3 = milli equivalents of acid = b   …(2)

From equation (1) and (2)

Milli equivalents of acid used by Na_2CO_3 = 2b $\equiv$ milli equivalents of Na_2CO_3

Milli equivalents of acid used by NaOH = a – b = milli equivalent of NaOH

Knowing the milli equivalents of Na_2CO_3 or NaOH and the volume of the solution titrated, their normality can be calculated.

Illustration 20:

NaOH and Na_2CO_3 are dissolved in 200 ml aqueous solution. In the presence of phenolphthalein indicator. 17.5 ml of 0.1 N HCl are used to titrate this solution. Now methyl orange is added in the same solution titrated and it requires 2.5 ml of the same HCl. Calculate the normality of NaOH and Na_2CO_3 and their mass present in the solution.

Solution:

Milli equivalents (a) of HCl used in the presence of phenolphthalein indicator.

$$= N \times V \text{ (ml)} = 0.1 \times 17.5 = 1.75$$

1.75 (a) = milli. equivalent. of NaOH + 1/2 milli equivalent. of Na_2CO_3 ...(1)

Milli equivalent. (b) of HCl used in the presence of methyl orange indicator

$$= N \times V \text{ (ml)}$$
$$= 0.1 \times 2.5 = 0.25$$

0.25 (b) = 1/2 milli equivalents of Na_2CO_3 …(2)

For Na_2CO_3 solution: From equation (2)

Milli equivalent. of acid used by Na_2CO_3 = 2b

$$= 2 \times 0.25 = 0.5$$

Volume of Na_2CO_3 solution = 200 ml

Suppose, Normality of Na_2CO_3 = N

Milli equivalents of Na_2CO_3 = N × V (ml) = 200 N

Putting equivalents of acid and Na_2CO_3 equal.

$$200 \text{ N} = 0.5$$

or (Normality of Na_2CO_3 solution) $N = \dfrac{1}{400}$

Mass of Na_2CO_3 = N × E × V (litre)

(E for Na_2CO_3 = 53) $= \dfrac{1}{400} \times 53 \times 0.2$

$$= \textbf{0.0265 gram}$$

For NaOH solution: From equation (1) and (2)

Milli equivalent. acid used by NaOH = a – b = 1.75 – 0.25

$$= 1.50$$

Volume of NaOH solution = 200 ml

Suppose, Normality of NaOH solution = N

Mili equivalent. of NaOH = N × V (ml) = 200 N

Putting the mili equivalent. of NaOH and acid used equal

$$200 \text{ N} = 1.5$$

(Normality of NaOH solution) $N = \dfrac{1.5}{200}$

Mass of NaOH = N × E × (V litres)

$$= \dfrac{1.5}{200} \times 40 \times 0.2$$

(E for NaOH = 40) = **0.06 g**

Titration of the solution containing both Na_2CO_3 and $NaHCO_3$:

Given volume of the solution is titrated by an acid using phenolphthalein indicator. Suppose 'a' milli equivalents of acid are used in the first end point. Then

1/2 milli equivalent of Na_2CO_3 = milli equivalents of acid = a ...(1)

Now in the same already titrated solution methyl orange indicator is added and again titrated to the end point. Suppose 'b' milli equivalents of the acid are used at the second end point. Then

1/2 milli equivalents of Na_2CO_3 + milli equivalents of $NaHCO_3$
= milli equivalents of acid = b ..(2)

From equation (1) and (2)

Milli equivalents of acid used by Na_2CO_3 = 2a

milli equivalents of Na_2CO_3

Milli equivalents of acid used by $NaHCO_3$ = b – a
= milli equivalent of $NaHCO_3$

Knowing the milli equivalents of the base and volume of the solution titrated, the normality (strength) of the bases can be calculated.

Illustration 21:

Both Na_2CO_3 and $NaHCO_3$ are present in an aqueous solution. In the presence of phenolphthalein indicator 10 ml of this solution requires 2.5 ml of 0.1M H_2SO_4 for titration. After this methyl orange is added in the same solution and titration requires 5 ml 0.1 M H_2SO_4. Calculate the concentration of Na_2CO_3 and $NaHCO_3$ in g/litre.

Solution:

Milli equivalent. (a) of H_2SO_4 used in the presence of phenolphthalein indicator
= N × V (ml) = 0.1 × 2 × 2.5 = 0.5

a = 0.5 =1/2 milli equivalents of Na_2CO_3 ...(1)

Milli. equivalent. (b) of $NaHCO_3$ + ½ milli equivalent. of Na_2CO_3 ...(2)

For Na_2CO_3 solution: From equation (1)

Milli equivalent. of acid used by Na_2CO_3 = 2 × 0.5 = 1

Suppose, Normality of Na_2CO_3 solution = N

Volume of Na_2CO_3 solution taken = 10 ml

Milli eq. of Na_2CO_3 taken = N × V (ml) = 10 N

Putting the milli eq. of H_2SO_4 and Na_2CO_3 equal,
1 = 10 N

or (Normality of Na_2CO_3) N = 0.1

Strength (S) in g/litre = N × E
= 0.1 × 53 (E for Na_2CO_3 = 53)
= **5.3 g/litre**

For $NaHCO_3$ solution: From equations (1) and (2) milli eq. of acid used by
$NaHCO_3$ = b – a = 1.0 – 0.5 = 0.5

Suppose, Normality of $NaHCO_3$ solution = N

Volume of $NaHCO_3$ solution taken = 10 ml

Milli equivalents of $NaHCO_3$ taken = 10 N

Putting the milli eq. of H_2SO_4 and $NaHCO_3$ equal, 0.5 = 10 N

or (Normality of $NaHCO_3$ solution) N = 0.05

Strength (S) in g/litre = N × E

(E for $NaHCO_3$ = 84) = 0.05 × 84 = **4.2g/litre**

Back Titration: Let us consider that we have an impure solid substance 'Z' weighing 'w' g and we are required to calculate the percentage purity of 'Z' in the sample. We are also provided with two solutions 'X' and 'Y', where the concentration of 'Y' is known (N_1) and that of 'X' is unknown. For the back titration to work, following conditions are to be satisfied

a) Compounds 'X', 'Y' and 'Z' should be such that 'X' and 'Y' reacts with each other.

b) 'X' and pure 'Z' also reacts with each other but the impurity present in 'Z' does not react with 'X'.

$$Z + X \text{ (excess)} \rightarrow \text{Product 1}$$

$$\text{Remaining (X)} + Y \rightarrow \text{Product 2}$$
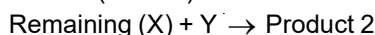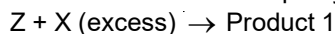
Note: Y should not react with Product 1

Milli equivalent of Y = N_2V_2

Where N_2 and V_2 (ml) is the normality and volume of Y

Initial mili equivalent of X = N_1V_1

Where N_1 and V_1 (ml) is the normality and volume of X

Remaining milli equivalents of X after reacting with Y = $N_1V_1 - N_2V_2$

Remaining milli equivalents of X = milli equivalents of Z

$$N_1V_1 - N_2V_2 = \frac{a \times 100}{\text{equivalent weight}}$$

Where 'a' is the weight of pure Z which is reacted.

$$a = \frac{\text{Molecular weight} \times (N_1V_1 - N_2V_2)}{n - \text{factor}}$$

∴ Percentage purity of 'Z' $= \dfrac{(N_1V_1 - N_1V_1)}{n - \text{factor}} \times \dfrac{\text{Molar mass of Z}}{w} \times 100$

Illustration 22: 20 g of a sample of $Ba(OH)_2$ is dissolved in 10 ml. of 0.5N HCl solution. The excess of HCl was titrated with 0.2N NaOH. The volume of NaOH used was 10 cc. Calculate the percentage of $Ba(OH)_2$ in the sample.
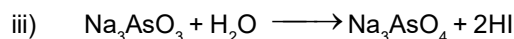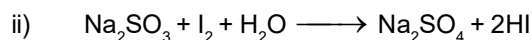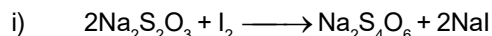
Solution:

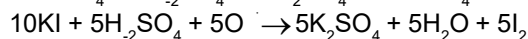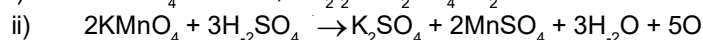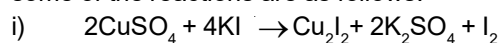|	
Milli eq. of HCl initially	= 10 × 0.5 = 5
Milli eq. of NaOH consumed	= Milli eq. of HCl in excess
	= 10 × 0.2 = 2
∴ Milli eq. of HCl consumed	= Milli eq. of $Ba(OH)_2$
	= 5-2=3
∴ eq. of $Ba(OH)_2$	= 3/1000 = 3 x 10⁻³
Mass of $Ba(OH)_2$	= 3·10⁻³(171/2) = 0.2565 g.
% $Ba(OH)_2$	= (0.2565/20) 100 = 1.28%

IODIMETRIC AND IODOMETRIC TITRATIONS

The redox-titration using iodine directly or indirectly as an oxidizing agent are called Iodine Titrations. These are of two types.
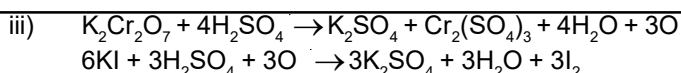
1. **Iodimetric Titrations:** Iodimetric titrations are defined as those iodine titrations in which a standard iodine solution is used as an oxidant and iodine is directly titrated against a reducing agent. Iodimetric procedures are used for the determination of strength of reducing agent like thiosulphates, sulphites, arsenites and stannous chloride etc., by titrating them against standard solution of iodine taken in a burette. Some cases of oxidation-reduction reactions are given as under:

   i) $2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$

   ii) $Na_2SO_3 + I_2 + H_2O \longrightarrow Na_2SO_4 + 2HI$

   iii) $Na_3AsO_3 + H_2O \longrightarrow Na_3AsO_4 + 2HI$

2. **Iodometric Titrations:** Iodometric titrations are defined as those iodine titrations in which some oxidizing agent liberates iodine from an iodine solution and then liberated iodine is titrated with a standard solution of a reducing agent added from a Burette. In such titrations, a neutral or an acidic solution of oxidizing agent is employed. The amount of iodine liberated from an iodide, (i.e. KI) is equivalent to the quantity of the oxidizing agent present. Iodometric titrations are used for the determination of $CuSO_4$, $K_2Cr_2O_7$, $KMnO_4$, ferric ions, antimonite ions, H_2O_2, MnO_2, bromine and chlorine etc. The equations for some of the reactions are as follows:

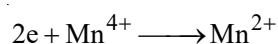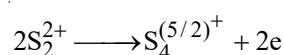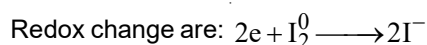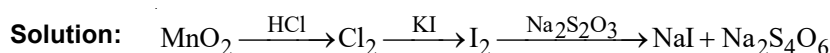   i) $2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$

   ii) $2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$

   $10KI + 5H_2SO_4 + 5O \longrightarrow 5K_2SO_4 + 5H_2O + 5I_2$

iii) $K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$

$6KI + 3H_2SO_4 + 3O \rightarrow 3K_2SO_4 + 3H_2O + 3I_2$

In the above reactions, the liberated iodine is titrated with a standard sodium thiosulphate.

$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$
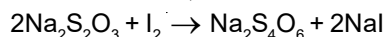
Illustration 23: 0.5 g sample containing MnO_2 is treated with HCl, liberating Cl_2. The Cl_2 is passed into a solution of KI and 30.0 cm³ of 0.1 M $Na_2S_2O_3$ are required to titrate the liberated iodine. Calculate the percentage of MnO_2 in sample. (At. Wt. of Mn = 55).

Solution: $MnO_2 \xrightarrow{HCl} Cl_2 \xrightarrow{KI} I_2 \xrightarrow{Na_2S_2O_3} NaI + Na_2S_4O_6$

Redox change are: $2e + I_2^0 \longrightarrow 2I^-$

$$2S_2^{2+} \longrightarrow S_4^{(5/2)^+} + 2e$$

$$2e + Mn^{4+} \longrightarrow Mn^{2+}$$

The reactions suggest that,

Meq. of MnO_2 = Meq. of Cl_2 formed = Meq. of I_2 liberated

= Meq. of $Na_2S_2O_3$ used

$\therefore \dfrac{w}{M/2} \times 1000 = 0.1 \times 1 \times 30$

$[\because N_{Na_2S_2O_3} = M_{Na_2S_2O_3}$ since valency factor = 1, see redox changes for $Na_2S_2O_3]$

or $w_{MnO_2} = \dfrac{0.1 \times 1 \times 30 \times M}{2000} = \dfrac{0.1 \times 1 \times 30 \times 87}{2000}$ $(\because M_{MnO_2} = 87)$

$w_{MnO_2} = 0.1305$

Purity of $MnO_2 = \dfrac{0.1305}{0.5} \times 100 = 26.1\%$

VOLUME STRENGTH OF H_2O_2 SOLUTION

The concentration of H_2O_2 is usually represented in terms of volume. If a sample of H_2O_2 is labeled as 'x volume', it means that 1 volume of H_2O_2 solution gives 'x volumes' of O_2 gas at STP on complete decomposition.

Consider the decomposition of H_2O_2 as $\underset{2 \times 34g}{2H_2O_2} \xrightarrow{\Delta} 2H_2O + \underset{22.4 \text{ L at STP}}{O_2}$
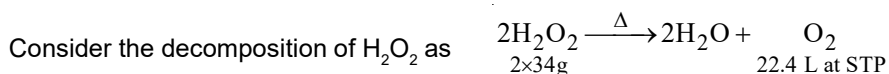
$\because$ 22400 ml of O_2 gas is liberated by 68g of H_2O_2 solution

$\therefore$ x ml of O_2 gas will be liberated by $= \dfrac{68x}{22400} = \dfrac{17x}{5600}$ g of H_2O_2

It means that $\dfrac{17x}{5600}$ g of H_2O_2 will be present in 1 ml of solution.

$\therefore$ 1000 ml of solution contains $H_2O_2 = \dfrac{17x}{5600} \times 1000 = \dfrac{17x}{5.6}$

Strength (g L⁻¹) = Normality × Equivalent weight

$\dfrac{17x}{5.6} = N \times \dfrac{34}{2}$ $(\because$ n-factor of $H_2O_2 = 2)$

x = 5.6 × N

i.e., Volume strength of $H_2O_2 = 5.6 \times$ Normality

Illustration 24:

A sample of H_2O_2 is x% by mass. x ml of $KMnO_4$ are required to oxidize one gram of this H_2O_2 sample. Calculate the normality of $KMnO_4$ solution.

Solution:

Suppose, Mass of H_2O_2 solution = 100g
Mass of H_2O_2 present $\qquad$ = x gram
Mass of H_2O_2 solution taken $\quad$ = 1 gram

Mass of H_2O_2 present in 1 gram solution = $\dfrac{x}{100}$

Equivalents of $H_2O_2 = \dfrac{w}{E}$

$$= \dfrac{x}{100 \times 17} \qquad ...(1)$$

(E for H_2O_2) = 17
Equivalents of $KMnO_4 \qquad = N \times V \text{ (litre)} = N \times x \times 10^{-3}$

Putting equivalents of H_2O_2 and $KMnO_4$ equal, $\dfrac{x}{100 \times 17} = N \times x \times 10^{-3}$

$\qquad$ N = 0.59 (Normality of $KMnO_4$)

PERCENTAGE LABELING OF OLEUM

Oleum or fuming sulphuric acid contains SO_3 gas dissolved in sulphuric acid. When water is added to oleum, $SO_3{}^-$ reacts with H_2O to form H_2SO_4, thus mass of the solution increases.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$
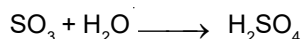
The total mass of H_2SO_4 obtained by diluting 100g of sample of oleum with desired amount of water, is equal to the percentage labeling of oleum.

% labeling of oleum = Total mass of H_2SO_4 present in oleum after dilution.

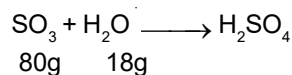$\qquad$ = mass of H_2SO_4 initially present + mass of H_2SO_4 produced on dilution.

Illustration 25:

Calculate the composition of 109% oleum.

Solution:

Let the mass of SO_3 in the sample be 'w' g, then the mass of H_2SO_4 would be $(100 - w)$g. On dilution,

$$SO_3 + H_2O \longrightarrow H_2SO_4$$
$\quad$ 80g $\quad$ 18g

Moles of SO_3 in oleum = $\dfrac{w}{80}$ = Moles of H_2SO_4 formed after dilution.

$\therefore$ Mass of H_2SO_4 formed on dilution = $\dfrac{98w}{80}$

Total mass of H_2SO_4 present in oleum after dilution = $\dfrac{98w}{80} + (100 - w) = 109$

$\therefore$ w = 40.

Thus oleum sample contains 40% SO_3 and 60% H_2SO_4.

HARDNESS OF WATER

Hardness of water is due to the presence of Ca^{++} and Mg^{++} in it. Hardness of water is of two types:

1. **Temporary Hardness:** It is due to the presence of dissolved $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ in water. To determine the temporary hardness a given volume of hard water is titrated with a strong acid (HCl or H_2SO_4) using methyl orange indicator.

2. **Permanent Hardness:** It is due to the presence of dissolved $CaCl_2$, $CaSO_4$, $MgCl_2$ and $MgSO_4$ in water. A known volume of hard water is taken and an excess of known equivalents of Na_2CO_3 are added in it. Na_2CO_3 reacts with Ca^{++} and Mg^{++} forming precipitates of $CaCO_3$ and $MgCO_3$. These precipitates are filtered off. The filtrate is titrated with a strong acid (HCl or H_2SO_4). Knowing the equivalents of Na_2CO_3 added and left unreacted, the equivalents of Na_2CO_3 consumed by hard water is known. The equivalents of Na_2CO_3 consumed is equal to the total equivalents of Ca^{++} and Mg^{++} ions present in hard water.

    Hardness of water is represented in ppm (mg/litre) of $CaCO_3$ i.e. milli grams of $CaCO_3$ present per litre of hard water. But hard water does not contain $CaCO_3$. Hard water contains $CaCl_2$, $MgCl_2$, $Ca(HCO_3)_2$ etc.

    One mole $CaCl_2 \equiv$ one mole $CaCO_3$ or 111g $CaCl_2 \equiv$ 100g $CaCO_3$
    Similarly,   120g $MgSO_4 \equiv$ 100g $CaCO_3$
    Thus mass of $CaCO_3$ corresponding to the mass of $CaCl_2$, $MgSO_4$ etc., present in hard water is calculated. Milligrams of $CaCO_3$ per litre of hard water is called hardness of water in ppm.

KEY POINTS

.   Relative Atomic Mass: It is the ratio of the mass of 1 atom of a substance and 1/12 of mass of 1 atom of C^{12} isotope.

.   Atomic Mass Unit (or amu): The atomic mass unit (amu) is equal to one twelfth $\left(\dfrac{1}{12}\right)$ of the mass of one atom of carbon-12 isotope.

.   Atomic Mass: It is the mass of 1 atom of a substance it is expressed in amu
    Atomic mass = RAM × 1 amu

.   Gram Atomic Mass: The atomic mass of an element expressed in gram is called gram atomic mass of the element.

.   Molecules: It is the smallest particle of matter which as free existence. Molecules can be further divided into its constituents atoms by physical and chemical process.

.   Molecular Mass: It is the mass of one molecule

.   Gram Molecular Mass: The molecular mass of a substance expressed in gram is called the gram-molecular mass of the substance.

.   MOLES: Gram-molecules and gram-atom are termed as a mole of molecules and a mole of atoms respectively, e.g., 1 gram-molecule of chlorine and 1 gram atom of chlorine are expressed as 1 mole of Cl_2 and 1 mole of Cl respectively.

.   Law of Conservation Of Mass: In a chemical change total mass remains conserved. i.e. mass before reaction is always equal to mass after reaction

- Law of Constant or Definite Proportion: All chemical compounds are found to have constant composition irrespective of their method of preparation or sources.

- Law of Multiple Proportion: When one element combines with the other elements to form two or more different compounds, the mass of one elements, which combines with a constant mass of the other, bear a simple ratio to one another.

- Gay Lussac's Law: Gas react or formed in the simple ratio of their volume. Provided all measurement are in the same condition of temperature and pressure.

- AVOGADRO'S HYPOTHESIS: Equal volume of all gases have equal number of molecules (not atoms) at same temperature and pressure conditions.

- PERCENTAGE COMPOSITION: percentage mass of an element

$$= \frac{\text{mass of that element in the compound}}{\text{molar mass of that compound}} \times 100$$

- EMPIRICAL FORMULA FOR MOLECULAR FORMULA

molecular formula = empirical formula × n ; where $n = \dfrac{\text{molecualr formula mass}}{\text{empirical formula mass}}$

- LIMITING REAGENT: The reactant which is consumed completely is known as limiting reagent.

- Molarity (M): The no. of moles of solute present in one litre of solution is called the molarity (M).

- Molality (m): No. of moles of solute present in one kilogram of solvent is know as molality

- Normality (N): No of equivalents of solute present in one litre of the solution is known as Normality (N).

- Mass-Mass Relationship: It relates the mass of a species (reactant or product) with the mass of another species (reactants or product)

- Mass-Volume Relationship: It relates the mass of a species (reactant or product) and the volume of a gaseous species (reactant or product) involved in a chemical reaction.

- Volume-Volume Relationship: It relates the volume of gaseous species (reactants or products) with the volume of another gaseous species (reactant or product) involved in a chemical reaction.

- "Oxidation" is defined as the addition of oxygen/ electronegative element to a substance or removal of hydrogen/ electropositive element from a substance.

- "Reduction" is defined as the addition of hydrogen / electropositive element to a substance or removal of oxygen / electronegative element from a substance.