Stoichiometry - 1

BASIC IDEAS Section - 1

In this chapter, we are going to build the basics of solving the numerical problems in chemistry. The concepts here involve, understanding of mole concept, gram equivalents and their applications in various chemical processes.

Concept of Gram Atom :

One gram-atom of an element means collection of 6.023×10^{23} atoms. This concept applies only to the elements, which exist in poly-atomic states (e.g. O as O_2, Cl as Cl_2, S as S_8, P as P_4 etc.).

$$\text{Atomic mass} = \frac{\text{Mass of 1 atom of an element}}{1/12^{\text{th}} \text{ the weight of } C^{12}}$$

(in a.m.u. where 1 a.m.u. = Atomic Mass Unit = 1.66×10^{-27} kg)

(a) The number of *gm*–atoms in ‘g’ gm of an element whose atomic mass is **A** is :

$$\boxed{\text{gm-atoms} = \frac{g}{A}}$$

Illustrating the Concept :

- gm-atoms in 142 grams of chlorine = $\frac{g}{A} = \frac{142}{35.5} = 4$
- gm-atoms in 16 grams of Oxygen = $\frac{g}{A} = \frac{16}{16} = 1$

(b) The number of atoms in ‘g’ gms of an element is given by :

$$\boxed{\text{No. of atoms} = \frac{g}{A} \times N_0} \quad (N_0 = \text{Avogadro number} = 6.023 \times 10^{23})$$

Note : *The concept of gm-atom is useful in Radioactivity as it gives us number of nuclei i.e.*

No. of nuclei = Number of atoms = gm-atoms × N_0 = $\frac{g}{A} \times N_0$

Illustrating the Concept :

Number of atoms in 56 grams of Nitrogen = $\frac{56}{14} \times 6.023 \times 10^{23} = 2.4092 \times 10^{24}$

Note : Atomic masses of some common elements are given at the end of this chapter.

Concept of Gram Mole :

The collection of 6.023×10^{23} molecules of an element or ions or a compound constitute 1 mole of that element or of ions or of compound. This magical number 6.023×10^{23} is known as Avogadro Number (N_0).

- The number of moles (**n**) in 'g' grams of a substance, whose molecular weight is M_0 is given by :

$$\text{Number of moles} = n = \frac{g}{M_0}$$

- The number of molecules in *n* moles :

$$\text{Number of molecules} = nN_0 = \frac{g}{M_0} \times N_0$$

- The number of millimoles :

$$\text{Millimoles (m.moles)} = \frac{g}{M_0} \times 1000$$

Illustrating the Concept :

- Number of moles in *46* grams of sodium (Na)

$$\text{moles} = \frac{g}{M_0} = \frac{46}{23} = 2$$ (Atomic Mass of Na = 23 = molecular mass as Na is monoatomic)

- Number of moles in *100* gm of Chlorine (Cl_2)

$$\text{moles} = \frac{g}{M_0} = \frac{100}{71} = 1.4$$ (Mol. Mass Cl_2 = 2 × 35.5 = 71)

- Number of moles in *54* grams of phosphorus (P_4)

$$\text{moles} = \frac{g}{M_0} = \frac{54}{124} = 0.4355$$ (Mol. Mass of P_4 = 4 × Atomic weight = 4 × 31 = 124)

- Number of moles in *49* grams of sulphuric acid (H_2SO_4)

$$\text{moles} = \frac{49}{98} = \frac{1}{2} = 0.5$$ (Mol. Mass = 2 × 1 + 32 + 16 × 4 = 98)

- Number of moles in *25* gm of $CaCO_3$ (calcium carbonate)

$$\text{moles} = \frac{25}{100} = 0.25$$ (Mol. Mass = 40 + 12 + 16 × 3 = 100)

Concept of Gram Equivalents :

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

$$\text{gram equivalents (gm.eq)} = \frac{\text{grams}}{\text{Equivalent weight}} = \frac{g}{E}$$

To understand the concept of gram equivalent, one must know the meaning of **equivalent weight** (**E**) of an element or a compound.

Theoretically, **Equivalent weight (E)** of an element or a compound is defined as *the weight of an element or a compound which would combine with or displace (by weight) 1 part of hydrogen or 8 parts of oxygen or 35.5 parts of chlorine.*

Analytically, **Equivalent weight (E)** is defined for elements/ions/compounds as :

$$\mathrm{E} = \frac{\text{Molecular Weight}}{x}$$

where x is known as Valence factor or 'n' factor and its value varies depending upon the compound being considered.

(i) Equivalent Weight (E) of an Element :

$$\mathrm{E} = \frac{\text{Atomic weight of an element}}{\text{Valency of element}}$$

$$\mathrm{E}_{(\text{Aluminium})} = \frac{27}{3} = 9 \qquad \mathrm{E}_{(\text{Magnesium})} = \frac{24}{2} = 12$$

$$\mathrm{E}_{(\text{Oxygen})} = \frac{16}{2} = 8 \qquad \mathrm{E}_{(\text{Chlorine})} = \frac{35.5}{1} = 35.5$$

(ii) Equivalent Weight (E) of an Acid :

$$\mathrm{E} = \frac{\text{Molecular weight of acid}}{\text{Basicity}}$$

Acid : A species capable of giving H^+ ions (protons) in its aqueous solution is an acid.
It is generally represented as HA. The number of H^+ ions furnished by an acid determines the **basicity** of acid.

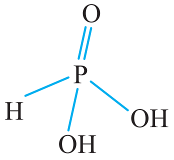
- Basicity of HCl (Hydrochloric acid) = 1 (As it furnishes only 1 H^+ ion)
- Basicity of H_2SO_4 (Sulphuric acid) = 2
- Basicity of H_3PO_4 (Phosphoric acid) = 3
- Basicity of $H_2C_2O_4$ (Oxalic acid) = 2

Note : *It is not necessary that basicity of an acid is equal to the number of H^+ ions contained in its formula. It is the number of* ***furnishable H^+ ions*** *which determines the basicity of an acid.*

Basicity of CH_3COOH (Acetic acid) = 1

Basicity of H_3PO_3 (Phosphorus acid) = 2

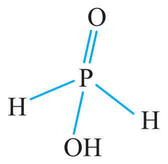
This can be deduced from its structure shown ($\longrightarrow$) :



As it can be seen that number of –OH groups are 2, the number of furnishable H^+ ions will also be 2.

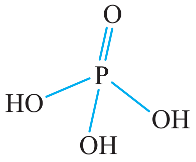
Note that bond between P and –OH will not break as it is a stronger bond compared to the bond strength between H and O in –OH group. So, H_3PO_3 is not a base although it contains 2 –OH groups. The H attached directly to P atom will not be able to furnish in the solution as this bond is quite strong.

On the similar grounds, try to calculate the basicity of H_3PO_2 (Hypophosphorus acid). Its structure is shown on right..



(*Ans*: *Basicity of* $H_3PO_2 = 1$)

Also, note the structure of H_3PO_4 (Phosphoric acid) and its basicity (= 3).



$$E_{HCl} = \frac{36.5}{1} = 36.5 \qquad E_{H_2SO_4} = \frac{98}{2} = 49.0 \qquad E_{H_2C_2O_4} = \frac{90}{2} = 45.0$$

(oxalic acid)

$$E_{H_3PO_4} = \frac{98}{3} = 32.6 \qquad E_{H_3PO_3} = \frac{82}{2} = 41.0 \qquad E_{CH_3COOH} = \frac{60}{1} = 60$$

(iii) Equivalent Weight (E) of a Base:

$$E = \frac{\text{Molecular weight of base}}{\text{Acidity}}$$

Base: A species capable of giving OH^- ions (hydroxyl) in its aqueous solution. It is generally represented as BOH. The number of OH^- ions furnished by a base determines the **acidity** of base.

- Acidity of NaOH (Sodium hydroxide) = 1
- Acidity of $Mg(OH)_2$ (Magnesium hydroxide) = 2
- Acidity of $Al(OH)_3$ (Aluminium hydroxide) = 3

$$E_{NaOH} = \frac{40}{1} = 40.0 \qquad E_{Mg(OH)_2} = \frac{58}{2} = 29 \qquad E_{Ca(OH)_2} = \frac{74}{2} = 37.0$$

(iv) Equivalent Weight (E) of an Ion :

E of an ion is determined by the charge on an ion irrespective of anion and cation.

$$\text{E of an ion} = \frac{\text{Molecular weight of ion}}{\text{Magnitude of charge on ion}}$$

$$E_{Cl^-} = \frac{35.5}{1} = 35.5 \qquad E_{O^{2-}} = \frac{16}{2} = 8 \qquad E_{Al^{3+}} = \frac{27}{3} = 9.0$$

$$E_{CO_3^{2-}} = \frac{60}{2} = 30.0 \qquad E_{PO_4^{3-}} = \frac{95}{3} = 31.66 \qquad E_{C_2O_4^{2-}} = \frac{88}{2} = 44.0$$

(oxalate)

(v) Equivalent Weight (E) of a Compound :

Equivalent of a compound (E) depends upon how a given compound reacts in a particular reaction. It means that equivalent weight can be variable. However, there are certain compounds for which equivalent weight remains constant. The equivalent weight of alkali metal salts (Na, K etc) and alkaline-earth metals salts (Mg, Ca etc) is constant. It depends upon the magnitude of total charge on cation or anion.

$$E = \frac{\text{Molecular weight}}{\text{Magnitude of total charge on cation or anion}}$$

$$E_{Na_2CO_3} = \frac{106}{2} = 53 \quad \text{(Magnitude of total charge on cation or anion = 2)}$$

$$E_{Al_2(CO_3)_3} = \frac{234}{6} = 39 \quad \text{(Magnitude of total charge on cation or anion = 6)}$$

(vi) Equivalent weight (E) of an Oxidising and Reducing Agent :

For the compounds taking part in redox reactions, the calculation of **E** becomes rather complex and one has to be very cautious. First, one should make sure which compound is acting as *oxidising agent* (**O.A.**) and which is acting as *reducing agent* (**R.A.**). Then find the number of electrons transferred by one mole of O.A. or R.A. in the reaction.

$$\text{E of compound} = \frac{\text{Molecular weight}}{\text{Electron transfer per mole of O.A or R.A}}$$

Note : We will discuss this concept in the study of **Redox Reactions** in more detail in upcoming modules.

Illustrating the Concept :

- gm. eq. in 71 gms of Chlorine atoms : $\text{gmeq.} = \frac{71}{35.5} = 2$ $(E_{Cl} = 35.5)$
- gm. eq in 16 gms. of Oxygen atoms : $\text{gm.eq} = \frac{g}{E} = \frac{16}{8} = 2$ $(E_O = 8)$
- gm. eq in 500 gms of H_3PO_4 : $\text{gm.eq} = \frac{g}{E} = \frac{500}{32.67} = 15.3$ $(E_a = \frac{M_0}{\text{basicity}})$
- gm. eq in 150 gms of $Mg(OH)_2$: $\text{gm.eq} = \frac{g}{E} = \frac{150}{29} = 5.17$ $(E_b = \frac{M_0}{\text{acidity}})$

Note : In practical cases, a smaller unit of moles and gram equivalent is used and is given by :

- The number of milli moles (*m.moles*) in *g* grams = $\frac{g}{M_0} \times 1000$
- The number of milli equivalents (*meq*) in *g* grams = $\frac{g}{E} \times 1000$

Relationship between Moles and Gram Equivalents :

$$\text{Gram equivalents} = \frac{g}{E} = \frac{g}{M_0 / x} = x \times \frac{g}{M_0} = x \times \text{moles}$$

IN-CHAPTER EXERCISE-A

1. *Fill in the blanks :*

(a) *gm atoms in 24 gm of Magnesium are* ________

(b) *gm atoms in 62 gm of* P_4 *are* __________

(c) *moles and gm equivalents in 196 gms of* H_3PO_4 *are* ________ *and* ___________

(d) *moles and gm equivalents in 196 gms of* $Ca(OH)_2$ *are* ________ *and* ___________

(e) *The weight of one mole of Sodium carbonate* (Na_2CO_3) *is*______________________

(f) *The number of molecules in 16 grams of Sulphur dioxide* (SO_2) *are* _______________

(g) *The mass of 1 molecule of water* (H_2O) *is* __________

2. *From 200 mg of* CO_2, 10^{21} *molecules are removed. How many grams of* CO_2 *are left ?*

(A) 0.5 *gm* *(B)* 0.25 *gm* *(C)* 0.126 *gm* *(D)* 0.063 *gm*

3. *A metal M of atomic weight 60 gm / mol has a density of* $10.0\,g/cm^3$. *Calculate the volume occupied by one atom.*

(A) $1\times10^{-23}\ cm^3$ *(B)* $2\times10^{-23}\ cm^3$ *(C)* $3\times10^{-23}\ cm^3$ *(D)* $4\times10^{-23}\ cm^3$

4. *Choose the correct option for each of the following :*

(i) *The simplest formula of a compound containing 50% of element A (atomic mass 10) and 50% of element B (atomic mass 20) is :* [**Hint :** *Assume weight of compound to be* 100 *gm*]

(A) *AB* *(B)* A_2B *(C)* AB_3 *(D)* A_2B_3

(ii) *The number of water molecules present in a drop of water (volume 0.0018 ml) at room temperature is :* *(Density of water* ~ 1.0 *g/cc)*

(A) 6.023×10^{19} *(B)* 1.084×10^{18} *(C)* 4.84×10^{17} *(D)* 5.023×10^{23}

(iii) *Which of the following has least mass :*

(A) *2 g atom of nitrogen* *(B)* 3×10^{23} *atoms of C*

(C) *1 mole of S* *(D)* *7.0 g of Ag*

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.

$$\text{Concentration of solute} = \frac{\text{Amount of solute}}{\text{Amount of solution (or solvent)}}$$

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

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

$$\text{mass fraction of } (W_B)\ B = \frac{g_B}{g_A + g_B} \qquad \text{mass fraction } (W_A)\ A = \frac{g_A}{g_A + g_B}$$

Note : $W_A + W_B = 1$

2. **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 a solution containing n_A moles of solvent and n_B moles of solute ;

$$\text{mole fraction of B } \chi_B = \frac{n_B}{n_A + n_B} \qquad \text{mole fraction of A } \chi_A = \frac{n_A}{n_A + n_B}$$

Note : $\chi_A + \chi_B = 1.$

Illustrating the Concept :

A given solution consists of 230 gm of C_2H_5OH (ethyl alcohol) and 720 gm of H_2O (water). How to determine the mole fraction of each component.

First, calculate moles of ethyl alcohol and water.

$$\text{moles of } C_2H_5OH = \frac{230}{46} = 5.0 \quad \text{and} \quad \text{moles of } H_2O = \frac{720}{18} = 40.0$$

Now let χ_A = mole fraction of H_2O and χ_B = mole fraction of C_2H_5OH

$$\chi_A = \frac{40}{40+5} = 0.88 \quad \text{and} \quad \chi_B = 1 - \chi_A = 0.12$$

3. **Molality (m)** is expressed as number of moles of solute dissolved in 1000 gms (1.0 Kg) of solvent. It is denoted by m. The unit is mol/kg. It can also be denoted by m.

i.e. $$m = \frac{\text{moles of solute}}{\text{kg of solvent}}$$

If n_B represent moles of solute and g_A represent gms of solvent, then, $m = \frac{n_B}{g_A} \times 1000$

Illustrating the Concept :

How to determine the molality of solution containing 87.7 gm of NaCl (sodium chloride) dissolved in 1500 gm of water ?

First, calculate moles of NaCl : $\text{moles} = \frac{g}{M} = \frac{87.7}{58.5} = 1.5$

$$\text{Now, molality (m)} = \frac{n_B}{g_A} \times 1000 = \frac{1.5}{1500} \times 1000 = 1.0\,\text{m}$$

4. **Molarity (M)** is expressed as moles of solute contained in one litre of solution *or* it is also taken as millimoles of solute in 1 cc (ml) of solution. Its unit is mol/ℓt. It is also denoted by M.

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

If n_B represents number of moles of solute and V_L be volume of solution in litres.

$$M = \frac{n_B}{V_L} = \frac{g_B/M_B}{V_L}$$

Note : moles of solute = Molarity × Volume in litres ⇒ $n_B = MV_L$ (M : molarity).

or m.moles of solute = Molarity × Volume in cm^3 (ml) = MV_{cc}

1 mL = 1 millilitre, 1 cc = 1 ml = 1 cubic centimetres

Illustrating the Concept :

How to determine the molarity of a solution containing 149 gram of KCl (potassium chloride) dissolved in sufficient water to make 1500mL of a solution?

$$\text{Molarity} = \frac{\text{moles of KCl}}{\text{litres of solution}} \qquad \left(\text{where moles} = \frac{g}{M_0}\right)$$

$$\text{moles of KCl} = \frac{149}{74.5} = 2.0 \quad \Rightarrow \quad \text{Molarity} = \frac{2.0}{1500/1000} = 1.33\,\text{molar} \text{ or written as } 1.33\text{ M}$$

How to calculate grams of solute (solid NaOH) in a 500 cc of 0.25M solution of NaOH ?

$\text{Moles} = MV_L$ M : molarity of solution; V_L : volume of solution in litres.

$$\text{Moles} = 0.25 \times \frac{500}{1000} = 0.125 \quad \Rightarrow \quad \text{gram of NaOH} = 0.125 \times 40 = 5\text{ gm} \qquad (\text{mass} = nM_0).$$

5. **Normality (N)** is expressed as the number of gram equivalents (gmeq) of solute contained in one litre of solution or it can also be taken as number of mill equivalents (meq) in 1 cc (mL) of solution. It is denoted by N.

$$\text{Normality of solution (N)} = \frac{\text{gmeq of solute}}{\text{litres of solution}} = \frac{\text{meq of solute}}{\text{millilitres of solution}}$$

If g_B represents grams of solute, *E* represents *Equivalent weight* of solute and V_L be volume of solution in litres,

$$\text{Normality} = \frac{\text{gmeq}}{V_L} = \frac{g_B/E}{V_L}$$

Important Concepts in Stoichiometric Calculations :

[A] **(a)** gm.eq. of solute = normality × volume in litres $= NV_L$

or meq of solute = normality × volume in cm^3 (mL) $= NV_{cc}$

(b) moles of solute $= \text{Molarity} \times V_L = MV_L$

or m.mol of solute $= \text{Molarity} \times V_{mL} = MV_{mL}$

[B] $$\text{Normality} = \frac{\text{gm.eq}}{V_L} = \frac{x \times \text{moles}}{V_L} = x \times \text{Molarity}$$

For acidic solutions : N = x M [x : basicity of acid ; M : molarity of acid]

For basic solutions : N = x M [x : acidity of base ; M : molarity of base]

For a mono acidic base (acidity =1) and mono basic acid (Basicity = 1) ⇒ Normality = Molarity

[C] **Relation between molality (m), molarity (M), density (d) of solution and molar mass of solute (M_0):**

Molarity (M) means M moles of the solute in 1 L of the solution. If density is in g/mL and M_0 is molar mass in $g\ mol^{-1}$, then

mass of solute $= MM_0$ grams ; mass of solution $= 1000 \times d$ grams

$\Rightarrow$ mass of solvent $= 1000d - MM_0$

$$\Rightarrow \quad \text{Molality (m)} = \frac{M}{1000d - MM_0} \times 1000$$

[D] Relationship between molality (m) and mole fraction (χ_B) of the solute :

$$\chi_B = \frac{n_B}{n_A + n_B} \quad ; \quad m = \frac{n_B}{g_A} \times 1000 = \frac{n_B}{n_A M_A} \times 1000$$

$$\Rightarrow \quad n_B = m n_A M_A/1000 \quad \text{or} \quad \chi_B = \frac{m n_A M_A/1000}{n_A + m n_A M_A/1000}$$

$$\Rightarrow \quad \chi_B = \frac{mM_A}{1000 + mM_A} \quad \Rightarrow \quad m = \frac{\chi_B}{1-\chi_B} \times \frac{1000}{M_A} \equiv \frac{1-\chi_A}{\chi_A} \times \frac{1000}{M_A}$$

Illustrating the Concept :

A solution was prepared by adding sufficient water to 100g of NaOH to make 0.50 L of solution. Calculate molarity and normality of solution.

$$\text{Normality} = \frac{\text{gmeq}}{V_L} = \frac{100/40}{0.5} = 5\,\text{N} \qquad \left(\text{gmeq} = \frac{g}{E},\ \ E = \frac{M_0}{\text{acidity}}\right)$$

Now using N = x M ;

$$\Rightarrow \quad M = \frac{5}{1} = 5\,\text{M solution} \qquad [x = 1 \text{ for NaOH (Mono-acidic base)}]$$

A solution was prepared containing 14.80 gm of Ca(OH)$_2$ in 3000 ml of solution. Calculate:

(a) molarity of solution *(b) normality of solution*

(c) moles in a 2.5 L of same solution *(d) gmeq contained in 1.5L of solution.*

(a) $$\text{Molarity} = \frac{\text{moles of } Ca(OH)_2}{V_L} = \frac{14.8/74}{3000/1000} = 0.067\text{M}$$

(b) $$\text{Normality} = \frac{\text{gmeq of } Ca(OH)_2}{V_L} = \frac{14.8/E}{3} = \frac{14.8/37}{3} = 0.133\text{N} \qquad \left[E = \frac{M_0}{\text{acidity}} = \frac{74}{2}\right]$$

(c) moles in 2.5 L of sample = MV_L = 0.067 × 2.5 = 0.167 moles (in 2.5 L sample).

(d) gmeq in 1.5 L of sample = NV_L = 0.133 × 1.5 = 0.2 gmeq (in 1.5 L).

6. Strength of a solution : It is expressed as grams of solute in 1 L of a solution.

$$\text{Strength} = \frac{\text{grams of solute}}{V_L}$$

We know, $$NV_L = \frac{g}{E} = \text{gmeq}$$

$$\text{Strength} = \frac{g}{V_L} = NE$$

Similarly, $$\text{Strength} = \frac{g}{V_L} = MM_0$$

Illustrating the Concept :

How to calculate normality when Strength is given ?

(i) HNO$_3$ containing 6.3 g/L of acid.

(ii) KOH solution containing 11.2 g/L of base.

(i) $E_{HNO_3} = \frac{63}{1} = 63 \quad \Rightarrow \quad N = \frac{6.3}{63} = 0.1N \quad \left(N = \frac{\text{strength}}{E}\right)$

(ii) $E_{KOH} = \frac{56}{1} = 56 \quad \Rightarrow \quad N = \frac{11.2}{56} = 0.2N$

How to calculate E when Strength is given ?

(i) ***10–N HCl acid solution containing 3.65 g/10 ml.***

(ii) ***N/3.5 H_2SO_4 acid solution containing 14 g/L.***

$$\text{Eq. wt} = \frac{\text{Strength}}{\text{Normality}}$$

(i) $E_{HCl} = ?$ Strength = 3.65 g /10 ml = 365 g /L

$$E_{HCl} = \frac{365}{10} = 36.5$$

(ii) Similarly, $E_{H_2SO_4} = \frac{14}{1/3.5} = 49$

Important Concepts in Stoichiometric Calculations :

1. If molarity of a solute $A_x B_y$ in a solution is 'M', assuming the solute to have complete dissociation (100%).

$$A_x B_y \longrightarrow x A^{y+} + y B^{x-}$$

Then, molarity of A^{y+} ions = x × M ; molarity of B^{x-} ions = y × M $\left[\because \text{ 1 mole } A_x B_y \text{ gives } x \text{ moles of } A^{y+} \text{ and } y \text{ moles of } B^{x-}\right]$

But, *same is not applicable to normality*.

If normality of solute $A_x B_y$ is 'N', assuming the solute to have complete dissociation (100%) :

$$A_x B_y \longrightarrow x A^{y+} + y B^{x-}$$

Then, normality of A^{y+} ions = N ; normality of B^{x-} ions = N $\left[\because \text{ gmeq. of } A_xB_y \equiv \text{gmeq. of } A^{y+} \equiv \text{gmeq. of } B^{x-}\right]$

(Correlate the above results, with the definitions of molarity and normality respectively).

Illustrating the Concept :

$0.1 \text{ M } H_2SO_4 \equiv 0.2 \text{ M } H^+ \equiv 0.1 \text{ M } SO_4^{2-}$ $\quad$ $0.1 \text{ N } H_2SO_4 \equiv 0.1 \text{ N } H^+ \equiv 0.1 \text{ N } SO_4^{2-}$

2. When Solute is Solid :

(a) ***x% by mass of solute (B) in the solution (A):*** It means *x* gm of solute (B) are present in 100 gm of solution (A).

(b) ***x% by volume of solute (B) in the solution (A):*** It means *x* gm of solute (B) are present in 100 cm^3 of solution (A).

3. When Solute is also a Liquid :

(a) ***x% by mass of solute (B) in the solution (A):*** It means *x* gm of solute (B) are present in 100 gm of solution (A).

(b) ***x% by volume of solute (B) in the solution (A):*** It means *x* cm^3 of solute are present in 100 cm^3 of solution (A).

Illustrating the Concept :

The molarity and normality of solution of H_2SO_4 containing x% H_2SO_4 by weight. ($d_{solution}$ = d gm/cc)

First, you must understand meaning of *x*% H_2SO_4 by weight.

This means *x* gms of actual amount of H_2SO_4 in 100 gms of solution or if *W* (in gms) be the be total mass of solution, then the mass of solute (H_2SO_4) contained = $\frac{x}{100} \times \text{W gms}$.

Now coming back to original problem ;

Let us consider 1 L or 1000 cc of solution

Mass of solution in 1 L = 1000 d $\left(d = \frac{\text{mass}}{\text{volume}}\right)$

Mass of actual H_2SO_4 in 1 L $= \frac{x}{100} \times (1000\,d) = 10\,x d$

$\Rightarrow$ moles of H_2SO_4 in 1 L = $\frac{10\,x d}{M_0}$ $\left[\text{moles} = \frac{g}{M_0}\right]$

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

Illustration - 1 ***(a) Concentrated acid H_2SO_4 has a density of 1.8 g/ml and contains 49% acid by weight. Compute molarity of the solution. Also calculate the number of gmeq of H_2SO_4 contained in 1 L solution.***

(b) What is the normality of a solution which is prepared by dissolving 100 ml of conc. H_2SO_4 in part (a) in sufficient water to make 500 ml of solution?

(c) If we take 50 ml sample of above solution [in part (b)], find number of milli moles and milli equivalents in the sample.

Solution : **(a)** We have : $\text{Molarity} = \frac{10 x d}{M_0}$

$\text{molarity}(M) = \frac{10 \times 49 \times 1.8}{98} = 9.0 M$ (*x* = 49, *d* = 1.8 g/mL = 1.8 g/cc, M_0 = 98)

To calculate gmeq, it is better to calculate normality first.

N = *x* M = 2 × 9 = 18 N *x* : Basicity of H_2SO_4 = 2

gm.eq. = NV_{cc} = 1 × 18 = 18 gmeq are contained in 1 L of given solution.

(b) N of H_2SO_4 = 18 [calculated above in part (a)]

gmeq in 100 cc of conc. $H_2SO_4 \equiv \frac{18.0 \times 100}{1000} = 1.8$

So, 1.8 gmeq of concentrated acid are to be added in water to make 500mL solution.

Normality of required solution $= (N) = \frac{\text{gmeq}}{V_L} = \frac{1.8}{500/1000} = 3.6$

(c) Milli equivalents = Normality × Volume (in ml) = $NV_{CC} = 3.6 \times 50 = 180$ meq.

Millimoles = Molarity × Volume (in ml) = MV_{CC}

$$= \frac{3.6}{2} \times 50 = 90\ m.moles \qquad [N = x\,M \text{ and } x = 2 \text{ for } H_2SO_4\text{, a dibasic acid}]$$

Note : If a naturally occurring atom exists in the form of isotopes (say of molecular masses A_1, A_2, ... etc) with their percentages as (x_1 %, x_2 % . . . . etc), then average atomic mass, A_{avg} of the atom is given as :

$$A_{avg} = \frac{x_1}{100} \times A_1 + \frac{x_2}{100} \times A_2 + \ldots\ldots\ldots\ldots$$

Illustrating the Concept :

The mass spectrum of carbon shows that 98.892% of carbon atom are C-12 with a mass of 12.000 amu and 1.108% are C-13 with a mass of 13.000335 amu. Calculate the atomic weight of naturally occurring carbon.

$$\text{Atomic weight of carbon} = \frac{98.892}{100} \times 12.000 + \frac{1.108}{100} \times 13.00335 = 12.011 \text{ amu}$$

If isotopic distribution of isotopes (relative abundance) C-12 and C-14 is 98% and 2% respectively then the number of C-14 atoms in 12g of carbon is :

(A) $\mathbf{1.20 \times 10^{22}}$ **(B)** $\mathbf{3.01 \times 10^{22}}$ **(C)** $\mathbf{5.55 \times 10^{23}}$ **(D)** $\mathbf{6.023 \times 10^{23}}$

$$\text{Average atomic mass} = \left(\frac{98}{100} \times 12\right) + \left(\frac{2}{100} \times 14\right) \approx 12$$

Total No. of C atoms in 12g of C = 6.023×10^{23}

$$\Rightarrow \quad \text{Total No. of C-14 atoms in 12g of C} = \frac{2}{100} \times 6.023 \times 10^{23} = 12.046 \times 10^{21} = 1.20 \times 10^{22} \quad \textbf{(A)}$$

There are two isotopes of an element with atomic mass z. Heavier one has atomic mass z + 2 and lighter one has z – 1, then abundance of lighter one is :

(A) **66.6%** **(B)** **96.7%** **(C)** **6.67%** **(D)** **33.3%**

$$\text{Let } x\% \text{ be abundance of lighter one. Then } \frac{(100 - x)}{100} \times (z + 2) + \frac{x}{100} \times (z - 1) = z$$

$$\Rightarrow \quad (100 - x)\,)\,(z + 2) + x\,(z - 1) = 100z \quad \Rightarrow \quad x = 66.6 \quad \textbf{(A)}$$

Note : A hydrated salt is a crystalline salt that has a certain number of water molecule trapped in the crystal.

For example : $CuSO_4.5H_2O$. The molecules of water contained in one such unit of hydrated salt is known as water of crystallisation. In the given example water of crystallisation in hydrated copper sulphate is 5. While calculating molecular mass of such a salt, we have to add molecular mass of water of crystallisation to overall molecular mass of salt.

For example : Consider hydrated oxalic acid ($H_2C_2O_4.2H_2O$). Its molecular mass will be = 90 + (2 × 18) = 126.

IN-CHAPTER EXERCISE - B

1. *Fill in the blanks :*

(a) *The % age composition (by mass) and mole fraction of each component in sugar solution containing 1000 gm of sugar in 2000 gm of water is ________.*

(b) *The mass of $MgCl_2$ should be dissolved in 750 gm of water in order to prepare a 1.05m solution is _______*

2. *49 grams of H_2SO_4 are dissolved in enough water to make one litre of a solution of density 1.049 g/cc. Find the molarity, normality, molality of H_2SO_4 in the solution.*

(A) (M, N, m) **(B)** (M/2, N/2, m/2) **(C)** (M/2, N, m/2) **(D)** (M, N/2, m/2)

3. *If x% of a solute of molecular mass (M_0) is present in a solution having density of 'd' gm/cm^3, calculate molarity, and molality, if*

(a) *x% is by mass* **(b)** *x% is by volume*

4. (a) *The molality of 1 M solution of sodium nitrate is 0.8 mol kg^{-1}. Determine the density of the solution.*

(b) *How much $BaCl_2$ would be needed to make 250 ml of a solution having same concentration of Cl^- as the one containing 2.92 g of NaCl per 100 ml? [1 molar $BaCl_2 \equiv 2$ molar Cl^- ions]*

5. *The density of 3 M solution of $Na_2S_2O_3$ is 1.2g ml^{-1}.*

(a) *the % by weight of $Na_2S_2O_3$ is __________*

mole fraction of $Na_2S_2O_3$ is ____________

(b) *the molalities of Na^+ and $S_2O_3^{2-}$ ions are ______ and ______*

6. Choose the correct alternative. Only one choice is correct. However, question marked '*' may have more than one correct option.

(i) *Hydrochloric acid solution A and B have concentration of 0.5 N and 0.1 N respectively. The volume of solution A and B required to make 2 litres of 0.2 N hydrochloric are :*

(A) 0.5 L of A + 1.5 L of B **(B)** 1.5 L of A + 0.5 L of B

(C) 1.0 L of A + 1.0 L of B **(D)** 0.75 L of A + 1.25 L of B

(ii) *The density of 1 M solution of NaCl is 1.0585 g/ml. The molality of the solution is :*

(A) 1.0585 **(B)** 1.00 **(C)** 0.10 **(D)** 0.0585

(iii) *0.2 mol of HCl and 0.1 mol of barium chloride dissolved in water to produce a 500 mL solution. The molarity of the Cl^- is :*

(A) 0.06 M **(B)** 0.09 M **(C)** 0.12 M **(D)** 0.80 M

(iv) *The hydrated salt $Na_2SO_4.nH_2O$ undergoes 55.9% loss in weight on heating and becomes anhydrous. The value of n will be :*

(A) 5 **(B)** 3 **(C)** 7 **(D)** 10

(v) *A sample of H_2SO_4 (density $1.8\,g\,mL^{-1}$) is 90% by weight. What is the volume of the acid that has to be used to make 1 L of 0.2 M H_2SO_4 ?*

(A) 16 mL **(B)** 10 mL **(C)** 12 mL **(D)** 18 mL

***(vi)** *Which of the following quantities are dependent on temperature ?*

(A) Molarity **(B)** Normality **(C)** Molality **(D)** Mole fraction

(vii) *An aqueous solution of urea (NH_2CONH_2) is 3.0 molal. The mole fraction of urea is :*

(A) 0.25 **(B)** 0.33 **(C)** 0.66 **(D)** 0.05

(viii) *The atomic mass of Cu is 63.546. There are only two naturally occurring isotopes of copper; Cu^{63} and Cu^{65}. The percentage of natural abundance of Cu^{63} is nearly :*

(A) 10 **(B)** 30 **(C)** 50 **(D)** 73

Important Concepts in Stoichiometric Calculations :

1. **Dilution :** Whenever a given solution of known concentration i.e., normality and molarity (known as standard solution) is diluted (adding solvent), the number of millimoles (or milli equivalents) of solute remain unchanged. The concentration of solution however changes.

In such a case if :

N_1 = normality of original solution ; V_1 = volume of original solution

and N_2 = normality of diluted solution ; V_2 = total volume of diluted solution

Since the number of milli equivalents remains same,

⇒ $N_1V_1 = N_2V_2$ (This also called equation of normality)

Also, $M_1V_1 = M_2V_2$ (This also called equation of molarity)

Illustrating the above concept :

0.2 M H_2SO_4 (1 mL) is diluted to 1000 times of its initial volume. Find normality of H_2SO_4.

$$M_1V_1 = M_2V_2 \Rightarrow M_2 = 0.2 \times \frac{1}{1000} = 2 \times 10^{-4} \Rightarrow N_2 = 2 \times 2 \times 10^{-4} = 4 \times 10^{-4}\ \text{N}\ \text{(Normality = n-factor × molarity)}$$

2. Whenever a small sample (volume) is taken from a standard solution, the concentration of sample is same as that of standard solution. However number of millimoles (or milli equivalents) in sample differs from that of standard solution.

From a 3.5 L of 0.5 N H_2SO_4 solution, a sample of 500mL is taken, then normality of a 500 mL solution is also 0.5N.

But meq in standard solution = 0.5 × 3500 = 1750 meq and meq in small sample = 0.5 × 500 = 250 meq

Illustration - 2 ***What volume of water must be added to a 0.5 litre of 10 N acid solution to make it exactly 0.5 N solution ?***

Solution : Let V_{cc} of water is added to given solution of acid.

Apply equation of normality (for dilution) i.e. $N_1V_1 = N_2V_2$

V_1 = vol. of original solution = 0.5L = 500 cc ; N_1 = normality of solution

V_2 = final volume of solution ; N_2 = normality of final solution

⇒ $10 \times 500 = 0.5 \times (500 + V_{cc})$ ⇒ $V_{cc} = 9500\ \text{cc} = 9.5\ \text{L}$

⇒ 9.5 L of H_2O will have to be added.

Illustration - 3 *A commercial sample of oxalic acid is labelled as 22.5% $H_2C_2O_4$ by weight (density = 1.5 g/cc). Calculate: (a) molarity (b) volume of acid having same amount of solute as in 1 L of 0.2 M $H_2C_2O_4$.*

Solution :

(a) Using standard formula : *molarity* = $\frac{10xd}{M_0}$

$$M = \frac{10 \times 22.5 \times 1.5}{90} = 3.75\ M$$

(b) Let V_{cc} of acid is required.

m.moles of concentrated sample = m.moles of desired sample

Using $M_1V_1 = M_2V_2$

$3.75 \times V_{cc} = 0.2 \times 1000 \quad \Rightarrow \quad V_{cc} = 53.34$ cc

Illustration - 4 *A 0.25 molar aqueous solution of NaOH is found to have a density of 1.26 g/cc. Determine its molality with respect to NaOH. Also determine its mole fraction.*

Solution :

0.25 M NaOH ≡ 0.25 moles/litre of NaOH

≡ 0.25 moles of NaOH in 1 L of solution

Use : $\left(m = \frac{\text{moles of solute}}{\text{gms of solvent}} \times 1000 \right)$

First find the mass of water.

Mass of solution = Volume × density

Mass of solution in 1.0 litre solution

= 1000 × 1.26 = 1260 g

Now mass of NaOH = (moles × M_0)

= 0.25 × 40 = 10 gm

⇒ Mass of H_2O = 1260 − 10 = 1250 g

Hence molality (m) = $\frac{0.25}{1250} \times 1000 = 0.2$ m

For conversion of molality into mole fraction, use the following relation.

$$m = \frac{\chi_B}{1 - \chi_B} \times \frac{1000}{M_A}$$

χ_B = mole fraction of solute

M_A = molecular mass of solvent.

Note : TRY to derive the above relation yourself.

In given case : m = 0.202, $M_A = M_{H_2O} = 18$

$$\Rightarrow \quad 0.2 = \frac{\chi_{NaOH}}{1 - \chi_{NaOH}} \times \frac{1000}{18}$$

Solve to get: $\chi_{NaOH} = 0.00358$

Illustration - 5 *An aqueous solution of ethyl alcohol (C_2H_5OH) is found to be 10/9 molal. If the density of the alcohol solution is 0.8 g/cc, find mole fraction and molarity of solution with respect to ethyl alcohol.*

Solution :

Use m $= \left(\dfrac{\chi_B}{1-\chi_B}\right)\dfrac{1000}{M_A}$

(χ = mole fraction of alcohol)

$$\Rightarrow \quad \frac{10}{9} = \left(\frac{\chi_B}{1-\chi_B}\right)\frac{1000}{18} \quad \Rightarrow \quad \chi = 0.0196$$

$\frac{10}{9}$ molal solution $\equiv \frac{10}{9}$ mol of C_2H_5OH

in 1000 gms of H_2O.

For molarity, find volume of solution and for volume of solution, first calculate mass of solution.

Mass of solution = mass of solute (C_2H_5OH) + mass of water.

$= (10/9 \times 46) + 1000$

$= 51.1 + 1000 = 1051.1$

$$\text{Volume (in cc)} = \frac{mass}{density} = \frac{1051.1}{0.8} = 1313.89 \text{ cc} = 1.314 \text{ L}$$

$$\Rightarrow \quad \text{Molarity} = \frac{\text{moles}}{V_L} = \frac{1019}{1.382} = \frac{10}{11.825} = 0.845 \text{ M}$$

Illustration - 6 *One litre solution of 0.5N is heated. The volume of the solution is reduced to 750cc and 2.675 gm of HCl is lost. Calculate :*

(i) ***normality of the resultant solution.***

(ii) ***number of meq of HCl in 100 cc of the original solution.***

Solution :

(i) First calculate grams of HCl in original solution

Use: $NV_L = \dfrac{g}{E}$

$$\Rightarrow \quad 0.5 \times 1 = \frac{g}{(36.5/1)}$$

$$\Rightarrow \quad g = 18.25 \text{ gm}$$

Now wt. of HCl lost due to heating = 2.675 gm

$\Rightarrow$ wt. of HCl in resultant solution

$\Rightarrow$ = 18.25 − 2.675 = 15.575 gm

Now normality of new solution, N :

$$N = \frac{g/E}{V_L} = \frac{15.575/36.5}{750/1000} = 0.57\text{N}$$

(ii) meq in 100 cc of original sample

$\text{meq} = NV_{cc} = 0.5 \times 100 = 50 \text{ meq}$