Unit 2

Stoichiometry

Dalton's atomic theory

John Dalton in 1808 proposed Dalton's atomic theory from the article. "A new system of chemical philosophy. The main postulates of this theory are as follows:-

1. All the matter are made up of very tiny, invisible and indivisible particles called atoms.

2. Atoms of the same element are entirely identical in all respect.

3. Atoms of different element are entirely different in all respect.

4. Atoms can neither be created nor be destroyed by any chemical process.

5. Atoms combine in simple whole number ratio in the compound.

Modification of Dalton's atomic theory.

At the end of 19^{th} century, J.J. Thomson, Neils Bohr and Chadwick modified Dalton's atomic theory.

The main modification of this theory are as follows:-

1. Atoms can be divided into sub-atomic particles like electron, proton and neutron.

2. Atoms of the same element may not be identical in all respect. For eg:-
Isotopes of chlorine :- ${}^{35}_{17}Cl$ and ${}^{37}_{17}Cl$

3. Atoms of different element may be similar in one or more respect. For eg:-
Isobars of ${}^{40}_{18}Ar$ and ${}^{40}_{20}Ca$

4. Atoms of one element can be converted into atoms of different element.

$${}^{14}_{7}N + {}^{4}_{2}He \longrightarrow {}^{17}_{8}O + {}^{1}_{1}H$$

5. Atoms combine in definite proportion but may not be in simple whole number ratio.
For eg:- $C_{12}H_{22}O_{11}$
Sucrose

- Stoichiometry.

↳ The chemical calculation based on mass, volume, no. of mole of reactant and product is called stoichiometry.

Stoichiometry → to measure an element.

There are five laws of stiochiometry.

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

• Law of conservation of mass.

↳ This law was proposed by Antonie Lavoision in 1774.

↳ It states that the total mass of reactant reacted is equal to total mass of product produced.

During chemical reaction, there is no loss of mass of any reactant or product.

This law is also known as law of indestructibility of matter. It is similar to law of conservation of energy.

For eg:-

$NaOH + HCl \rightarrow NaCl + H_2O$.

40 gm   38.5g   58.5g   18g.

Total mass of reactant = (40 + 36.5 gm)

= 76.5 gm

Total mass of product = (58.5 + 18 gm)

76.5 gm..

∴ Total mass of reactant = Total mass of product.

- 12gm of carbon combines with 32gm of oxygen to produce 44gm of CO_2. What chemical law those detail illustrate. State the law.

$C + O_2 \longrightarrow CO_2$
12gm   32gm   44 gm

Total mass of reactant = (12gm + 32gm)
44gm

Total mass of product = 44gm

∴ Total mass of reactant = total mass of product.

2. Law of constant composition or law of definite proportion.
↳ This law was studied by louis procost in 1799. It states that in a chemically pure compound, the composition of an element always remains fixed or the percentage composition of an element in a compound always remains fixed. It means whether the sources and methods of preparation of compound are different but the composition of element in a compound doesn't varies.

For eg:- Carbon dioxide can be obtained as follows:

1. By heating coke with oxygen.

$C + O_2 \longrightarrow CO_2 \uparrow$

2. By heating calcium carbonate.

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \uparrow$

3. By reacting $CaCO_3$ with dil. HCl

$CaCO_3 + \text{dil. } 2HCl \rightarrow CaCl_2 + H_2O + CO_2$

In above three reaction, the ratio of weight of carbon and oxygen ~~is~~ in CO_2 is 12 : 32 or, 3 : 8 which is same. Hence, verifies law of constant composition.

Law of multiple proportion

↳ This law was proposed by John Dalton in 1804. It states that when two different element combine to form two or more than two compounds, then the weight of one element which combines with constant weight of other element, bears a simple whole number ratio to one another.

For eg:-

When hydrogen and oxygen combine together to form H_2O and H_2O_2.

In H_2O,

2 parts by weight two of hydrogen combines with 16 parts by weight of oxygen.

In H_2O_2.

classmate

2 part by weight of hydrogen combines with 32 parts by weight of oxygen.

Then the ratio of weight of oxygen which combines with constant weight of hydrogen is
16 : 32 . or 1 : 2
which is simple whole number ratio.

Hence, verifies the law of multiple proportion.

Eg:- $C + O_2 \rightarrow \begin{cases} CO \\ CO_2 \end{cases}$

When carbon and oxygen combines together to produce CO and CO_2.
In CO,
12 part by weight of carbon combines with 16 part by weight of oxygen.

In CO_2.
12 parts by weight of carbon combines with 32 parts by weight of oxygen.

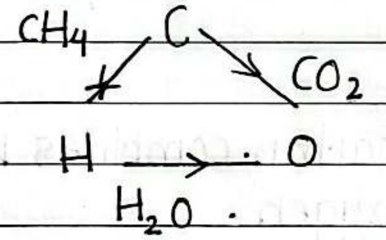
Then, the ratio of weight of oxygen which combines with constant weight of carbon is,
16 : 32 or 1 : 2 which is simple whole number ratio.
Hence, verifies the law of multiple proportion.

Law of reciprocal proportion or law of equivalent composition.

- This law was developed by Richter in 1792.
- It states that when two different elements combines separately with constant weight of third element, the ratio in which they combine is same or simple multiple of the ratio with one another.

Eg:-

When hydrogen, oxygen and carbon combines separately in a cyclic way gives different compound as follows:-



- In CH_4

12 part by weight of carbon combines with 4 part by weight of Hydrogen.

- In CO_2

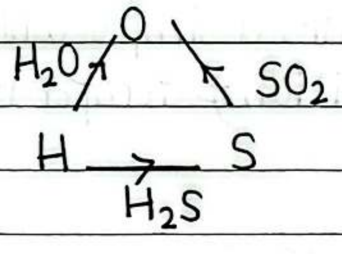
12 part by weight of carbon combines with 32 parts by weight of oxygen.

The ratio of weight of hydrogen and oxygen which combines with constant weight of carbon is 4:32 or 1:8. — (i)

In H_2O
2 parts by weight of hydrogen combines with 16 parts ~~by~~ weight of oxygen.

then, ratio of hydrogen and oxygen is 2:18 or 1:8 ,, ... (ii)
Hence, eq (i) and (ii) are same and verifies the law of reciprocal proportion

When, hydrogen, oxygen and sulphur combines separately in a cyclic way gives following compound.



In H_2O : When 2 parts by the weight of hydrogen combines with 16 parts by weight of oxygen.

In H_2S : 2 parts by weight of hydrogen combines with 32 parts by weight of ~~ox~~ sulphur.

Then, the ratio of weight of oxygen and sulphur ~~with~~ which combines with constant weight of hydrogen is 1:2 ... (i)

In SO_2
32 parts by weight of sulphur combines with 32 parts by weight of oxygen.
then, the ratio of oxygen and sulphur is 32:32 or 1:1 ... (ii)

Hence, eq. (i) and (ii) are in simple multiple ratio and verifies the law of reciprocal proportion.

- law of gaseous volume

This law was developed by Joseph Gay Lussac in 1805.

↳ It states that when gaseous substance reacts together to give gaseous product then, the volume of reactant and product bears a simple whole number ratio under similar condition of temperature and pressure.

Eg:- $H_2 + Cl_2 \rightarrow 2HCl$
(g) (g) (g)
1 vol. 1 vol. 2 vol

∴ The rate of volume of reactant and product is 1:1:2, which is simple whole number ratio and verifies the law of gaseous volume.

Q.N.

CH_4 contains 75 % C

CO contains 42.86 % C

H_2O contains 11.11 % H

- so that above data illustrate the law of reciprocal proportion.

↳ In CH_4,

% of C = 75 %

% of H = (100 − 75) %

= 25 %

75 %

75 parts by weight of carbon combines with 25 parts by weight of hydrogen.

↳ 1 part by weight of carbon combines with $\frac{25}{75}$ parts by weight of hydrogen.

= 0.33 parts by Weight of hydrogen.

In CO,

% of C = 42.86 %

% of O = (100 − 42.86) %

= 57.14 %

42.86 parts by weight of carbon combines with 57.14 parts by weight of oxygen

1 part by weight of carbon combines with $\frac{57.14}{42.86}$ parts by weight of oxygen

= 1.33 parts by weight of oxygen.

$\therefore$ The ratio of weight of hydrogen and oxygen which combines with constant weight of carbon.

$0.33 : 1.33$

$\frac{0.33}{0.33} = \frac{1.33}{0.33}$

$1 : 4 \quad -(i)$

In H_2O:

% of H = 11.11

% of Oxygen = 100 − 11.11%

= 88.89%

11.11 part of hydrogen combines with 88.89 part of oxygen.

The ratio of hydrogen and oxygen is

$11.11 : 88.89$

$= \frac{11.11}{11.11} : \frac{88.89}{11.11}$

$= 1 : 8 \quad -(ii)$

$\therefore$ The eqn (i) and eq. (ii) are in multiple proportion and verifies the law of reciprocal proportion.

explain quantum no.

application of avogardo's hypothesis with example for solid & liquid concentration is unity

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$CaCO_3 \rightleftharpoons CaO + CO_2$

$K_c = \frac{[CaO][CO_2]}{[CaCO_3]} = \frac{1 \times [CO_2]}{1}$

Mole Concept.

N_A (No. of atoms) = 6.023×10^{23} (atom, molecule, proton, electron, neutron)

Any amount of substance which contains Avogardo's number of particle (atom, molecule, ion, proton, electron, neutron) is called mole.

Avogardo's no. of particle = 6.023×10^{23}
One mole of O_2 = 6.023×10^{23} molecules
One mole of Na^+ = 6.023×10^{23} ion
One mole of CO_2 = 6.023×10^{23} molecules.

- Gram atomic mass
  - The atomic mass expressed in gram is called gram atomic mass.

- Mole concept in terms of gram atomic mass.

$$\left.\begin{array}{l}\text{1 mole of carbon} = 12\,gm \\ \text{1 mole of Na} = 23\,gm\end{array}\right\} = 6.023 \times 10^{23} \text{ atom.}$$

$$\text{No. of mole} = \frac{\text{given mass (g)}}{\text{gram atomic mass}}$$

Qno: Calculate no. of mole present in a 2gm of carbon.

$$\text{No. of mole} = \frac{2\,gm}{12\,gm}$$

$$= \frac{1}{6} = 0.167 \text{ mole}$$

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- Gram molecular mass

↳ The molecular mass expressed in gram is called gram molecular mass.

- Mole in terms of gram molecular mass.

One mole of CO = 28gm

One mole of NH_3 = 17gm.

$$\text{No. of moles} = \frac{\text{Given mass (g)}}{\text{Gram atomic mass}}$$

× 2.5gm of Oxygen

$$\text{No. of moles} = \frac{2.5\,gm}{32\,gm}$$

$= 0.078$ mole

- Mole in terms of volume

↳ 1 mole of any gaseous substance at NTP = 22.4l

so,

1 mole of CO_2 = 22.4l = 44gm = 6.023×10^{23} molecule

$$\text{No. of mole} = \frac{\text{given volume (litre)}}{22.4\,l}$$

Calculate, no. of mole

5.6l of NH_3

$$\text{No. of mole} = \frac{5.6}{22.4}$$

$= 0.25$ mol

2.00cc of HCl

$$\text{No. of mole} = \frac{0.002}{22.4}$$

$= 8.92 \times 10^{-5}$ mole

· Mole in terms of particles.

→ 1 mole of gaseous substance = 6.023×10^{23} no. of particles.

$$\text{No. of mole} = \frac{\text{given particle}}{6.023 \times 10^{23}}$$

$$\text{No. of mole in } 1 \times 10^{20} \text{ molecules} = \frac{1 \times 10^{20}}{6.023 \times 10^{23}}$$

$= 1.66 \times 10^{-4}$ mole.

· Limiting reagent or limiting reaction.

↳ The chemical species which is present in lesser amount and finished first or consumed first is called limiting reagent
It limits whole chemical reaction and gives an idea about product formation.

· Excess reagent

↳ The chemical species which is present in large amount and don't finish at the end of reaction is called excess reagent.

53 gram of Na_2CO_3 combines with 7.5 gm of HCl

i) find limiting reagent.

ii) calculate the mass of excess reagent left over unre acted.

iii. what mass of salt is produced?

iv. find the volume of CO_2 produced.

v. Calculate no. of molecules of water produced.

→ $Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2 \uparrow$
106 gm 73gm 117gm 18gm 44gm.

→ 106gm of Na_2CO_3 combines with 73 gm of HCl
5.3gm of Na_2CO_3 combines with $\frac{73}{106} \times 5.3$ gm of HCl.
3.65gm of HCl.

∴ 5.3gm of Na_2CO_3 combines with 3.65gm of HCl
but given 5.3gm of Na_2CO_3 combines with 7.5gm of HCl

Hence, Na_2CO_3 is limiting reagent.

(ii) Mass of excess reagent = 7.5 − 3.65
= 3.85 gm.

(iii) 106gm of Na_2CO_3 produces 117gm of NaCl
5.3gm of Na_2CO_3 produces $\frac{117gm}{106} \times 5.3$ g of NaCl
= 5.85 gm of NaCl.

(iii) 106gm of Na_2CO_3 produces 22.4l of CO_2
5.3gm of Na_2CO_3 produces $\frac{22.4}{106} \times 5.3$ l of CO_2
= 1.12 l of CO_2

(v) 106 gm of Na_2CO_3 produces 6.023×10^{23} molecules
5.3 gm of Na_2CO_3 produces $\frac{6.023 \times 10^{23}}{106} \times 5.3$ molecule
$= 3.0115 \times 10^{22}$ molecule of H_2O.

Percentage yield
↳ The ratio of actual yield to the theoretical yield is called percentage yield.

$$\text{Percentage yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100\%$$

* **Actual** yield:
The amount of product obtained from a chemical reaction.

* Theoritical yield:
The amount of product obtained from stoichiometric equation using the limiting reactant to determine product.

• 20.8g of barium chloride is treated with excess of sulphuric acid and 18gm $BaSO_4$ is product. What is percentage yield of the reaction. (At. weight of Barium = 137)

↳ $BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl$
(208gm) (98gm) (233gm) + 73(gm)

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208 gm of $BaCl_2$ produces 233 gm of $BaSO_4$.
20.8 gm of $BaCl_2$ produces $\frac{233}{208} \times 20.8$ gm of $BaSO_4$

= 23.3 gm of $BaSO_4$.

Actual yield = 18 gm
Theoretical yield = 23.3 gm.

Percentage yield = $\frac{18}{23.3} \times 100\%$

= 77.25%.

2. 11.1 gm of $CaCl_2$ reacts with excess of Na_2CO_3.
Percentage yield = 70%, Actual yield = ?

$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$
(111 gm) - (106 gm) (100 gm) (117 gm).

111 gm of $CaCl_2$ produces 100 gm of $CaCO_3$
11.1 gm of $CaCl_2$ produces $\frac{100}{111} \times 11.1$ gm of $CaCO_3$

= 10 gm of $CaCO_3$

Percentage yield = $\frac{A}{10} \times 100\%$

or, $70 = \frac{A}{10} \times 100\%$

$A = 7$ gm.

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- Empherical formula.

↳ It is the simplest formula obtained by taking simple whole number ratio of the element present in the molecule.

For eg:-

Molecular formula of glucose

$C_6H_{12}O_6$

Simple whole ~~rat~~ number = 1:2:1

Empherical formula = ~~C6~~ CH_2O

* Relationship between molecular formula and emphirical formula.

Molecular formula = n x Emphirical formula.

$$n = \frac{\text{Molecular formula weight}}{\text{Emphirical formula weight}} = \frac{M.F.W}{E.F.W}$$

- From following composition, find emphirical formula

C = 27.27%

O = 72.72%

Name of element	% compo-sition	At. weight	Rel. no. of mole	Simplest ratio
C	27.27%	12	2.27	$\frac{2.27}{2.27} = 1$
O	72.72%	16	4.5	$\frac{4.5}{2.27} = 2$

∴ Simple whole no. ratio = 1:2

Emphirical formula = CO_2.

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An inorganic salt has following composition.
Na = 29·11%
S = 40·51%
O = 30·38%
Calculate the emphirical f yield.

No. of element	% of composition	At. weight	Relative no. of mole	Simplest ratio.
Na	29·11%	23	1.26	1 X2 = 2
S	40·51%	32	1.26	1 X2 = 2
O	30·38%	16	1.86	1.5X2 = 3

Simple whole no. ratio = 2:2:3
Emphirical formula = $Na_2S_2O_3$.

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Development of Avogadro's Hypothesis.

• Berzelius hypothesis

→ It states that "equal volume of all gases contains equal ~~volume~~ number of atom under similar conditions of temperature and pressure.

i.e, $n \propto V$

For eg:-

$$H_2 + Cl_2 \longrightarrow 2HCl$$

1 vol. 1 vol. 2 vol.

[1 atom] [1 atom] [2 compound atom]

($\frac{1}{2}$ atom) ($\frac{1}{2}$ atom) (1 compound atom)

↳ It shows that 1 compound atom of HCl is obtained from $\frac{1}{2}$ (half) atom of hydrogen and $\frac{1}{2}$ (half) atom of chlorine.

↳ Splitting of atom is against with Dalton's atomic theory, so this hypothesis was failed or discarded.

Avogadro's Hypothesis

↳ In 1811, Amedeo Avogadro, an Italian scientist introduced term molecules instead of atom. He modified berzelius hypothesis.

↳ It states that "Equal volume of all gases contains equal number of molecules per mole under similar condition of temperature and pressure".

For example,

$H_2 + Cl_2 \rightarrow 2HCl$
1vol. 1vol. 2vol.

If 'v' volume consists 'n' molecules, then
$H_2 + Cl_2 \longrightarrow 2HCl$
n molecule n molecule 2n molecule

If n = 1.
$H_2 + Cl_2 \longrightarrow HCl$
1 molecule 1 molecule 2 molecule.
$\frac{1}{2}$ molecule $\frac{1}{2}$ molecule 1 molecule

↳ It shows that 1 molecule of HCl is obtained from half ($\frac{1}{2}$) molecule of hydrogen and half ($\frac{1}{2}$) molecule of chlorine.

↳ Splitting of molecules is in accordance with Dalton's atomic theory because 1 molecule contains more than one atom. Hence, Avogadro's hypothesis was accepted forever.

- Application of Avogadro's law (Hypothesis)

1. Determination of Atomicity of molecules.

- Atomicity

↳ Total number of atoms present in a molecule is called atomicity.

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- Show that hydrogen is diatomic in nature.

$H_2 + Cl_2 \longrightarrow 2HCl$ - from eg. (avogadro's hypothesis)

1 molecule 1 molecule 2 molecules

$\frac{1}{2}$ molecule $\frac{1}{2}$ molecule 1 molecule

It shows that 1 molecule of HCl is obtained from half ($\frac{1}{2}$) molecules of hydrogen and half ($\frac{1}{2}$) molecules of chlorine.

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

1 molecule of hydrogen = 2 atom

Hence, hydrogen is diatomic in nature.

- Show that oxygen is diatomic in nature.

$2H_2 + O_2 \longrightarrow 2H_2O$

2 vol. 1 vol. 2 vol.

If 'v' volume contains 'n' molecules.

$2H_2 + O_2 \longrightarrow 2H_2O$

2n' molecule n molecule 2n molecule.

If n = 1,

2 molecule : 1 molecule → 2 molecule.

1 molecule : $\frac{1}{2}$ molecule → 1 molecule

↳ It shows that 1 molecule of H_2O is obtained from 1 molecule of hydrogen and half ($\frac{1}{2}$) molecule of oxygen.

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

1 molecule of oxygen = 2 atom.

Hence, oxygen is diatomic in nature.

- To determine relationship between molecular mass and vapour density.
  [molecular mass = 2 × d] → (vapour density)

- Molecular mass:

→ It is defined as the ratio of weight of one molecules of gas to the weight of one atom of hydrogen gas.

- Formula:

$$\text{Molecular mass} = \frac{\text{Weight of 1 molecule of gas}}{\text{Weight of 1 atom of hydrogen gas}}$$

- Vapour density:

→ It is defined as the ratio of weight of certain volume of gas to the weight of same volume of hydrogen gas.

$$\text{V.D.} = \frac{\text{Wt. of certain volume of gas}}{\text{Wt. of same volume of hydrogen gas}}$$

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If 'v' be the volume of gas.

$$V.D = \frac{\text{Wt. of 'v' volume of gas}}{\text{Wt. of 'v' volume of hydrogen gas}}$$

Applying Avogadro's hypothesis.

↳ If 'v' volume contains 'n' molecules.

$$V.D = \frac{\text{Wt. of 'n' molecules of gas}}{\text{Wt. of 'n' molecule of hydrogen gas}}$$

If n = 1.

$$V.D. = \frac{\text{Wt. of 1 molecule of gas}}{\text{Wt. of 1 molecule of hydrogen gas.}}$$

$$V.D. = \frac{\text{Wt. of 1 molecule of gas}}{\text{Wt. of 2 atom of hydrogen gas}}$$ [∵ hydrogen is diatomic in nature]

$$V.D = \frac{\text{Wt. of 1 molecule of gas}}{2 \times \text{Wt. of 1 atom of hydrogen gas}}$$

$$V.D. = \frac{1}{2} \cdot \text{molecular mass}$$ $$\left[\text{m. mass} = \frac{\text{Wt. of 1 m. gas}}{\text{Wt. of 1 atom of hydrogen gas}}\right.$$

or, $2 \cdot V.D = \text{molecular mass}$.

∴ molecular mass = 2 × vapour density.

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Determine the relationship of:

- Gram molecular mass and volume of the gas.

↳ We know,

Molecular mass = 2 X V.D (vapour density).

$$= 2 \times \frac{\text{Wt. of certain volume of gas}}{\text{Wt. of same volume of hydrogen gas}}$$

If 'v' be the volume of gas.

$$\text{Molecular mass} = 2 \times \frac{\text{Wt. of 'v' volume of gas}}{\text{Wt. of 'v' volume of hydrogen gas}}$$

If 'v' contains 1l volume

$$\text{Molecular mass} = 2 \times \frac{\text{Wt. of 1l volume of gas}}{\text{Wt. of 1l volume of hydrogen gas}}$$

$$\text{Molecular mass} = \frac{2 \times \text{Wt. of 1l of gas}}{0.089 \text{ gm}}$$

$$\left[\begin{array}{l} \because 22.4l \text{ of } H = 2gm \\ \quad 1l = \frac{2}{22.4} \\ \quad\quad = 0.089 \end{array} \right]$$

Molecular mass in gm = 22.4 [Wt. of 1l of gas]

Gram molecular mass = Weight of 22.4l of gas.

↳ Gram molecular mass = 22.4l of gas at NTP.

To determine molecular formula from its volume composition.

↳ A nitrious oxide contain same volume of nitrogen. The vapour density of nitrous oxide is 54. Determine molecular formula.

Nitrogen + oxygen ⟶ Nitrious oxide

↳ If 'v' volume of Nitrous oxide contains 'v' volume of nitrogen.

↳ If 'v' volume contains 'n' molecules,
n molecules of nitrous oxide contains 'n' molecules of nitrogen.

If n = 1,
1 molecule of nitrous oxide contains 1 molecule of nitrogen.

Let, x be the number of atom of oxygen.
∴ molecular formula is:
N_2O_x

↳ Vapour density = 54.

Molecular mass = 2 X 54
or, Molecular mass = 108
$N_2O_x = 108$
or, $28 + 16x = 108$
or, $16x = 80$
or, $x = \frac{80}{16}$

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$\therefore x = 5$

N_2O_5

- Percentage composition

→ It is defined as the number of parts by the weight of an element present in 100 parts by weight of the compound.

$$\text{Percentage composition} = \frac{\text{Wt. of an element}}{\text{Wt. of compound}} \times 100\%$$