THE MOLE CONCEPT AND STOICHIOMETRY

(I) The Mole Concept and Stoichiometry

Content

- Relative masses of atoms and molecules
- The mole, the Avogadro constant
- The calculation of empirical and molecular formulae
- Reacting masses and volumes (of solutions and gases)

Learning Outcomes required for H2 (9729) and H1 (8873) Chemistry:

[The term relative formula mass or M_r will be used for ionic compounds]

Candidates should be able to

(a) Define the terms *relative atomic*, *isotopic*, *molecular* and *formula mass,* based on the ^{12}C scale;

(b) Define the term *mole* in terms of the Avogadro constant;

(c) Calculate the relative atomic mass of an element given the relative abundances of its isotopes;

(d) Define the terms *empirical* and *molecular formula*;

(e) Calculate empirical and molecular formulae using combustion data or composition by mass;

(f) Write and /or construct balanced equations;

(g) Perform calculations, including use of the mole concept, involving:

  (i) reacting masses (from formulae and equations);

  (ii) volumes of gases (e.g. in the burning of hydrocarbons);

  (iii) volumes and concentrations of solutions;

  [when performing calculations, candidates' answers should reflect the no. of significant figures given or asked for in the question]

(h) Deduce stoichiometric relationships from calculations such as those in (g).

1. RELATIVE MASSES OF ATOMS AND MOLECULES

Success Criteria:

- Able to define the terms *relative atomic*, *isotopic*, *molecular* and *formula mass,* based on the ^{12}C scale.
- Able to calculate the relative atomic mass of an element given the relative abundances of its isotopes.

1.1 Relative Atomic Mass Scale: The Carbon–12 scale

Atoms are too small to be weighed directly and it is inconvenient to express masses of individual atoms in terms of kilograms, *kg*, or grams, *g* (e.g. mass of one H atom = 1.67×10^{-27} kg). It is more practical to consider its mass relative to that of another atom known as the standard. The most abundant isotope of carbon, ^{12}C, is the chosen standard. In this scale, an atom of carbon–12 is assigned a mass of exactly 12 atomic mass units (a.m.u).

1.1.1 Relative Isotopic Mass (NO UNITS)

Isotopes are **atoms** of the same element whose nuclei have the **same number of protons but different number of neutrons**; e.g. $^{35}_{17}Cl$ and $^{37}_{17}Cl$.

Relative isotopic mass is the **mass of one atom of the isotope relative to $\frac{1}{12}$ the mass of one atom of carbon-12.**

Note:
Values of A_r are to be given to **1 decimal place** unless otherwise stated.

1.1.2 Relative Atomic Mass of an element (symbol: A_r, NO UNITS)

Many elements consist of isotopes of varying abundances. The weighted average of their mass numbers and abundances need to be taken into consideration when calculating the relative atomic mass of an element.

Relative atomic mass is the **weighted average of the isotopic masses of one atom of an element relative to $\frac{1}{12}$ the mass of one atom of carbon-12.**

Worked Example 1

Calculate the relative atomic mass of chlorine from the isotopic abundances data:

Isotope	Relative isotopic mass	Natural abundance (%)
^{35}Cl	34.9689	75.77
^{37}Cl	36.9658	24.23

$$A_r \text{ of } Cl = \frac{(34.9689 \times 75.77 + 36.9658 \times 24.23)}{100} = 35.5$$

Worked Example 2

Given the A_r of copper is 63.54, determine the relative abundances of the two isotopes of copper, ^{63}Cu and ^{65}Cu.

Let % abundance of ^{63}Cu be x and ^{65}Cu be (100 – x).

$$\frac{63(x) + 65(100 - x)}{100} = 63.54$$

$$x = 73.0\%$$

Relative abundances of ^{63}Cu and ^{65}Cu are 73.0 % and 27.0 % respectively.

<u>Checkpoint 1</u> 

1. Naturally occurring gallium, Ga, is a mixture of two isotopes, gallium-69 and gallium-71. Given that the relative atomic mass of gallium is 69.7, calculate the percentage abundance of each isotope.

[^{69}Ga: 65.0%, ^{71}Ga: 35.0%]

2. Calculate the relative atomic mass of neon using the following data.

[20.2]

Isotope	**Natural abundance (%)**
Neon-20	90.5
Neon-21	0.3
Neon-22	9.2

3. [2016/P1/Q3]

Shakudo is a Japanese alloy of copper and gold. The information in the table was obtained by mass spectrometry of a sample of shakudo.

Mass number	63	65	197
% abundance	65	29	6

What A_r value for copper is given by these figures?

A 59.8 **B** 63.5 **C** 63.6 **D** 71.6

Note:
Values of A_r and M_r are to be given to **1 decimal place** unless otherwise stated.

1.1.3 Relative Molecular Mass (symbol: M_r, NO UNITS)

Relative molecular mass is the **weighted average of the masses of one molecule of a substance relative to $\frac{1}{12}$ the mass of one atom of carbon-12.**

Worked Example 3
Calculate the relative molecular mass of glucose, $C_6H_{12}O_6$.

M_r of $C_6H_{12}O_6$ = 6(12.0) + 12(1.0) + 6(16.0) = 180.0

1.1.4 Relative Formula Mass (symbol: M_r, NO UNITS)

Relative Formula Mass is used for compounds with giant lattices.

Relative formula mass is the **weighted average of the masses of one formula unit relative to $\frac{1}{12}$ the mass of one atom of carbon-12.**

Worked Example 4
Calculate the relative formula mass of Na_2SO_4.

M_r of Na_2SO_4 = 2(23.0) + 32.1 + 4(16.0) = 142.1

2. THE MOLE, THE AVOGADRO CONSTANT

Success Criteria:
- Able to define the term *mole* in terms of the Avogadro constant.
- Able to calculate the amount of particles present using Avogadro's constant, *L*
- Able to calculate the amount of gas using molar volumes at r.t.p. & s.t.p conditions
- Able to express a quantity in terms of parts per million (ppm)

Unit for mole: **mol**

Avogadro constant, $L = 6.02 \times 10^{23}$ mol^{-1}

(This value is given in the *Data Booklet*)

One mole of *a substance* is the amount of that substance which contains the same number of particles as there are atoms in 12.0 g of ^{12}C isotopes.

The term "***particles***" could refer to atoms, molecules, ions or electrons etc.

This number is known as **Avogadro's constant, *L***, and has a value of **6.02×10^{23}**.

2.1 Calculation of amount (i.e. no. of moles) from number of particles

Note:
The term **"amount"** is used to represent "**number of moles"**

$$\text{amount of particles (in mol)} = \frac{\text{number of particles}}{6.02 \times 10^{23} (\text{in mol}^{-1})}$$

When the mole is used, the elementary entities *must* be specified, which may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.

In 1 mole of water (H_2O), there are: 6.02×10^{23} H_2O molecules
$2 \times 6.02 \times 10^{23} = 1.20 \times 10^{24}$ H atoms
6.02×10^{23} O atoms

In 1 mole of magnesium chloride ($MgCl_2$), there are: 6.02×10^{23} Mg^{2+} ions
$2 \times 6.02 \times 10^{23}$ Cl^- ions

2.2 Molar mass (units: g mol^{-1})

Molar mass is the mass of one mole of substance and is *numerically equal* to the A_r or M_r of the substance.

relative atomic mass of sodium = 23.0
$\Rightarrow$ molar mass of sodium = 23.0 g mol^{-1}

relative formula mass of $MgSO_4$ = 120.4
$\Rightarrow$ molar mass of $MgSO_4$ = 120.4 g mol^{-1}

2.3 Calculation of *Amount* using *Mass* of substance

$$\text{amount of } \mathbf{A} \text{ (in mol)} = \frac{\text{mass of } \mathbf{A} \text{ (in g)}}{\text{molar mass of } \mathbf{A} \text{ (in g mol}^{-1})}$$

Worked Example 5
Calculate the amount of $CaCl_2$ in 2.54 g of $CaCl_2$.

$$\textbf{Amount of } \mathbf{CaCl_2} = \frac{\mathbf{2.54}}{\mathbf{40.1 + 2(35.5)}} = \mathbf{0.0229 \ mol}$$

2.4 Molar volume of Gas (V_m) (units: dm^3 mol^{-1})

The molar volume of any **gas** is the volume occupied by 1 mole of the gas under the **same temperature and pressure**.

Note:
The molar volume and the conditions for r.t.p & s.t.p are given in the ***Data Booklet***.

T (in K) = T (in °C) + 273

Conditions	V_m
room temperature & pressure (**r.t.p**) **20 °C [293K], 1 atm [101325 Pa]**	**24.0 dm^3 mol^{-1}**
standard temperature & pressure (**s.t.p**) **0 °C [273K], 1 bar [10^5 Pa]**	**22.7 dm^3 mol^{-1}**

Note:

1 dm^3 = 10^3 cm^3

$$\text{At } \textbf{r.t.p.}\text{, Amount of } \mathbf{A} \text{ (in mol)} = \frac{\textbf{Volume of gas A (in dm}^3\textbf{)}}{\mathbf{24.0 \ dm^3}}$$

$$\text{At } \textbf{s.t.p.}\text{, Amount of } \mathbf{A} \text{ (in mol)} = \frac{\textbf{Volume of gas A (in dm}^3\textbf{)}}{\mathbf{22.7 \ dm^3}}$$

Note:
Intermediate answers are to be recorded to **4 significant figures.**

Final answers are to be recorded to **3 significant figures** unless otherwise stated.

Worked Example 6

Calculate the volume of carbon dioxide produced at s.t.p. from the decomposition of 15.0 g of calcium carbonate. [A_r: Ca, 40.1; C, 12.0; O, 16.0]

$$\mathbf{CaCO_3\ (s) \longrightarrow CaO\ (s) + CO_2\ (g)}$$

Amount of $CaCO_3$ = $\frac{15.0}{100.1}$
= 0.1498 mol (4 s.f.)
= Amount of CO_2

Volume of CO_2 = 0.1498 × 22.7
= 3.40 dm^3 (3 s.f.)

Checkpoint 2 

[A_r: H, 1.0; C, 12.0; O, 16.0; Na, 23.0; N, 14.0; Mg, 24.3; S, 32.1]

1(a)(i) Calculate the amount of CH_4 present in 4.0 g of methane. **[0.250]**

(ii) Calculate the number of methane molecules present in 4.0 g of methane. **[1.51 × 10^{23}]**

(iii) Calculate the number of hydrogen atoms present in 4.0 g of methane. **[6.02 × 10^{23}]**

(b) Calculate the number of hydroxide ions present in 8.0 g of magnesium hydroxide. **[1.65 × 10^{23}]**

(c) Calculate the number of sodium ions present in 8.0 g of sodium sulfate. **[6.78 × 10^{22}]**

2. For each of the following pairs, which balloon has a greater volume?

[(a) S, (b) T]

	Balloon **S**	Balloon **T**	Answer
(a)	15 g of O_2 under r.t.p	10.6 dm^3 of CO_2 under r.t.p	
(b)	3.01×10^{22} CH_4 molecules at s.t.p	0.4 mol of N_2 at s.t.p	

<u>Note: Since gases are measured under the same conditions, number of moles can be used for comparison.</u>

3. How many moles of propane, C_3H_8, are there in 600 cm^3 of the gas at s.t.p. and r.t.p?

[0.0264; 0.0250]

2.5 Parts per million (ppm)

Parts per million is a fraction out of one million. When expressing a quantity in terms of ppm, you must make sure that the units of both quantities are the same.

For solutions: 1 ppm $\Rightarrow$ 1 g of solute A in 10^6 g of water
For gases: 1 ppm $\Rightarrow$ 1 cm^3 of gas A in 10^6 cm^3 of air

E.g. When the volume of carbon monoxide in air is 20 ppm,

It means that $\frac{\textbf{20 cm}^3}{\textbf{1000000 cm}^3}$ **or** $\frac{\textbf{20 dm}^3}{\textbf{1000000 dm}^3}$ **or** $\frac{\textbf{20 m}^3}{\textbf{1000000 m}^3}$ **of air is CO.**

Note:
Convert units of both quantities to be the same before doing further calculations.

1 m^3 = 10^3 dm^3
= 10^6 cm^3

Worked Example 7
In a factory area where hydrogen cyanide gas is released into the environment, it is estimated that there are about 20 cm^3 of hydrogen cyanide gas per 50 m^3 of air. Calculate the volume of hydrogen cyanide in the air in terms of ppm.

Conversion of units: 50 m^3 = 50×10^6 cm^3

$\Rightarrow$ In 50×10^6 cm^3 of air, there are 20 cm^3 of hydrogen cyanide gas

$\Rightarrow$ In 10^6 cm^3 of air : $\frac{20}{50\ x\ 10^6}$ **x 10^6 = 0.400 ppm of hydrogen cyanide gas**

3. STOICHIOMETRY

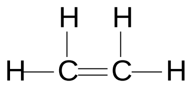
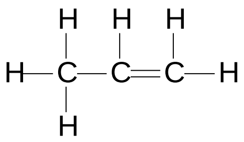
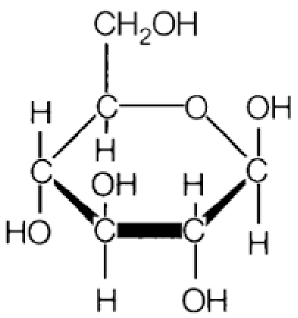
Stoichiometry refers to the study of the **quantitative** aspects of chemical reactions. It involves both the determination of chemical formulae as well as calculations using balanced chemical equations based on the central idea of the mole.

3.1 Empirical and Molecular Formulae

<u>Success Criteria:</u>
- Able to define the terms *empirical* and *molecular formula*.

The **empirical formula** of a compound is the simplest formula that shows the <u>simplest whole number ratio</u> of the atoms of each element present in the compound.

The **molecular formula** of a compound shows the <u>actual number of atoms</u> of each element in <u>one molecule</u> of the compound. It is a simple multiple of the empirical formula and can only be obtained if the molar mass is known.

Compound	Molecular formula	Empirical formula	Molar Mass (g mol^{-1})
Ethene 	C_2H_4	CH_2	28.0
Propene 	C_3H_6	CH_2	42.0
Glucose 	$C_6H_{12}O_6$	CH_2O	180.0

Success Criteria:
- Able to calculate empirical and molecular formulae using combustion data or composition by mass.

Worked Example 8

A substance **X** was found to have the following composition (% by mass): 50 % carbon, 5.6 % hydrogen and 44.4 % oxygen. Find the empirical formula of **X**.

If the relative molecular mass of **X** is 144, deduce its molecular formula.
[A_r: H, 1.0; C, 12.0; O, 16.0]

Note:
If the simplest ratio ends with certain decimals (.33, .5 or .67), you should **not** round up or down, but to multiply it throughout by a factor to obtain a whole number instead.
Eg. .33 × 3, .5 × 2, .67 × 3

Element	C	H	O
% by mass	50	5.6	44.4
Amount / mol	$\frac{50}{12.0} = 4.167$	$\frac{5.6}{1.0} = 5.6$	$\frac{44.4}{16.0} = 2.775$
Mole ratio	$\frac{4.167}{2.775} = 1.50$	$\frac{5.6}{2.775} = 2.02$	$\frac{2.775}{2.775} = 1$
Simplest whole number mole ratio	3	4	2

The empirical formula of X is $C_3H_4O_2$.

Let molecular formula of X be $(C_3H_4O_2)n$

$$\begin{aligned} M_r \text{ of } (C_3H_4O_2)n &= 144 \\ \{3(12.0) + 4(1.0) + 2(16.0)\}n &= 144 \\ 72n &= 144 \\ n &= 2 \end{aligned}$$

∴ Molecular formula of X is $C_6H_8O_4$.

3.2 Percentage composition by mass

From the formula of a compound and the relative atomic masses of the elements in it, the percentage composition by mass of each element in the compound can be calculated.

Worked Example 9

The molecular formula of chlorophyll is $C_{55}H_{72}MgN_4O_5$. Calculate the percentage by mass of magnesium present in chlorophyll.

$$M_r \text{ of } C_{55}H_{72}MgN_4O_5 = 55(12.0) + 72(1.0) + 24.3 + 4(14.0) + 5(16.0) = 892.3$$

$$\therefore \text{ Percentage by mass of Mg} = \frac{24.3}{892.3} \times 100\% = 2.72\ \%$$

Checkpoint 3

1. Caproic acid (M_r = 116) is present in goat's milk and has the following composition by mass:

C, 62.1%; H, 10.3%; O, 27.6%.

Determine the empirical formula and molecular formula of Caproic acid.

[A_r : C, 12.0 ; H, 1.0; O, 16.0]

[C_3H_6O; $C_6H_{12}O_2$]

2. A compound **Y**, containing only carbon, hydrogen and oxygen, is subjected to combustion analysis. Complete combustion of 1.000 g of compound **Y** gave 1.500 g of carbon dioxide and 0.405 g of water. Calculate the mass of C, H and O present in compound **Y** and hence determine its empirical formula.

[A_r : C, 12.0 ; H, 1.0; O, 16.0]

[$C_3H_4O_3$]

[***Hint: C in CO_2 and H in H_2O come from the hydrocarbon only]

Checkpoint 3 (Continued)

3. $Ca_5(PO_4)_3F$ and $(NH_4)_2HPO_4$ are both used as fertilizers. Suggest which compound contains a higher percentage by mass of phosphorus: $Ca_5(PO_4)_3F$ or $(NH_4)_2HPO_4$.
[A_r: H, 1.0; Ca, 40.1; O, 16.0 ; P, 31.0; F, 19.0; N, 14.0]

[$(NH_4)_2HPO_4$]

3.3 Reacting Masses & Limiting Agents

Success Criteria:

- Able to construct balanced equations;
- Able to calculate using mole concept, involving reacting masses (from formulae and equations);
- Able to deduce stoichiometric relationships from calculations.

In a chemical reaction, the atoms involved are not destroyed or created but rearranged to give new products. All the atoms are thus accounted for and obey the law of conservation of matter.

These chemicals react in stoichiometric amounts according to the balanced chemical equation. They are expressed in term of moles and are not easily measured quantities in the laboratory. In practice, chemicals are measured by masses or volumes, which can be converted into amounts (i.e. moles). Often, the reactants may not be added in stoichiometric amounts; i.e. one of the reagents would be present in limited amount while the rest would be in excess.

A **limiting reagent** is **completely consumed** when the reaction goes to completion while the **excess reagents** are not. The reaction stops when the limiting reagent is used up. The limiting agent thus limits how much product is formed.

Steps in determining the limiting and excess reagents in a chemical reaction:

1. Write the balanced chemical equation.
2. Calculate the amount of each reagent added into the reaction.
3. Compare the ratio of the amount of reactants with the mole ratio in the balanced equation to determine the limiting reagent.

Worked Example 10

When 34.6 g of red lead oxide, Pb_3O_4, was heated with 1 mol of hydrogen, lead and water was produced. Calculate the mass of water formed.
[A_r: H, 1.0; O, 16.0; Pb, 207.2]

$$\mathbf{Pb_3O_4 + 4H_2 \longrightarrow 3Pb + 4H_2O}$$

Amount of Pb_3O_4 present in 34.6 g = $\mathbf{\dfrac{34.6}{3(207.2) + 4(16.0)}}$ **= 0.05046 mol**

0.05046 mol of Pb_3O_4 will require 4(0.05046) = 0.2018 mol of H_2,
Since 1 mole of H_2 is present (excess), hence Pb_3O_4 is the limiting reagent.

Amount of H_2O formed = 0.05046 × 4 = 0.2018 mol
∴ Mass of H_2O formed = 0.2018 × 18.0 = <u>3.63 g</u>

Worked Example 11

Given the balanced equation:

$$3CuO(s) + 2NH_3(g) \longrightarrow N_2(g) + 3Cu(s) + 3H_2O(l)$$

If 30 dm^3 of NH_3 is reacted with excess solid CuO at r.t.p, calculate the amount of N_2 produced and the mass of Cu produced.

Amount of NH_3 = $\dfrac{30\ dm^3}{24.0\ dm^3 mol^{-1}}$ **= 1.25 mol**

$$\mathbf{\frac{\text{Amount of } N_2}{\text{Amount of } NH_3} = \frac{1}{2} \qquad \frac{\text{Amount of Cu}}{\text{Amount of } NH_3} = \frac{3}{2}}$$

Amount of N_2 produced = $\mathbf{\dfrac{1}{2}}$ **× 1.25 = 0.625 mol**

Amount of Cu produced = $\mathbf{\dfrac{3}{2}}$ **× 1.25 = 1.875 mol**

Mass of Cu produced = 1.875 × 63.5 = 119 g

Worked Example 12

Sodium peroxide, Na_2O_2, is used in submarines for absorbing atmospheric carbon dioxide and generating oxygen, producing sodium carbonate as a by-product.

(a) Write a balanced equation for the reaction.

$$\mathbf{2Na_2O_2 + 2CO_2 \longrightarrow O_2 + 2Na_2CO_3}$$

(b) Calculate the mass of sodium peroxide needed per day to absorb the carbon dioxide produced by the submariners who exhale a total of 4.80 m^3 of CO_2 per day. Assume all measurements are made at r.t.p.

4.80 m^3 = 4800 dm^3

Amount of CO_2 exhaled = $\mathbf{\dfrac{4800}{24.0}}$ **= 200 mol**

Amount of Na_2O_2 needed = 200 mol

Mass of Na_2O_2 needed = 200 × 78.0 = 15600 g

3.3.1 Calculations using Volumes of Gases

Volumes of gases are **dependent on temperature and pressure**.

Avogadro's Law: At the **same temperature and pressure**, the **same volume of all gases** contains the **same amount of gas particles**.

Hence, for **GASEOUS** substances **only**:

VOLUME RATIO = MOLE RATIO

E.g. Given the equation $2CO\ (g) + O_2\ (g) \longrightarrow 2CO_2\ (g)$
The balanced equation tells us that 20 cm^3 of carbon monoxide reacts with 10 cm^3 of oxygen to give 20 cm^3 of carbon dioxide.

Note that the ratio of volumes **20 cm^3 : 10 cm^3 : 20 cm^3** is the same as the mole ratio **2:1:2** indicated by the stoichiometric coefficients in the balanced equation.

Worked Example 13

A mixture of 10 cm^3 of oxygen and 50 cm^3 of hydrogen is sparked. Calculate the final volume of gas after the reaction goes to completion.

Assume all volumes are measured under r.t.p.

Note:
For gaseous reactions, volume ratio = mole ratio

"Change" in amount of reactants and product will **always follow mol ratio** in the balanced equation.

	$2H_2(g)$	+	$O_2(g)$	$\longrightarrow$	$2H_2O(l)$
Initial vol /cm^3	**50**		**10**		–
Change in vol / cm^3	**–20**		**–10**		–
Final vol / cm^3	**30**		**0**		–

O_2 is the limiting reagent. 1 mol of O_2 reacts with 2 mol of H_2.
Hence, 10 cm^3 O_2 reacts with 20 cm^3 of H_2.

Volume of H_2 left = 50 – 20 = 30 cm^3

Checkpoint 4

Aluminium sulfide solid, Al_2S_3, reacts with water to give hydrogen sulfide gas, H_2S, and aluminium hydroxide solid.
[A_r: Al, 27.0; S, 32.1; O, 16.0 ; H, 1.0]

(a) Write a balanced equation, with state symbols, for the reaction.

(b) What is the maximum mass of H_2S that can form when 158 g of aluminium sulfide reacts with 131 g of water?

[108 g]

(c) Calculate the amount of excess reagent remaining at the end of the reaction.

[0.972 mol]

3.4 Percentage Yield & Percentage Purity

Theoretical yield is the maximum quantity of the product that can be obtained in a reaction from the given amount of the limiting reagent reacted. This can be calculated using stoichiometric ratios.

Experimental yield / actual yield is the actual quantity of the product obtained in a reaction experimentally. It may be much less than the theoretical yield due to various reasons such as incomplete reaction, unwanted by-products, loss in chemicals during the reaction (e.g. when transferring reagents from one container to another).

$$\text{Percentage Yield} = \frac{\textbf{actual mass of product}}{\textbf{theoretical expected mass of product}} \times \textbf{100\%}$$

Worked Example 14

Calculate the percentage yield of the reaction between 5.00 g iron and excess sulfur if 4.21 g of iron(II) sulfide was obtained.

$$Fe(s) + S(s) \longrightarrow FeS(s)$$

Amount of Fe = $\mathbf{\frac{5.00}{55.8}}$ **= 0.08960 mol = Theoretical amount of FeS formed**

Theoretical yield of FeS = 0.08960 × 87.9 = 7.876 g

Percentage yield = $\mathbf{\frac{4.21}{7.876}}$ **× 100% = 53.5%**

Likewise, percentage purity may be calculated using:

$$\text{Percentage Purity} = \frac{\textbf{mass of pure compound}}{\textbf{mass of sample mixture}} \times \mathbf{100\%}$$

Worked Example 15

The mineral dolomite is a double carbonate of magnesium and calcium, with the formula $CaMg(CO_3)_2$. When 1.00 g of an impure sample of dolomite was completely dissolved in an excess hydrochloric acid, 0.420 g of carbon dioxide was given off.

$$CaMg(CO_3)_2 + 4HCl \longrightarrow CaCl_2 + MgCl_2 + 2CO_2 + 2H_2O$$

Determine the percentage purity of the sample. (Molar mass of dolomite = 184.4 g mol^{-1})

Amount of CO_2 = $\mathbf{\frac{0.420}{44.0}}$ **= 0.009545 mol**

Amount of $CaMg(CO_3)_2$ = $\mathbf{\frac{0.009545}{2}}$ **= 0.004772 mol**

Mass of $CaMg(CO_3)_2$ present in sample = 0.004772 × 184.4 = 0.8800 g

Percentage purity of sample = $\mathbf{\frac{0.8800}{1.00}}$ **× 100% = 88.0%**

<u>Checkpoint 5</u> 

When 41.5 g of tungsten(VI) oxide (WO_3, M_r = 231.8) was reacted with excess hydrogen gas, metallic tungsten (W, A_r = 183.8) and 9.50 cm^3 of water was produced.

$$WO_3\ (s) + 3H_2\ (g) \longrightarrow W\ (s) + 3H_2O\ (l)$$

Given that the density of water is 1.00 g cm^{-3}, find the mass of tungsten obtained and the percentage yield.

[32.3 g, 98.3 %]

3.5 Calculations using Volumes of Gases in Combustion reactions

Success Criteria:

- Able to write the general equation for complete combustion of hydrocarbon and calculate using mole concept, involving volumes of gases;
- Able to deduce stoichiometric relationships from calculations and hence deduce molecular formula of the hydrocarbon

Hydrocarbons (C_xH_y) burn completely in excess oxygen (complete combustion) to form **CO_2 and H_2O** as the ***only products***.

Note:
If volume measurement is done at temperature ≥ 100°C, $H_2O(\mathbf{g})$ is obtained instead.

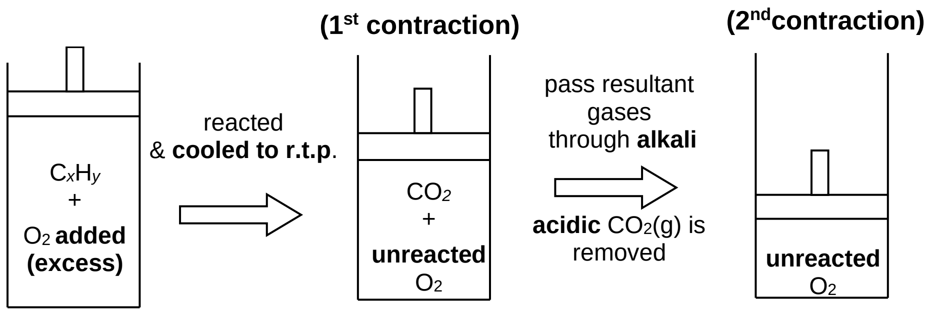
General equation for the complete combustion of a hydrocarbon:
[All vol measured at r.t.p.]

$$C_xH_y(\mathbf{g}) + (\boldsymbol{x} + \tfrac{\mathbf{y}}{\mathbf{4}})\, O_2(\mathbf{g}) \longrightarrow \boldsymbol{x}\, CO_2(\mathbf{g}) + \tfrac{\mathbf{y}}{\mathbf{2}}\, H_2O(\boldsymbol{l})$$

$$\text{Mole ratio = vol ratio of gas} = \quad 1 \quad : \quad \boldsymbol{x} + \tfrac{\mathbf{y}}{\mathbf{4}} \quad : \quad \boldsymbol{x}$$

Usually after complete combustion, there is a **contraction** (i.e. decrease) in volume of gases.
When an excess amount of alkali such as NaOH(aq) or KOH(aq) is added to the resultant gases that remain after combustion (unreacted O_2 and CO_2), only CO_2 (acidic) will be absorbed (reacted) by the alkali. This results in a **second contraction** in volume.

Illustration



Excess oxygen is required to ensure complete combustion so that CO_2 and H_2O are the only products.

Worked Example 16

10.0 cm^3 of a gaseous hydrocarbon, C_xH_y, was burnt in 100 cm^3 of oxygen. The total volume after the reaction was 80.0 cm^3, which decreased to 50.0 cm^3 on shaking with excess sodium hydroxide solution. All volumes were measured at r.t.p. Determine the molecular formula of the hydrocarbon.

C_xH_y + $O_2(g)$ (**10 cm^3**, **100 cm^3**) $\xrightarrow{\text{reacted \& cooled to r.t.p.}}$ **$CO_2(g)$ + unreacted $O_2(g)$** (**80 cm^3**) $\xrightarrow{\text{pass through NaOH(aq)}}$ **unreacted $O_2(g)$** (**50 cm^3**)

Steps in determining molecular formula of hydrocarbon:

1. Write combustion equation.
2. Determine the "Initial", "Final", "Reacting vol"
3. Derive simplest ratio.
4. Determine x and y using the ratio.

Vol of unreacted O_2 + Vol of CO_2 = 80.0 cm^3
Vol of unreacted O_2 = 50.0 cm^3

Hence, vol of O_2 reacted = 100 – 50 = 50 cm^3
Hence, vol of CO_2 produced = (80 – 50) = 30 cm^3

	$C_xH_y(g)$	**+ $(x + \frac{y}{4})O_2(g)$**	**$\longrightarrow$ $x\,CO_2(g)$**	**+ $\frac{y}{2}H_2O(l)$**
Initial vol /cm^3	10	100	0	
Change in vol / cm^3	–10	– 50	30	
Final vol / cm^3	0	50	30	
Reacting vol / cm^3	10	50	30	
Mole ratio	$\frac{10}{10} = 1$	$\frac{50}{10} = 5$	$\frac{30}{10} = 3$	

$\therefore$ x = 3, $x + \frac{y}{4} = 5 \Rightarrow$ hence y = 8, hence molecular formula is C_3H_8.

Worked Example 17

20 cm^3 of a gaseous hydrocarbon, C_xH_y, was exploded with an excess of oxygen. A contraction of 50 cm^3 occurred. On treating the cooled resulting mixture with excess potassium hydroxide, a further contraction of 80 cm^3 occurred. All volumes were measured at r.t.p.

Deduce the molecular formula of the hydrocarbon.

C_xH_y + $O_2(g)$; 20 cm^3, excess $\xrightarrow[\text{Contraction of 50 cm}^3]{\text{reacted \& cooled to r.t.p.}}$ **$CO_2(g)$ + unreacted $O_2(g)$** $\xrightarrow[\text{Contraction of 80 cm}^3]{\text{pass through KOH(aq)}}$ **unreacted $O_2(g)$**

Vol of CO_2 = 80 cm^3 (from 2nd contraction)
Initial vol – Final vol = 50 cm^3 (1st contraction)
(Vol of C_xH_y + Total Vol of O_2) – (Vol of unreacted O_2 + Vol of CO_2) = 50 cm^3
(20 + Total Vol of O_2) – (Vol of unreacted O_2 + 80) = 50 cm^3
Total Vol of O_2 – Vol of unreacted O_2 = 80 + 50 – 20 = 110
Vol of O_2 reacted = 110 cm^3

	$C_xH_y(g)$	+	$(x + \frac{y}{4})\ O_2(g)$	$\longrightarrow$	$x\ CO_2(g)$	+	$\frac{y}{2}\ H_2O(l)$
Reacting vol / cm^3	**20**		**110**		**80**		
Mole ratio	$\frac{20}{20} = 1$		$\frac{110}{20} = 5.5$		$\frac{80}{20} = 4$		

$\therefore$ ***x* = 4,**

$x + \frac{y}{4} = 5.5 \Rightarrow y = 6$

$\therefore$ The molecular formula of the hydrocarbon is C_4H_6.

<u>Checkpoint 6</u>

20 cm^3 of a gaseous hydrocarbon was exploded with 150 cm^3 of oxygen. The resulting gaseous mixture had a total volume of 130 cm^3. When this mixture was passed through aqueous sodium hydroxide, the final volume of the mixture decreased to 90 cm^3.
The volumes of all gases were measured at r.t.p.
Deduce the molecular formula of the hydrocarbon.

[C_2H_4]

C_xH_y + O_2(g)
20 cm^3 150 cm^3

$\xrightarrow{\text{reacted \& cooled to r.t.p.}}$

CO_2(g) + unreacted O_2(g)
130 cm^3

$\xrightarrow{\text{pass through NaOH(aq)}}$

unreacted O_2(g)
90 cm^3

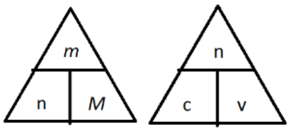
Note:
Notation for concentration of solute X in a solution is [X]

3.6 Stoichiometry involving Solutions (Volumetric Analysis)

When a **solute** is dissolved in a solvent, a **solution** is formed. If the solvent is water, an **aqueous solution** is formed. The **concentration** of a solution shows the amount of solute dissolved in a given volume of solution.
Molarity of a solution refers to the concentration of the solution in **mol dm^{-3}**.

A **standard solution** is a solution whose concentration is accurately known.

Use these triangles by simply placing your thumb over the term you intend to find and carry out the multiplication or division of the remaining terms.



3.6.1 Important Relationships

1. Volume of solution in dm^3 = $\dfrac{\text{volume of solution in cm}^3}{1000}$
2. Concentration of X (in mol dm^{-3}), [X] = $\dfrac{\text{amount of X (in mol)}}{\text{volume of solution, V (in dm}^3\text{)}}$
3. Concentration of X (in g dm^{-3}) = concentration of X in mol dm^{-3} × M
   where M = molar mass in g mol^{-1}
4. Amount (no of moles), $\eta = \dfrac{m}{M}$ where m = mass in g, M = molar mass in g mol^{-1}
5. Amount (no of moles), η = cv where c = concentration in mol dm^{-3}, v = volume in dm^3

<u>**Checkpoint 7**</u>

1. Convert the following to **mol dm^{-3}**

(a) 0.913 g dm^{-3} of dilute HC*l* **[0.0250]** **(b)** 2 kg of $CuSO_4$ in 500 cm^3 of water **[25.1]**

2. Calculate the amount of NaOH present in a 1 m^3 solution of 0.50 mol dm^{-3} NaOH. **[500 mol]**

3. Calculate the mass of KOH present in a 100 cm^3 solution of 0.20 mol dm^{-3} KOH. **[1.12 g]**

4. Calculate the volume, in cm^3, required to provide 0.85 g of ethanoic acid (M_r = 60.0) from a 0.30 mol dm^{-3} solution. **[47.2 cm^3]**

3.6.2 Dilution

Dilution of a solution involves the addition of more solvent e.g. water, to a known volume of the solution. The amount of solute present **DOES NOT** change but the concentration of the solution changes.

To find the concentration of a diluted solution, use the following formula:

c = concentration in mol dm^{-3}
V = volume in dm^3

Amount of solute in original solution = Amount of solute in diluted solution
c_1V_1 (before dilution) = c_2V_2 (after dilution)

Worked Example 18

A 50.0 cm^3 solution of 1.00 mol dm^{-3} $CuSO_4$ was transferred into a 250 cm^3 volumetric flask and the content made up to the 250 cm^3 mark using deionized water. Calculate the new concentration of the $CuSO_4$ solution.

Amount of $CuSO_4$ = $\frac{50.0}{1000} \times 1.00 = 0.05$ mol

After dilution, concentration of $CuSO_4$ = $\frac{0.05}{(^{250}/_{1000})}$ =0.200 mol dm^{-3}

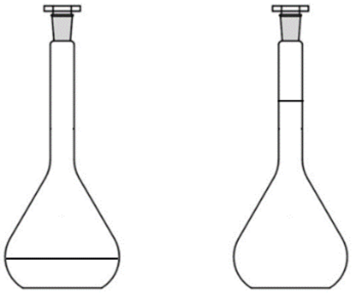
<u>Alternative method using 'dilution factor':</u>

Dilution factor = $\frac{\textit{volume after dilution}}{\textit{volume before dilution}} = \frac{250.0}{50.0} = \frac{5}{1}$

After dilution, [$CuSO_4$] = 1.0 ÷ 5 = 0.200 mol dm^{-3}

Note:

Concentration of $CuSO_4$ decreases after dilution, BUT amount of $CuSO_4$ present in the 50 cm^3 and 250 cm^3 solution are the same.



50.0 cm^3 of $CuSO_4$ in volumetric flask

250.0 cm^3 diluted $CuSO_4$ in volumetric flask

	Success Criteria	Relevant Tutorial Qns	What do you still struggle with? Write your queries here.
	I am able to:		
(a)	Define the following terms based on the ^{12}C scale:		
	1) *relative atomic mass*		
	2) *isotopic mass*		
	3) *molecula*r mass		
	4) *formula mass*		
(b)	Define the term *mole* in terms of the Avogadro constant.		
(c)	Define the terms *empirical* and *molecular formula*.		
(d)	Calculate the relative atomic mass of an element given the relative abundances of its isotopes.	**DQ1**	
(e)	Calculate the number of particles present using Avogadro's constant, *L.*		
(f)	Calculate the volumes of gas under r.t.p or s.t.p conditions.		
(g)	Calculate empirical and molecular formulae using combustion data or composition by mass.	**DQ6,7, 8, 9**	
(h)	Construct balanced equations and perform calculations using mole concept:	**DQ3, 6, 7, 8, 9 ,10**	
	1) involving limiting agent	**DQ3**	
	2) involving combustion (using volumes of gases) to deduce molecular formula of the hydrocarbon	**DQ8, 9**	
	3) involving stoichiometry of solutions (Volumetric Analysis), taking into account any dilution		
(i)	Perform calculations to express a quantity in terms of parts per million.	**DQ2**	
(j)	Perform calculation to obtain:	**DQ4, 5**	
	1) % yield		
	2) % purity		
(k)	Present answers for intermediate steps correct to 4 significant figures, final answer to 3 significant figures unless instructed otherwise & include relevant units.		

DISCUSSION QUESTIONS

Calculation of Relative Molecular Mass

1 Bromine consists of two isotopes, ^{79}Br and ^{81}Br, in the relative abundance ratio of 1:1. Bromine exists as diatomic molecule, Br_2, at room temperature and pressure.
Calculate the possible relative molecular masses, M_r, of Br_2 molecules formed by these two isotopes and their relative abundance ratio.

[1:2:1]

Calculation involving Parts Per Million

2 Gardeners sometimes fumigate their greenhouses to rid them of pests and moulds by burning a sulfur 'candle'. A gaseous concentration of sulfur dioxide of 50 ppm (parts per million) by volume is effective.

Calculate how many grams of sulfur a gardener needs to burn in order to produce a concentration of 50 ppm of SO_2 in a greenhouse that measures 2 m × 3 m × 4 m. Assume room conditions.

[1.61 g]

Calculation using Mole Concept

3 Phosgene, $COCl_2$, was once used as a war gas. It is poisonous because when inhaled, it reacts with water in the lungs to produce carbon dioxide gas and hydrochloric acid which causes severe lung damage, leading to death ultimately.

(a) Calculate the percentage by mass of chlorine in $COCl_2$. [71.7%]

(b) Write a balanced equation for the reaction between $COCl_2$ and H_2O.

(c) Calculate the amount of HCl that will be produced by the complete reaction of 0.430 mol of $COCl_2$.

[0.860]

(d) Identify the limiting reagent when 0.200 mol of $COCl_2$ is mixed with 6.20 g of H_2O.
Hence, calculate the amount of HCl produced at the end of the reaction.

[0.400]

Calculation involving % purity & % yield

4 The mineral phosphorite, $Ca_3(PO_4)_2$, exists as phosphate rock in its impure form.
Elemental phosphorus can be prepared from phosphate rock by reduction using carbon in the presence of sand, SiO_2. The reduction of phosphorite also produces solid **A** and carbon monoxide.

(a) **A** has the following composition by mass:

Ca: 34.2% Si: 24.5% O: 41.3%

Calculate the empirical formula for solid **A**.

[$CaSiO_3$]

(b) Write a balanced equation for the reaction.

(c) A 30.0 g sample of phosphate rock was subjected to the above reaction and produced 5.3 g of phosphorus. Calculate the percentage purity of phosphorite in the rock sample.

[88.4%]

5 In the Solvay process, ammonia is recovered by the reaction:

$$2NH_4Cl\ (aq) + CaO\ (s) \rightarrow CaCl_2\ (aq) + H_2O\ (l) + 2NH_3\ (g)$$

(a) What is the maximum volume of ammonia that can be recovered, at s.t.p., from 20.0 g of NH_4Cl and 4.50 g of CaO?
State the limiting reagent, if any, and assume that any impurity present is unreactive.
[3.64 dm^3]

(b) What is the percentage yield if only 3.03 dm^3 of NH_3 is obtained experimentally at s.t.p.?
[83.2%]

Calculation involving % composition by mass

6 In small quantities, nicotine in tobacco is addictive. In large quantities, it is a deadly poison. Determine the molecular formula of nicotine, $C_xH_yN_z$, if 4.38 mg of nicotine burns to form 11.9 mg of carbon dioxide and 3.41 mg of water. [M_r of nicotine = 162.0] [$C_{10}H_{14}N_2$]

Calculation involving Volumes of gas

7 Buckminsterfullerene, C_{60}, is a molecule with 60 carbon atoms arranged in pentagons and hexagons that are similar to those in a football. C_{60} reacts with hydrogen to form hydrofullerenes with the molecular formula $C_{60}H_n$.
When 60 g of C_{60} is reacted with hydrogen gas at 273 K and 1 bar, the volume of hydrogen gas is decreased by 34 dm^3. Find the value of n in the formula of hydrofullerene, $C_{60}H_n$. [36]

Calculation using Volumes of gas in Combustion reactions

8 20 cm^3 of a gaseous hydrocarbon **A**, C_xH_y, was exploded with an excess of oxygen. Upon cooling to room temperature, there was a contraction in volume of 50 cm^3. When the products were treated with excess potassium hydroxide, there was a further contraction of 60 cm^3.

Deduce the molecular formula of **A**. All volumes were measured at r.t.p. [C_3H_6]

9 A 20 cm^3 mixture containing methane (CH_4) and ethane (C_2H_6) was burnt completely in excess oxygen. On passing the residual gas through aqueous sodium hydroxide, there was a reduction in volume by 25 cm^3. All volumes were measured at room temperature and pressure.

Calculate the percentage by mass of methane in the original gaseous mixture. [61.5%]

Calculation using Mole Concept in Solutions

10 **(a)** What is the mass of NaOH(s) required to prepare 250 cm^3 of 0.120 mol dm^{-3} NaOH(aq)?
[1.20 g]

(b) What volume of water must be added to 900 cm^3 of 0.120 mol dm^{-3} $NaCl$ solution to dilute it to 0.100 mol dm^{-3}? [180 cm^3]