1 Atoms, Molecules and Stoichiometry

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Syllabus

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

[the term relative formula mass or Mr 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 number of significant figures given or asked for in the question]

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

References

1. *Chemistry for Advanced level, Peter Cann and Peter Hughes*
2. *General Chemistry (7th ed), Darrell D Ebbing and Steven D Gammon, Houghton Mifflin Company,*

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1 Introduction

particles	***absolute mass / kg***	***relative mass***
proton	1.67×10^{-27}	1
neutron	1.67×10^{-27}	1
electron	9.11×10^{-31}	1/1836

- Being so small, atoms are also very light. Their masses could range from 10^{-27} kg (e.g. hydrogen) to 10^{-25} (e.g. lawrencium). It is impossible to weigh them out individually, but we can measure accurately their **relative masses**, i.e. how heavy one atom is compared with another.

2 Relative Mass

2.1 Relative Isotopic Mass

- Isotopes are atoms having the same number of protons and electrons but different number of ____________.
- The relative isotopic mass, A_r, of an isotope is defined as:

$$\text{Relative isotopic mass} = \frac{\text{mass of one atom of the isotope}}{\text{1/12 the mass of a } ^{12}\text{C atom}}$$

e.g. relative isotopic mass of ^{35}Cl = 34.97; ^{37}Cl = 36.95 (values obtained from experiment)

2.2 Relative Atomic Mass

- Some elements have several isotopes in different abundancies. Hence, the different isotopic masses of the element have to be considered so as to obtain its relative atomic mass.
- The relative atomic mass, A_r, of an element is defined as:

$$\text{Relative atomic mass, } A_r = \frac{\text{mass of an atom of the element}}{\text{1/12 the mass of a } ^{12}\text{C atom}}$$

Example 1 (working out A_r from data)

(a) Chlorine has 2 isotopes, ^{35}Cl and ^{37}Cl in the ratio 3:1 in abundancies. What is the relative atomic mass of chlorine?

A_r of C*l* =

Note:
- Relative masses do not have units!
- Calculate A_r to 1 d.p.

(b) Calculate the relative atomic mass of neon using the following data.

isotope	*Natural abundance (%)*
neon-20	90.5
neon-21	0.3
neon-22	9.2

A_r of Ne=

2.3 Relative Molecular Mass

- The relative molecular mass, M_r, of an element or compound is defined as:

$$\text{Relative molecular mass, } M_r = \frac{\textbf{average} \text{ mass of one molecule of the element / compound}}{\text{1/12 the mass of a } ^{12}\text{C atom}}$$

2.4 Relative Formula Mass

- The relative formula mass, M_r, of an *ionic compound* is defined as:

$$\text{Relative formula mass, } M_r = \frac{\textbf{average} \text{ mass of one formula unit of the compound}}{\text{1/12 the mass of a } ^{12}\text{C atom}}$$

Example 2 (working out M_r from data)

Chlorine and sodium have relative atomic masses of 35.5 and 23.0 respectively.

(a) What is the relative molecular mass of Cl_2?

(b) What is the relative formula mass of NaC*l*?

(a) M_r of Cl_2

(c) M_r of NaC*l*

Note:
- A_r and M_r values are given to 1 decimal place.

3 The Mole and Avogadro Constant

Many properties depend on the number of molecules in the sample, and not on the mass of the sample. Counting the molecules individually would be completely impractical. Even if you had a way to see the individual molecules, there are just too many, even in a tiny sample.

The unit 'mole' was defined to solve the problem of counting large numbers of molecules. *With moles, you can count the number of molecules in the sample by simply weighing it.*

Definition: The **mole** is the measure of the **amount** of a substance (notation: **n**, unit: **mol**).

*One **mole** of a substance is the amount of substance that contains the same number of particles as there are atoms in 12 g of the carbon-12 isotope.*

The number of carbon atoms in exactly 12.0 g of ^{12}C is called the **Avogadro constant, L.**

Avogadro constant, L *= 6.02×10^{23} mol^{-1}*

Amount of substance, $n = \dfrac{N}{L}$

where n: amount of the substance in mol
N: no. of particles in the substance
L: Avogadro constant

Example 3 (working out *n*, the amount of substance from number of particles)

(a) How many moles of carbon atoms are there in 3.01×10^{23} atoms of carbon?

$n_C = N / L =$

(b) How many moles of **oxygen atoms** are there in 1.08×10^{24} molecules of O_3, ozone?

$n_{O_3} = N / L =$

$n_O =$

- When the mole is used, the elementary entities ***must*** be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.
- **To avoid ambiguity, specify particles or the chemical formula**. If particles or chemical formula is not specified, *assume that the particles are those that are normally present in the substance under room conditions*.

For example,

1 mole of carbon consists of 6.02×10^{23} ________ of carbon.

1 mole of water (H_2O) consists of 6.02×10^{23} ______________of water.

1 mole of oxygen consists of 6.02×10^{23} _____________ of oxygen.

1 mole of magnesium chloride ($MgCl_2$) consists of 6.02×10^{23} formula units of $MgCl_2$

i.e. 6.02×10^{23} ______________________ and $2 \times 6.02 \times 10^{23} = 12.04 \times 10^{23}$ ___________________.

3.1 Converting mass to mole

- The molar mass, M, is the mass (in g) of one mole of a substance.
  - It is numerically equal to the A_r or M_r of the substance.
  - Unit for M is g mol^{-1}.

The amount of substance can be quantified as follows:

Amount of substance, $n = \dfrac{m}{M}$

where n: amount of the substance in mol
m: mass of the substance in g
M: molar mass of the substance in g mol^{-1}

Example 4 (working out *n*, amount of substance from mass)

(a) How many moles of **fluorine molecules** are there in 38.0 g of fluorine gas?
[A_r of F = 19.0]

$n_{F_2} = \frac{m}{M}$ **= 38.0 / 2(19.0) = 1.00 mol**

(b) How many moles of **oxygen atoms** are there in 25.6 g of oxygen gas?
[A_r of O = 16.0]

$n_{O_2} = \frac{m}{M}$ =

n_O =

(c) How many moles of **fluoride ions** are there in 20 g of aluminium fluoride?
[A_r of Al = 27.0; F = 19.0]

$n_{AlF_3} = \frac{m}{M}$ =

n_{F^-} =

4 The Calculation of Empirical and Molecular Formulae

Definitions

The **empirical formula** of a compound is a formula that gives the **simplest ratio** of the **elements** in one molecule of the compound.

The **molecular formula** of a compound is a formula that gives the **actual number** of **atoms** present in one molecule of the compound.

For example,

Compound	Empirical formula	Molecular formula
Ethanoic acid	CH_2O	$C_2H_4O_2$
butene	CH_2	C_4H_8
cyclohexane	CH_2	C_6H_{12}

Empirical and molecular formulae of a compound can be calculated from:

(a) composition by mass data

(b) combustion data (or eudiometry)

4.1 Calculation using Composition by Mass Data

<u>Example 5 (working out empirical formula and molecular formula from mass data)</u>

An organic compound, **A**, with relative molecular mass of 60.0 has the following composition by mass:

C, 40.0 %; H, 6.65 %; O, 53.3 %

Calculate the **(i)** empirical formula and **(ii)** molecular formula of **A**.

(i)

Elements	C	H	O
Composition / %			
Mole ratio			
Simplest ratio			

<u>Example 6 (working out empirical formula and molecular formula from mass data)</u>

A compound, **X**, with an M_r of 86.0 has the following composition by mass:

C, 83.7 %; H, 16.3 %

Calculate the empirical and molecular formulae of **X**.

Elements	C	H
Composition / %		
Mole ratio		
Simplest ratio		

Example 7 **(working out empirical formula from mass data)**

0.4764 g of a sample of oxide of iron was reduced by a stream of carbon monoxide. 0.3450 g of iron metal remained after reduction. What is the empirical formula of the oxide?

Elements	Fe	O
Composition / g		
Mole ratio		
Simplest ratio		

Hence, the empirical formula of the oxide is .

4.2 Calculation using Combustion Data

Organic compounds, on complete combustion with oxygen, form CO_2 and H_2O. By measuring and calculating the amount of reactants used (i.e. the compound and oxygen) and products formed (CO_2 and H_2O) in a combustion experiment, the **empirical** and **molecular formula** of the organic compound can be obtained.

4.2.1 Simple Combustion Data

Example 8 **(working out empirical formula from combustion data)**

Complete combustion of a hydrocarbon, **Y**, yields 2.64 g of CO_2 and 2.16 g of H_2O. What is the empirical formula of the hydrocarbon?

Elements	C	H
Composition / g		
Mole ratio		
Simplest ratio		

Hence, the empirical formula of the hydrocarbon is .

Example 9 **(working out empirical formula from combustion data)**

0.100 g of a compound, **Z**, containing only carbon, hydrogen and oxygen, was completely burnt in excess oxygen to give 0.228 g of CO_2 and 0.0931 g of H_2O.
(i) Calculate the empirical formula of the compound.
(ii) Given that Z has molar mass of 116, determine its molecular formula.

Elements	C	H	O
Composition / g			
Mole ratio			
Simplest ratio			

5 Stoichiometry and Calculations involving Mole Concept

5.1 General symbols used

Symbols	Meaning	Units	Example
m	Mass	g	mass of NaC*l*: m_{NaCl} = 20.0 g
v	Volume	cm^3 or dm^3	volume of HC*l*: v_{HCl} = 25.0 cm^3
n	amount of substance	mol	amount of NaC*l*: n_{NaCl} = 0.01 mol
M	molar mass	g mol^{-1}	molar mass of NaC*l*: M_{NaCl} = 58.5 g mol^{-1} (note: M_r of NaCl =58.5)
c	concentration	mol dm^{-3} or g dm^{-3}	concentration of HC*l*: c_{HCl} = 0.02 mol dm^{-3}

5.2 Calculations using Reacting Masses (based on formulae and equations)

Example 10

The pollutant, SO_2, can be removed form the air by the following reaction:

$$2CaCO_3\ (s) + 2SO_2\ (g) + O_2\ (g) \rightarrow 2CaSO_4\ (s) + 2CO_2\ (g)$$

What is the mass of $CaCO_3$ needed to remove 10.0 g of SO_2? [Ca = 40.1; S = 32.1; C = 12.0; O = 16.0;]

$$n_{SO_2} = \frac{m}{M} = \frac{10.0}{64.1} = 0.1560 \text{ mol}$$

From equation, $n_{CaCO_3} = n_{SO_2}$ =0.1560 mol

m_{CaCO_3} = $n \times M$

= 0.156 x 100.1

= <u>15.6 g</u>

Example 11

What is the mass of silver carbonate, Ag_2CO_3, that can be precipitated from a solution containing 1.00 x 10^{-3} mol of silver ions? [Ag = 108.0; C = 12.0; O = 16.0; H=1.0]

$$2Ag^+\ (aq) + CO_3^{2-}\ (aq) \rightarrow Ag_2CO_3\ (s)$$

$n_{Ag_2CO_3}$ =

$m_{Ag_2CO_3}$ = $n_{Ag_2CO_3} \times M_{Ag_2CO_3}$

Example 12

When a 1.01 g sample of potassium nitrate is heated above its melting point, oxygen gas is evolved. The mass of the sample decreases by 0.16 g. suggest the identity for the residue and hence construct a balanced equation for this decomposition reaction.

[K = 39.1; N = 14.0; O = 16.0]

n_{KNO_3} =

n_{O_2} =

$n_{KNO_3} : n_{O_2}$ =

Example 13

Sulphur and chlorine can react together to form S_2Cl_2. When 1.00 g of this sulphur chloride reacted with water, 0.36 g of a yellow precipitate of sulphur was formed, together with a solution containing a mixture of sulphurous acid, H_2SO_3, and hydrochloric acid. Use the above data to deduce the equation for the reaction between S_2Cl_2 and water. [S= 32.1; Cl = 35.5]

5.3 Limiting and Excess Reagents

- The **limiting reagent** is the reactant that is **completely used up** when a reaction goes to completion.
- The **excess reagent** is the reactant that is **not completely used up** when a reaction stops.
- For calculation purposes, the amount or **yield of products** formed is always determined by the **amount of limiting reagents** used.

General Steps in Stoichiometery
(i) Write the balanced equation for reaction
(ii) Convert quantities of reactants to moles and determine the limiting reagent.
(iii) Calculate the required quantity of reactant or product.

Example 14

What is the mass of Zn obtained when 50.0 g of ZnO is reduced by 50.0 g of charcoal?

$$\mathbf{ZnO + C \rightarrow Zn + CO}$$

$$n_{ZnO} = \frac{50.0}{81.0} = 0.6172\ mol$$

$$n_C = \frac{50.0}{12.0} = 4.166\ mol$$

5.4 Theoretical, Experimental and Percentage Yield

- The **theoretical yield** of a product is the **maximum amount of product** that can be obtained by a reaction from the given amounts of reactants. It is obtained by calculations.
- The **experimental yield** of a product is the **amount of product** that can be obtained by a reaction from the given amounts of reactants under stated experimental conditions. It is usually smaller than the theoretical yield.

$$\boxed{Percentage\ yield = \frac{Experimental\ \ yield}{Theoretical\ \ yield} \times 100\%}$$

Example 15

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 → FeS

$n_{Fe} = \frac{5.00}{55.8} = 0.08960\ mol$

$\therefore n_{FeS} = n_{Fe} = 0.0896\ mol$

Expected mass of FeS, m_{FeS} = 0.08960 x 87.9 = 7.876 g

% yield =

Example 16

If 0.50 g of magnesium is burnt in 12 dm^3 of oxygen at room conditions, determine the limiting and excess reagents. Hence, calculate the amount of MgO formed. During the experiment, the actual mass of MgO obtained is 0.769 g. What is the percentage yield of MgO?

5.5 Calculations based on Reacting Gas Volumes

- Avogadro's Law states that equal volumes of all gases, at the ***same temperature and pressure***, contain the same number of particles (e.g. atoms or molecules).
- The volume occupied by 1 mole of any gas (L particles) is called the molar volume of the gas, V_m.

> - V_m is 22.4 dm^3 mol^{-1} at s.t.p. (i.e. 101 kPa and 273 K)
> - V_m is 24 dm^3 mol^{-1} at r.t.p. (i.e. 101 kPa and 298 K)

When the reaction involves gases, we usually consider the **volumes** of the gases rather than masses.

We can directly relate the volume ratio of the gaseous substances involved to their mole ratio:

example:

	H_2 (g)	+	Cl_2 (g)	→	2HC*l* (g)
Mole ratio	**1**		**1**		**2**
Volume ratio	**1**		**1**		**2**
Volume of gas at r.t.p / dm^3	**24**		**24**		**48**

Example 17

A mixture of 10 cm^3 of oxygen and 50 cm^3 of hydrogen is sparked continuously. What is the maximum decrease in volume? All gas volumes are recorded at 293 K and standard pressure.

	$2H_2$ (g)	+	O_2 (g)	→	$2H_2O$ (l)
Initial volume/ cm^3	**50**		**10**		**0**
Volume ratio	**5**		**1**		**Negligible**
Mole ratio of gases	**5**		**1**		

From equation,____mol of O_2 requires ____mol of H_2.
10 cm^3 O_2 requires (2 x 10=) 20 cm^3 of H_2.
∴ Vol of H_2 left = 50 – 20 = 30 cm^3
Decrease in volume = Initial vol – Final Vol = (50+ 10) – 30 = 30 cm^3

Example 18

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

$$CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g)$$

$n_{CaCO_3} = \frac{m}{M}$ **= 15.0 / [40.1 + 12.0 + 3(16.0)]**

= 0.1498 mol

n_{CO_2} **=**

V_{CO_2} **=**

Example 19

Sodium azide, NaN_3, is made for use in car 'air-bags'. When this compound is heated to 300 °C, it rapidly decomposes into its elements according to the following equation. $2NaN_3\,(s) \rightarrow 2Na\,(s) + 3N_2\,(g)$

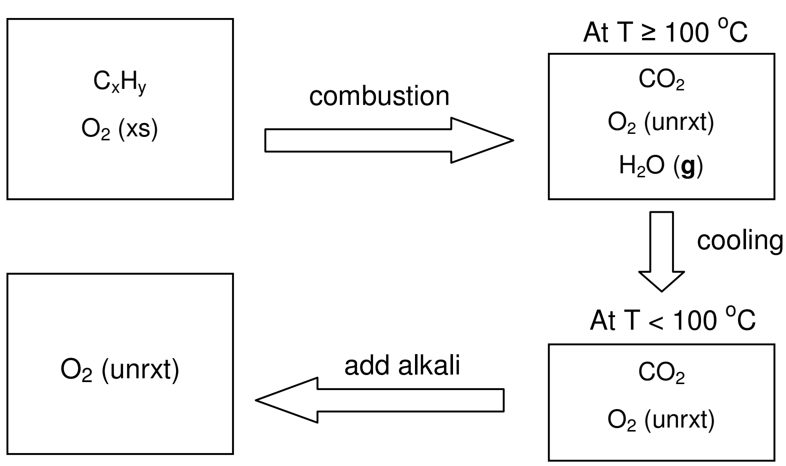
What is the volume of nitrogen produced at r.t.p. from the decomposition of 10.0 g of sodium azide? [Na, 23.0; N, 14.0]

6 Eudiometry

- Eudiometry is a process of determining the constituents of a gaseous mixture by means of a eudiometer (an instrument for the volumetric measurement of gases).
- This method can be used to **determine the molecular formulae** of gaseous hydrocarbons. The **volumes of the gases are determined at <u>each stage</u>** so that the molecular formula of the unknown hydrocarbon can be found. This process is shown in the schematic diagram in *Figure 1*.
- When a gaseous hydrocarbon (C_xH_y) is completely burnt in *excess* oxygen, only carbon dioxide and water are formed in the reaction (at T < 100 °C).

$$C_xH_y\,(g) + (x + y/4)\,O_2\,(g) \rightarrow x\,CO_2\,(g) + (y/2)\,H_2O\,(l)$$

- $(x + y/4)\,O_2$ in the equation above represents the *reacted* oxygen.
- Since excess oxygen is used for combustion, some *unreacted* oxygen will be left.



O_2 (xs) = excess oxygen
O_2 (rxt) = reacted oxygen
O_2 (unrxt) = unreacted oxygen

Note:
- Only *volumes of the gaseous products* are calculated at each stage.
- $v(O_2\,(xs)) = v(O_2\,(rxt)) + v(O_2\,(unrxt))$

Figure 1: Schematic diagram of eudiometry in molecular formulae determination

Example 20

15 cm^3 of a gaseous hydrocarbon, **W**, was burnt with 95 cm^3 of oxygen. After cooling to room temperature, the residual gaseous products occupied a volume of 80 cm^3. On adding aqueous NaOH, the volume decreased to 50 cm^3. Find the molecular formula of the hydrocarbon, **W**.

	C_xH_y (g)	+ (x + y/4) O_2 (g)	→	x CO_2 (g)	+ (y/2) H_2O (l)
Initial vol /cm^3					
After burning & cooling /cm^3					
After NaOH /cm^3					

Volume of reacted O_2 =
Volume of CO_2 produced =

By comparing the mole ratios:
For C_xH_y (g) and CO_2 (g):
For C_xH_y (g) and O_2 (g):

Hence, the molecular formula of the hydrocarbon, **W**, is .

Example 21

When 20 cm^3 of a gaseous hydrocarbon, **P**, was completely burnt with 150 cm^3 of oxygen, the residual gaseous products occupied a volume of 110 cm^3. On adding aqueous KOH, the volume decreased to 50 cm^3. Find the molecular formula of the hydrocarbon, **P**. [All gas volumes are measured under room conditions]

	C_xH_y (g)	+ (x + y/4) O_2 (g)	→	x CO_2 (g)	+ (y/2) H_2O (l)
Initial vol /cm^3					
After burning & cooling /cm^3					
After KOH /cm^3					

Volume of reacted O_2 =
Volume of CO_2 produced =

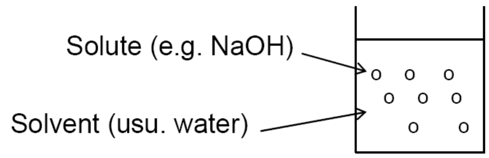
By comparing the mole ratios:
For C_xH_y (g) and CO_2 (g):
For C_xH_y (g) and O_2 (g):

Hence, the molecular formula of the hydrocarbon, **P**, is .

Section 2 Solutions and Volumetric Analysis

1 Calculations based on solutions

An aqueous solution is made up of a **solute** and a **solvent**.



- The concentration of an aqueous solution may be stated as

(i) mass concentration (g dm^{-3}) $= \dfrac{\text{mass of solute (g)}}{\text{volume of solution (dm}^3)} = \dfrac{m}{V}$

(ii) Molarity / molar concentration (mol dm^{-3}) $= \dfrac{\text{amount of solute (mol)}}{\text{volume of solution (dm}^3)} = \dfrac{n}{V}$

- In a solution, there are two terms to consider:
  i. amount (number of moles) of solute, n in mol and
  ii. concentration of solution, c in mol dm^{-3}
- **n and c are related by the following relationship:**

$$\boxed{n = c\,V}$$

where n = amount of solute (mol)
c = concentration of solution (mol dm^{-3})
V = volume of solution (dm^3)

The table below summarises the common symbols used to represent the terms used in calculation

Terms	***Units***	***Symbols (case sensitive)***	***Examples***
Amount (no of moles)	mol	n	n_{NaOH}
concentration	mol dm^{-3}	c or [ ]	c_{NaOH} or [NaOH]
Mass	g	m	m_{NaOH}
Volume	cm^3 or dm^3	V	V_{NaOH}
molar mass	g mol^{-1}	M	M_{NaOH}

For calculations, present your values of intermediate working to 4 s.f. and values of final answers to 3 s.f.

Example 1 (Finding mass and molar concentration)

Find the mass and molar concentration of the solution formed by dissolving 4.00 g of NaOH in 500 cm^3 of solution.

$$\text{mass concentration} = \frac{m}{V} = \frac{4.00}{500/1000} = 8.00 \text{ g dm}^{-3}$$

$$\text{molar concentration} = \frac{n}{V} = \frac{m/M}{V} = \frac{4.00/40.0}{500/1000} = 0.200 \text{ mol dm}^{-3}$$

Example 2 (Finding the concentration of ions)

Calculate the concentration of each ion in each of the following solutions:

(i) 2.30 mol dm^{-3} NaBr

(ii) 0.020 mol dm^{-3} $Al_2(SO_4)_3$ solution

(iii) 10 g of $MgCl_2$ dissolved in 100 cm^3 of water [M_{MgCl_2} = 95.3 g mol^{-1}]

(i) $NaBr \rightarrow Na^+ + Br^-$

$[Na^+]$ = 2.30 mol dm^{-3} $[Br^-]$ = 2.30 mol dm^{-3}

(ii) $Al_2(SO_4)_3 \rightarrow$

(iii) $MgCl_2 \rightarrow$

Note:

- It is important to state the ***exact species*** in which the concentration is referring to. e.g. 1.00 mol dm^{-3} $Al_2(SO_4)_3$ solution is not the same as 1.00 mol dm^{-3} of Al^{3+} or 1.00 mol dm^{-3} of SO_4^{2-} ions.
- The concentration of the ions is determined through the mole ratio of the ionic compounds to its respective ions per dm^3 of solution.

2 Standard solutions

- A solution of ____________________________ is called a **standard solution**.
- They are prepared carefully by weighing out a known mass of the sample and dissolving it in a known volume of solvent in a standard / volumetric flask.

Example 3 (Preparation of a standard solution)

You are given a sample of hydrated copper sulphate crystals, $CuSO_4.5H_2O$.
Describe how you would prepare 250 cm^3 of a standard solution of 0.20 mol dm^{-3} $CuSO_4$.
Show clearly your calculations. [Mr of $CuSO_4.5H_2O$ = 249.6]
[Note: $CuSO_4.5H_2O \rightarrow CuSO_4 + 5\ H_2O$]

Pictures taken from General Chemistry by Ebbing & Gammon

Calculations:

Using $n = cV$ and $n = \frac{m}{M}$,

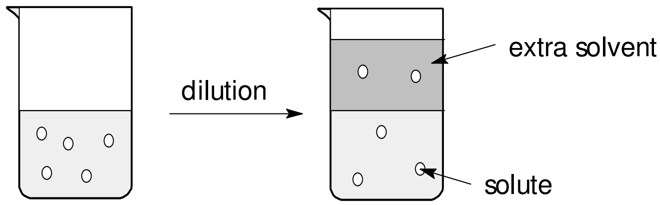
mass of $CuSO_4.5H_2O$ required = $n \times M = cV \times M = \left(0.200 \times \frac{250}{1000}\right) \times 249.6 = \underline{12.48\ g}$

Procedure:

1) Weigh out 12.48 g of $CuSO_4.5H_2O$ accurately using a mass balance.
2) Pour the solid $CuSO_4.5H_2O$ into a clean and dry 100 ml beaker. Dissolve it with distilled water, by stirring with a glass rod. Transfer the solution and its washings to a clean and dry volumetric flask.
3) Top up the volumetric flask with distilled water. Mix the solution thoroughly by shaking and inverting the flask.

3 Dilution

- When a solution is diluted (by adding more solvent), the concentration of the solution ____________ but the amount of solute in the diluted solution ________________.



- Dilution formula:

$$n_{\text{before dilution}} = n_{\text{after dilution}}$$
$$c_1V_1 = c_2V_2$$

Example 4 (Finding the new concentration after dilution)

250 cm^3 of 0.450 mol dm^{-3} aqueous hydrochloric acid is diluted to 750 cm^3. Calculate the new concentration of the diluted acid.

$$n_{\text{before dilution}} = n_{\text{after dilution}}$$
$$c_1V_1 = c_2V_2$$
$$0.450 \times \frac{250}{1000} = c_2 \times \frac{750}{1000}$$
$$c_2 = 0.150 \text{ mol dm}^{-3}$$

Example 5 (Finding the volume of stock solution and solvent needed for dilution)

(a) Calculate the volume (in cm^3) of 18.0 mol dm^{-3} sulfuric acid that is required to prepare 2.00 dm^3 of a 0.300 mol dm^{-3} sulfuric acid solution.

$$n_{\text{before dilution}} = n_{\text{after dilution}}$$
$$c_1V_1 = c_2V_2$$

b) What is *the volume of water* that must be added to 150 cm^3 of 0.0262 mol dm^{-3} NaOH to obtain a 0.0100 mol dm^{-3} NaOH solution?

$$n_{\text{before dilution}} = n_{\text{after dilution}}$$
$$c_1V_1 = c_2V_2$$

Example 6 (Applying dilution formula on ions)

250 cm^3 of 0.020 mol dm^{-3} KOH(aq) is added to 100 cm^3 of 0.100 mol dm^{-3} NaOH(aq)

(i) What is the final concentration of NaOH(aq) after the two solutions have been **mixed**?

Calculate the concentration of (ii) K^+ and (iii) OH^- in the mixture.

[Note: there is NO reaction between NaOH and KOH]

(i) Final volume = 250 + 100 = 350 cm^3

For NaOH, $n_{\text{before dilution}} = n_{\text{after dilution}}$

$$c_1V_1 = c_2V_2$$

$$0.100 \times \frac{100}{1000} = c_2 \times \frac{350}{1000}$$

$$c_2 = 0.02857 \text{ mol dm}^{-3}$$

Final concentration of NaOH = **<u>0.0286 mol dm^{-3}</u>**

(ii) For KOH, $n_{\text{before dilution}} = n_{\text{after dilution}}$

$$c_1V_1 = c_2V_2$$

$$0.020 \times \frac{250}{1000} = c_2 \times \frac{350}{1000}$$

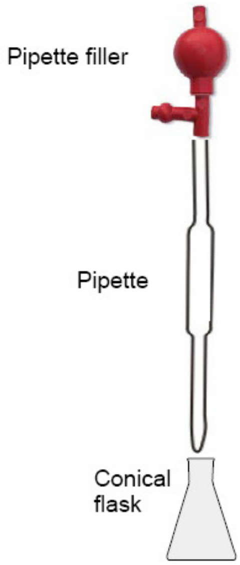
$$c_2 = 0.01429 \text{ mol dm}^{-3}$$

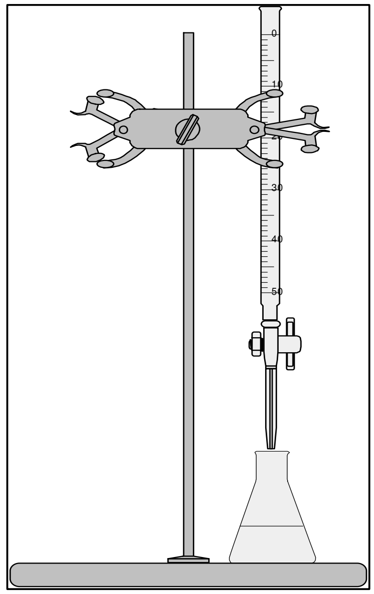
Final concentration of KOH = 0.0143 mol dm^{-3}

Hence $[K^+]$ = **<u>0.0143 mol dm^{-3}</u>**

(iii) OH^- comes from two sources, NaOH and KOH.

4 Volumetric Analysis





Titration is the process whereby a solution is added from a **burette** to a **known volume** of another solution in a **conical flask**.
The concentration of one of the two solutions must be known.

- **Titration** is a common laboratory method of **quantitative** chemical analysis that is used to determine the unknown concentration of a known reactant or to establish the stoichiometry of a reaction**.** Because volume measurements play a key role in titration, it is also known as ***volumetric analysis***.
- In a typical titration, a **known volume** of a **standard solution** of one reactant is measured into a conical flask, using a **pipette**. A solution of the other reactant (with **unknown concentration**) is added, from a **burette,** slowly into the flask, until the reaction between the two substances are complete.
- If we know the balanced equation for the reaction, then we can find out the amount of each reactant that have reacted and hence calculate the concentration of the other solution.
- Titrations can be carried out for :
  - (i) **acid/base reactions** e.g. reaction of HCl (aq) and NaOH (aq)
    For acid/base reactions, an indicator is usually needed to signify the end point of the titration. Some indicators used are **methyl orange** and **phenolphthalein**.
  - (ii) **redox reactions** e.g. reaction of $KMnO_4$ (aq) and $FeSO_4$ (aq)
  - (iii) **precipitation reactions**. e.g. reaction of $AgNO_3$ (aq) and NaCl (aq)

General Steps in Volumetric Analysis

(i) Write a balanced equation for the reaction.
(ii) Apply mole ratio and use mole concept to solve.

Example 7 (Acid-Base Titration)

25.0 cm^3 of NaOH solution required 10.00 cm^3 of a 0.100 mol dm^{-3} solution of H_2SO_4 solution for complete neutralization using phenolphthlalein as indicator. Calculate the concentration of the NaOH solution in mol dm^{-3}.

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + H_2O$$

$$\frac{n_{NaOH}}{n_{H_2SO_4}} = \frac{2}{1}$$

$$\therefore \frac{(cV)_{NaOH}}{(cV)_{H_2SO_4}} = \frac{2}{1}$$

$$c_{NaOH} = \frac{2 \times 0.100 \times {}^{10.0}/_{1000}}{{}^{25.0}/_{1000}} = 0.0800 \text{ mol dm}^{-3}$$

Example 8 (Dilution & Acid-Base Titration)

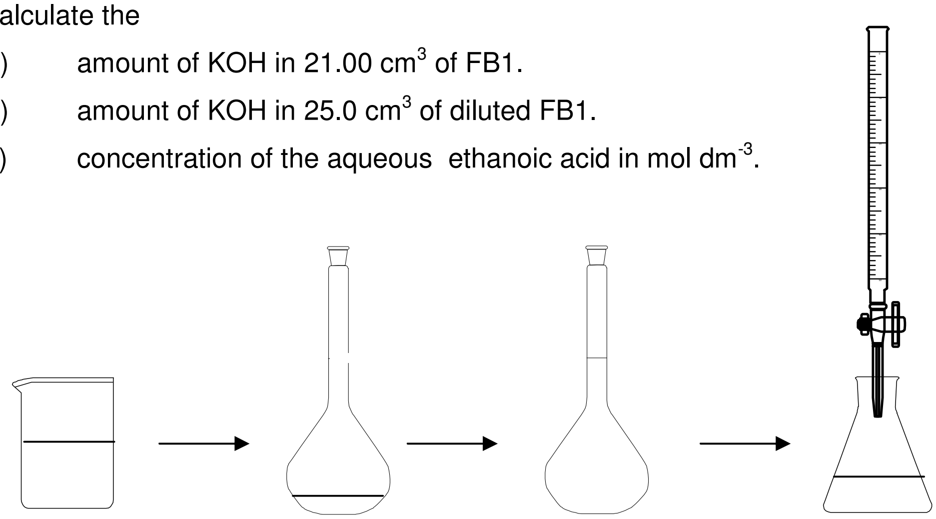
FB1 is a solution containing 14.0 g of KOH(s) dissolved in 250 cm^3 solution. 21.00 cm^3 of FB1 is put into a volumetric flask and then made up to 100 cm^3 with water. Diluted FB1 is then titrated with aqueous ethanoic acid using phenolphthalein indicator. 25.0 cm^3 of diluted FB1 required 27.50 cm^3 of aqueous ethanoic acid for neutralization.

Calculate the

(a) amount of KOH in 21.00 cm^3 of FB1.

(b) amount of KOH in 25.0 cm^3 of diluted FB1.

(c) concentration of the aqueous ethanoic acid in mol dm^{-3}.



(a) n_{KOH} in 250 cm^3 FB1 = $\frac{m}{M} = \frac{14.0}{56.0}$ mol

n_{KOH} in 21.00 cm^3 FB1 = $\frac{14.0}{56.0} \times \frac{21.00}{250}$ = 0.02100 mol = <u>0.0210 mol</u>

(b) $n_{\text{before dilution}} = n_{\text{after dilution}}$

n_{KOH} in 100 cm^3 diluted FB1 = n_{KOH} in 21.00 cm^3 FB1 =

n_{KOH} in 25.0 cm^3 of diluted FB1 =

(c) $CH_3COOH + KOH \rightarrow CH_3COO^-K^+ + 2H_2O$

n_{CH_3COOH} in 27.50 cm^3 = n_{KOH} in 25.0 cm^3 =

$c_{CH_3COOH} = \dfrac{n}{V} =$

5 Back Titration

Some substances (such $CaCO_3$) are insoluble in water and would be difficult to titrate directly. These difficulties can be overcome by dissolving a known amount of the substance in an <u>excess</u> of acid, for example, and determining the amount of excess by ***back titration*** with alkali.

Examples of back titration are:

- determination of the purity of a Group II carbonate and
- determination of the solubility of an ammonium salt

<u>Example 9 (Back Titration for the identification of a Gp II carbonate)</u>

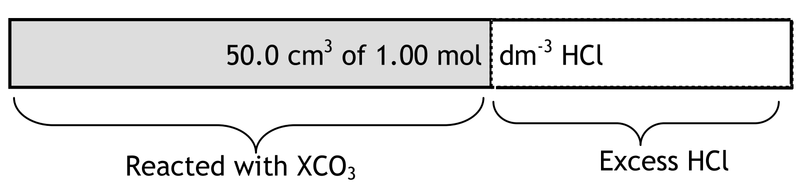
1.00 g of a group II carbonate, XCO_3 is dissolved in 50.0 cm^3 of 1.00 mol dm^{-3} HCl and the remaining acid requires 30.00 cm^3 of 1.00 mol dm^{-3} NaOH for neutralization. By determining the A_r of X, identify element X.

The two reactions which have taken place are

$$XCO_3 + 2HCl \rightarrow XCl_2 + CO_2 + H_2O \quad \text{......eqn (i)}$$

$$NaOH + HCl \rightarrow NaCl + H_2O \quad \text{......eqn (ii)}$$

30.00 cm^3



n_{HCl}, (initial) = cV = $1.00 \times \dfrac{50.0}{1000} = 0.05000$ mol from eqn (ii), $\dfrac{n_{HCl}(\text{excess})}{n_{NaOH}} = \dfrac{n_{HCl}(\text{excess})}{1.00 \times {}^{30.00}/_{1000}} = \dfrac{1}{1}$

$\therefore n_{HCl}$ (excess) = 0.03000 mol

n_{HCl} that reacted with XCO_3 =

from eqn (i), $\dfrac{n_{XCO_3}}{n_{HCl}} = \dfrac{{}^{m}/_{M}}{0.02000} = \dfrac{{}^{1.00}/_{M}}{0.02000} = \dfrac{1}{2}$

$M_{XCO_3} = 100.0 \text{ g mol}^{-1}$

hence, $A_r(X) + 12.0 + 16.0 \times 3 = 100.0$

$A_r(X) =$

<u>Example 10 (Back titration for determination of mass of an ammonium salt)</u>

A sample containing ammonium chloride was warmed with 100 cm^3 of 1.00 mol dm^{-3} sodium hydroxide solution. After all the ammonia had been driven off, the excess sodium hydroxide required 50.00 cm^3 of 0.250 mol dm^{-3} sulfuric acid for neutralization. What mass of ammonium chloride did the sample contain?

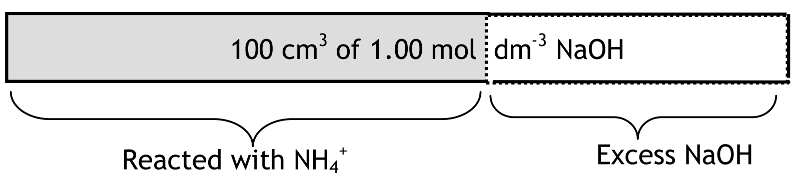
The two reactions which have taken place are

(a) reaction between ammonium salt and alkali:

$NH_4^+ \quad + \quad OH^- \rightarrow NH_3 \quad + \quad H_2O$……eqn (i)

(b) neutralization of the excess alkali:

$2NaOH \quad + \quad H_2SO_4 \rightarrow Na_2SO_4 \quad + \quad 2H_2O$…..eqn (ii)



n_{NaOH} initially present = cV =

The amount of NaOH left unused is titrated against sulfuric acid.

from eqn (ii), $\dfrac{n_{NaOH}(\text{excess})}{n_{H_2SO_4}} = \dfrac{n_{NaOH}}{0.250 \times {}^{50.00}/_{1000}} = \dfrac{1}{2}$

$\therefore n_{NaOH}$ (excess) = 0.02500 mol

n_{NaOH} used in eqn (i) $= n_{NaOH}$ (Initial) $- n_{NaOH}$ (excess)

=

From equation (i), $\dfrac{n_{NH_4Cl}}{n_{NaOH}} = \dfrac{1}{1}$, $\quad n_{NH_4Cl} =$

Mass of ammonium chloride = n x M =