

Stoichiometry

unit: 2

Physical Chemistry

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Law of multiple proportions:

In 1803 John Dalton put forth the law of multiple proportions.

It states that one element combine with other element to form two or more different compounds, then the weights of one of the elements which combine with the constant weight of the other bear a simple whole number ratio to one another.

Illustrations:

1. Water and hydrogen peroxide:

Hydrogen and oxygen two different elements combine to give two different compounds water and hydrogen peroxide.

In water:

2 parts by weight of hydrogen combine with 16 parts by weight of oxygen

In Hydrogen peroxide:

2 parts by weight of hydrogen combine with 32 parts by weight of oxygen

2. Oxide of Nitrogen:

Nitrogen combines with oxygen to give five different oxides of Nitrogen. Here the weight of oxygen which combine with 14 grams of nitrogen in the five oxides of nitrogen are given as below:

S.No.	Oxides	Weight of Nitrogen	Weight of Oxygen
1	Nitrous oxide (N_2O)	14	8
2	Nitric oxide (NO)	14	16
3	Nitrogen trioxide (N_2O_3)	14	24
4	Nitrogen peroxide (NO_2)	14	32
5	Nitrogen pentoxide (N_2O_5)	14	40

Thus, the weight of oxygen which combine with 14 grams of nitrogen in the five oxides of nitrogen are in the ratio of 8:16:24:32:40 or 1:2:3:4:5 which is a simple ratio, and it illustrate the law of multiple proportions.

Numerical:

A metal forms two oxides, A and B. 1 gm of A on reduction gave 0.881 gm of metal, while 1 gm of B yielded 0.788 gm of metal. Show that these facts are in agreement with the law of multiple proportions.

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Solution

In oxide A

Weight of oxide A = 1 gm

Weight of the metal = 0.881 gm

Therefore, weight of oxygen = $(1 - 0.881) = 0.119$ gm

In oxide B

Weight of oxide B = 1 gm

Weight of the metal = 0.788 gm

Therefore, weight of oxygen = $(1 - 0.788) = 0.212$ gm

In oxide A

0.119 gm of oxygen combine with 0.881 gm of metal.

1 gm of oxygen combines with $0.881/0.119 = 7.403$ gm

In oxide B

0.212 gm of oxygen combine with 0.788 gm of metal.

1 gm of oxygen combines with $0.788/0.212 = 3.717$ gm

Therefore, the masses of metal combining with fixed mass of oxygen (1gm) are in the ratio of 7.403:3.717 or $7.403/3.717 : 3.717/3.717$ or 1.99 : 1 or nearly 2:1. These figures are in accordance with the law of multiple proportions.

Law of reciprocal proportion or equivalent proportions

Or

Law of combining weights

This law was first introduced by Richter in 1792

This states that when two different elements combine separately with the same weight of the third elements, the ratio in which they do so will be the same or some simple multiple of ratio in which they unit with each other.

Illustration;

Let us consider three different elements Sulphur, Hydrogen and Oxygen which combine to give hydrogen sulphide, water and sulphur dioxide.

In Hydrogen sulphide (H₂S):

2 parts by weight of Hydrogen combine with 32 parts by weight of Sulphur.

In water(H₂O):

2 parts by weight of Hydrogen combine with 16 parts by weight of Oxygen.

The ratio of weights of Sulphur and Oxygen which combine separately with the fixed weight (2 parts by weight) of Hydrogen are in the ratio of 32 : 16 = 2 : 1

Sulphur : Oxygen = 2 : 1(1)

Then according to the reciprocal proportions, whenever Sulphur and Oxygen combine they should do so in the ratio of 2:1 or some simple multiple of this ratio.

In SO_2 , Sulphur and Oxygen combine in the ratio of 32 : 32 or 1 : 1

Sulphur : Oxygen = 1 : 1(2)

The ratios from equations (1) and (2) are related to each other as 2/1 : 1/1 or 2:1 which are simple multiples to one another and this illustrates the law of reciprocal proportions.

Examples;

Consider three elements Hydrogen, Carbon and Oxygen which combine with one another to give methane, water and carbon dioxide.

H, C and O form CH_4 , H_2O and CO_2

In CH_4

4g of Hydrogen combine with 12 gm of Carbon

1 gm of Hydrogen combine with 3 gm of Carbon

In H_2O

2g of Hydrogen combine with 16 gm of Oxygen

1 gm of Hydrogen combine with 8 gm of Oxygen

Therefore, ratio of Carbon and Oxygen combined with fix weight of Hydrogen = 3 : 8

In CO_2

12 gram of Carbon combined with 32 gram of Oxygen .
So, in CO_2 Carbon and Oxygen combine in the ratio of 12 : 32 or 3 : 8

This also verifies law of reciprocal proportions.

1. Numerical problem:

Carbondioxide contains 27.27 % carbon carbondisulphide contains 15.97% of carbon and Sulphurdioxide contains 50 % of sulphur. Show that these data are in agreement with the law of reciprocal proportions.

Solution

In Carbondioxide,

% of Carbon = 27.27
% of Oxygen = $(100 - 27.27) = 72.73$

In Carbondisulphide,

% of Carbon = 15.97
% of Sulphur = $(100 - 15.97) = 84.03$

In Sulphurdioxide

% of Sulphur = 50
% of Oxygen = $(100 - 50) = 50$

In CO_2 27.27 gm of Carbon combine with 72.73 gm of Oxygen
1 gm carbon combine with $72.73/27.27 = 2.667$ gm of Oxygen

In CS_2 15.97 gm of Carbon combine with 84.03 gm of Sulphur
1 gm carbon combine with $84.03/15.97 = 5.262$ gm of Sulphur

Therefore the weight of Sulphur and Oxygen which combine with fixed weight (1gm) Carbon is in the ratio of $5.262 : 2.667 = 2:1$

In case of SO_2 , the ratio of Sulphur to the Oxygen is $50 : 50 = 1:1$. Therefore, the ratio 2:1 is a simple multiple of 1:1 and these figures illustrate the law of reciprocal proportions.

2. Numerical problem:

Illustrate the law of reciprocal proportions from the composition of the following compounds.

H_2S	S = 94.11 %	H = 5.89 %
SO_2	S = 50 %	O = 50 %
H_2O	H = 11.11 %	O = 88.89 %

The law of gaseous volumes(Gay-Lussac's law):

This law deals with a relationship between the volumes of gaseous reactants and gaseous products. Gay Lussac had stated this law in 1805.

It states that when gases unite to form new compounds, the volumes of the reacting gases as well as those of the products, if gaseous, are in the ratio of simple whole numbers under similar condition of temperature and pressure.

Illustration:

For example, Hydrogen and Chlorine both gases combine together to give Hydrogen chloride gas.



Experimentally, it has been found that one volume of H_2 combine with one volume of Cl_2 to give two volumes of HCl . Therefore, the volume ratios of $\text{H}_2:\text{Cl}_2:\text{HCl} = 1:1:2$, which is simple ratio.

Hydrogen combine with Nitrogen to give Ammonia is another example that varifies Gay-Lussac's law of gaseous volume.



Here, three volumes of H_2 combine with one volume of N_2 to give two volume of NH_3 . Therefore, the volume ratio of $\text{H}_2:\text{N}_2:\text{NH}_3$ is 3:1:2. This is a simple whole number ratio, actually varifies Gay-Lussac's law of gaseous volume.

Avogadro's Law and Some Deductions

- DALTON'S ATOMIC THEORY
- BERZELIUS HYPOTHESIS
- AVOGADRO'S HYPOTHESIS
- APPLICATIONS OF AVOGADRO'S HYPOTHESIS

Stoichiometry:

Dalton's atomic theory and its postulates:

All matters are made up of tiny, discrete, invisible particles called atoms. In 1808, John Dalton put forward the atomic theory, and successfully explained laws of chemical combination.

Postulates of Dalton's atomic theory:

1. All matter consists of extremely small invisible particles called atoms.
2. Atoms of same elements are all alike.
3. Atoms of different elements are entirely different and have different properties.
4. Atoms can not be destroyed, created or transformed into atoms of other elements.
5. Atoms combine together in a simple whole number ratio to give compounds.
6. The relative number and kind of atoms are constant in a given compounds.



DALTON'S ATOMIC THEORY

□ Introduction

Dalton's atomic theory was the first scientific theory which successfully explained the concept of atomic character of matter.

• **Postulates:** The main postulates of this theory are:

1. All matter consists of extremely small, indivisible and discrete particles called atoms.
2. Atoms cannot be created, destroyed or transformed into atoms of other elements by any physical or chemical process.
3. Atoms of the same element are identical in all respects while atoms of different elements have different masses and properties.
4. Atoms combine with each other in simple whole number ratios to form compound atoms, nowadays called molecules.

BERZELIUS HYPOTHESIS

□ Statement

According to Berzelius hypothesis, “*Under similar conditions of temperature and pressure, equal volumes of all gases contain equal number of atoms.*”

Example:

Hydrogen + Chlorine → Hydrogen chloride

1 vol	1 vol	2 vol
n atoms	n atoms	2n atoms
1 atom	1 atom	2 compound atom
1/2 atom	1/2 atom	1 compound atom

But, according to Dalton's theory, an atom is not divisible and therefore, fractional or half atom is not possible. On this account, Berzelius hypothesis was rejected.

AVOGADRO'S HYPOTHESIS

□ Statement

According to Avogadro's hypothesis, "*Under similar conditions of temperature and pressure, equal volumes of all gases contain equal number of molecules.*"

Example:

Hydrogen + Chlorine → Hydrogen chloride

1 vol	1 vol	2 vol
n molecules	n molecules	2n molecules
1 molecule	1 molecule	2 molecules
1/2 molecule	1/2 molecule	1 molecule

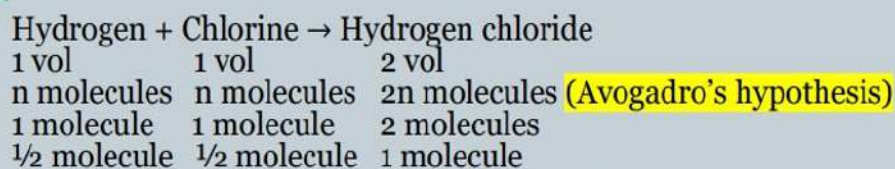
Now, this fact does not contradict the atomic theory, since molecules can be divided into atoms. The Avogadro's hypothesis has been experimentally verified and hence is now regarded as law.

APPLICATIONS OF AVOGADRO'S HYPOTHESIS

□ Deduction of Atomicity of Elementary Gases

The number of atoms present in a molecule of a gas is called its atomicity. With the help of Avogadro's hypothesis it can be shown that elementary gases such as hydrogen, oxygen, nitrogen, chlorine etc. are diatomic.

Example:



Since, one molecule of hydrogen chloride is found to contain one atom of hydrogen and one atom of chlorine,

$\frac{1}{2}$ molecule of hydrogen = 1 atom of hydrogen

∴ 1 molecule of hydrogen = 2 atoms of hydrogen

Similarly,

$\frac{1}{2}$ molecule of chlorine = 1 atom of chlorine

∴ 1 molecule of chlorine = 2 atoms of chlorine

Thus, atomicity of both hydrogen and chlorine is two.

APPLICATIONS OF AVOGADRO'S HYPOTHESIS

□ Deduction of Relationship Between Molecular Mass and Vapour Density of Gas

The vapour density or relative density of a gas is defined as the ratio of the mass of a certain volume of the gas to the mass of the same volume of hydrogen gas under similar conditions of temperature and pressure. Mathematically,

$$\text{Vapour density (V. D.)} = \frac{\text{Mass of certain volume of gas}}{\text{Mass of same volume of hydrogen}}$$

(At same temperature and pressure)

APPLICATIONS OF AVOGADRO'S HYPOTHESIS

• Derivation of Relationship

$$\begin{aligned} \text{V. D.} &= \frac{\text{Mass of } V \text{ litre of gas}}{\text{Mass of } V \text{ litre of hydrogen}} \quad (\text{At same T and P}) \\ &= \frac{\text{Mass of } n \text{ molecules of gas}}{\text{Mass of } n \text{ molecules of hydrogen}} \quad (\text{Avogadro's hypothesis}) \\ &= \frac{\text{Mass of 1 molecule of gas}}{\text{Mass of 1 molecule of hydrogen}} \\ &= \frac{\text{Mass of 1 molecule of gas}}{\text{Mass of 2 atoms of hydrogen}} \\ &= \frac{\text{Molecular mass of gas}}{2 \times \text{Mass of 1 atom of hydrogen}} \\ &= \frac{\text{Molecular mass of gas}}{2} \end{aligned}$$

$$\therefore \text{Molecular mass} = 2 \times \text{V. D.}$$

APPLICATIONS OF AVOGADRO'S HYPOTHESIS

□ Deduction of Molar Volume of Gas at NTP

We know,

$$\text{Vapour density (V. D.)} = \frac{\text{Mass of certain volume of gas}}{\text{Mass of same volume of hydrogen}} \quad (\text{At same T and P})$$

$$\text{Or, V. D.} = \frac{\text{Mass of 1 litre of gas at NTP}}{\text{Mass of 1 litre of hydrogen at NTP}}$$

$$\text{Or, V. D.} = \frac{\text{Mass of 1 litre of gas at NTP}}{0.089 \text{ g}} \quad (\text{Mass of 1 litre of hydrogen at NTP} = 0.089 \text{ g})$$

$$\text{Or, Mass of 1 litre of gas at NTP} = (0.089 \times \text{V. D.}) \text{ g}$$

$$\text{Or, Mass of 1 litre of gas at NTP} = (0.089 \times M/2) \text{ g}$$

Now,

$(0.089 \times M/2)$ g of gas occupies a volume of 1 litre at NTP

$$\text{Or, } M \text{ g (i.e. 1 mole) of gas occupies a volume of } \frac{1}{0.089 \times M/2} \times M \text{ litre at NTP}$$

$$= \frac{2}{0.089} \text{ litre at NTP}$$

$$= 22.4 \text{ litre at NTP}$$

∴ Molar volume of gas at NTP = 22.4 L

APPLICATIONS OF AVOGADRO' HYPOTHESIS

□ Deduction of Molecular Formula of Gaseous Compound From Its Volumetric Composition

The Avogadro's hypothesis can also be used to determine the molecular formula of a gaseous compound if the volumes of the reactants and products are known. For example, it has been found that one volume of nitrogen reacts with three volumes of hydrogen to form two volumes of ammonia. Thus,

Nitrogen	+	Hydrogen	→	Ammonia
1 vol		3 vol		2 vol
n molecules		3n molecules		2n molecules (Avogadro's hypothesis)
1 molecule		3 molecules		2 molecules
1/2 molecule		3/2 molecule		1 molecule
1 atom		3 atoms		1 molecule (Nitrogen and hydrogen are diatomic)

It shows that one molecule of ammonia contains one atom of nitrogen and three atoms of hydrogen. Therefore, molecular formula of ammonia is NH_3 .

NUMERICAL PROBLEMS

- **Sample Problem:** Nitric oxide contains half of its own volume of nitrogen and has a vapour density equal to 15. Determine its molecular formula.

Soln: Here, 1 vol. of nitric oxide contains $\frac{1}{2}$ vol. of nitrogen.

Or, n molecules of nitric oxide contains $n/2$ molecules of nitrogen. (Applying Avogadro's hypothesis)

Or, 1 molecule of nitric oxide contains $\frac{1}{2}$ molecule of nitrogen.

Or, 1 molecule of nitric oxide contains 1 atom of nitrogen. (Nitrogen is diatomic molecule)

Let, 1 molecule of nitric oxide contains x atoms of oxygen. Hence, molecular formula will be NO_x .

Molecular mass of nitric oxide = $2 \times \text{V. D.} = 2 \times 15 = 30$

Now, Mol. mass of $\text{NO}_x = \text{At. mass of N} + x \times \text{At. mass of O}$

$$\text{Or, } 30 = 14 + 16x$$

$$\text{Or, } x = 1$$

\therefore Molecular formula of nitric oxide is NO.

- **Follow up problems**

1. An oxide of carbon contains its own volume of oxygen. Its vapour density is 22. Find the molecular formula of the oxide. [Ans: CO_2]
2. A hydride of nitrogen contains half volume of nitrogen. The vapour density of the hydride is 8.5. Find the molecular formula of the hydride. [Ans: NH_3]

Chemical Arithmetic

- 1. Atomic Mass and Molecular Mass**
- 2. Mole Concept**
- 3. Empirical, Molecular formula and Limiting reactants**
- 4. Equivalent Mass**
- 5. Avogadro's Hypothesis and Its Applications**
- 6. Dalton's Atomic Theory and Laws Of stoichiometry**

Limitations of Dalton's Atomic Theory

- **It does not account for subatomic particles:** Dalton's atomic theory stated that atoms were indivisible. However, the discovery of [subatomic particles](#) (such as protons, electrons, and neutrons) disproved this postulate.
- **It does not account for isotopes:** As per Dalton's atomic theory, all atoms of an element have identical masses and densities. However, different isotopes of elements have different atomic masses (Example: hydrogen, deuterium, and tritium).
- **It does not account for isobars:** This theory states that the masses of the atoms of two different elements must differ. However, it is possible for two different elements to share the same mass number. Such atoms are called isobars (Example: ^{40}Ar and ^{40}Ca).
- **Elements need not combine in simple, whole-number ratios to form compounds:** Certain complex organic compounds do not feature simple ratios of constituent atoms. Example: sugar/sucrose ($\text{C}_{11}\text{H}_{22}\text{O}_{11}$).
- **The theory does not account for allotropes:** The differences in the properties of diamond and graphite, both of which contain only carbon, cannot be explained by Dalton's atomic theory.



Chemical Arithmetic

Some important basic terms you must know for this chapter:

i. Atomic Number:

It is the total numbers of proton present in the nucleus of an atom. (It is also the number of electrons present in neutral atom).

ii. Mass number :

It is the sum of number of protons and neutrons present in an atom of an element.
i.e. Mass number(A) = no. of protons (p)+ no.of neutrons (n)

iii. Isotopes :

Atoms of same element having different mass number are called isotopes. It arises due to difference in number of neutron.

For ex: ${}^1_1\text{H}$, ${}^2_1\text{H}$, ${}^3_1\text{H}$ (isotopes of hydrogen)
 ${}^{12}_6\text{C}$, ${}^{13}_6\text{C}$, ${}^{14}_6\text{C}$ (Isotopes of Carbon)

iv. Isotones :

Atoms of different elements having same number of neutrons are called Isotones.

For ex: ${}^{14}_6\text{C}$, ${}^{15}_7\text{N}$, ${}^{16}_8\text{O}$ (8 neutrons each)

v. Isobar:

Atoms of different elements having same mass number are called isobars.

For ex: ${}^{40}_{18}\text{Ar}$, ${}^{40}_{19}\text{K}$, ${}^{40}_{20}\text{Ca}$

1. Atomic Mass and Molecular mass

Q. Why concept of atomic mass came?

Atom is the smallest particle of an element which takes part in a chemical reaction. Atoms are so small that their actual masses are unimaginably small. So, it is inconvenient to use in common practice and their weight have no practical meaning. For ex: the atomic mass of hydrogen is $1.66 \times 10^{-24}\text{g}$.

To overcome the difficulty, the weights of atoms of different elements are expressed by

taking one of the elements as the standard reference.

For convenience, the international union for pure and applied chemistry (IUPAC) in 1961 recommended to express the atomic mass of an element in terms of C-12 isotope as standard comparison.

In terms of C-12,

Atomic mass of an element is defined as the number which shows how many times an atom of an element is heavier than one –twelfth($\frac{1}{12}$)th mass of an atom of C-12 isotope.

$$\text{Atomic Mass} = \frac{\text{mass of an atom of the element}}{\frac{1}{12} \text{ mass of an atom of C-12 isotope}}$$

Atomic Mass Unit (amu)

Mass of one atom of C-12 is assigned as 12amu. One twelfth the mass of one atom of C-12 is called **atomic mass unit (amu).**

1amu = $\frac{1}{12}$ of mass of C-12 isotope

Q. What do you mean by atomic mass of magnesium is 24 amu?

Ans: It means one atom of magnesium is 24 times as heavy as one twelfth ($\frac{1}{12}$)th mass of an atom of C-12 isotopes.

Calculation of absolute value of 1 amu

1 mole of C-12 = 12g

1 mol of C-12 = 6.022×10^{23} (number of carbon atoms)

Or, 12 g = 6.022×10^{23} number of carbon

atoms Or, 6.022×10^{23} number of carbon

Or, 1 carbon atom = $\frac{12}{6.022 \times 10^{23}}$ g

atoms = 12 g

So, mass of $\frac{1}{12}$ carbon atom = $\frac{12}{6.022 \times 10^{23}} \times \frac{1}{12}$ g

Therefore, 1 amu = 1.66×10^{-24} g

Q. Calculate the molecular mass of the following compound.

HCl, H₂SO₄, NaOH, KOH, HNO₃, NaCl, KCl, C₆H₁₂O₆, C₁₂H₂₂O₁₁

Q. What do you mean by molecular mass of Oxygen is 32?

Ans: It means one molecule of oxygen is 32 times as heavy as one twelfth ($\frac{1}{12}$)th mass of an atom of C-12 isotope.

Q. what do you mean by molecular mass of CO₂ is 44 amu?

Gram atomic mass (Gram atoms/mole)


Atomic mass expressed in gram is called Gram atomic mass (GAM).

For ex: Gram atomic mass (1 gram atom) of sodium is 23g

How??

Atomic mass of sodium = 23 amu

So, Gram atomic mass = 1 gram atoms = 1mole = 23g

 Remember

1 gram atom of sodium is also known as 1 mole of sodium.

Note: 1 gram atoms of sodium does not mean 1 gram of sodium atoms. It is actually atomic mass of sodium expressed in gram.

$$\text{Number of gram atoms (mole)} = \frac{\text{mass of element in gram}}{\text{Gram atomic Mass}}$$

Q. Calculate the no. of gram atoms of the following.

a) 3.2g of sulphur b) 4 g of calcium c) 23 gram of sodium d) 0.2 g of hydrogen

Gram Molecular Mass (Gram Mole)

Molecular mass of a substance expressed in gram is call gram molecular mass or 1 gram mole or simply mole.

For ex: Gram molecular mass of oxygen =32g

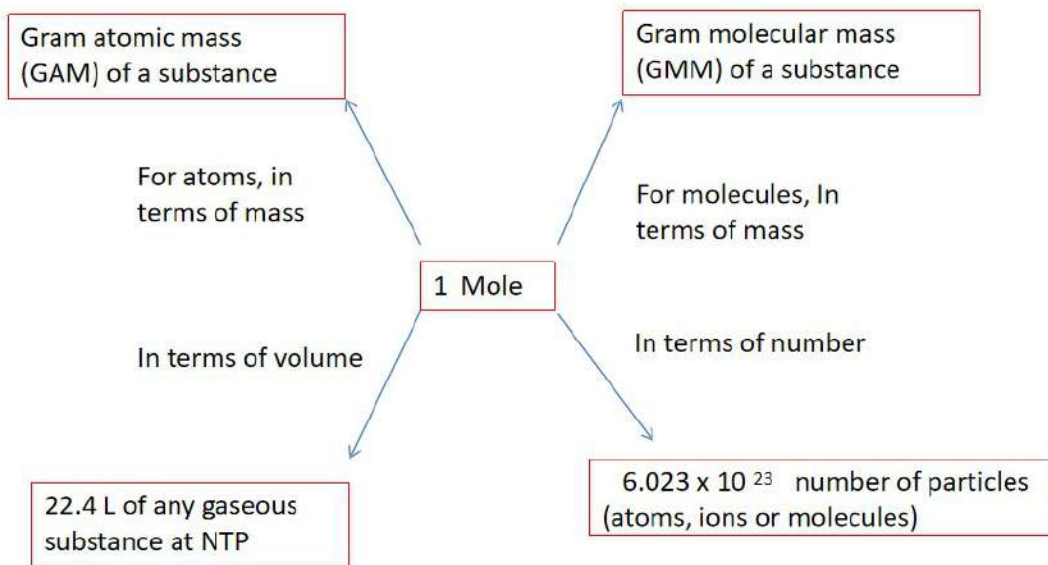
Gram molecular mass of CO_2 = 1 gram mole
= 1 mole = 44g

$$\text{No. of gram mole (mole)} = \frac{\text{Mass in gram}}{\text{Gram Molecular Mass}}$$

Q. Calculate the number of gram mole (mole) in 4.4 g of CO_2 , 32 gram of Oxygen and 73 gram of HCl .

Mole Concept

A mole is simply collection of Avogadro's number (N_A) i.e. 6.023×10^{23} number of particles (atoms, ions or molecules).



Significance of mole

1. A mole gives number of particles i.e. 1 mole = 6.022×10^{23} particles

2. A mole gives mass of a substance in gram

i.e. 1 mole of atoms = 6.022×10^{23} atoms = Gram atomic mass (GAM) of element

Similarly,

1 mole of molecule = 6.022×10^{23} molecules = Gram molecular mass (GMM) of molecules

3. A mole gives volume of gaseous substance

i.e. 1 mole of any gas at NTP = 22.4 L (Molar Volume)

The volume occupied by one mole of any gaseous substance at 0°C (273 K) and 1 atmospheric pressure (760 mmHg) is called Molar volume.

Note: The standard or normal temperature pressure (STP or NTP) refers to 0°C or 273K and 1 atm or 760 mmHg.

Calculation based on mole concept

$$\begin{aligned} \text{No. of mole (n)} &= \frac{\text{Given mass in gram}}{\text{molar mass}} = \frac{\text{Given number of particles}}{6.022 \times 10^{23}} = \frac{\text{Volume of gas in L at NTP}}{22.4 \text{ L}} \\ &= \frac{\text{no of discrete particles}}{6.023 \times 10^{23}} \end{aligned}$$

Note : The mass occupied by 1 mole of any substance is called Molar mass. **Molar mass** can be used instead of **gram molecular mass** or **gram atomic mass** as the term is applicable for both atoms and molecules. The unit of molar mass is g/mol.

For ex: Molar mass of sodium (Na) = 23 g/mol (it indicates mass of 1 mole of sodium is 23g)

Similarly, Molar mass of CO₂ = 44 g/mol (it indicates mass of 1 mole of CO₂ is 44g)

▪ No. of particle present in 'n' mole of substance = $n \times N_A$

(Avogadro's Number)

▪ Total number of atoms present in 'n' mole of any molecule = $n \times N_A$
x total no. of atoms present per molecule

Stoichiometry is the branch of chemistry that deals with the calculation involving mass and volume relationship among reactant and product in a chemical reaction.

Some laws of stoichiometry

1. Law of conservation of mass
2. Law of constant proportion
3. Law of multiple proportions
4. Law of reciprocal proportions
5. Gay Lussac's law of gaseous volume

The law of conservation of mass (law of indestructibility of matter):

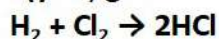
It states that "Mass is neither created nor destroyed in a chemical reaction or The total mass of reactant is equal to the total mass of product in a chemical reaction".

For a general reaction, $A + B = C + D$

let w gm of A reacts with x gm of B to give y gm of C and z gm of D, then according to this law,

$$(w+x) \text{ gm} = (y+z) \text{ gm}$$

For example:



$$\begin{aligned} \text{Mass of reactant} &= 2 \times \text{mass of H} + 2 \times \text{mass of Cl} \\ &= 2 \times 1 + 2 \times 35.5 \\ &= 73 \end{aligned}$$

$$\begin{aligned} \text{Mass of product} &= 2(\text{mass of H} + \text{mass of Cl}) \\ &= 2(1 + 35.5) \\ &= 73 \end{aligned}$$



Calculation based on mole concept

- Calculate the mass of an atom of S (atomic mass=32)
- How many gram atom are present in 100 g calcium?
- One atom of an element weighs 6.644×10^{-12} g. Calculate the number of g atom in 40 kg of it.
- Calculate the number of molecules in 4.4g of CO₂. (hint no. of moles of CO₂= $4.4/44 = 0.1$ mole, 0.1 mol of CO₂ contains $N \times 0.1$ molecules)
- Calculate a) number of mole b) number of mL at NTP and c) total number of atoms present in 1×10^{-2} g of CH₄



Calculation in Stoichiometric Chemical Equation from Mole Concept

- **Mass-Mass relationship:** the mass of one of the reactant or product is to be calculated if that of the other reactant or product are given

Q. Calculate the mass of iron, which will be converted into oxide(Fe_2O_3) by the action of 18g of steam on it.

Solution,



now, 72g of steam reacts with 168 g of iron

or, 18 g of steam reacts with $(168 \times 18) / 72$ g of iron

thus, the mass of iron required = 42 g



- **Mass-Volume relationship:** mass or volume of one of the reactant or product is calculated if that of the other reactant or products are given

Q. What volume of CO₂ measured at NTP would be obtained by treating 10 g of pure marble with dilute hydrochloric acid?

Solution,



here, 100g of CaCO₃ gives 22.4L of CO₂ at NTP

or, 10 g of CaCO₃ gives (22.4x 10)/100 L

= 2.24L of CO₂ at NTP



Chemical Arithmetic

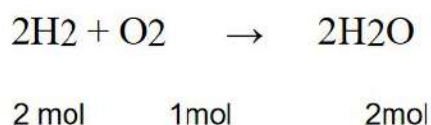
- 1. Limiting reactant and excess reactant**
- 2. Theoretical yield, experimental yield and percentage yield**
- 3. Empirical and Molecular formula**

LIMITING REACTANT

In many cases, the substances in a mixture are not present in exactly the same amount as required by the balanced chemical equation. In such situations, one reactant is in excess over the other. The reactant which is present in lesser amount gets consumed after sometime and after that no further reaction takes place even though the other reactant is present. Thus,

the reactant which gets completely consumed in a reaction is called limiting reactant.

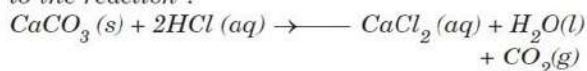
The concentration of the limiting reactant limits the amount of products formed. The other reactants present in quantities greater than those needed to react with the quantity of the limiting reagent present would be left unreacted. It is also called excess reagent. For example, in the reaction



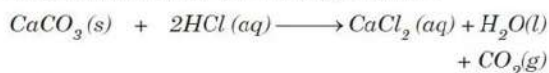
if 2 mol of hydrogen are mixed with 2 mol of O_2 , then only 1 mol of O_2 will be used up and 1 mol of O_2 will be left over. Therefore, in this case, hydrogen is the limiting reactant. Oxygen is excess reactant.

□ **Example**

If 20.0 g of CaCO_3 is treated with 20.0 g of HCl , how many grams of CO_2 can be produced according to the reaction :



Solution: In this problem, CO_2 can be calculated by using either of the reactants CaCO_3 or HCl . So, first of all we are to calculate the limiting reactant.



$$\begin{array}{cc} 1 \text{ mol} & 2 \text{ mol} \\ 40 + 12 + 3 \times 16 & 2 \times (1 + 35.5) \\ = 100 \text{ g} & = 73 \text{ g} \end{array}$$

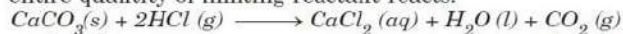
According to above equation,
100 g of CaCO_3 require 73 g of HCl

$$20 \text{ g of } \text{CaCO}_3 \text{ require} = \frac{73}{100} \times 20 = 14.6 \text{ g}$$

But amount of HCl actually present = 20.0 g

Therefore, CaCO_3 is limiting reactant and HCl is excess reactant.

Now let us calculate the amount of CO_2 produced when entire quantity of limiting reactant reacts.



$$\begin{array}{ccc} 1 \text{ mol} & & 1 \text{ mol} \\ 100 \text{ g} & & 44 \text{ g} \\ 20 \text{ g} & & ? \end{array}$$

$$100 \text{ g of } \text{CaCO}_3 \text{ produces } \text{CO}_2 = 44 \text{ g}$$

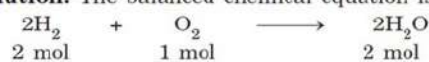
$$20 \text{ g of } \text{CaCO}_3 \text{ will produce } \text{CO}_2 = \frac{44}{100} \times 20 = 8.80 \text{ g}$$

□ **Example**

3.0 g of H_2 react with 29.0 g of O_2 to yield H_2O .

- Which is the limiting reactant ?
- Calculate the maximum amount of H_2O that can be formed.
- Calculate the amount of one of the reactants which remains unreacted.

Solution: The balanced chemical equation is



$$\begin{array}{ccc} 2 \text{ mol} & 1 \text{ mol} & 2 \text{ mol} \end{array}$$

$$\text{Moles of } \text{H}_2 = \frac{\text{Wt. of } \text{H}_2}{\text{Molecular mass of } \text{H}_2} = \frac{3.0}{2} = 1.50 \text{ mol}$$

$$\text{Moles of } \text{O}_2 = \frac{\text{Wt. of } \text{O}_2}{\text{Molecular mass of } \text{O}_2} = \frac{29.0}{32.0} = 0.906 \text{ mol}$$

(i) **Calculation of limiting reactant**

According to the above equation, 2 mol of H_2 require $\text{O}_2 = 1 \text{ mol}$

$$\therefore 1.50 \text{ mol of } \text{H}_2 \text{ require } \text{O}_2 = \frac{1.50}{2} = 0.75 \text{ mol}$$

But moles of O_2 actually present = 0.906 mol

Therefore, O_2 is in excess and H_2 is the **limiting reactant**.

(ii) **Calculation of maximum amount of H_2O formed.**

Now, 2 mol of H_2 form $\text{H}_2\text{O} = 2 \text{ mol}$

$$\therefore 1.50 \text{ mol of } \text{H}_2 \text{ form } \text{H}_2\text{O} = 1.50 \text{ mol}$$

Thus, the maximum amount of H_2O formed = **1.50 mol**

(iii) **Calculation of the amount of one of the reactants which remains unreacted i.e., O_2**

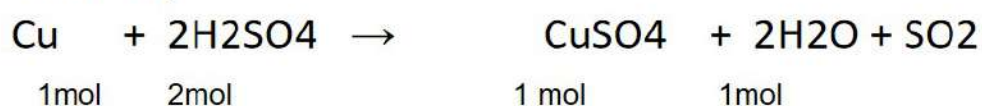
Number of moles of O_2 added = 0.906 mol

Number of moles of O_2 used up = 0.75 mol

$$\therefore \text{Number of moles of } \text{O}_2 \text{ unreacted} = 0.906 - 0.75 = 0.156 \text{ mol.}$$

What mass of copper sulphate can be obtained by the action of 2.94g of sulphuric acid on excess of copper?

Solution,



given, mass of $\text{H}_2\text{SO}_4 = 2.94 \text{ g}$

no of moles of $\text{H}_2\text{SO}_4 = 2.94/98 = 0.03 \text{ mol}$

from reaction,

2 mol of H_2SO_4 gives 1 mol of CuSO_4

0.03 mol of H_2SO_4 gives $1 \times 0.03 / 2$ mol of CuSO_4

$= 0.5 \times 0.03 \times 159.5 \text{ g of CuSO}_4 = 2.3925 \text{ g of CuSO}_4$

so , mass of copper sulphate formed us 2.3925 g.



You are given 100 g of each HCl and NaOH and they are mixed together. How much NaCl would be formed? Identify the limiting reactant. How much excess reactant is left unreacted?

solution,



mass of HCl = 100g

no of mol = $100/36.5 = 2.74$ mol

mass of NaOH = 100g

no of mol = $100/40 = 2.5$ mol

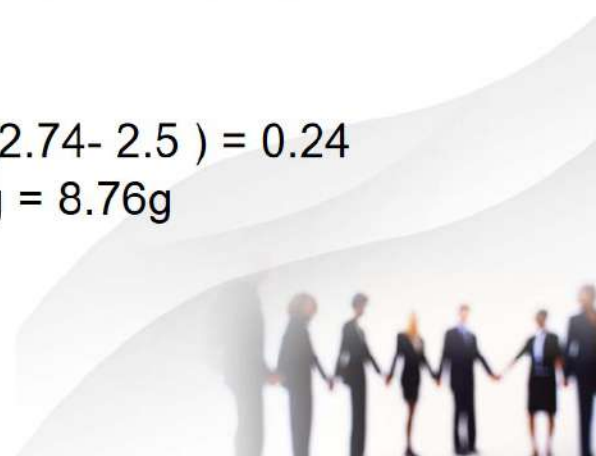
hence, no of mol of NaOH is less than HCl, NaOH is limiting reactant

2.5 mol of NaOH gives 2.5 mol of NaCl

or, 2.5×58.5 g of NaCl = 146.25 g of NaCl

now, no of mol of excess reagent HCl left = $(2.74 - 2.5) = 0.24$

mass of excess reagent(HCl) = 0.24×36.5 g = 8.76g



Theoretical yield:

The maximum amount of a particular product that could be formed from the balanced chemical reaction using the limiting reactant to determine the product is called theoretical yield or stoichiometric yield.

Experimental yield

The actual or experimentally obtained amount of particular product, when total amount of limiting reactant gets consumed completely is called experimental yield.

The amount of product formed may be slightly different from the calculated or theoretical value. The amount of theoretical yield is the function of limiting reagents. Therefore, theoretical yield always should be calculated based on the limiting reagent. The experimental or actual product yield will be always less from those calculated theoretically.

Percentage yield

Percent yield or percentage yield is the ratio of experimental yield to the theoretical yield expressed in hundred part. Mathematically, it is expressed as,

$$\% \text{ yield} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100\%$$

This law is also known as law of indestrutibility of matter.

The truth of this law had been established by following scientist;

(a) Lavoisier's experiment:

This is the original experiment performed by Lavoisier himself to verify the law. Lavoisier heated tin with air in a closed container and it was experimentally found that there was no change in weight even though the tin united with the oxygen of the air to form white powder of tin oxide.

Tin + Oxygen \longrightarrow Tin Oxide

This result verify the truth of law of conservation of mass.

(a) Landolt's experiment:

This was the typical experiment that Landolt had done to verify the law of conservation of mass. Here, the solutions of sodium chloride and silver nitrate were taken in two limbs of Y-shaped tube known as Landolt's tube.

The tube is sealed and subsequently weighted out accurately. The solutions were then mixed together by turning the tube upside down.

1 gram of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Mol. Mass 393.833, and atomic mass of gold is 199.966) was reduced to gold nanoparticles using sodium citrate. After subsequent purification and drying, the mass of gold nanoparticle was 0.325 g. Calculate the percentage yield of gold nanoparticles.

⇒ 393.833 gram of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ consists of 199.966 g gold.

1 gram of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ consists of $\frac{199,966}{393,833} = 0.507$ g.

Therefore, theoretical yield = 0.507 g

Experimental yield = 0.325 g (given)

Percentage yield = $\frac{\text{Experimental yield}}{\text{Theoretical yield}} \times 100\% = \frac{0.325}{0.507} \times 100\% = 64.10\%$

Percentage composition

The mass of each element present in the compound expressed in percent by mass is known as percentage composition.

$$\text{Percent composition} = \frac{\text{mass of element in the sample}}{\text{total mass of the sample}} \times 100$$

For eg.

The weight of hydrogen is 2 and oxygen is 16 in water molecule (H₂O)

Molecular mass of water = 18

$$\begin{aligned} \text{Hence the percentage of H in H}_2\text{O} &= \frac{\text{wt of H}}{\text{wt of H}_2\text{O}} \times 100 \\ &= \frac{2}{18} \times 100 \\ &= 11.11\% \end{aligned}$$

$$\begin{aligned} \text{And percentage of O in H}_2\text{O} &= \frac{\text{wt of O}}{\text{wt of H}_2\text{O}} \times 100 \\ &= \frac{16}{18} \times 100 \\ &= 88.89\% \end{aligned}$$

Find the percentage composition of CO₂??

% of C = 27.27

% of O = 72.72

Calculate the percentage composition of each elements in

Na_2CO_3 ? Molecular mass of $\text{Na}_2\text{CO}_3 = 23 \times 2 + 12 + 16 \times 3 = 106$

$$\% \text{ of Na} = \frac{46}{106} \times 100 =$$

$$43.39\% \quad \% \text{ of C} = \frac{12}{106} \times 100 =$$

$$11.32\% \quad \% \text{ of O} = \frac{48}{106} \times 100 =$$

$$45.28\%$$

Calculate the percentage of water of crystallization in blue vitriol ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) ??

Solution: Molecular mass of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

$$= 63.5 + 32 + 16 \times 4 + (1 \times 2 + 16) \times 5$$

$$= 63.5 + 32 + 64 + 90$$

$$249.5$$

$$\% \text{ of water} = \frac{\text{mass of water}}{\text{mass of blue vitriol}} \times 100$$

$$= \frac{18 \times 5}{249.5} \times 100$$

$$= 36.07\%$$

Empirical formula

The formula which shows the simplest whole no. ratio of atoms of various element present in the molecule of the compound is called empirical formula.

For example: empirical formula of hydrogen peroxide is HO (molecular formula H_2O_2).

Empirical formula of ethane is CH_3 (molecular formula C_2H_6)

Empirical formula of benzene is CH (molecular formula C_6H_6)

Relationship between molecular formula and empirical formula.

Molecular formula of a compound is the simple whole number multiple of empirical formula.

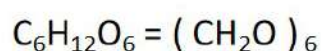
$$\text{Molecular formula} = (\text{Empirical formula})_n \quad n = \frac{\text{molecular mass}}{\text{empirical formula mass}}$$

For eg:

$$\begin{aligned} \text{Molecular formula of benzene} &= (\text{Empirical formula of benzene})_n \\ (C_6H_6) &= (CH)_6 \end{aligned}$$

$$\begin{aligned} n &= \frac{\text{molecular mass of benzene}}{\text{empirical formula mass of benzene}} \\ n &= \frac{78}{13} \\ n &= 6 \end{aligned}$$

Find the empirical formula of glucose and the value of common factor (n)



$$n = \frac{180}{30} = 6$$

• Rule for determining the Empirical formula

1. At first determine the mass percentage of each elements in the compound.
2. Divide the mass percentage of each element by its atomic mass to get relative number of moles of atoms.
3. Divide each relative number of moles of all atoms by smallest number to get simplest ratio of moles.
4. If value is near to whole number, make it to the nearest whole number.

[If necessary, multiply all values by a common number to change them into simplest whole number. The simplest whole number ratio, thus obtained, gives the empirical formula of the compound.]

1. Compound which is made up of oxygen and carbon contains 27.27% C and 72.72% oxygen by mass. Calculate the empirical formula of the compound.

Solution:

Element	Percentage(%)	Atomic mass	Relative no. of moles = $\frac{\%}{\text{Atomic mass}}$	Simplest ratio of moles	Simplest whole number of moles
C	27.27	12	$\frac{27.27}{12} = 2.27$	$\frac{2.27}{2.27} = 1$	1
O	72.72	16	$\frac{72.72}{16} = 4.54$	$\frac{4.54}{2.27} = 2$	2

Thus the empirical formula of the compound is CO_2

2. An inorganic salt gave the following percentage composition. Na = 29.11%,
 S = 40.51%, O = 30.38%
 Calculate the empirical formula of the salt?

Element	Percentage(%)	Atomic mass	Relative no. of moles = $\frac{\%}{\text{Atomic mass}}$	Simplest ratio of moles	Simplest whole number of moles
Na	29.11	23	$\frac{29.11}{23} = 1.26$	$\frac{1.26}{1.26} = 1$	2
S	40.51	32	$\frac{40.51}{32} = 1.26$	$\frac{1.26}{1.26} = 1$	2
O	30.38	16	$\frac{30.38}{16} = 1.89$	$\frac{1.89}{1.26} = 1.5$	3

Thus the empirical formula of the compound is $\text{Na}_2\text{S}_2\text{O}_3$

3.74g of oxide of iron when heated in a current of hydrogen gave 1.161g of water.
Determine the simplest formula of the compound.(Empirical formula)

Mass of iron oxide = 3.74g

Mass of water formed = 1.161g

Mass of oxygen in 1.161g H₂O = $\frac{16}{18} \times 1.161 =$

1.032g Hence mass of oxygen in 3.74g of iron oxide =

~~1.032g~~ oxide + hydrogen \longrightarrow Iron + water

Mass of Fe in 3.74g iron oxide = (3.74 – 1.032)g = 2.708g

% of oxygen in iron oxide = $= \frac{1.032}{3.74} \times 100 =$

% of Fe in iron oxide = $= \frac{2.708}{3.74} \times 100 =$
27.59%
72.40%

Element	Percentage(%)	Atomic mass	Relative no. of moles = $\frac{\%}{\text{Atomic mass}}$	Simplest ratio of moles	Simplest whole number of moles
Fe	72.40	56	$\frac{72.40}{56} = 1.29$	$\frac{1.29}{1.29} = 1$	$1 \times 3 = 3$
O	27.59	16	$\frac{27.59}{16} = 1.72$	$\frac{1.72}{1.29} = 1.33$	$1.33 \times 3 = 4$

Hence the empirical or the simplest formula of iron oxide is Fe_3O_4

An organic compound contains C, H, and O. When 1.265g of the compound was burned, 2.417g of carbondioxide and 1.484g of water were formed. The molecular mass of the compound is 46. Determine its molecular formula?

Mass of organic compound = 1.265g

Mass of CO_2 formed = 2.417g

Mass of H_2O formed = 1.484g

Organic compound + oxygen = carbondioxide + water

Mass of C in 2.417g of $\text{CO}_2 = \frac{12}{44} \times 2.417\text{g} = 0.6592\text{g}$

Mass of H in 1.484g of $\text{H}_2\text{O} = \frac{2}{18} \times 1.484\text{g} = 0.1649\text{g}$

Mass of oxygen in organic compound = $1.265 - 0.6592 - 0.1649 = 0.4409\text{g}$

% of C = $\frac{0.6592}{1.265} \times 100 = 52.11$

% of H = $\frac{0.1649}{1.265} \times 100 = 13.03$

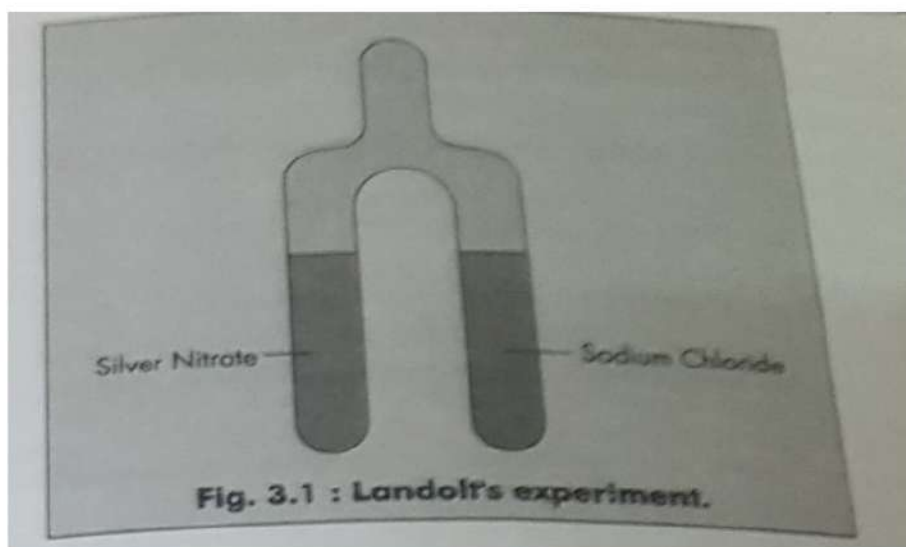
% of O = $\frac{0.4409}{1.265} \times 100 = 34.85$

Then the reaction between the solutions of sodium chloride and silver nitrate occurs spontaneously forming curdy white precipitate of silver chloride.



Curdy white ppt.

After an experiment Landolt's tube was weighted out again. No change in weight was observed. This results verify the truth of the law of conservation of mass.



Element	Percentage(%)	Atomic mass	Relative no. of moles = $\frac{\%}{\text{Atomic mass}}$	Simplest ratio of moles	Simplest whole number of moles
C	52.11	12	$\frac{52.11}{12} = 4.34$	$\frac{4.34}{2.17} = 2$	2
H	13.03	1	$\frac{13.03}{1} = 13.03$	$\frac{13.03}{2.17} = 6$	6
O	34.85	16	$\frac{34.85}{16} = 2.17$	$\frac{2.17}{2.17} = 1$	1

Empirical formula of the compound is $\text{C}_2\text{H}_6\text{O}$

Molecular mass = 46

Empirical formula mass = $\text{C}_2\text{H}_6\text{O} = 12 \times 2 + 1 \times 6 + 16 = 46$

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}}$$

$$n = \frac{46}{46} = 1$$

Molecular formula = (Empirical formula) \times
n

Molecular formula = ($\text{C}_2\text{H}_6\text{O}$) \times 1

Hence, Molecular formula = $\text{C}_2\text{H}_6\text{O}$

Butyric acid contains C, H, and O. 4.24mg sample of butyric acid is completely burned, it gives 8.45mg of CO₂ and 3.46mg of H₂O. The molecular mass of butyric acid was determined by experiment to be 88amu. What is the molecular formula?

Mass of butyric acid = 4.24mg

Mass of CO₂ formed = 8.45mg

Mass of H₂O formed = 3.46mg

Butyric acid + oxygen = carbon dioxide + water

Mass of C in 8.45mg of CO₂ = $\frac{12}{44} \times 8.45 \text{ mg} =$
2.304mg

Mass of H in 3.46mg of H₂O = $\frac{2}{18} \times 3.46 \text{ mg} =$
0.3844mg

Mass of oxygen in Butyric acid = (4.24 - 2.304 - 0.3844) = 1.552mg

% of C = $\frac{2.304}{4.24} \times 100 = 54.33$

% of H = $\frac{0.3844}{4.24} \times 100 = 9.066$

% of O = $\frac{1.552}{4.24} \times 100 = 36.60$

%

Element	Percentage(%)	Atomic mass	Relative no. of moles = $\frac{\%}{\text{Atomic mass}}$	Simplest ratio of moles	Simplest whole number of moles
C	54.33	12	$\frac{54.33}{12} = 4.52$	$\frac{4.52}{2.28} = 2$	2
H	9.066	1	$\frac{9.066}{1} = 9.066$	$\frac{9.066}{2.28} = 4$	4
O	36.60	16	$\frac{36.60}{16} = 2.28$	$\frac{2.28}{2.28} = 1$	1

Thus, the empirical formula of butyric acid is C_2H_4O .

Molecular mass of butyric acid = 88 amu

Empirical formula mass = $C_2H_4O = 12 \times 2 + 1 \times 4 + 16 = 44$
amu

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}}$$

$$n = \frac{88}{44} = 2$$

Molecular formula = (Empirical formula) \times n

Molecular formula = (C_2H_4O) \times 2

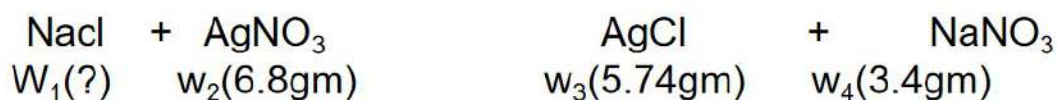
Hence, Molecular formula of butyric acid = $C_4H_8O_2$

Solved examples

Q.

What weight of sodium chloride reacts with 6.8 gm of silver nitrate, if 5.74 gm of silver chloride and 3.4 gm of sodium nitrate are formed?

Solution:



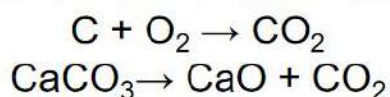
According to law of conservation of mass,

$$\begin{aligned} W_1 + w_2 &= w_3 + w_4 \\ \text{or, } W_1 + 6.8 &= 5.74 + 3.4 \\ \therefore W_1 &= 2.34 \text{ gm} \end{aligned}$$

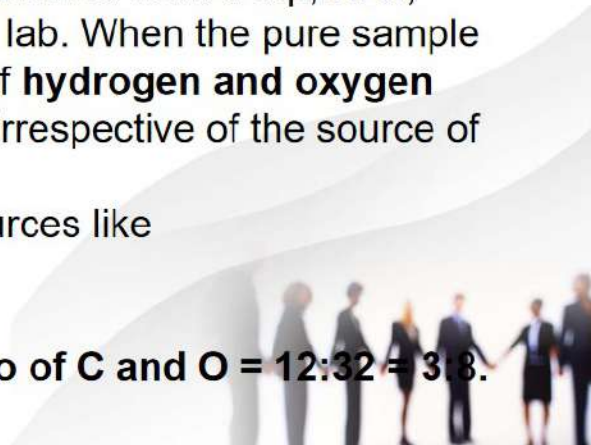
Law of constant composition or definite proportion

It states that "The same compound always contains the same elements combined together in the same proportion by weight whatever the origin or mode of formation of compound".

1. Let us take an example of **water**: Water can be obtained from a tap, river, ocean, lake, etc. It also can be synthesized in the lab. When the pure sample of water is analyzed, it is found to be composed of **hydrogen and oxygen which combine together in a 1:8** ratio by mass irrespective of the source of water.
2. Carbon dioxide may be obtained from various sources like



Regardless of the source of CO_2 , the mass ratio of C and O = 12:32 = 3:8.



Solved example:

Q. copper oxide was prepared by following method:

a. 1.75 g of metal were dissolved in nitric acid and igniting the residual copper nitrate yielded 2.19 g of copperoxide.

b. 1.45 g of copper when strongly heated in a current of air yielded 1.83 g of copperoxide. Prove law of constant composition.

Solution,

1st case,

wt of Cu= 1.75 g

wt of CuO= 2.19 g

so, wt of O= 2.19 - 1.75g = 0.44g

% of O = $(0.44/2.19) \times 100\%$

= 20.09%

% of Cu= $(1.75/2.19) \times 100\%$

= 79.90%

2nd case,

wt of Cu= 1.45g

wt of CuO= 1.83g

so, wt of O= 1.83- 1.45 = 0.38g

% of Cu= $(1.45/1.83) \times 100\%$

= 79.23%

% of O= $(0.38/1.83) \times 100\%$

= 20.67%

% of Cu and O are equivalent in both cases, hence proved.



Solved Example

Q. 1.81 gm of copper was obtained by heating 2.26 gm of copper oxide. In a separate experiment, 2.13 gm of copper was dissolved on nitric acid, copper nitrate so formed was ignited to give 2.67 gm of copper oxide. Show that the above experimental data explain the law of definite proportion.

solution:

Case I:

Weight of copper oxide = 2.26 gm

Weight of copper = 1.81 gm

Weight of oxygen = $2.26 - 1.81 = 0.45$ gm

Ratio of weight of copper to oxygen = 4:1

Case II:

Weight of copper oxide = 2.67 gm

Weight of copper = 2.13 gm

Weight of oxygen = $2.67 - 2.13 = 0.54$ gm

Ratio of weight of copper to oxygen = 4:1

In both the case ratio of the weight of copper to oxygen is the same. So the given data explain the law of definite proportion.

Limitations

i) This law of definite proportion does not hold good for non-stoichiometric compounds like ZnO, FeO and also in some compounds which are formed by the different isotopes of the same element.

