Chapter-1
STOICHIOMETRY

Law of conservation of mass :

"In all physical and chemical changes, the total mass of the reactants is equal to that of the products" or "Matter can neither be created nor destroyed".

Law of constant composition or definite proportions :

"A chemical compound is always found to be made up of the same elements combined together in the same fixed ratio by weight".

Law of multiple proportions :

"When two elements combine together to form two or more chemical compounds, then the weights of one of the elements which combine with a fixed weight of the other bear a simple ratio to one another".

Law of Reciprocal Proportions :

The ratio of the weights of two elements A and B which combine with a fixed weight of the third element C is either the same or a simple multiple of the ratio of the weights of A and B which directly combine with each other.

Gay Lussac's law of gaseous volumes :

"When gases react together, they always do so in volumes which bear a simple ratio to one another and to the volumes of the products, if gaseous, all measurements are made under the same conditions of temperature and pressure".

Avogadro's hypothesis :

"Equal volumes of all gases under similar conditions of temperature and pressure contain equal number of molecules".

Atom :

It is the smallest particle of an element that takes part in a chemical reaction. It may or may not be capable of free existence.

Atomic mass unit (a.m.u) :

It is equal to $\frac{1}{12}$ th of the mass of an atom of C-12. It is equal to 1.6606×10^{-24} g.

Atomic mass :

It is the average relative mass of its atoms as compared with an atom of carbon – 12 isotope taken as 12.

Calculation of average atomic mass :

If an element exists in two isotopes having atomic masses 'a' and 'b' in the ratio *m*: *n*, then average atomic mass = $\frac{m \times a + n \times b}{m + n}$.

Gram atomic mass (G.A.M.):

The atomic mass of an element expressed in grams is called gram atomic mass. This amount of the element is called one gram atom. This amount of the element can also be called one mole atom.

Method of determining atomic weight

(i) **By application of the relation**

$$\textbf{At. wt. = Eq. wt. } \times \textbf{ Valency}$$

Knowing the exact eq. wt. and approximate atomic weight, valency can be calculated (which is a whole number). Knowing exact eq. wt. and valency, exact atomic weight can be calculated.

(ii) **Dulong and Petit's method:** According to Dulong and Petit's law, for solid elements (except Be, B, C and Si)

At. wt. × Specific heat = 6.4 (approx.)

$$\therefore \quad \text{Approx at. wt.} = \frac{6.4}{\text{Sp. heat}}$$

$$= \frac{\text{Approx. At. wt.}}{\text{Eq. wt.}} = \text{approx. Valency.}$$

The approx. valency is converted to the nearest whole number which is called exact valence.
Eq. wt. × exact valency = exact Atomic Weight.

(iii) **Specific heat/molar heat capacity method:** For gases, $\gamma = \frac{C_p}{C_v}$ is 1.66 for monoatomic, 1.40 for diatomic and 1.30 for triatomic gases. Thus having known the atomicity of the gas from the value of γ, Atomic wt. of the gaseous element = $\frac{\text{Mol. wt.}}{\text{Atomicity}}$

Molecular wt. = 2 × Vapour density.

(iv) **Volatile chloride method:** This method can be used for those elements whose chlorides are volatile so that their vapour densities can be determined. Then

Mol. wt. of the chloride = 2 × V.D.

If x is the valency of the element (M), then the formula of its chloride will be MCl_x. Hence

Mo. wt. of the Chloride MCl_x = *At. wt.* of $M + x \times 35.5$

$$= \text{Eq. wt. of M} \times \text{Valency of M} + x \times 35.5$$

$$= E \times x + x \times 35.5$$

$$= x\,(E + 35.5)$$

$$\therefore \quad x\,(E + 35.5) = 2 \times \text{V.D.} \quad \text{or} \quad x = \frac{2 \times \text{V.D.}}{E + 35.5}$$

Knowing the eq. wt. E of the element, the valency x can be calculated. Then Atomic weight = eq. wt. × Valency.

(v) **Isomorphism method:** Compounds having similar molecular formulae and identical crystal structure are called isomorphs. The method is based upon the fact that elements in isomorphous compounds have same valencies e.g.,

(a) K_2SO_4, K_2CrO_4 and K_2SeO_4 are isomorphous. Hence valency of S, Cr and Se = 6.

(b) $ZnSO_4, 7H_2O, FeSO_4, 7H_2O, MgSO_4, 7H_2O$ are isomorphous. Hence valency of Zn, Fe and Mg = 2.

(c) Alums, $M_2SO_4.M'_2(SO_4)_3.24H_2O$ in which M is monovalent and M′ is trivalent are isomorphous.

Knowing the valency, Atomic wt. = Eq. wt. × Valency

Molecules :

It is the smallest particle of an element or a compound that is capable of free existence.

Molecular mass :

Molecular mass of a substance is the average relative mass of its molecules as compared with an atom of C–12 isotope taken as 12.

Gram molecular mass or molar mass (G.M.M.):

The molecular mass of a substance expressed in gram is called gram molecular mass or molar mass. This amount of the substance is called one gram molecule. This amount of the substance is called one mole of the substance.

Methods of determining molecular weight

(i) **Gram Molecular Volume (G.M.V.)** method, 22.4 litres of every gas or vapour at STP weigh equal to molecular weight expressed in grams. This is the principle of Victor Meyer method used for volatile liquids.

(ii) **Vapour density method**

Molecular weight = 2 × Vapour Density

$$\text{where Vapour Density} = \frac{\text{Wt. of certain volume of the vapour}}{\text{Wt. of same volume of H under same conditions of temp. and pressure}}$$

(iii) **Diffusion method:** According to Graham's law of diffusion, rates of diffusion of different gases under similar conditions of temperature and pressure are inversely proportional to the square root of their densities or molecular weights i.e.,

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{2 \times d_2}{2 \times d_1}} = \sqrt{\frac{M_2}{M_1}}$$

Knowing the molecular weight of one gas, that of the other can be calculated.

(iv) **Colligative property method:** Discussed in the unit of 'Solutions'.

Moles :

The collection of 6.023×10^{23} molecules of an element or ions or compounds constitute one mole of that element, ion or compound. This number, 6.023×10^{23} is known as Avogadro's number. This is called mole-particle relationship.

Mole-Particle Relationship :

e.g. (i) one mole of Na contains 6.023×10^{23} atoms of Na.

(ii) one mole of oxygen i.e. one mole of O_2 contains 6.023×10^{23} molecules of oxygen.

(iii) one mole of CCl_4 carbontetrachloride contains 6.023×10^{23} molecule of CCl_4 (carbon tetrachloride)

Mole-Weight Relationship :

(i) one mole of an element weighs equal to gram atomic weight of the element
e.g. one mole of Na weighs 23 gm (Gram atomic wt. of Na = 23)

(ii) one mole of Mg weighs 24 gms (GAM of Mg = 24)

(iii) one mole of substance (molecular state) weighs equal to the gram molecular weight of the substance.
e.g. one mole of O_2 weighs 32 gms (GMM of O_2 = 32)
one mole of SO_2 weighs 64 gms.

Mole-Volume Relationship :

(i) one mole of every gas at STP occupies 22.4 litres of volume.
e.g. one mole of CO_2 at STP occupies 22.4 litres of volume.

(ii) one mole of SO_2 at STP occupies 22.4 litres of volume.

GRAM-ATOMS :

One gram-atom of an element means collection of 6.023×10^{23} atoms. This concept applies only to the elements which exists in polyatomic states (e.g. O, Cl, S, P etc.). It is meaningless for metals and compounds.

* The number of atoms in w gms of an element whose atomic mass is A is :

$$\text{gm} - \text{atom} = \frac{w}{A} = \text{mole atom}$$

* The number of atoms is given by:

$$\text{No. of atoms} = \frac{w}{A} \times N_0$$

Avogadro's number :

It is the number of atoms present in one gram atom of an element or the number of molecules present in one gram molecule of the substance. In general, it is the number of particles present in one mol of the substance. Its value is 6.02×10^{23}.

Equivalent weight :

The equivalent weight of a substance is the number of parts by weight of the substance that combine with or displace directly or indirectly 1.008 parts by weight of hydrogen or 8 parts by weight of oxygen or 35.5 parts by weight of chlorine.

$$\text{Eq. wt. of an acid} = \frac{\text{Mol. wt. of the acid}}{\text{Basicity}}$$

$$\text{Eq. wt. of a base} = \frac{\text{Mol. wt. of the base}}{\text{acidity}}$$

Gram equivalent weight :

The equivalent weight of a substance expressed in grams is called gram eq. wt. or one gram equivalent.

Now we can define **gram-equivalent (gm eq)** in **g** gms of a substance whose equivalent weight is **E** as follows:

$$\text{No. of } \boldsymbol{eq} = \frac{\mathbf{g}}{\mathbf{E}}$$

* The number of **milliequivalents** (**meq**) in **g** gms is given by:

$$meq = \frac{g}{E} \times 1000$$

Methods of determining equivalent weight

(i) **Hydrogen displacement method:** This method is used for metals which react with an acid to evolve hydrogen gas.

Eq. wt. of the metal is the weight of the metal which displace 1.008 g of H_2 or 11200 c.c. of H_2 at STP.

$$\text{Eq. wt. of metal} = \frac{\text{Wt. of metal}}{\text{Wt. of } H_2 \text{ displaced}} \times 1.008$$

$$\text{or} \quad = \frac{\text{Wt. of metal}}{\text{Vol. of } H_2 \text{ in ml displaced at STP}} \times 11200$$

(ii) **Oxide formation or reduction of the oxide method:** In this method a known weight of the metal is converted into its oxide directly or indirectly. Knowing the weight of the metal oxide formed, the weight of oxygen combined can be calculated. Alternatively, a known weight of the metal oxide may be reduced to metal whose weight is determined.

$$\text{Eq. wt. of metal} = \frac{\text{Wt. of metal}}{\text{Wt. of oxygen combined}} \times 8$$

$$\text{or} \quad = \frac{\text{Wt. of metal}}{\text{Vol. of } O_2 \text{ displaced/combined in ml at STP}} \times 5600$$

$$\text{Eq. wt. of metal} = \frac{\text{Wq. of metal}}{\text{Wt. of chlorine combined}} \times 35.5$$

$$\text{or} \quad \frac{\text{Wt. of metal}}{\text{Vol. of } Cl_2 \text{ combined in ml at STP}} \times 11200$$

(iii) **Double decomposition method:** For a reaction of the type

$$AB + CD \rightarrow AD \downarrow + BC$$

$$(\text{e.q. } AgNO_3 + NaCl \rightarrow AgCl \downarrow + NaNO_3)$$

$$\frac{\text{Weight of AB taken}}{\text{Weight of AD formed}} = \frac{\text{Eq. wt. of AB}}{\text{Eq. wt. of AD}} = \frac{\text{Eq. wt. of A} + \text{Eq. wt. of B}}{\text{Eq. wt. of A} + \text{Eq. wt. of D}}$$

Knowing the equivalent weights of any two radicals out of A, B and D, that of the third can be calculated.

(iv) **Electrolytic method (based on Faraday's laws of electrolysis)**

1 Faraday (96500 coulombs) deposit one gram equivalent of the substance.

Electrochemical equivalent of a substance is the weight of the substance deposited by one coulomb.

When the same quantity of electricity flows through solutions of different electrolytes,

$$\frac{\text{Wt. of X deposited}}{\text{Wt. of Y deposited}} = \frac{\text{Eq. wt. of X}}{\text{Eq. wt. of Y}}$$

(v) **Neutralization method:** This is based on the fact that acids and bases react in equivalent amounts. Hence equivalent weight of an acid is the weight of the acid which is neutralized by 1000 cc of 1N base solution (which contains 1g eq. of the base) Likewise equivalent weight of a base can be determined.

(vi) **Silver salt method:** (*for organic acids only*) The organic acid is converted into its silver salt (RCOOAg), a known weight of which is ignited to give residue of Ag which is weighed. Then

$$\frac{\text{Eq. wt. of RCOOAg}}{\text{Eq. wt. of Ag (108)}} = \frac{\text{Wt. of silver salt}}{\text{Wt. of silver}}$$

Eq. wt. of acid (RCOOH) = Eq. wt. of RCOOAg–107.

(vii) **Conversion method:** When one compound of a metal is converted into another compound of the same metal (e.g. metal carbonate → metal oxide), then

$$\frac{\text{Weight of compound I}}{\text{Weight of compound II}} = \frac{\text{Eq. wt. of metal + Eq. wt. of anion of compound I}}{\text{Eq. wt. of metal + Eq. wt. of anion of compound II}}$$

Relationship between eq. wt. atomic wt. and valency of an element: Eq. wt. = $\frac{\text{Atomic weight}}{\text{Valency}}$

Equivalent weight of oxidizing/reducing agent = $\frac{\text{Molecular weight of the substance}}{\text{No. of electrons gained/lost by one molecule}}$

Expressing concentration of solutions

Solution is a homogenous mixture of two or more components in which intermingling particles are of atomic or molecular dimensions. A solution consists of a dissolved substance known as **solute** and the substance in which the solute is dissolved is known as **solvent.** The **concentration** of a solution means the quantity of solute dissolved per unit volume of solution, or per unit quantity of solvent.

concentration of solution = $\frac{\text{quantity of solute}}{\text{quantity of solvent or solution}}$

Note: While discussing various methods for expressing concentration, we have taken solute as **B** dissolved in solvent **A** and g_A as grams of solute and e_B as grams of solvent.

Mass fraction is the fractional part of a component that is contributed by it to the total mass of solution.

$$\text{mass fraction of B} = \frac{w_B}{w_A + w_B}$$

$$\text{mass fraction of A} = \frac{w_B}{w_A + w_B}$$

Mole fraction is the fractional part of the moles that is contributed by each component to the total number of moles that comprises the solution. In containing n_A moles of solvent and n_B moles of solute:

$$\text{mole fraction of B} = x_B = \frac{n_B}{n_A + n_B}$$

$$\text{mole fraction of A} = x_B = \frac{n_A}{n_A + n_B}$$

Molality (m) is expressed as number of moles of solute dissolved in 1000 gms (1 Kg) of solvent. It is denoted by **m**.

$$m = \frac{n_B}{w_A} \times 1000$$

Molarity (m) is expressed as moles of solute contained in one litre of solution or it is also taken as millimoles of solute in 1000 cc (ml) of solution. It is denoted by **M.**

$$\textit{molarity}\ (M) = \frac{\text{moles of solute}}{\text{litres of solution}} = \frac{\text{millimoles of solute}}{\text{millilitres of solution}}$$

$$M = \frac{n_B}{V_{lt}} = \frac{g_B / m_B}{V_{lt}}$$

Normality (N) is expressed as the number of gram equivalents (gm eq) of solute contained in one litre of solution or it can also be taken as number of milliequivalents (meq) in 1000 cc (ml) of solution. It is denoted by **N.**

$$\text{normality of solution (N)} = \frac{\text{gm} - \text{eq of solute}}{\text{litres of solution}} = \frac{\text{meq of solute}}{\text{millilitres of solution}}$$

$$N = \frac{\text{gm} - \text{eq}}{V_{lt}}$$

Note : The following results should be remembered and used directly

(1) $$\text{moles} = M\ V_{lt} = \frac{w_B}{M_B}$$

$$\text{milimoles} = M\ V_{cc} = \frac{w_B}{M_B} \times 1000$$

(2) $$\text{gm-eq} = N\ V_{lt} = \frac{w_B}{E_B}$$

$$\text{meq} = N\ V_{cc} = \frac{w_B}{E_B} \times 1000$$

(3) $$\text{Molarity (M)} = \frac{10\ x d}{M_0} \qquad \text{Normality (N)} = \frac{10\ x d}{E}$$

d : density of solution in g/cc x :% age strength of solution (by weight)

(4) $N = z \times M$

(5) $$m = \frac{1000 \times x_B}{M_A \times x_A}$$

x : acidity for base or basicity for acid or electron transfer / mole for O.A. and R.A.

Strength of a solution is generally expressed as grams of solute in one litre of solution.

$$\text{strength} = \frac{w_B}{\text{litres of solution}}$$

strength = Normality × Eq. wt. = Molarity × Mole wt.

Diluting a solution:

Whenever a given solution of known concentration i.e. normality & molarity (known as standard solution) is diluted by adding more of solvent, the number of millimoles (or millequivalents) of solutes remain unchanged. The concentration of solution however changes.

In such cases $M_1\ V_1 = M_2\ V_2$ (M_1 & V_1a re molarity and volume of original solution)

(M_2 & V_2 are molarity and volume of diluted solution)

STOICHIOMETRIC CALCULATIONS:

(Quantitative analysis of a balance chemical equation)

Consider a balanced chemical reaction of equation:

$$mA + nB \rightarrow pC + qD$$

A and B are reactants; C and D are products; *m*, *n*, *p*, *q* are the stiochiometric coefficients.

The above balanced reaction is analysed as:

***m* moles of A react with *n* moles of B to produce *p* moles of C plus *q* moles of D.**

This can be represented as:

m moles of a ≡ n moles of B ≡ p moles of C ≡ q moles of d

It is also observed that when a substance takes part in a chemical reaction then the amount of the substance taking part is proportional to its equivalent weight

i.e. 1 equivalent of every substance combines (displaces, double displaces, exidises, reduces, neutralizes) are equivalent of another substance. Hence in a chemical reaction of the type

$$aA + bB \longrightarrow mC + nD$$

1 eq. of A combines with 1 eq. of B to form 1 eq of C and 1 eq of D or

n_{eq} of A ≡ n_{eq} of B ≡ n_{eq} of C ≡ n_{eq} of D.

In general, there are two types of stiochiometric reactions (which are most common):

Neutralisation Reactions and **Redox Reactions**

The analysis of two types of reactions is generally carried out in the form of mass of reactants (or products) taking part in a given reaction (gravimetric analysis) or in terms of concentrations of reactants (or products) taking part in a given reaction (**volumetric analysis).**

Neutralisation:

A reaction in which an acid (or a base) completely reacts with a base (or an acid) to form salt and water. If HA be the acid, BOH be the base and BA be the salt, then neutralisation reaction can be represented as follows:

$$\mathbf{HA + BOH \rightarrow BA + H_2O}$$

As we known that an acid may be monobasic (HCl, HNO_3, etc.), dibasic (H_2SO_4, $H_2C_2O_4$ etc.) or tribasic (H_3PO_4 etc.) and similarly a base may be monoacidic (NaOH, $NaHCO_3$ etc.), diacidic ($Ca(OH)_2$, Na_2CO_3 etc.) or triacidic ($Al(OH)_3$ etc.), so it is better to define the neutralisation reaction in the following manner.

A reaction in which 1 gram equivalent (or 1 meq of an acid (or a base) completely reacts with 1 gram equivalent (or 1 meq) of a base (or an acid) to form 1 gram equivalent (or 1 meq) of corresponding salt.

A stage at which the process of neutralisation is complete is known as **end point** or **equivalence point.** At equivalence point:

gm eq. (or meq) of acid = gm eq. (or meq) of base.

$N_a V_a = N_b V_b$ (N : normality, V: volume in ml of *l*t, at acid, b:)

SOLVED EXAMPLES

Example 1 : What amount of substance containing 60% NaCl, 37% KCl should be weighed out for analysis so that after the action of 25 ml of 0.1 N $AgNO_3$ solution, excess of Ag^+ is back titrated with 5 ml of NH_4SCN solution ? Given that 1 ml of NH_4SCN = 1.1 ml of $AgNO_3$.

Solution : Let *a* g of the given sample be weighed out for the purpose

$\therefore$ Wt of NaCl = $\frac{60}{100} \times a = 0.6\ a$ g $\quad\quad \therefore$ Wt of KCl = $\frac{37}{100} \times a = 0.37\ a$ g

Now this mixture reacts with $AgNO_3$, the excess of $AgNO_3$ is back titrated with NH_4SCN.

$\therefore$ Meq. of $AgNO_3$ added to mixture = $25 \times 0.1 = 2.5$

Normality of NH_4SCN can be derived as

$$\text{Meq. of } NH_4SCN = \text{Meq. of } AgNO_3$$
$$N \times 1 = 0.1 \times 1.1$$
$$\therefore \quad N = 0.11$$
$$\text{Meq. of } AgNO_3 \text{ left} = \text{Meq. of } NH_4SCN$$
$$= 5 \times N$$
$$\therefore \quad \text{Meq. of } AgNO_3 \text{ left} = 5 \times 0.11 = 0.55$$
$$\therefore \quad \text{Meq. of } AgNO_3 \text{ used for mixture} = 2.5 - 0.55 = 1.95$$
$$\therefore \quad \text{Meq. of KCl + Meq. of NaCl in mixture} = 1.95$$
$$\frac{0.37a}{74.5} \times 1000 + \frac{0.6a}{58.5} \times 1000 = 1.95$$
$$\therefore \quad a = \mathbf{0.128\ g}$$

Example 2 : A solution contains Na_2CO_3 and NaOH. Using phenolphthalein as indicator, 25 ml of a mixture requires 19.5 ml of 0.005 *N* HCl for the end point. If methyl orange is indicator, then 25 ml of solution requires 25.9 ml of the same HCl for end point. Calculate concentration of each substance in g per litre.

Solution : Meq. of HCl for 25 ml mixture using phenolphthalein indicator

$$= 19.5 \times 0.005$$

$\therefore$ Meq. of NaOH + $\frac{1}{2}$ Meq. of $Na_2CO_3 = 19.5 \times 0.005$

$$= 0.0975 \quad \text{.....(1)}$$

Now Meq. of HCl used for 25 ml mixture using methyl orange as indicator

$$= 25.9 \times 0.005 = 0.1295$$

$\therefore$ Meq. of NaOH + Meq. of $Na_2CO_3 = 0.1295$ .....(2)

$\therefore$ By Eqs. (1) and (2),

Meq. of NaOH = 0.0655 $\quad\quad$ Meq. of $Na_2CO_3 = 0.064$

$\frac{w}{40} \times 1000 = 0.0655$ $\quad\quad$ $\frac{w}{106/2} \times 1000 = 0.064$

$\therefore$ Weight of NaOH = 2.62×10^{-3} g/25 ml $\quad\quad \therefore$ Wt of $Na_2CO_3 = 3.392 \times 10^{-3}$ g/25 ml

$\therefore$ Strength of NaOH = **0.1048 g/litre**. $\quad\quad \therefore$ Strength of Na_2CO_3 = **0.1357 g/litre**

Example 3 : A mixture of $H_2C_2O_4$ and $NaHC_2O_4$ weighing 2.02 g was dissovled in water and the solution made upto one litre. 10 ml of this solution required 3.0 ml of 0.1 *N* NaOH solution for complete neutralization. In another experiment 10 ml of same solution in hot dilute H_2SO_4 medium required 4 ml of 0.1 *N* $KMnO_4$ for complete neutralization. Calculate the amount of $H_2C_2O_4$ and $NaHC_2O_4$ in mixture.

Solution : Let wt. of $H_2C_2O_4$ = a g in 1 litre

wt. of $NaHC_2O_4$ = b g in 1 litre

For acid base reaction :

Now (Meq. of $H_2C_2O_4$ + Meq. of $NaHC_2O_4$) in 10 ml = 3 × 0.1

$\therefore$ Meq. of $H_2C_2O_4$ + Meq. of $NaHC_2O_4$ in one litre = 3 × 0.1 × 100 = 30

$\therefore \quad \frac{a}{45} \times 1000 + \frac{b}{112/1} \times 1000 = 30$ .....(1)

Eq. wt. of $H_2C_2O_4 = \frac{M}{2} = \frac{90}{2} = 45$

Eq. wt. of $NaHC_2O_4 = \frac{M}{1} = \frac{112}{1} = 112$ (as acid salt)

Meq of $H_2C_2O_4$ + Meq of $NaHC_2O_4$ in 10 ml = Meq of $KMnO_4$

For redox change : $C_2^{+3} \rightarrow 2C^{+4} + 2e$

$5e + Mn^{+7} \rightarrow Mn^{+2}$

Meq. of $H_2C_2O_4$ + Meq. of $NaHC_2O_4$ in 10 ml = 4 × 0.1

$\therefore$ Meq. of $H_2C_2O_4$ + Meq. of $NaHC_2O_4$ in 1 litre = 4 × 0.1 × 100 = 40

$\therefore \quad \frac{a}{45} \times 1000 + \frac{b}{112/2} \times 1000 = 40$ .....(2)

$\therefore$ Eq. wt. of $H_2C_2O_4 = M/2$

and Eq. wt. of $NaHC_2O_4 = M/2$ (as reductant)

Sovling Eqs. (1) and (2), we get, a = **0.90 g** and b = **1.12 g**

Note : Also given a + b = 2.02 and thus Eq. (1) or (2) can be used to find a and b by using a + b = 2.02.

Example 4 : A 1 g sample of Fe_2O_3 solid of 55.2% purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made upto 100 ml. An aliquot of 25 ml of this solution requires 17 ml of 0.0167 *M* solution of an oxidant for titration. Calculate number of electrons taken up by oxidant in the above titration.

Solution : The redox changes are :

For reduction of Fe_2O_3 by zinc dust

$2e + Fe_3^{2+} \rightarrow 2Fe^{+2}$

$Fe^{+2} \rightarrow Fe^{+3} + e$

Oxidant + $ne \rightarrow$ Reductant

Meq. of Fe_2O_3 in 25 ml = Meq. of Fe^{+3} in Fe_2O_3 = Meq. of Fe^{+2} formed

= Meq. of oxidant used to oxidize Fe^{+2} again

$\therefore$ Meq. of Fe_2O_3 in 25 ml = Meq. of oxidant

$= 17 \times 0.0167 \times n$

where n is number of electrons gained by 1 molecule of oxidant.

$\therefore$ Meq. of Fe_2O_3 in 100 ml = $17 \times 0.0167 \times n \times \frac{100}{25}$

$\therefore$ $\frac{1 \times 55.2 \times 1000}{100 \times M/2} = 17 \times 0.0167 \times n \times 4$

$\because$ M. wt. of $Fe_2O_3 = 160$

$\therefore$ $n =$ $= 6$

$\therefore$ Number of electrons gained by one molecule of oxidant = **6**.

Example 5 : The equivalent weight of an element is 13.16. It forms an acidic oxide which with KOH forms a salt, isomorphous with K_2SO_4. Deduce at. wt. of element.

Solution : The element forming acidic oxide is non-metal say A. It forms isomorphous of K_2SO_4 with KOH *i.e.* K_2AO_4.

$\therefore$ $A^o \rightarrow A^{+6} + 6e$

$\therefore$ At. wt. of A = Eq. wt. of A × no. of 'e' lost

= 13.16 × 6 = **78.96**.

OBJECTIVE

1. If 'x' gms of an element A reacts with 16 gms of oxygen then the equivalent weight of element A is

   (a) $\frac{x}{4}$ (b) $\frac{x}{2}$ (c) x (d) $2x$

2. The mass of CO containing the same amount of oxygen as in 88 gms of CO_2 is

   (a) 56 gms (b) 28 gms (c) 112 gm (d) 14 gm

3. When 8 gms of oxygen reacts with magnesium then the amount of MgO formed is

   (a) 18 gm (b) 20 gm (c) 24 gm (d) 32 gm

4. An hydride of nitrogen decomposes to give nitrogen and hydrogen. It was formed that one volume of the hydride gave one volume of N_2 and 2 volumes of H_2 at STP. The hydride of nitrogen is

   (a) NH_3 (b) N_2H_6 (c) NH_2 (d) N_2H_4

5. 5 volumes of a hydrocarbon on complete combustion consumed 10 volumes of oxygen giving 5 volumes of CO_2 at STP. The hydrocarbon is

   (a) C_2H_6 (b) C_2H_4 (c) CH_4 (d) C_2H_4

6. The volume of oxygen used when x gms of Zn is converted to ZnO is

   (a) $\frac{x\times 2}{65} \times 5.6$ litres (b) $\frac{x}{65} \times 5.6$ litres (c) $\frac{4x}{65} \times 5.6$ litres (d) None of these

7. 'x' gms of an element 'A' on heating in a jar of chlorine give 'y' gms of ACl_2 the atomic weight of element A is

   (a) $\left(\frac{x}{y-71}\right) \times \frac{35.5}{2}$ (b) $\frac{71x}{y-71}$ (c) $\frac{35.5x}{y-71}$ (d) None of these

8. A sample of clay was partially dried and then contained 50% silica and 7% water. The original clay contained 12% water. The silica in original sample is :

   (a) 51.69 (b) 47.31 (c) 63.31 (d) None of these

9. The amount of H_2SO_4 present in 1200 ml of 0.2 N solution is

   (a) 10.76 gms (b) 11.76 gms (c) 12.76 gms (d) 14.76 gm

10. 300 ml of 0.1 M HCl and 200 ml of 0.3 M H_2SO_4 are mixed. The normality of the resulting mixture is:

    (a) 0.4 N (b) 0.1 N (c) 0.3 N (d) 0.2 N

11. The volume of water which should be added to 300 ml of 0.5 M NaOH solution so as to get a solution of 0.2 M is:

    (a) 550 ml (b) 350 ml (c) 750 ml (d) 450 ml

12. The mole fraction of a solution containing 3.0 gms of urea per 250 gms of water would be

    (a) 0.00357 (b) 0.99643 (c) 0.00643 (d) None of these

13. The molality of a solution of conc. HCl containing 36.5% by weight of HCl would be

    (a) 16.75 (b) 17.75 (c) 15.75 (d) 14.75

14. 0.35 gms of a sample of $Na_2CO_3 \cdot xH_2O$ were dissolved in water and the volume was made to 50 ml. 10 ml of this solution required 9.9 ml of $\frac{N}{10}$ HCl for complete neutralization. Calculate the value of x.
(a) 1 (b) 2 (c) 3 (d) None of these

15. 1.2 gms of a sample of washing soda was dissolved in water and volume was made upto 250 cc. 25 cc of this solution when titrated against $\frac{N}{10}$ HCl for required 17 ml. The percentage of carbonate is given sample is:
(a) Approximately 70% (b) Approximately 66%
(c) Approximately 76% (d) None of these

16. 25 c.c. of solution containing NaOH and Na_2CO_3 when titrated against $\frac{N}{10}$ HCl. Using phenolphthatein as indicator required 40 c.c. of HCl. The same volume of mixture when titrated against $\frac{N}{10}$ HCl using methyl orange required 45 cc of this HCl. The amount of NaOH and Na_2CO_3 in one liter mixture is.
(a) NaOH = 28 gm/ L
Na_2CO_3 = 10.6 gm/L
(b) NaOH = 10.6 gm/L
Na_2CO_3 = 28 gm/L
(c) NaOH = 14 gm/L
Na_2CO_3 = 5.3 gm/L
(d) None of these

17. 0.5 gms of a mixture of K_2CO_3 and Li_2CO_3 requires 30 ml of 0.25 NHCl solution for neutrilization. The percentage compsition of mixture would be
(a) K_2CO_3 = 96%, Li_2CO_3 = 4%
(b) K_2CO_3 = 4%, Li_2CO_3 = 96%
(c) K_2CO_3 = 50%, Li_2CO_3 = 50%
(d) K_2CO_3 = 25%, Li_2CO_3 = 74%

18. How many ml. of a 0.05 M $KMnO_4$ solution are required to oxidise 2.0 g of $FeSO_4$ in a dilute acid solution ?
(a) 5.263 (b) 0.5263 (c) 52.63 (d) None of these

19. The normality of 10 ml of a 20 V H_2O_2 is
(a) 1.79 (b) 3.58 (c) 6.086 (d) None of these

20. Two elements, X (at. wt. 75) and Y (at. wt. 16) combine to give a compound having 75.8% of X. The formula of the compound is
(a) X Y (b) X_2Y (c) X_2Y_2 (d) X_2Y_3

21. The weight of quick lime obtianed by strongly heating 25 gm of marble is
(a) 14 gm (b) 28 gm (c) 42 gm (d) 56 gm

22. Ther percentage of oxygen in NaOH is
(a) 40 (b) 16 (c) 8 (d) 1

23. 56 gm of CaO has been mixed with 63 gm of HNO_3, the amount of $Ca(NO_3)_2$ formed is
(a) 4 gm (b) 3.28 gm (c) 164 gm (d) 82 gm

24. The haemoglobin from the red corpuscles of most mammals contains app. 0.33% of iron by weight. The physical measurement indicates the molecular weight of haemoglobin 7000. The number of iron atoms in each molecule of haemoglobin is (At. wt. of Fe = 56)
    (a) 2 (b) 3 (c) 4 (d) None of these

25. If 0.5 mol of $BaCl_2$ is mixed with 0.2 mol of Na_3PO_4, the maximum number of mole of $Ba_3(PO_4)_2$ that can be formed is
    (a) 0.7 (b) 0.5 (c) 0.30 (d) 0.10

26. One g of a mixture of Na_2CO_3 and $NaHCO_3$ consumes *y* equivalent of HCl for complete neutralisation. One g of the mixture is strongly heated, then cooled and the residue treated with HCl. How many equivalent of HCl would be required for complete neutralisation:
    (a) 2*y* equivalent (b) *y* equivalent (c) 3*y*/4 equivalent (d) None of these

27. Six gm of magnesium (atomic weight 24) reacts with excess of an acid, the amount of hydrogen produced would be
    (a) 0.5 gm (b) 1.0 gm (c) 2 gmn (d) 4 gm

28. A gas of mixture of 3.0 litres of propane and butane on complete combustion at 25ºC produced 10 litres of CO_2. Find out the composition of the gas mixture.
    (a) 70%, 30% respectively (b) 66.66%, 33.33% respectively
    (c) 30%, 70% respectively (d) None of these

29. Molecular weight of a gas, 11.2 litre fo which at NTP weighs 14 g is
    (a) 14 (b) 28 (c) 11/11.2 (d) 14 × 11.2

30. The empirical formula of a compound is CH. Its molecular weight is 78. The molecular formula of the compound will be
    (a) C_2H_4 (b) C_3H_3 (c) C_4H_4 (d) C_6H_6

31. 1.60 g of a metal were dissolved in HNO_3 to prepare its nitrate. The nitrate on strong heating gives 2 g oxide. The equivalent weight of metal is
    (a) 16 (b) 32 (c) 48 (d) 12

32. Amount of oxygen required for complete combustion of 27 g Al is
    (a) 24 g (b) 12 g (c) 20 g (d) 6 g

33. 6.022×10^{22} molecules of N_2 at NTP will occupy a volume of
    (a) 22.4 litre (b) 2.24 litre (c) 6.02 litre (d) 6.02 ml

34. One mole of a mixture of CO and CO_2 required exactly 20 g of NaOH in solution for complete conversion of all the CO_2 into Na_2CO_3. How much NaOH would it require for conversion into Na_2CO_3 if the mixture (one mole) is completely oxidised to CO_2:

(a) 60 g (b) 80 g (c) 40 g (d) 20 g

35. 2.76 g of silver carbonate on being strongly heated yields a residue weighing

(a) 2.16 g of Ag (b) 2.16 gm of Ag_2O (c) Both of these (d) None of these

MISCELLANEOUS ASSIGNMENT

Comprehension

Normality is number of gram equivalents dissolved per litre of solution. It changes with change in temperature. In case of monobasic acid, normality and molarity are equal but in case of dibasic acid, normality is twice the molarity. In neutralization and redox reactions, number of milliequivalents of reactants as well as products are always equal

1. On heating a litre of a N/2 HCl solution, 2.750 g of HCl is lost and the volume of solution becomes 750 mL. The normality of resulting solution will be

(a) 0.58 (b) 0.75 (c) 0.057 (d) 5.7

2. The volume of 0.1 M $Ca(OH)_2$ required to neutralize 10 mL of 0.1 N HCl will be

(a) 10 mL (b) 20 mL (c) 5 ml (d) 40 mL

3. Molarity of 0.5 N Na_2CO_3 is

(a) 0.25 (b) 1.0 (c) 0.5 (d) 0.125

4. 6.90 N KOH solution in water contains 30% by weight of KOH. The density of solution will be

(a) 1.288 (b) 2.88 (c) 0.1288 (d) 12.88

5. The amount of ferrous ammonium sulphate required to prepare 250 mL of 0.1 N solution is

(a) 1.96 g (b) 1.8 g (c) 9.8 g (d) 0.196 g

Each of the questions given below consists of two statements, an assertion (*A*) and reason (*R*). Select the number corresponding to the appropriate alternative as follows

(a) If both **A** and **R** are true and **R** is the correct explanation of **A**, then mark **(a)**

(b) If both **A** and **R** are true but **R** is not the correct explanation of **A**, then mark **(b)**

(c) If **A** is true but **R** is false, then mark **(c)**

(d) If both **A** and **R** are false, then mark **(d)**

6. **A.** 0.28 g of N_2 has equal volume as 0.44 g of another gas at same conditions of temperature and pressure.

R. Molecular mass of another gas is 44 g mol^{-1}.

7. **A.** Boron has relative atomic mass 10.81.

R. Borons two isotopes $^{10}_{5}B$ and $^{11}_{5}B$ and their relative abundance is 19% and 81%.

8. **A.** The percentage of nitrogen in urea is 46%

R. Urea is Ionic compound.

9. **A.** The oxidation state of central sulfur of $Na_2S_2O_3$ is + 6

R. Oxidation state of an element should be determined from structures.

10. **A.** Molarity of a solution and molality of a solution both change with density.

R. Density of the solution changes when percentage by mass of solution changes.

SUBJECTIVE PROBLEMS

1. What weight of Na_2CO_3 of 95% purity would be required to neutralize 45.6 mL of 0.235 *N* acid ?

2. How much $BaCl_2.2H_2O$ and pure water are to be mixed to prepare 50 g of 12.0% (by wt.) $BaCl_2$ solution.

3. To 50 litre of 0.2 *N* NaOH, 5 litre of 1 *N* HCl and 15 litre of 0.1 *N* $FeCl_3$ solution are added. What weight of Fe_2O_3 can be obtained from the precipitate ? Also report the normality of NaOH left in the resultant solution.

4. 0.5 g fuming H_2SO_4 (oleum) is diluted with water. The solution requires 26.7 mL of 0.4 *N* NaOH for complete neutralization. Find the percentage of free SO_3 in the sample of oleum.

5. 200 mL of a solution of mixture of NaOH and Na_2CO_3 was first titrated with phenolphthalein and *N*/10 HCl. 17.5 mL of HCl was required for the end point. After this methyl orange was added and 2.5 mL of same HCl was again required for next end point. Find out amounts of NaOH and Na_2CO_3 in mixture.

6. A precipitate of AgCl and AgBr weighs 0.4066 g. On heating in a current of chlorine, the AgBr is converted to AgCl and the mixture loses 0.0725 g in weight. Find the percentage of Cl in original mixture.

7. How many milli-litre of 0.5 *M* H_2SO_4 are needed to dissolve 0.5 g of copper II carbonate ?

8. What is the strength in g per litre of a solution of H_2SO_4, 12 mL of which neutralized 15 mL of *N*/10 NaOH solution.

9. *n*-butane is produced by the monobromination of ethane followed by Wurtz reaction. Calculate the volume of ethane at NTP required to produce 55 g *n*-butane if the bromination takes place with 90% yield and the Wurtz reaction with 85% yield.

10. 0.50 g of a mixture of K_2CO_3 and Li_2CO_3 required 30 mL of 0.25 *N* HCl solution for neutralization. What is percentage composition of mixture ?

11. 5 mL of 8 *N* HNO_3, 4.8 mL of 5 *N* HCl and a certain volume of 17 *M* H_2SO_4 are mixed together and made upto 2 litre. 30 mL of this acid mixture exactly neutralizes 42.9 mL of Na_2CO_3 solution containing 1 g $Na_2CO_3.10H_2O$ in 100 mL of water. Calculate the amount of sulphate ions in g present in solution.

12. A sample of Mg was burnt in air to give a mixture of MgO and Mg_3N_2. The ash was dissolved in 60 Meq of HCl and the resulting solution was back titrated with NaOH. 12 Meq of NaOH were required to reach the end point. An excess of NaOH was then added and the solution distilled. The ammonia released was then trapped in 10 Meq of second acid solution. Back titration of this solution required 6 Meq of the base. Calculate the percentage of Mg burnt to the nitride.

13. A mixture of ethane (C_2H_6) and ethene (C_2H_4) occupies 40 litre at 1.00 atm and at 400 K. The mixture reacts completely with 130 g of O_2 to produce CO_2 and H_2O. Assuming ideal gas behaviour, calculate the mole fractions of C_2H_4 and C_2H_6 in the mixture.

14. A solid mixture 5 g consists of lead nitrate and sodium nitrate was heated below 600ºC until weight of residue was constant. If the loss in weight is 28%, find the amount of lead nitrate and sodium nitrate in mixture.

15. Upon mixing 45.0 mL of 0.25 *M* lead nitrate solution with 25 mL of 0.10 *M* chromic sulphate, precipitation of lead sulphate takes place. How many moles of lead sulphate are formed ? Also calculate the molar concentrations of the species left behind in final solution. Assume that lead sulphate is completely insoluble.

ANSWERS

Objectives

1.	(b)	2.	(c)	3.	(b)	4.	(d)	5.	(c)
6.	(a)	7.	(d)	8.	(b)	9.	(b)	10.	(c)
11.	(d)	12.	(a)	13.	(c)	14.	(b)	15.	(c)
16.	(d)	17.	(a)	18.	(c)	19.	(b)	20.	(d)
21.	(a)	22.	(a)	23.	(c)	24.	(c)	25.	(d)
26.	(b)	27.	(a)	28.	(b)	29.	(b)	30.	(d)
31.	(b)	32.	(a)	33.	(b)	34.	(b)	35.	(a)

Miscellaneous Assignment

1.	(a)	2.	(c)	3.	(a)	4.	(a)	5.	(c)
6.	(b)	7.	(a)	8.	(c)	9.	(b)	10.	(a)

Subjective Problems

1. 0.597 g
2. $BaCl_2.2H_2O$ = 7.038 g , H_2O = 42.962 g
3. 40 g, 0.05 N
4. 20.78%
5. NaOH = 0.06 g per 200 mL, Na_2CO_3 = 0.0265 g per 200 mL.
6. 6%
7. 8.097 mL
8. 6.125 g/litre
9. 55.53 litre
10. K_2CO_3 = 96%, Li_2CO_3 = 4%
11. SO_4^{2-} ion concentration = 6.528
12. 27.27%
13. C_2H_6 = 0.66, C_2H_4 = 0.34
14. $Pb(NO_3)_2$ = 3.32 g, $NaNO_3$ = 1.68 g
15. 0.0075, $[Pb^{2+}]$ = 0.0536 *M*, $[NO_3^-]$ = 0.32 *M*, $[Cr^{3+}]$ = 0.0714 *M*