# CHAPTER 1

# CHEMICAL ARITHMETIC

## 1.1 MOLE CONCEPT

The 'mole' in Latin means heap or mass or pile. A mole is a collection of atoms or molecules or ions whose total weight in grams is equal to the atomic weight of an element or molecular weight of a compound or formula weight of an ion respectively.

Equal number of mole of different elements contains equal number of atoms. Therefore, it is convenient to express amounts of the elements in terms of moles. The concept of mole is based upon **Avogadro's hypothesis.**

**Avogadro's hypothesis:** Under similar conditions of temperature and pressure, equal volumes of all gases contain equal number of molecules and hence equal number of moles.

e.g., $v \mu n$ if P and T are constant

$$v = kn \text{ at STP } k = \frac{v}{n} = 22.4 \text{ litres/mole}$$

**Standard molar volume:** Volume of 1 mole of gas at STP is called standard molar volume. Numerically, it is equal to 22.4 litres.

### 1.1.1 Application of Avogadro vs Hypothesis

1. **Determination of Atomicity:** Atomicity means number of atoms present in one molecule of an elementary gas, e.g., $H_2$, $N_2$ and $O_2$ have atomicity of 2 while noble gases have atomicity of 1 etc. However, atomicity is not defined for a compound.
2. **Relationship between molecular mass and vapour density:** The vapour density of any gas is the ratio of densities of the gas and hydrogen under similar conditions of temperature and pressure.

$$VD = \frac{\rho_{gas}}{\rho_{H_2}} = \frac{\text{Mol. mass}}{2}.$$

**Avogadro number:** The number of atoms of carbon present in 12 g of C–12 has been found experimentally to be $6.02 \times 10^{23}$. This number is also known as Avogadro's number.

### 1.1.2 Different Ways of Expressing Mole

(i) Number of g mole or g molecule or mole of molecule $= \dfrac{\text{Weight in gram}}{\text{Molecular weight}}$

$= \dfrac{\text{Number of molecule}}{\text{Avogadro number } (N_A)}$

(ii) Number of g mole or g atom or mole of atoms $= \dfrac{\text{Weight in gram}}{\text{Atomic weight}} = \dfrac{\text{Number of atoms}}{\text{Avogadro number } (N_A)}$

(iii) Number of moles of gases $= \dfrac{\text{Volume of gas at NTP}}{\text{Standard molar volume}} = \dfrac{\text{Number of molecules}}{\text{Avogadro number } (N_A)}$

## 1.2 LAWS OF CHEMICAL COMBINATION

Formation of chemical substances occurs through certain rules. These rules are called law of chemical combination.

(a) **Law of conservation of mass:** This law was given by Lavoisier in 1774. It is also known as law of indestructibility of matter.

| | A | + | B | → | C | + | D |
|---|---|---|---|---|---|---|---|
| t = 0 | $w_A$ | | $w_B$ | | 0 | | 0 |
| $y = t_{comp}$ | 0 | | 0 | | $w_C$ | | $w_D$ |

from law of conservation of mass, $w_A + w_B = w_C + w_D$

The more generalized form of law of conservation of mass is the principle of atomic conservation.

**Principle of atomic conservation (POAC):** According to this principle during a chemical change atoms remain conserved and if atoms remain conserve, then mole of atom will also be conserved.

i.e., number of atoms of an element in a reactant = number of atoms of that element in a product.

⇒ Mole of atoms of element in a reactant = mole of atoms of that element in a product.

e.g., if we consider the decomposition of $KClO_3$

$KClO_{3(s)} \rightarrow KCl_{(s)} + O_{2(g)}$

If we want to relate amount of $KClO_3$ with amount of $O_2$, then we apply POAC for O atom

Mole of atom of O in $KClO_3$ = Mole of atom of O in $O_2$.

⇒ $3 \times$ mole of $KClO_3 = 2 \times$ mole of $O_2$

$$\Rightarrow \quad 3 \times \frac{W_{KClO_3}}{M_{KClO_3}} = 2 \times \frac{W_{O_2}}{M_{O_2}}$$

**Advantages of POAC over other methods:**

1. POAC can be applied even in an unbalanced reaction.
2. POAC can be applied in those cases where all reaction steps and their sequence are not given in the problem.

(b) **Law of definite or constant proportion:** 'A chemical compound always contains the same elements combined together in fixed proportion by mass,' i.e., chemical compound has a fixed composition and it does not depend on the method of its preparation or the source from which it has been obtained. It is observed that C and O are always combined in the ratio of 3:8. to form $CO_2$.

## Note:

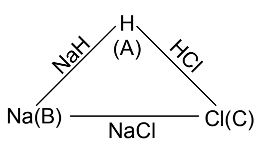
*This law is not followed for isomers.*

(c) **Law of multiple proportions:** This law was given by Dalton in 1808. According to this law, 'if two elements combine to form more than one compound, then the different masses of one element which combine with a fixed masses of the other element bear a simple ratio to one another.'
N and O combine to form five products as tabutated hereunder.

| | N | O | Simple ratio |
|---|---|---|---|
| $N_2O$ | 28 parts | 16 parts | 1 |
| $N_2O_2$ | 28 parts | 32 parts | 2 |
| $N_2O_3$ | 28 parts | 48 parts | 3 |
| $N_2O_4$ | 28 parts | 64 parts | 4 |
| $N_2O_5$ | 28 parts | 80 parts | 5 |

The masses of oxygen which combine with same mass of nitrogen in the five compounds bear a ratio of 1:2:3:4:5.

(d) **Law of reciprocal proportions:** This law was given by Richter in 1794. According to this law, 'when definite mass of an element A combines with two other elements B and C to form a compound, their combining masses are in same proportion or bear a simple ratio to the masses of B and C which combine with a constant mass of A.'
e.g., Na, H and Cl




when Na and Cl combine with 1 part of hydrogen, then the ratio of their weight will be some whole number multiple of ratio in which they combine themselves.

(e) **Law of gaseous volumes:** 'Gases react with each other in the simple ratio of their volumes and if the product is also in gaseous state, the volume of the product also bears a simple ratio with the volume of gaseous reactants, when all volumes are measured under similar conditions of temperature and pressure.'

$N_{2(g)} + 3H_{2(g)} \longrightarrow + 2NH_{2(g)}$

Example: 1 volume 3 volume 2 volume

1 : 3 : 2

## 1.3 TERMS USED IN STOICHIOMETRY

(a) **Limiting reactant:** Reactant that is present in the smallest stoichiometric amount.

**or**

If two or more reactants are mixed and if the reaction were to proceed according to the chemical equation to completion whether it does or not, the reactant that would first disappear is termed as the limiting reactant.

$2H_2(g) + O_2(g) \rightarrow 2\ H_2O(v)$

| | | | |
|---|---|---|---|
| Moles before reaction | 10 | 7 | 0 |
| Moles after reaction | 0 | 2 | 10 |

The reaction stops only after consumption of 5 moles of $O_2$ as no further amount of $H_2$ is left to react with untreated $O_2$. Thus, $H_2$ is a limiting reagent in this reaction.

(b) **Per cent Yield:** The amount of product obtained by assuming that the reaction goes cleanly and completely is called theoretical yield. The actual yield of a product is the amount present after separating it from other products and reactants and purifying it. It is always less than the theoretical yield.

$$\textbf{per cent Yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

## 1.4 LAW OF CHEMICAL EQUIVALENCE

During a chemical change, number of gram equivalent of reactants and products involved are always equal.

| A | + | B | $\rightleftharpoons$ | C | + | D |
|---|---|---|---|---|---|---|
| $w_A$ | | $w_B$ | | $w_C$ | | $w_D$ |
| $E_A$ | | $E_B$ | | $E_C$ | | $E_D$ |

$$\Rightarrow \text{Number of gram equivalent of a substance} = \frac{\text{Amount of substance in gram}}{\text{Equivalent mass of the substance}}.$$

From law of chemical equivalence, $\frac{w_A}{E_A} = \frac{w_B}{E_B} = \frac{w_C}{E_C} = \frac{w_D}{E_D}$

## 1.5 EQUIVALENT MASS

**Equivalent mass or chemical equivalent:** The number of parts by mass of the substance which combine or displace directly or indirectly 1.008 parts by mass of hydrogen or 8 parts by mass of oxygen or 35.5 parts by mass of chlorine or 108 parts by mass of silver.

**Relation between atomic mass, equivalent mass and valency:**

$$\text{Equivalent mass} = \frac{\text{Atomic mass}}{n}\ ;\ \text{Atomic mass} = \text{equivalent mass} \times \text{valency}$$

$$\text{Equivalent weight of element} = \frac{\text{Atomic weight}}{\text{Valency}}; \text{Compound} = \frac{\text{Molecular weight}}{\text{Valency factor}}$$

$$\text{Acid} = \frac{\text{Molecular weight}}{\text{Basicity}}; \text{Base} = \frac{\text{Molecular weight}}{\text{Acidity}};$$

$$\text{Ion} = \frac{\text{Formula weight}}{\text{Charge}}; \text{Acid salt} = \frac{\text{Molecular weight}}{\text{Replacable H-atoms}}$$

## 1.6 METHOD OF DETERMINING EQUIVALENT WEIGHT

(i) **Hydrogen displacement method:** This method is used for metals which react with an acid to evolve hydrogen gas. Equivalent weight of the metal is the weight of the metal which displaces 1.008 g of $H_2$ or 11200 c.c. of $H_2$ at STP.

(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.
Equivalent of the metal is the weight of the metal which combines with 8 g of oxygen.

(iii) **Chloride formation method:** A known weight of the element is convered into its chloride directly or indirectly whose weight is determined.
Equivalent weight of element is the weight of the elements which combines with 35.5 g of chlorine.

(iv) **Metal displacement method:** This method is based upon the fact that a more electropositive metal displaces a less electropositive metal from its salt and one gram equivalent of the metal added displaces one gram equivalent of the metal. Hence, $\dfrac{\text{Weight of metal added}}{\text{Weight of metal displaced}}$

$$= \frac{\text{Equivalent weight of metal added}}{\text{Equivalent weight of metal displaced}}$$

(v) **Double decomposition method:** For a reaction of the type
$AB + CD \rightarrow AD\downarrow + BC$
(e.g., $AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3$)

$$\frac{\text{Weight of AB taken}}{\text{Weight of AD formed}} \quad \frac{\text{Equivalent weight of AB}}{\text{Equivalent weight of AD}}$$

$$= \frac{\text{Equivalent weight of A} + \text{Equivalent weight of B}}{\text{Equivalent weight of A} + \text{Equivalent weight of D}}$$

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

## 1.7 METHODS OF DETERMINING ATOMIC WEIGHT

**Dulong and petit's method:** According to dulong and petit's law, for solid elements (except Be, B, C and Si), Atomic weight × Specific heat = 6.4 approx.

$\therefore$ Approx. atomic weight = $\dfrac{6.4}{\text{Sp. heat}}$

Exact atomic weight = Equivalent weight × Valency

$\therefore$ Valency = $\dfrac{\text{Approx. atomic weight}}{\text{Equivalent weight}}$

**Vapour density method:** If we consider a chloride of formula $XCl_n$ with vapour density D, then

$$\text{Valency (n)} = \frac{2 \times D}{E_x t\ 35.5}$$

$\Rightarrow$ $A_x - n \times E_x$

## 1.8 EMPIRICAL AND MOLECULAR FORMULA

**Empirical formula:** It is the simplest formula of a compound which gives the simplest whole number ratio of the atoms of the various elements present in one molecule of the compound, e.g., empirical formula of glucose ($C_6H_{12}O_6$) is $CH_2O$.

(i) **Molecular formula:** It is the actual formula of a compound which gives the actual number of atoms of various elements present in one molecule of the compound, e.g., molecular formula of glucose is $C_6H_{12}O_6$.

(ii) **Relationship between empirical formula and molecular formula**
Molecular formula = n × empirical formula where n is any integer such as 1,2,3 ......etc.

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

(iii) **Calculation of empirical formula mass**: It is obtained by adding the atomic masses of the various atoms present in the empirical formula.

(iv) Calculation of molecular mass
Molecular mass = 2 × Vapour density (VD)

**Calculation of empirical formula:** First calculate percentage of oxygen = 100 – Sum of percentages of all other elements, then EF is calculated through the following steps:

| Element | Percentage | Relative number of atoms $= \dfrac{\%\text{ age}}{\text{Atomic mass}}$ | Simplest atomic ratio | Simplest whole number ratio |
|---|---|---|---|---|

## 1.9 VOLUMETRIC ANALYSIS

It is a method which involves quantitative determination of the amount of any substance present in a solution through volume measurements. For the analysis, a standard solution is required. The purpose of any titration is to make a non-standard solution standard or for identification of an unknown compound. All volumetric calculations are based upon law of chemical equivalence.

Different types of titrations are possible which are summarized as follows:

(i) **Redox titrations:** To determine the strength of oxidizing agents or reducing agents by titration with the help of standard solution of reducing agents or oxidizing agents.

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

**Examples:**
$$\frac{[2\,FeSP_4 + H_2SO_4 + O \rightarrow Fe_2(SO_4)_3 + H_2O] \times 3}{6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 \rightarrow 3Fe(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 7H_2O}$$

Number of g equation of oxidizing agent used = Number of g equation of reducing agent used

(ii) **Acid–base titrations:** To determine the strength of acid or base with the help of standard solution of base or acid.

**Example:** $NaOH + HCl \rightarrow NaCl + H_2O$ and $NaOH + CH_3COOH \rightarrow CH_3COONa + H_2O$, etc.

Solution required to bring about the completion of the reaction with a measured volume of the unknown solution.

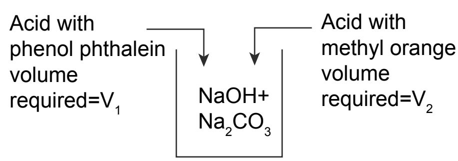
**Simple titration** $N_1V_1 = N_2V_2$, $\therefore\ N_1 = \dfrac{N_2 \times V_2}{V_1}$

**Back titration:** Back titration is used to find the percentage purity of the impure substance.

The g equation of substance under estimation = $(N_1V_1 - N_2V_2)$

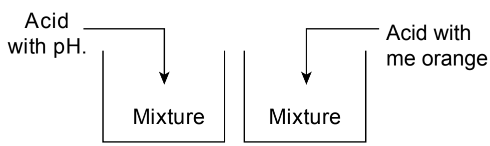
**Double titration:** Mixture of NaOH and $Na_2CO_3$ in a solution:

For Same beaker problem




$NV_1 \equiv$ Meq of NaOH + meq of 1/2
$Na_2CO_3$ $NV_2 \equiv$ Meq of 1/2 $Na_2CO_3$

For separate beaker problem




$NV_1 \equiv$ Meq of (NaOH + 1/2 $Na_2CO_3$)
$NV_2 \equiv$ Meq of (NaOH + $Na_2CO_3$)

## 1.10 VOLUME STRENGTH OF $H_2O_2$

Hydrogen peroxide is highly reactive and unstable, and hence, it is packed and sold in the form of its aqueous solutions. The concentration of such solutions is expressed as 'volume strength'.

$\therefore$ Molarity of solution, $(M) = \dfrac{v}{11.2}$

$\Rightarrow$ Normality of solution, $(N) = \dfrac{v}{5.6}$

$\Rightarrow$ Strength of solution $\dfrac{17v}{5.6}$

## 1.11 PER CENT STRENGTH OF OLEUM

Mixture of $H_2SO_4$ and $SO_3$ is called oleum. It is also known as fuming $H_2SO_4$. Concentration of oleum sample is expressed in terms of per cent strength of oleum.

X per cent of oleum means 100 g of oleum sample on dissolving in water that produces x g of $H_2SO_4$.

$$\underbrace{\underset{100-y}{H_2SO_4} + \underset{y}{SO_3}}_{100\text{ g}} + H_2O \longrightarrow \underset{x\text{ g}}{H_2SO_4}$$

$$\Rightarrow X-100 = y\left(\frac{98}{80}-1\right) = y \times \frac{18}{80}$$

$$\Rightarrow y = \frac{(X-100)\times 80}{18} = \frac{(X-100)\times 40}{9}$$

$$\therefore \text{ per cent of free } SO_3 \text{ in oleum} = \frac{(X-100)\times 40}{9}$$