Anderson Serangoon Junior College
JC1 H2 Chemistry
THE MOLE CONCEPT, STOICHIOMETRY & REDOX REACTIONS

Learning Outcomes

[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*

(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)

(i) describe and explain redox processes in terms of electron transfer and/or of changes in oxidation number (oxidation state)

(j) construct redox equations using the relevant half−equations

(k) Describe and explain the use of Fe^{3+}/Fe^{2+}, MnO_4^-/Mn^{2+}, $Cr_2O_7^{2-}/Cr^{3+}$ and iodometric titration as examples of redox systems

References

1. Chemistry for Advanced Level, Peter Cann & Peter Hughes
2. Chemistry, JGR Briggs
3. Chemistry in Context, 5th edition, Graham Hill & John Holman
4. A−Level Chemistry, Fourth Edition, E.N. Ramsden
5. Chemistry, Sixth Edition, Steven S. Zumdahl & Susan A. Zumdahl
6. Chemistry: The Molecular Nature of Matter and Change, 4th Edition, Martin S. Silberberg

TABLE OF CONTENTS **Pg**

Introduction

Chemistry is observed all the time. The chemical reactions occurring in your brain allows you to read and understand this statement. The food you ate is now providing you with energy through chemical reactions.

In the study of Chemistry, we learn about the structure and properties of matter, its interactions and transformation. During transformation of matter, a chemical and/or physical change takes place. ***Matter and energy are conserved in all of such transformations***.

In this topic, we will focus on the ***stoichiometry*** − study of the quantitative relationship between the amounts of reactants and products − in chemical reactions. This key concept is an important tool for chemists in the area of food, health, medicine and engineering.

1. Relative Masses of Atoms And Molecules

- What do the terms *relative isotopic*, *atomic*, *molecular* and *formula mass* mean?
- Can you calculate the relative atomic mass of an element given the relative abundances of its isotopes?

1.1 Relative Masses of Atoms

Atoms have very small masses. For example, a hydrogen atom weighs 1.66 x 10^{-24} g.
Instead of using their actual masses, we measure how heavy one atom is compared with another atom. The carbon−12 isotope, ^{12}C is used as the standard of reference.

$$\textbf{Relative isotopic mass} \text{ of an isotope} = \frac{\text{mass of one atom of the isotope}}{\frac{1}{12} \times \text{mass of one atom of } ^{12}\text{C isotope}}$$

Example: Relative isotopic mass of ^{13}C = 13
Relative isotopic mass of ^{37}Cl = 37

$$\textbf{Relative atomic mass} \text{ of an element, } A_r = \frac{\text{average mass of one atom of the element}}{\frac{1}{12} \times \text{mass of one atom of } ^{12}\text{C isotope}}$$

Most elements consist of a mixture of isotopes. The average of the relative isotopic masses of the element is equal to the relative atomic mass of the element.

Recall: Isotopes are atoms of the same element with different number of neutrons. They have identical atomic (proton) numbers but different mass numbers.

1.2 Relative Molecular Mass and Relative Formula Mass

Relative molecular mass of a substance, $M_r = \dfrac{\text{average mass of one molecule of the substance}}{\frac{1}{12} \times \text{mass of one atom of } ^{12}\text{C isotope}}$

The relative molecular mass of a compound is also the sum of the relative atomic masses of all the atoms in a molecule of a compound.

Example: M_r of HC*l* = 1 x 1.0 + 1 x 35.5 = 36.5 (1 d.p.)
M_r of O_2 = 2 x 16.0 = 32.0 (1 d.p.)

For giant ionic and giant covalent compounds, they do not consist of individual molecules. Relative formula mass, with the same symbol $\boldsymbol{M_r}$ is used for such substances.

Relative formula mass of a substance, $M_r = \dfrac{\text{average mass of one formula unit of the substance}}{\frac{1}{12} \times \text{mass of one atom of } ^{12}\text{C isotope}}$

Similarly, the relative formula mass of a compound is the sum of the relative atomic masses of all the atoms in one formula unit of a giant ionic/giant covalent compound.

Example: M_r of NaC*l* = 1 x 23.0 + 1 x 35.5 = 58.5 (1 d.p.)
M_r of SiO_2 = 1 x 28.1 + 2 x 16.0 = 60.1 (1 d.p.)

Note

- Since ***relative*** masses are the ***ratio*** of two masses, they have ***no units***.
- Relative masses are given to ***1 decimal place***.
- *You will learn more about the structures of giant ionic, giant covalent compounds in the topic of Chemical Bonding.*

Worked Example 1

Natural samples of krypton consist of mixtures of isotopes in the following percentage abundances.

Relative isotopic mass	Percentage abundance (%)
80	2.6
82	11.6
83	11.5
84	56.9
86	17.4

Calculate the relative atomic mass of Kr using the data above.

$$A_r \text{ of Kr} = \frac{(80\times2.6)+(82\times11.6)+(83\times11.5)+(84\times56.9)+(86\times17.4)}{(2.6+11.6+11.5+56.9+17.4)}$$

= **83.9** (1 d.p)

Checkpoint 1

Boron (A_r 10.8) occurs naturally as two isotopes, ${}^{10}_{5}B$ and ${}^{11}_{5}B$.

What is the percentage of ${}^{11}_{5}B$ atoms in a sample of naturally−occurring boron?

Let x be the percentage of ${}^{11}_{5}B$

A_r of B =

10.8 =

x =

Percentage of ${}^{11}_{5}B$ atoms in the sample =

Answer: 80.0%

2. <u>The Mole, The Avogadro Constant And Molar Mass</u>

Chemists are often interested in measuring quantities of substances. In a chemical reaction, the number of particles (atoms, ions or molecules) involved is very large; hence the ‘mole’ is used to describe a very large number. It is just like ‘pair’ refers to 2 items and ‘dozen’ refers to 12 items.

Questions to ponder:

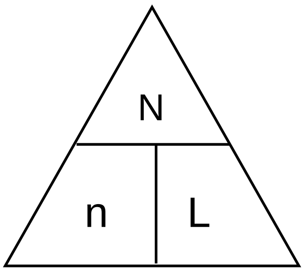
- *What is a mole?*
- *Is the phrase “the mass of one mole of oxygen” ambiguous? Why?*

2.1 <u>The Mole, The Avogadro Constant</u>

The chemist’s **unit** of amount is the mole, with symbol **<u>mol</u>**, is defined as such,

> One **mole** contains exactly 6.02 x 10^{23} (or Avogadro constant) elementary entities.
>
> *An elementary entity may be an atom, a molecule, an ion, an electron, any other particle or specified group of particles.*

The number of particles (denoted by **N**) in one mole of any substance is a constant, known as **Avogadro constant** (denoted by **L** or **N_A**), which is equal to **6.02×10^{23} mol^{-1}**.



N = number of particles

L = Avogadro’s constant (mol^{-1})

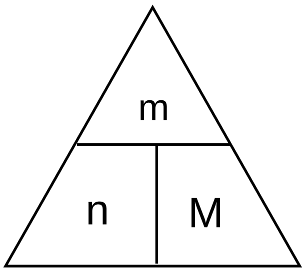
n = amount / number of moles (mol)

<u>Example:</u>

- 1 mole of ^{12}C atoms (i.e. 12 g of ^{12}C) contains <u>6.02 x 10^{23} ^{12}C</u> atoms.
- 1 mole of H_2O molecules contains 6.02 x 10^{23} H_2O molecules which are made up of <u>6.02 x 10^{23}</u> O atoms and <u>**2 x** 6.02 x 10^{23}</u> H atoms.
- 1 mole of Na_2CO_3 contains <u>6.02 x 10^{23}</u> CO_3^{2-} ions and <u>**2 x** 6.02 x 10^{23}</u> Na^+ ions.

2.2 <u>Molar Mass</u>

- The mass of <u>one mole</u> of a substance is called the **molar mass** (unit: g mol^{-1}).
- Molar mass of a substance is **<u>numerically equal</u>** to the relative atomic mass, A_r, relative molecular mass or relative formula mass, M_r of the substance.



m = mass (g)

M = molar mass (g mol^{-1})

n = amount / number of moles (mol)

Worked Example 2

What is the mass of 0.3 mol of $CuSO_4 \bullet 5H_2O$?

5 moles of water

M_r of $CuSO_4 \bullet 5H_2O$ = 63.5 + 32.1 + (4 x 16.0) **+** (5 x 18.0) = 249.6
mass of 0.3 mol of $CuSO_4.5H_2O$ = 0.3 x 249.6 = **<u>74.9 g</u>**

Checkpoint 2

1. How many moles of H_2O molecules are there in 25 g of $CuSO_4 \bullet 5H_2O$?

   n($CuSO_4 \bullet 5H_2O$) in 25 g =

   n(H_2O) =

2. How many copper atoms are there in 6.24 g of $CuSO_4 \bullet 5H_2O$?

   n($CuSO_4 \bullet 5H_2O$) in 6.24 g =

   n(Cu atoms) = n($CuSO_4 \bullet 5H_2O$) =

   number of Cu atoms =

3. How many oxygen atoms are there in 0.1 mol of $CuSO_4 \bullet 5H_2O$?

   n(O atoms) =

   number of O atoms =

Answers: Q1) 0.501 mol Q2) 1.51 x 10^{22} Q3) 5.42 x 10^{23}

3. Stoichiometry

Stoichiometry refers to the relationship (usually specified by the mole ratio) between the amounts of reactants and products involved in a chemical reaction. A reaction is stoichiometric if it proceeds exactly as in the balanced equation.

Questions to ponder:

- *What is the significance of a balanced equation?*
- *How do you determine the amount of reactants and products in a chemical reaction?*

3.1 Balancing Chemical Equations (Self−directed learning)

Before understanding and applying stoichiometry, a chemical equation must be constructed. A chemical equation is a statement in formulas that expresses the identities and quantities of substances involved in a chemical or physical change.

In a chemical process, **atoms cannot be created, destroyed or changed.** Atoms can only be arranged into different combinations. Hence, **the number of atoms on left hand side of equation must equal to the number of atoms on right hand side of equation.**

Writing Balanced equations

Step 1: **Translate** the statement/phenomenon.

Step 2: **Balance the atoms**. Start with the most complex substance, and end with the least complex substance (i.e. an element by itself)

Step 3: **Adjust balancing (stoichiometric) coefficients.** The smallest whole−number coefficients are preferred, unless the equations need to fulfill other functions (such as describing a specific definition e.g. enthalpy change).

Step 4: **Checking** to ensure balancing of atoms on the left and right side of the equation (Mass Balance).

Step 5: **Specify the states of matter**. The abbreviations are solid (s), liquid (l), gas (g) and aqueous solution (aq). (Note: only if specified by the question)

Worked Example 3

Magnesium burned in air to produce white magnesium oxide.

Step 1: **Translate** the statement/phenomenon.

__ Mg + __ O_2 → __ MgO

Step 2: **Balance the atoms**.

__ Mg + __ O_2 → 1 MgO

1 Mg + __ O_2 → 1 MgO

1 Mg + ½ O_2 → 1 MgO

Step 3: **Adjust balancing (stoichiometric) coefficients**.

(x2) 1 Mg + ½ O_2 → 1 MgO

2 Mg + 1 O_2 → 2 MgO

Step 4: **Checking** (Mass Balance)

Step 5: **Specify the states of matter (if specified by question).**

Answer: **2 Mg (s) + O_2 (g) → 2 MgO (s)**

3.2 Stoichiometry involving Gases

3.2.1 Relationship between the Mole and Volume of Gases

Avogadro's Law states that equal volumes of all gases **under the same conditions of temperature and pressure** contain the same number of molecules/atoms (valid for gases that behave ideally).

This means that 6.02×10^{23} (Avogadro number) molecules/atoms (i.e. 1 mole) of any gas will occupy the same volume under the same conditions of temperature and pressure.

Eg. Volume of **1 mol** (or 20.2 g) of neon (Ne) gas = **x cm^3**
Volume of **1 mol** (or 2.00 g) of hydrogen (H_2) gas = **x cm^3**

In a chemical equation, the **mole ratio** of gases involved in the chemical reaction is the same as the **volume ratio** of the gases involved.

Eg. $3H_2(g) + N_2(g) \rightarrow 2NH_3(g)$

Volume ratio = mole ratio: $3H_2 \equiv N_2 \equiv 2NH_3$

3 moles of H_2 reacts with **1** mole of N_2 to give **2** moles of NH_3.

3y dm^3 of H_2 reacts with **y** dm^3 of N_2 to give **2y** dm^3 of NH_3 under the same conditions.

3.2.2 Molar Volumes of Gases

- From Avogadro's Law, the number of moles of gas can be determined by:

$$n = \frac{V}{V_m}$$

n = number of moles of gas
V = volume of gas (dm^3)
V_m = molar volume (dm^3)

Scan this **QR code** to watch a video on how the knowledge of molar volume of gases is needed in everyday life.

- Molar volume is the **volume** that is occupied by **1 mole of any gas**
  - At **s.t.p**.
    standard **t**emperature and **p**ressure of **10^5 Pa [1 bar] and 273 K [0 °C]**,
    molar volume is **22.7 dm^3 mol^{-1}**.
  - At **r.t.p**
    room **t**emperature and **p**ressure of **101325 Pa [1 atm] and 293 K [20 °C]**,
    molar volume is **24 dm^3 mol^{-1}**.

  (This information can be found in the Data Booklet.)

  Conversion of volumes:
  1000 cm^3 = 1 dm^3 = 10^{-3} m^3
  1 x 10^6 cm^3 = 1000 dm^3 = 1 m^3

Worked Example 4

1. How many methane (CH_4) molecules are there in 5.6 dm^3 of the gas at s.t.p?

   (Volume of 1 mol of CH_4 molecules (or molar volume) at s.t.p. = 22.7 dm^3)
   n(CH_4) in 5.6 dm^3 at s.t.p. = $\frac{5.6}{22.7}$ = 0.2467 mol
   No. of CH_4 molecules in 5.6 dm^3 at s.t.p. = n × L = 0.2467 × 6.02 × 10^{23}
   = **1.49×10^{23}**

2. What is the volume of 6.55 g of xenon (Xe) gas at r.t.p?

   n(Xe) in 6.55 g = $\frac{6.55}{131.3}$ = 0.04989 mol
   (Volume of 1 mol of Xe atoms at r.t.p. = 24 dm^3)
   Volume of Xe at r.t.p. = 0.04989 × 24 = **1.20 dm^3**

3. Determine the volume ratio of 1.70 g of ammonia (NH_3) gas compared to 3.01 x 10^{23} helium (He) atoms at s.t.p.

   n(NH_3) = $\frac{1.70}{14.0 + 1.0 \times 3}$ = 0.1000 mol
   n(He) = $\frac{3.01 \times 10^{23}}{6.02 \times 10^{23}}$ = 0.5000 mol
   Mole ratio: $NH_3 \equiv He$
   $0.1000 \equiv 0.5000$
   $1 \equiv 5$
   Volume ratio of NH_3 to He = **1 : 5**

Checkpoint 3

1. Determine the volume (in cm^3) occupied by 3.80 × 10^{23} bromine gas molecules (Br_2) at r.t.p.

   n(Br_2) =

   volume of Br_2 =

2. What volume of oxygen (O_2) is required to react completely with 24 g of methane (CH_4) at s.t.p?

   Chemical equation: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$
   Reacting mole ratio:

   n(CH_4) in 24 g =

   n(O_2) required =

   volume of O_2 at s.t.p. =

Answer: 1) 1.52 x 10^4 cm^3; 2) 68.1 dm^3

3.3 Calculations involving Reacting Masses

- A balanced chemical equation gives the mole ratio between the reactants and products involved in the chemical reaction.

$$a\mathbf{A} + b\mathbf{B} \rightarrow c\mathbf{C} + d\mathbf{D}$$

(reactants: **A** & **B**; products: **C** & **D**; a, b, c & d are stoichiometric coefficients)

- General steps in solving problems involving chemical reactions.

Worked Example 5

Barium carbonate ($BaCO_3$) decomposes to form barium oxide (BaO) and carbon dioxide gas. What mass of barium oxide would be formed from decomposing 39.4 g of barium carbonate?

Step 1: Write a balanced chemical equation for the reaction.

Chemical equation: $BaCO_3(s) \rightarrow BaO(s) + CO_2(g)$

Step 2: Determine the mole ratio involved in the reaction.

Mole ratio: $BaCO_3 \equiv BaO$

Step 3: Work out the answer based on stoichiometry.

! Always use **mole ratio** to perform calculations and **not mass ratio.**

n($BaCO_3$) in 39.4 g = $\dfrac{39.4}{137.3+12.0+16.0\times3}$ = 0.2000 mol

n(BaO) = 0.2000 mol

mass of BaO = 0.2000 × (137.3 + 16.0) = **<u>30.6 g</u>**

Checkpoint 4

1. Calculate the mass of copper carbonate that can be precipitated from a solution containing 0.002 mol of copper ions. [A_r of Cu = 63.5; A_r of O = 16.0; A_r of C = 12.0]

   $Cu^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CuCO_3(s)$

   Mole ratio:

   n($CuCO_3$) =

   mass of $CuCO_3$ =

2. A hydrate of potassium carbonate has the formula $K_2CO_3.xH_2O$. When 10.0 g of the hydrate was heated until all the water is driven off, the residue (K_2CO_3) weighed 7.93 g. Deduce the formula of the hydrate. [A_r of K = 39.1]

   $K_2CO_3.xH_2O(s) \rightarrow K_2CO_3(s) + xH_2O(g)$

   n(K_2CO_3) =

   mass of H_2O =

   n(H_2O) =

   x =

   $\Rightarrow$ the formula of the hydrate is ____________________

3. Sulfur and chlorine can react together to form S_2Cl_2. When 1.00 g of this sulfur chloride reacted with water, 0.36 g of a yellow precipitate (i.e. sulfur) was formed together with a solution containing a mixture of sulfurous acid, H_2SO_3 and HC*l*. Use the data to deduce the equation for the reaction between S_2Cl_2 and water. [A_r of S = 32.1; A_r of C*l* = 35.5]

   n(S_2Cl_2) =

   n(S: yellow ppt.) =

   Mole ratio of S_2Cl_2 : S =

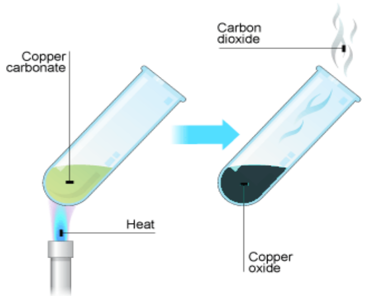
   Balanced equation:

Answer: 1) 0.247 g; 2) $K_2CO_3.2H_2O$

<table>
<tr><td colspan="3"><u>Link to Laboratory Experiments (Practical work):</u>
Checkpoint 4 Question 2 is an example of gravimetric analysis – analysis by measuring masses.</td></tr>
<tr><td>Types of gravimetric analysis</td><td><u>Thermal decomposition</u></td><td><u>Precipitation</u></td></tr>
<tr><td>General description</td><td>Heating a known mass of a solid sample (e.g. hydrated salts, carbonates) and <u>measuring the mass loss</u></td><td><u>weighing</u> the mass of precipitate formed when solutions are mixed</td></tr>
<tr><td colspan="3">More details on the experimental procedures for each analysis will be covered in the laboratory.</td></tr>
<tr><td>Examples</td><td>(1) $CuSO_4.nH_2O \rightarrow CuSO_4(s) + nH_2O(g)$
The value of n can be determined by measuring the mass loss due to H_2O.

(2) decomposition of some carbonates on heating:
$MCO_3(s) \rightarrow MO(s) + CO_2(g)$

The identity of M can be determined by measuring the mass loss due to $CO_2(g)$.



Bbc.co.uk,. (2016). BBC – GCSE Bitesize: Thermal decomposition. Retrieved 22 January 2016, from <u>http://www.bbc.co.uk/schools/gcsebitesize/science/aqa_pre_2011/rocks/limestonerev1.shtml</u></td><td>$Na_2SO_4 + BaCl_2 \rightarrow BaSO_4(\mathbf{s}) + 2\ NaCl$

The amount of Na_2SO_4 present in a solution can be determined by adding $BaCl_2$ solution and weighing the mass of $BaSO_4$ precipitate formed.</td></tr>
</table>

3.4 <u>Calculations involving Limiting Reagents</u>

- Most of the time, the amount of reactants added is not according to the stoichiometric ratio of the reactions. Therefore, the reactions will go on until one of the reactants is exhausted and the reactions will cease. This reactant is called the limiting reagent.

- **<u>Definition of Limiting Reagent</u>**
  The reactant that is completely used up in a reaction (i.e. not in excess). The amount of limiting reagent (in mole) determines the amount of product (in mole) formed.

- General steps in solving problems involving reactions with limiting reagent:

Step 1: Write a balanced chemical equation for the reaction.
Step 2: Calculate the number of moles of each reactant.

Eg:	**A**	+	2**B**	→	4**C**
Given	0.6 mol		0.5 mol		

Step 3: Assume either A (or B) is limiting, and calculate amount of B (or A) needed to react completely with A (or B). Identify the limiting reagent.

<u>EITHER:</u>	**<u>OR:</u>**
If all of **A** is used up, Mole Ratio: **A** ≡ 2**B** n(B) required = 0.6 × 2 = 1.2 mol Since n(B) available < n(B) required (0.5 mol) (1.2 mol) ⇒ **<u>B is the limiting reagent</u>**	If all of **B** is used up, Mole Ratio: **A** ≡ 2**B** n(A) required = 0.5 × ½ = 0.25 mol Since n(A) available > n(A) required (0.6 mol) (0.25 mol) ⇒ **A** is **in excess** hence, **<u>B is the limiting reagent</u>**

Step 4: Determine the amount of product formed (in mole) using limiting reagent.
Based on the amount of limiting reagent,
Reacting Mole Ratio: 2B (limiting reagent) ≡ 4C (product)
n(C) = 2 × 0.5 = **<u>1.00 mol</u>**

Worked Example 6

5.00 g of iron (Fe) and 5.00 g of sulfur (S) were heated together to form iron(II) sulfide (FeS). What is the mass of iron sulfide formed?

Step 1: Chemical equation: **Fe(s) + S(s) → FeS(s)**
Step 2: Mole ratio: Fe ≡ S ≡ FeS
Step 3: n(Fe) in 5.00 g = $\frac{5.00}{55.8}$ = 0.08961 mol   n(S) in 5.00 g = $\frac{5.00}{32.1}$ = 0.1558 mol
Step 4: Determine the limiting reagent.
If all of S is used up, n(Fe) required = 0.1558 mol
n(Fe) available **<** n(Fe) required ⇒ Limiting reagent: **Fe**
Step 5: Work out the answer based on stoichiometry with reference to the amount of the limiting reagent (in mole) available.
Since Fe ≡ FeS
n(FeS) = 0.08961 mol
m(FeS) = 0.08961 × (55.8 + 32.1) = **<u>7.88 g</u>**

3.5 Theoretical, Experimental and Percentage Yield

- The **theoretical yield** of a product is the maximum amount of substance that can be obtained by a chemical reaction from the given amount of reactants. It is obtained by calculations.

- The **experimental yield** of a product is the amount of substance that can be obtained by a chemical reaction from the given amount of reactants under stated conditions. It is obtained only by experiments. It should be smaller than the theoretical yield.

$$\text{Percentage Yield (\%)} = \frac{\text{Experimental Yield}}{\text{Theoretical Yield}} \times 100\%$$

Worked Example 7

2.00 g lead(II) nitrate, $Pb(NO_3)_2$ is added to a solution containing 1.00 g potassium iodide (KI). A bright yellow precipitate of lead(II) iodide (PbI_2) is formed.

(a) Calculate the mass of lead(II) iodide formed.

(b) During the experiment, 1.10 g of PbI_2 is formed. Calculate the percentage yield of PbI_2.

(a) $Pb(NO_3)_2(s) + 2KI(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$

Mole ratio: $Pb(NO_3)_2 \equiv 2KI$

$n(Pb(NO_3)_2)$ in 2.00 g $= \frac{2.00}{331.2} = 6.039 \times 10^{-3}$ mol

$n(KI)$ in 1.00 g $= \frac{1.00}{166.0} = 6.024 \times 10^{-3}$ mol

If all of KI is used up, $n(Pb(NO_3)_2)$ required $= \frac{1}{2} \times 6.024 \times 10^{-3}$
$= 3.012 \times 10^{-3}$ mol

$n(Pb(NO_3)_2)$ available **>** $n(Pb(NO_3)_2)$ required
$\Rightarrow$ Limiting reagent: KI
Since $2KI \equiv PbI_2$

$n(PbI_2) = \frac{6.024 \times 10^{-3}}{2} = 3.012 \times 10^{-3}$ mol

mass of $PbI_2 = 3.012 \times 10^{-3} \times 461.0 =$ **1.39 g**

(b) Percentage Yield (%) $= \frac{1.10}{1.39} \times 100\% =$ **79.2 %**

Checkpoint 5

The mass of MgO was found to be 6.01 g when 6 g of magnesium is reacted with 3 g of oxygen. Calculate the percentage yield of MgO.

$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$
Mole ratio:

n(Mg) used =

n(O_2) used =

If all of Mg is used up, n(O_2) required =

n(O_2) available **<** n(O_2) required

$\Rightarrow$ Limiting reagent:

Since $O_2 \equiv 2MgO$

n(MgO) formed =

mass of MgO formed =

Percentage yield =

Answer: 79.5%

Practices of Science: Real World Applications

Example 1:
The nutrition label found on the container of many food products uses the concept of percent composition.

Sample Label for Macaroni and Cheese

Nutrition Facts
Serving Size 1 cup (228g)
Servings Per Container 2

Amount Per Serving

Calories 250	Calories from Fat 110
	% Daily Value*
Total Fat 12g	18%
Saturated Fat 3g	15%
Trans Fat 1.5g	
Cholesterol 30mg	10%
Sodium 470mg	20%
Total Carbohydrate 31g	10%
Dietary Fiber 0g	0%
Sugars 5g	
Protein 5g	
Vitamin A	4%
Vitamin C	2%
Calcium	20%
Iron	4%

* Percent Daily Values are based on a 2,000 calorie diet. Your Daily Values may be higher or lower depending on your calorie needs:

	Calories:	2,000	2,500
Total Fat	Less than	65g	80g
Sat Fat	Less than	20g	25g
Cholesterol	Less than	300mg	300mg
Sodium	Less than	2,400mg	2,400mg
Total Carbohydrate		300g	375g
Dietary Fiber		25g	30g

e.g. The fat content of this particular food product can be read in this way:
For 1 serving of approx. 1 cup of macaroni and cheese, the total fat content is 12 g. The % Daily Value (DV) is computed based on a 2000 calories diet.

Hence % DV of Total Fat

$$= \frac{\text{total fat content in 1 serving}}{\text{total fat content in a 2000 calories diet}} \times 100\%$$

$$= \frac{12}{65} \times 100\% \approx 18\%$$

Fda.gov,. (2016). Trans Fat Now Listed With Saturated Fat and Cholesterol. Retrieved 22 January 2016, from
http://www.fda.gov/food/ingredientspackaginglabeling/labelingnutrition/ucm274590.htm

Example 2:
Do you know how to tell the percentage purity of gold?
Do you know how to test the purity of gold?

CARAT	MILLESIMAL	% GOLD
24	999	99.9
22	916	91.6
20	833	83.3
18	750	75.0
15	625	62.5
14	585	58.5
10	417	41.7
9	375	37.5
8	333	33.3
1	42	0.42

Many countries quantify gold's purity by carat.

$$\text{Carat} = \frac{\text{mass of gold}}{\text{total mass}} \times 24$$

- 24 Carat gold has a minimum of 99 % gold
.
- 18 Carat gold has a minimum of 75 % gold and 25 % of other metals (e.g. copper or silver)
- FYI: The purity of gold can be determined via measurements of impurity using advanced spectroscopy methods or acid testing kits (containing acids with different strength).

The table above is obtained from:
Understanding the World Around Through Simple Mathematics, M. Kemal Atesmen, p25.

4. Empirical and Molecular Formulae

- *What are the definitions of empirical and molecular formula?*
- *Is empirical formula always the same as molecular formula?*
- *How do we determine empirical and molecular formula using combustion data or composition by mass?*

The empirical formula is the ***simplest*** formula that shows the relative number of atoms of each element present in a compound.

The molecular formula shows the ***actual number*** of atoms of each element present in one molecule of the compound.

Note:
The molecular formula may be the same as the empirical formula or is an integral multiple of it.

4.1 Determination of Empirical and Molecular Formulae using Composition by Mass

Worked Example 8

A hydrocarbon is found to contain 85.72% carbon and its relative molecular mass is 28.0. Calculate the empirical and molecular formula of the hydrocarbon.

*To find an **empirical formula**, you need to work out the ratio of the amounts (in moles) of atoms of each element present.*

	C	H
Mass (%) (assuming 100 g sample)	85.72	14.28
Amount (mol) (i.e. mass/A_r)	$\frac{85.72}{12.0}$ = 7.143	$\frac{14.28}{1.0}$ = 14.28
simplest ratio	1	2

∴ empirical formula is $\mathbf{CH_2}$.

__Molecular formula__ is an integral multiple of the empirical formula.

Let the molecular formula be $(CH_2)_n$

M_r = n(12.0 + 2 x 1.0) = 28.0 ⇒ 14n = 28 ⇒ n = 2

∴ molecular formula is $\mathbf{C_2H_4}$.

Note:
From the formula of the 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

20.882 g sample of an ionic compound is found to contain 6.072 g of Na, 8.474 g of S and 6.336 g of O. What is its empirical formula?

	Na	**S**	**O**
Mass (g)	6.072	8.474	6.336
Amount (mol) (i.e. mass/A_r)	$\frac{6.072}{23.0} = 0.2640$	$\frac{8.474}{32.1} = 0.2640$	$\frac{6.336}{16.0} = 0.3960$
Division by the smallest mol	$\frac{0.2640}{0.2640} = 1.0$	$\frac{0.2640}{0.2640} = 1.0$	$\frac{0.3960}{0.2640} = 1.5$
Simplest mol ratio	1 × 2 = 2	1 × 2 = 2	1.5 × 2 = 3

Empirical formula of compound: **$\underline{Na_2S_2O_3}$**

Worked Example 10 (self-read)

A compound has the following composition: C, 58.8%, H, 9.8%, O, 31.4%. The relative molecular mass is known to be 102.0. What is its molecular formula?

	C	**H**	**O**
Mass (%) (assuming 100 g sample)	58.8	9.8	31.4
Amount (mol) (i.e. % mass/A_r)	$\frac{58.8}{12.0} = 4.900$	$\frac{9.8}{1.0} = 9.800$	$\frac{31.4}{16.0} = 1.9625$
Division by the smallest mol	$\frac{4.900}{1.9625} = 2.5$	$\frac{9.800}{1.9625} = 5$	$\frac{1.9625}{1.9625} = 1$
Simplest mol ratio	2.5 × 2 = 5	5 × 2 = 10	1 × 2 = 2

Empirical formula of compound: $C_5H_{10}O_2$
Let the molecular formula be $(C_5H_{10}O_2)_n$
Therefore, $n \times [5(12.0) + 10(1.0) + 2(16.0)] = 102.0$
$\Rightarrow n = 1$
Molecular formula: **$\underline{C_5H_{10}O_2}$**

Checkpoint 6

Calculate the empirical formula of an oxide of iron that contains 70% Fe by mass. If the molar mass of the oxide is 159.6 g mol^{-1}, calculate the molecular formula of the oxide.

	Fe	**O**
% mass		
no. of moles		
division by the smallest mol		
simplest mol ratio		

∴ empirical formula is ________.

Let the molecular formula be ____________
M_r =

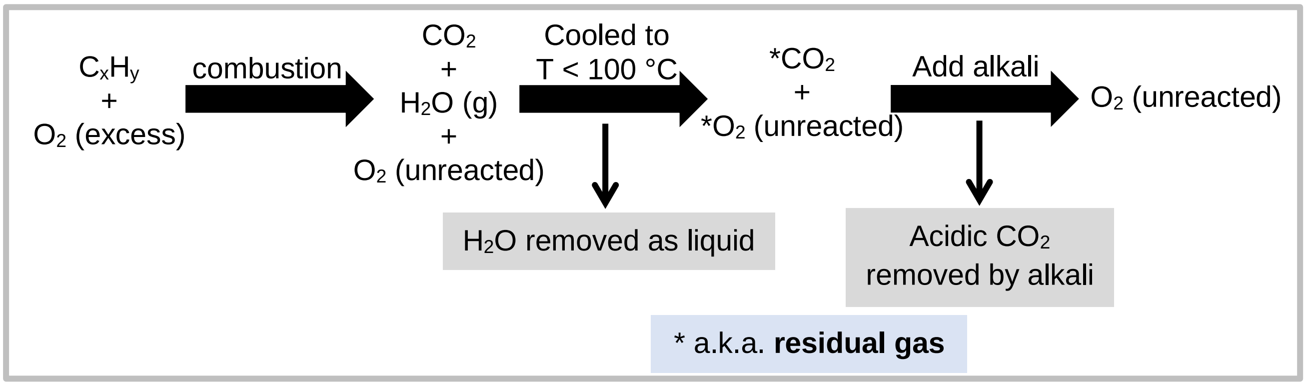
∴ molecular formula is _________.

4.2 <u>Determination of Molecular Formula using Combustion Data</u>

- Sometimes, the molecular formula of a gaseous hydrocarbon, C_xH_y, can also be determined if the volumes of the gases at each stage can be found. The following general chemical equation may be applied when the gaseous hydrocarbon is completely burnt in **<u>excess</u>** oxygen (and cooled to T < 100 °C)

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

Note:
$(x + \frac{y}{4})\ O_2$ in the above equation represents the <u>reacted</u> oxygen.
Since excess oxygen is used for combustion, some unreacted oxygen will be left.
If the organic compound contains C, H and O, CO_2 and H_2O will be formed upon complete combustion.
If there is incomplete combustion, other carbon containing product e.g C and CO may be formed.



Worked Example 11

15 cm^3 of a gaseous hydrocarbon were mixed with 90 cm^3 of oxygen and exploded. After cooling to room temperature, the residual gas occupied a volume of 75 cm^3 and after passing through an alkali, the volume was reduced to 45 cm^3. Explain the function of the alkali and determine the molecular formula of the hydrocarbon.

Function of alkali: ***to absorb the acidic CO_2***

Chemical equation: $C_xH_y\,(g) + (x + \frac{y}{4})\,O_2\,(g) \rightarrow x\,CO_2\,(g) + \frac{y}{2}\,H_2O\,(l)$

15 cm^3	45 cm^3	30 cm^3	liquid

$V_{\text{residual gas } (CO_2 \text{ and unused } O_2)} = 75\ \text{cm}^3$

V_{CO_2} produced = 75 – 45 = 30 cm^3 $\qquad$ V_{O_2} reacted = 90 – 45 = 45 cm^3

By Avogadro's Law: **volume ratio ≡ mole ratio**

$$\frac{n_{CO_2}}{n_{C_xH_y}} = \frac{V_{CO_2}}{V_{C_xH_y}}$$

$$\frac{x}{1} = \frac{30}{15} \quad \Rightarrow x = 2$$

$$\frac{n_{O_2}}{n_{C_xH_y}} = \frac{V_{O_2}}{V_{C_xH_y}}$$

$$\frac{x + y/4}{1} = \frac{45}{15} \Rightarrow y = 4$$

Molecular formula of hydrocarbon: **<u>C_2H_4</u>**

Checkpoint 7

10 cm^3 of a gaseous hydrocarbon were mixed with 100 cm^3 of oxygen and exploded. After cooling to room temperature, the residual gas occupied a volume of 80 cm^3 and after passing through aqueous potassium hydroxide, a reduction of 30 cm^3 in gaseous volume was noted. Determine the molecular formula of the hydrocarbon.

$$C_xH_y \;+\; (x + \frac{y}{4})\,O_2 \;\rightarrow\; x\,CO_2 \;+\; \frac{y}{2}\,H_2O$$

$V_{\text{residual gas }(CO_2\text{ and unused }O_2)} =$

$V_{CO_2\text{ produced}} =$

$V_{\text{unused }O_2} =$

$V_{\text{reacted }O_2} =$

By Avogadro's Law: **volume ratio ≡ mole ratio**

$\frac{n_{CO_2}}{n_{C_xH_y}} = \frac{V_{CO_2}}{V_{C_xH_y}} \Rightarrow \frac{x}{1} = \frac{30}{10} \Rightarrow x = 3$

$\frac{n_{O_2}}{n_{C_xH_y}} = \frac{V_{O_2}}{V_{C_xH_y}} \Rightarrow$

Molecular formula of hydrocarbon: __________

- Empirical formulae can be determined from combustion data, especially for organic compounds. In the case of ***complete*** combustion of one mole of any hydrocarbon (i.e. an organic compound containing only carbon and hydrogen) with oxygen, CO_2 and H_2O will be formed.

Worked Example 12 (self-read)

A 1.500 g sample of an organic compound containing only C, H and O was burned completely. The only combustion products were 1.738 g carbon dioxide and 0.715 g water. What would be its empirical formula?

n(CO_2) in 1.738 g = $\frac{1.738}{44.0}$ = 0.03950 mol
Since $CO_2 \equiv C$
n(C) in 1.738 g = 0.03950 mol
mass of C in 1.500 g compound = 0.03950 × 12.0 = **0.4740 g**

n(H_2O) in 0.715 g = $\frac{0.715}{18.0}$ = 0.03972 mol
Since $H_2O \equiv 2H$
n(H) in 0.715 g = 0.03972 × 2 = 0.07944 mol
mass of H in 1.500 g = 0.07944 x 1.0 = **0.07944 g**

mass of O in 1.500 g = 1.500 – 0.4740 – 0.07944 = **0.9466 g**

	C	H	O
Mass (g)	0.4740	0.07944	0.9466
Amount (mol) (i.e. mass/A_r)	$\frac{0.4740}{12.0}$ = 0.03950	$\frac{0.07944}{1.0}$ = 0.07944	$\frac{0.9466}{16.0}$ = 0.05916
Division by the smallest mol	$\frac{0.03950}{0.03950}$ = 1.0	$\frac{0.07944}{0.03950}$ = 2.01	$\frac{0.05916}{0.03950}$ = 1.50
Simplest mol ratio	1 × 2 = 2	2 × 2 = 4	1.5 × 2 = 3

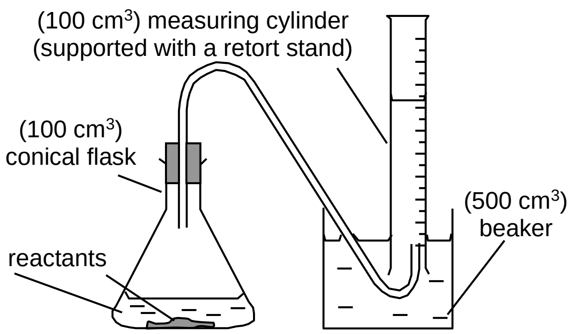
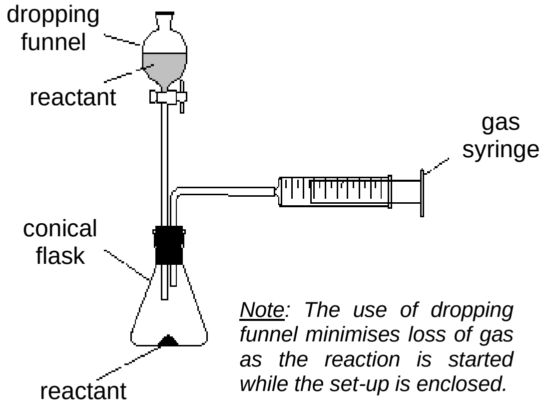
The empirical formula is **$\underline{C_2H_4O_3}$**.

<u>Link to Laboratory Experiments (Practical Work)</u>

Some reactions which produce a gas:

- acid + metal → H_2
- acid + carbonate → CO_2
- H_2O_2 + oxidising agent → O_2

The volume of gas evolved can be measured with a **gas syringe** or by the **displacement of water**.

Method	*by displacement of water*	*using gas syringe*
Set-up		 *<u>Note</u>: The use of dropping funnel minimises loss of gas as the reaction is started while the set-up is enclosed.*
Apparatus required & their common capacities	▪ conical flask (100 cm^3, 250 cm^3) ▪ stopper & delivery tube ▪ burette (50 cm^3) or ▪ measuring cylinder (10, 25, 50, 100 cm^3) ▪ beaker or water trough ▪ retort stand	▪ conical flask (100 cm^3, 250 cm^3) ▪ stopper & delivery tube ▪ <u>dry</u>, <u>well lubricated</u> gas syringe (50 cm^3, 100 cm^3) ▪ retort stand
Remarks	▪ more difficult to set up ▪ **suitable for gases that are <u>insoluble</u> in water** ▪ not suitable for soluble gases like NH_3, HCl, SO_2	▪ easier to set up ▪ suitable for all gases

Qn: What do you need to consider when choosing a suitable gas collection method?
*Ans: The method used to collect and measure the volume of gas evolved depends on several factors such as the **solubility of the gas in water** and the **volume of gas expected**.*

Qn: What other considerations do you need to take to ensure reliability of the volume measured?
*Ans: The gas collected must be left to **equilibrate** to standard conditions (298 K and 1 bar) before recording the volume collected.*

5. Volumetric Analysis

5.1 Theory of Volumetric Analysis

Volumetric analysis or **titration** is a method of quantitative analysis which depends on the accurate measurement of volumes of two reacting solutions.

A measured volume of one solution placed in a conical flask (also known as analyte) and a second solution (also known as titrant) added bit by bit from a burette until the reaction is complete. The two solutions (**A** and **B**) have such characteristics.

- Solution **A**: **Standard** solution whose concentration is **accurately known** (usually known as the titrant).
- Solution **B**: **Unknown** concentration (usually known as the analyte).
- Once the two solutions have reacted in **stoichiometric amounts**, the solution undergoes a **colour change**. (In some reactions, the change in colour can be detected using a suitable indicator)

There are essentially four types of reactions that can be analysed using titrations:

- **Acid−base reaction:** involves the neutralisation of a base with an acid.

Arrhenius theory of acids and bases
An **Arrhenius** **acid** is a substance that **releases H^+ ions** and an **Arrhenius** **base** is a substance that **releases OH^-** when they are dissolved in water.

- **Redox reaction:** involves the transfer of electrons from a reducing agent to an oxidising agent.
- **Precipitation:** involves the formation of an insoluble salt.
- **Complexation reaction:** involves the reaction between a metal ion and ligand to form a complex.

Note:
For acid−base titrations,

- In cases where both solutions are colourless, a suitable indicator is used to detect the end−point. Do not use too much indicator. 2 − 3 drops of indicator is usually sufficient for an acid−base titration.

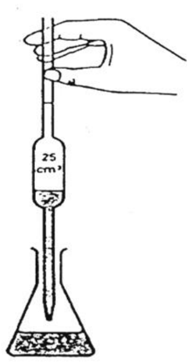
For redox titrations (to be discussed later),

- For all manganate(VII) titrations, an acid is added in excess. No indicator is required. (*refer to pg 44*)
- For iodometric titrations, I_2(aq) is titrated against $Na_2S_2O_3$(aq) until the solution changes from brown to pale yellow. 1 cm^3 of starch solution (the indicator) is then added which gives an intense dark blue−black colour. After which, the titration is continued until the blue−black colouration disappears. (*refer to pg 47*)

<u>Link to Laboratory Experiments (Practical Work)</u>

<u>Steps in performing a titration (to be covered in laboratory exercise)</u>

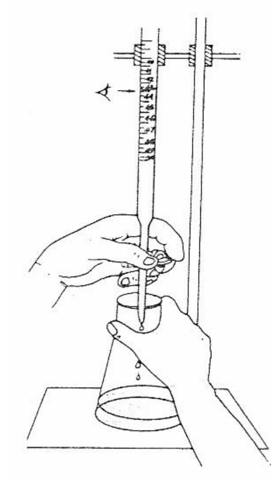
<u>Step 1:</u> Measure 25.0 cm^3 of solution with a *pipette*.



<u>Step 2:</u>

Titrate the solution with another solution from a *burette*.

The titration is repeated until ***consistent*** titre values (difference ≤ 0.10 cm^3) are obtained.



Note: A good titration is one with a titre of less than 50.00 cm^3, preferably close to the volume of the pipette used (usually 25.0 cm^3).

5.2 <u>Solutions and Standard solutions</u>

- A ***standard solution*** is a solution of ***known*** concentration. It can be prepared from
  - a **solid** (of known mass) or
  - a **solution** (of known concentration).
- A **standard flask** (also called volumetric flask or graduated flask) is used to prepare a standard solution.
- The **concentration** of a solution is measured in terms of the amount of solute (in g or mol) contained in a given volume of solution.

$$\text{Concentration}\left(\text{g dm}^{-3}\right) = \frac{\text{mass of solute (g)}}{\text{volume of solution}\left(\text{dm}^3\right)}$$

$$\text{Concentration}\left(\text{mol dm}^{-3}\right) = \frac{\text{amount of solute (mol)}}{\text{volume of solution}\left(\text{dm}^3\right)}$$

Conversion of volumes:

1000 cm^3 = 1 dm^3 = 10^{-3} m^3

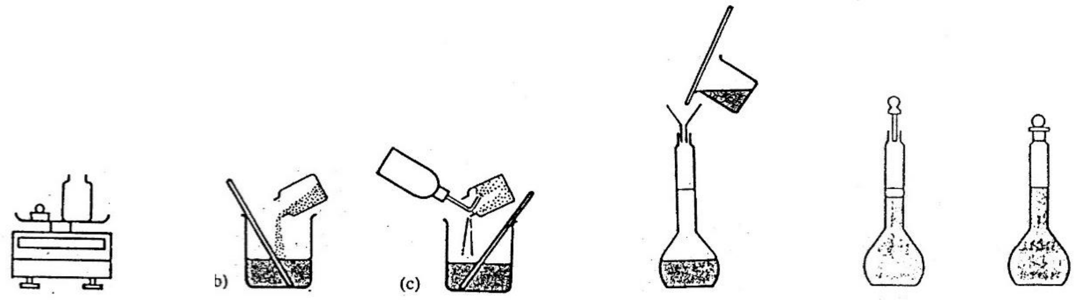
1 x 10^6 cm^3 = 1000 dm^3 = 1 m^3

- Relationship between concentrations in mol dm^{-3} and g dm^{-3}:

Concentration in g dm^{-3} = Concentration (mol dm^{-3}) × molar mass (g mol^{-1})

<u>Link to Laboratory Experiments (Practical Work)</u>

<u>Steps in preparing a standard solution from a solid (to be covered in laboratory exercise)</u>



Weigh the solid in a **dry** *weighing bottle.*	Dissolve the solid in a **small** amount of distilled water.	Transfer the solution, **including washings**, using glass rod (and funnel) into a *volumetric flask*.	Top up to the mark with a dropper and **shake solution thoroughly** to obtain a homogeneous solution

Worked Example 13

What is the concentration of a solution in mol dm^{-3} containing 1.26 g of nitric acid (HNO_3) in 500 cm^3?

n_{HNO_3} in 500 cm^3 = $\frac{1.26}{63.0}$ = 0.02000 mol

$[HNO_3]$= $\frac{0.0200}{500/1000}$ = **<u>0.0400</u>** mol dm^{-3}

<u>Note:</u> The square bracket [ ] stands for the concentration of a substance in <u>mol dm^{-3}</u>.

5.3 <u>Dilution and Sampling</u>

- **<u>Dilution</u>** is the process of adding solvent (e.g. water) to a known volume of the solution.
- **Concentration of solute decreases** but **amount of solute (mol) is unchanged**.

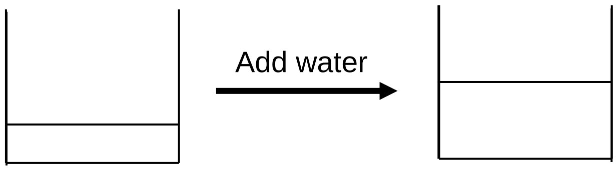
Amount of solute in original solution	=	Amount of solute in diluted solution
$\mathbf{C_oV_o}$	**=**	$\mathbf{C_dV_d}$

where C_o: original concentration
V_o: original volume
C_d: diluted concentration
V_d: diluted volume

Note: V_d **<u>is the diluted volume or final volume</u>**, NOT the volume of water to be added to the original solution.

<u>Example:</u>
Determine the concentration of the diluted solution as prepared below.

C_o = 0.1 mol dm^{-3}
V_o = 100 cm^3



C_d = ???
V_d = 500 cm^3

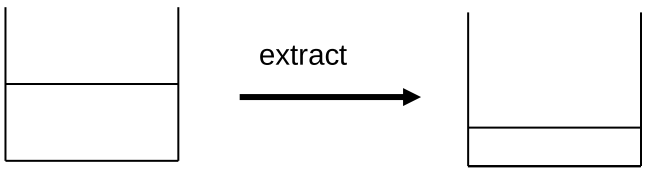
Applying $C_oV_o = C_dV_d$ $\Rightarrow$ 0.1 × (100/1000) = C_d × (500/1000)
Concentration of diluted solution, C_d = **<u>0.0200 mol dm^{-3}</u>**

- **<u>Sampling</u>** is the process of extraction a small portion of the solution for analysis. This portion that is sampled will have the **<u>same concentration</u>** but containing a different **<u>amount of solute</u>**.

$$\text{Sampled amount (mol)} = \frac{\text{Volume of portion sampled}}{\text{Original Volume}} \times \text{Original Amount (mol)}$$

<u>Example:</u>
Given a 250 cm^3 solution containing 0.10 mol of hydrochloric acid, calculate the amount of hydrochloric acid present when 25 cm^3 is extracted from the beaker?

n = 0.1 mol
V = 250 cm^3



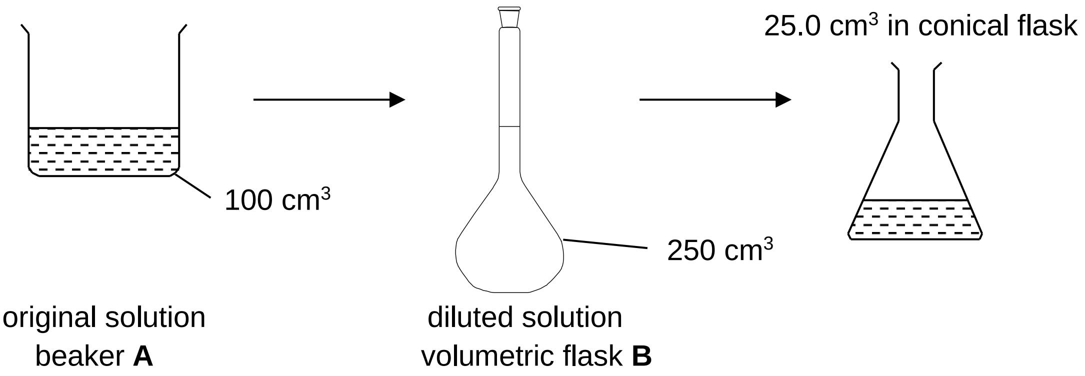
n = ???
V = 25 cm^3

n(HC*l*) in 25 cm^3 extracted sample = (25/250) x 0.10 = **<u>0.0100 mol</u>**

Worked Example 14 (dilution and finding the amount in a portion)

1. 29.64 g of calcium hydroxide, $Ca(OH)_2$ is dissolved in water to make 100 cm^3 solution in beaker **A**. The solution is then diluted to 250 cm^3 in volumetric flask **B**. A 25.0 cm^3 aliquot (portion) is then pipetted out into a conical flask for titration.

   (a) What is the amount of calcium hydroxide (in mole) in beaker **A**?
   (b) What is the initial concentration, in mol dm^{-3}, of the original solution in beaker **A**?
   (c) What is the amount of calcium hydroxide (in mole) in volumetric flask **B**?
   (d) Calculate the amount of calcium hydroxide (in mole) pipetted into the conical flask.



(a) $n(Ca(OH)_2)$ in 29.64 g in beaker **A** = $\frac{29.64}{74.1}$ = **<u>0.400 mol</u>**

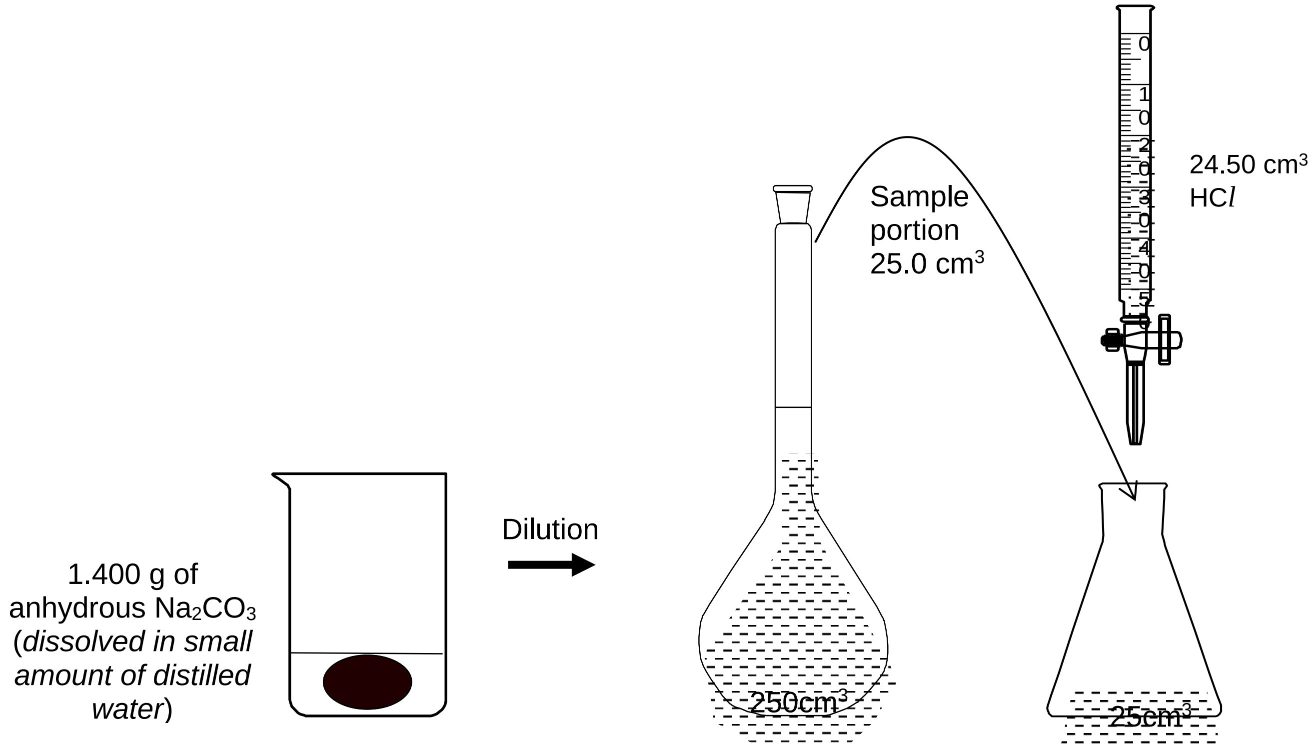
(b) [original solution in beaker **A**] = $\frac{0.400}{100/1000}$ = **<u>4.00 mol dm^{-3}</u>**

(c) $n(Ca(OH)_2)$ after dilution in volumetric flask **B** = **<u>0.400 mol</u>**
(*the amount (in moles) does <u>not</u> change after dilution)*

(d) $n(Ca(OH)_2)$ in 25.0 cm^3 = (25.0/250) × 0.400 = **<u>0.0400 mol</u>**

2. 1.400 g of anhydrous sodium carbonate (Na_2CO_3) was made up to 250 cm^3 of solution. 25.0 cm^3 of this solution required 24.50 cm^3 hydrochloric acid (HCl) for neutralisation.

(a) Write the balanced equation for the acid−base reaction.
(b) Calculate the amount of sodium carbonate (in mole) used in the titration.
(c) Calculate the concentration, in mol dm^{-3}, of hydrochloric acid.
(d) Calculate the concentration, in g dm^{-3}, of hydrochloric acid.
(e) Calculate the mass of chloride ions in 1 dm^3 of hydrochloric acid.



Step 1: Write the balanced chemical equation for the reaction.

(a) Chemical equation:

$Na_2CO_3\,(aq) + 2HCl\,(aq) \rightarrow 2NaCl\,(aq) + CO_2\,(g) + H_2O\,(l)$

(b) $n(Na_2CO_3)$ in 250 cm^3 = $\frac{1.400}{106.0}$ = 0.01321 mol

$n(Na_2CO_3)$ in 25.0 cm^3 = $\frac{25.0}{250}$ × 0.01321 = <u>**1.32×10^{-3} mol**</u>

Step 2: Determine the mole ratio involved.

(c) Mole ratio: $Na_2CO_3 \equiv 2HCl$

$n(HCl)$ in 24.50 cm^3 = 2 × 1.3208 × 10^{-3} = 2.6416 × 10^{-3} mol

$[HCl] = \frac{2.6416 \times 10^{-3}}{24.50/1000}$ = <u>**0.108 mol dm^{-3}**</u>

Step 3: Work out the answer based on stoichiometry.

(d) $[HCl]$ in g dm^{-3} = conc in mol dm^{-3} × molar mass

= 0.1078 × 36.5 = <u>**3.94 g dm^{-3}**</u>

(e) $HCl \rightarrow H^+ + Cl^-$

Since $HCl \equiv Cl^-$

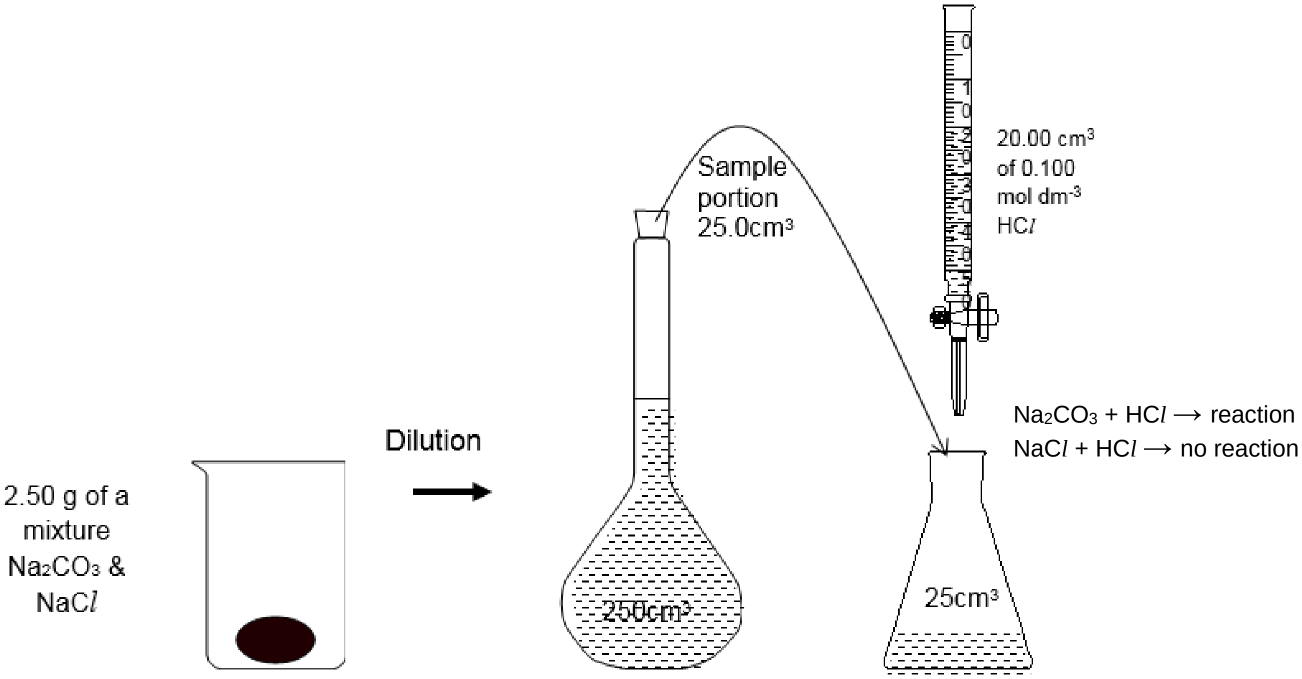
$n(HCl)$ in 1 dm^3 = 0.1078 mol

$n(Cl^-)$ in 1 dm^3 = 0.1078 mol

∴ mass of Cl^- ions in 1 dm^3 = 0.1078 × 35.5 = <u>**3.83 g**</u>

Checkpoint 8

1. 2.50 g of a mixture of anhydrous sodium carbonate (Na_2CO_3) and sodium chloride ($NaCl$) were made up to 250 cm^3 with distilled water. 25.0 cm^3 of this solution required 20.00 cm^3 of 0.100 mol dm^{-3} hydrochloric acid (HCl) for titration. Calculate the percentage by mass of sodium chloride in the anhydrous mixture.



Step 1: Write the balanced chemical equation for the reaction.
Chemical equation:
$Na_2CO_3(aq) + 2HCl\,(aq) \rightarrow 2NaCl\,(aq) + CO_2(g) + H_2O(l)$

Step 2: Determine the mole ratio involved.
Mole ratio: _____ Na_2CO_3 ≡ _____ HCl

Step 3: Work out the answer based on stoichiometry.
n(HCl) in 20.00 cm^3 =

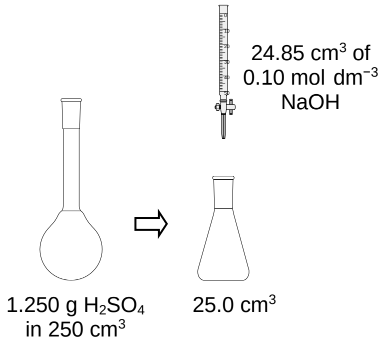
n(Na_2CO_3) in 25.0 cm^3 =
n(Na_2CO_3) in 250 cm^3 =

mass of Na_2CO_3 in 2.50 g mixture =
mass of $NaCl$ in 2.50 g mixture =

Percentage by mass of $NaCl$ in mixture =

Answer: 57.6%

2. 1.250 g of concentrated sulfuric acid were made up to 250 cm^3. 25.0 cm^3 of this solution were neutralised by 24.85 cm^3 of 0.10 mol dm^{-3} sodium hydroxide.
Calculate the percentage purity of the concentrated sulfuric acid.



Chemical Equation: ____NaOH + _____H_2SO_4 →

n(NaOH) used $= 0.10 \times \frac{24.85}{1000}$
$= 2.485 \times 10^{-3}$ mol

$n(H_2SO_4)$ in 25 cm^3 = _______ x n(NaOH)
$= 1.243 \times 10^{-3}$ mol

$n(H_2SO_4)$ in 250 cm^3 =
=

mass of H_2SO_4 in 250 cm^3 =
=

% purity of H_2SO_4 =
= **<u>97.5 %</u>**

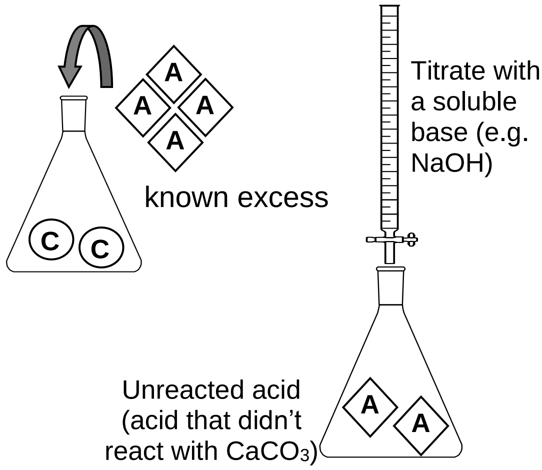
5.4 <u>Back titration</u>

Back titrations are used in cases where a direct titration is **not** possible, due to one of the reactants being an **<u>insoluble solid</u>, <u>slow reaction between reactants</u>, <u>end−point is not distinct and sharp</u>,** or a **<u>lack of a suitable indicator</u>** for the titration.

For example, calcium carbonate, being insoluble in water, reacts slowly with acid. As a result, there is no sharp end−point if titrated with an acid directly.

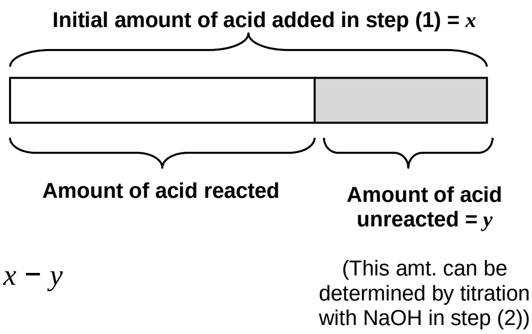
This problem is overcome by **<u>back titration</u>** via the following steps:

1) Add **<u>known amount of acid (added in excess)</u>** to dissolve calcium carbonate, $CaCO_3$.



2) The amount of **<u>unreacted acid</u>** (acid that did not react with $CaCO_3$) can be found by titrating it with a soluble base such as sodium hydroxide.

3) The amount of acid that reacted with $CaCO_3$ is the **<u>amount of acid added in (1) minus the amount of unreacted acid</u>**

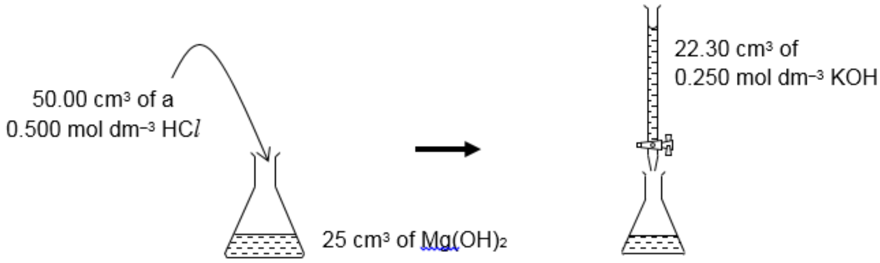


amount (in mol) of acid reacted with $CaCO_3$ = $x - y$

4) The amount of $CaCO_3$ present can then be calculated based on stoichiometry for the reaction between $CaCO_3$ and acid.

Worked Example 15 (self-read)

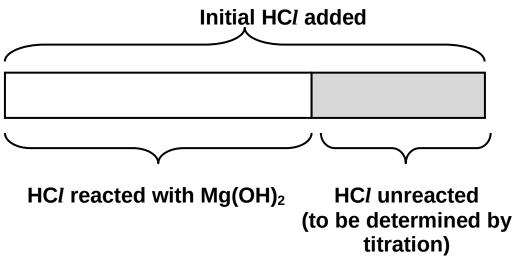
1. To 25.0 cm^3 of a solution of magnesium hydroxide $Mg(OH)_2$, 50.00 cm^3 of 0.500 mol dm^{-3} hydrochloric acid were added. The resulting solution required 22.30 cm^3 of 0.250 mol dm^{-3} potassium hydroxide for neutralisation. Calculate the concentration of magnesium hydroxide solution in mol dm^{-3}.



Step 1: Write the balanced chemical equations for the reactions.
Chemical equations:

$Mg(OH)_2(aq) + 2HCl(aq)_{reacted} \rightarrow MgCl_2(aq) + 2H_2O(l)$ ––––– *(1)*

$KOH(aq) + HCl(aq)_{remaining} \rightarrow KCl(aq) + H_2O(l)$ ––––– *(2)*



Step 2: Determine the mole ratio involved.
Mole ratio: $Mg(OH)_2 \equiv 2HCl_{\text{ reacted}}$ *from (1)*
$KOH \equiv HCl_{\text{ remaining}}$ *from (2)*

Step 3: Determine the amount of the reactant remaining after reaction by titration with the standard reagent.

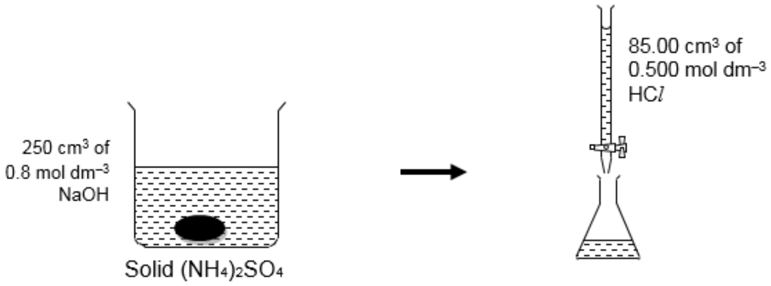
n(KOH) in 22.30 cm^3 = (22.30 / 1000) × 0.250 = 0.005575 mol

remaining n(HCl) for titration with KOH = 0.005575 mol
initial n(HCl) in 50.00 cm^3 = (50/1000) × 0.500 = 0.02500 mol

n(HCl) reacted with $Mg(OH)_2$ = ***initial n(HCl) – remaining n(HCl)***
= 0.02500 – 0.005575
= 0.019425 mol

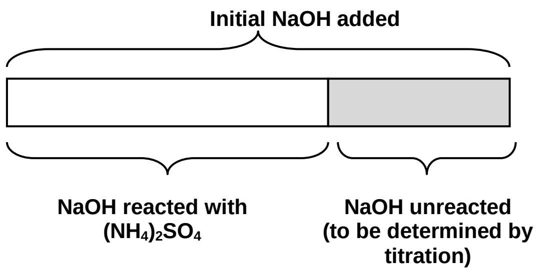
Step 4: Work out the answer based on stoichiometry.
n($Mg(OH)_2$) in 25.0 cm^3 = 0.019425 ÷ 2 = 0.0097125 mol
$[Mg(OH)_2] = \frac{0.0097125}{\frac{25.0}{1000}}$ = **0.389 mol dm^{-3}**

2. A sample containing acidic ammonium sulfate, $(NH_4)_2SO_4$ was warmed with 250 cm^3 of 0.800 mol dm^{-3} sodium hydroxide (NaOH). After the evolution of ammonia has ceased, the remaining sodium hydroxide solution was neutralised by 85.00 cm^3 of 0.500 mol dm^{-3} hydrochloric acid (HC*l*). What mass of ammonium sulfate did the sample contain?



Step 1: Write the balanced chemical equations for the reactions.

Chemical equations:
$(NH_4)_2SO_4$ (s) + 2NaOH $(aq)_{reacted}$ → Na_2SO_4 (aq) + $2NH_3$ (g) + $2H_2O$ *(l)* −*(1)*
HC*l* (aq) + NaOH $(aq)_{remaining}$ → NaC*l* (aq) + H_2O *(l)* −*(2)*



Step 2: Determine the mole ratio involved.

Mole Ratio: $(NH_4)_2SO_4 \equiv 2NaOH$
HC*l* ≡ NaOH

Step 3: Determine the amount of the reactant remaining after reaction by titration with the standard reagent.

n(HC*l*) in 85.00 cm^3 = (85.00/1000) × 0.500 = 0.04250 mol
n(NaOH) **remaining** for titration with HC*l* = 0.04250 mol

Initial n(NaOH) in 250 cm^3 = (250/1000) × 0.800 = 0.2000 mol

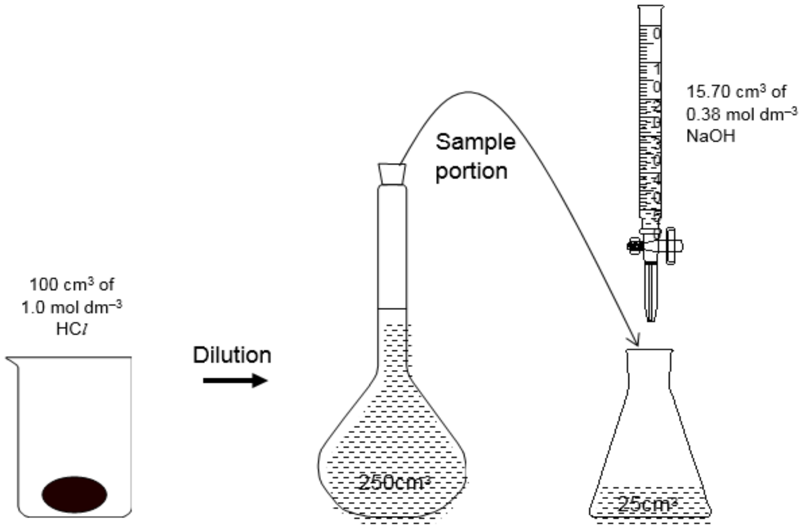
n(NaOH) **reacted with $(NH_4)_2SO_4$ = initial** n(NaOH) **– remaining** n(NaOH)
= 0.2000 – 0.04250
= 0.1575 mol

Step 4: Work out the answer based on stoichiometry.

n($(NH_4)_2SO_4$) = ½ x 0.1575 = 0.07875 mol
mass of $(NH_4)_2SO_4$ = 0.07875 × 132.1 = **<u>10.4 g</u>**

Checkpoint 9

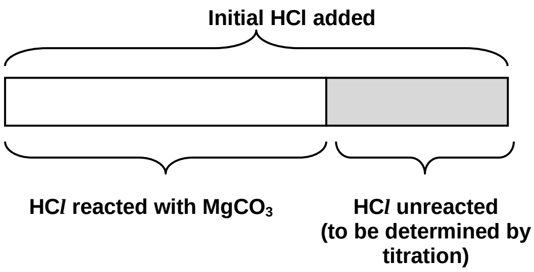
A sample of magnesium carbonate was dissolved in 100 cm^3 of 1.0 mol dm^{-3} hydrochloric acid. The resulting solution was made up to 250 cm^3 with distilled water. 25.0 cm^3 of the solution required 15.70 cm^3 of 0.38 mol dm^{-3} aqueous sodium hydroxide for neutralisation. Determine the mass of magnesium carbonate used.



Chemical equations:

$MgCO_3$ (aq) + 2HCl (aq)$_{reacted}$ → MgCl_2 (aq) + CO_2(g) + H_2O(l) -----*(1)*

HCl (aq)$_{remaining}$ + NaOH (aq) → NaCl (aq) + H_2O (l) -----*(2)*



Mole ratio: $MgCO_3 \equiv 2HCl$

$HCl \equiv NaOH$

n(NaOH) in 15.70 cm^3 =

n(HCl) **remaining** in 25.0 cm^3 for titration with NaOH =

n(HCl) **remaining** in 250 cm^3 =

Initial n(HCl) = $\frac{100}{1000} \times 1 = 0.1000$ mol

n(HCl) **reacted with** $\mathbf{MgCO_3}$ **= initial** n_{HCl} **– remaining** n_{HCl}

=

n($MgCO_3$) =

mass of $MgCO_3$ used =

Answer: 1.70 g

6. <u>Redox Processes</u>

It is important to first understand redox processes before performing calculations for redox titrations.

- What happens in a redox reaction?
- How to construct a balanced redox equation using oxidation number method and half−equation method?

6.1 <u>Definition of Oxidation and Reduction</u>

Oxidation	Reduction
• **Gain** of **oxygen** • **Loss** of **hydrogen** • **Loss** of **electrons** • **Increase** in **oxidation number**	• **Loss** of **oxygen** • **Gain** of **hydrogen** • **Gain** of **electrons** • **Decrease** in **oxidation number**

6.2 <u>Oxidation Number</u>

6.2.1 <u>Definition of Oxidation Number</u>

Each atom in a molecule (or ionic compound) is assigned an ***oxidation number*** or ***oxidation state***, which is the charge the atom would have *if* electrons were not shared but were transferred completely. Note that an oxidation number contains <u>both the sign and the number</u>. The '+' and '–' signs must be indicated <u>before</u> the number.

All atoms in elements, ions/compounds can be assigned an oxidation number according to a set of rules as shown in **6.2.2**.

6.2.2 <u>Rules for Assigning Oxidation Number (O.N.)</u>

- The oxidation number of an atom in its **<u>elemental state</u>** is **<u>zero</u>**.
  e.g. **<u>0</u>** in Fe **<u>0</u>** in O_2 **<u>0</u>** in P_4

- The oxidation number of any **<u>monoatomic ion</u>** is equal to the **<u>charge on the ion</u>**.
  e.g. **<u>–2</u>** in O^{2-} **<u>–1</u>** in F^- **<u>+3</u>** in Al^{3+} **<u>+2</u>** in Fe^{2+}

- The **<u>algebraic sum</u>** of the oxidation numbers of all atoms in a **<u>neutral (uncharged) compound</u>** must be **<u>zero</u>**.

Substance	Sum of O.N.
$FeCl_2$	(+2) + 2(–1) = 0
NH_3	–3 + 3(+1) = 0
H_2SO_4	2(+1) + (+6) + 4(–2) = 0

- The **algebraic sum** of the oxidation numbers of all atoms in a **polyatomic ion** (ion containing more than one atom) is equal to the **charge on the ion**.

Substance	**Sum of O.N.**
MnO_4^-	(+7) + 4(–2) = –1
$Cr_2O_7^{2-}$	2(+6) + 7(–2) = –2
CO_3^{2-}	(+4) + 3(–2) = –2

- **Standard (fixed) oxidation numbers** for some elements in their compounds.

Elements	**O.N.**	**Examples**	**Exceptions**
Group 1	**+1**	$\mathbf{K}_2O$, **Li**C*l*	Nil
Group 2	**+2**	**Mg**Cl_2 , **Ca**$(OH)_2$	Nil
Group 13	**+3**	**A*l***F_3	Nil
Hydrogen	**+1**	$\mathbf{H}_2O$, $C_2\mathbf{H}_6$, O**H**$^-$	Metal hydride e.g. NaH (O.N. of **H** is **–1**)
Oxygen	**–2**	$H_2\mathbf{O}$, Ca**O**	**a)** peroxides e.g. H_2O_2, Na_2O_2 (O.N. of **O** is **–1**) **b)** when oxygen is bonded to fluorine (e.g. OF_2) (O.N. of **O** is **+2**)
Fluorine	**–1**	H**F**, Mg$\mathbf{F}_2$	Nil
Other halogens (C*l*, Br, I...)	**–1**	Fe**C*l***$_3$, H**Br**	When bonded to more electronegative element e.g. Cl_2O (O.N. of **C*l*** is **+1**) BrO_3^- (O.N. of **Br** is **+5**)

- The **most electronegative atom** is assigned the same O.N. in all their compounds. Electronegativity is the ability of an atom in a molecule to attract shared electrons in a covalent bond.

  Electronegativity trends: **increases across the period,**
  decreases down the group (**F > C*l* > Br > I**)
  Very electronegative elements retain the same O.N. in their compounds. They are used as reference in assigning O.N. to other elements.
  In general, electronegativity: **F > O > N ≈ C*l* > Br**

O.N. of	***Fluorine***	***Oxygen***	***Nitrogen***
Fluorine	$\mathbf{F}_2$ (0)	$F_2\mathbf{O}$ (+2)	$\mathbf{N}F_3$ (+3)
Oxygen	$\mathbf{F}_2O$ (–1)	$\mathbf{O}_2$ (0)	$\mathbf{N}O_2$ **N**O (+4), (+2)
Nitrogen	N$\mathbf{F}_3$ (–1)	N**O** N$\mathbf{O}_2$ (–2), (–2)	$\mathbf{N}_2$ (0)
Hydrogen	H**F** (–1)	$H_2\mathbf{O}$ (–2)	$\mathbf{N}H_3$ (–3)

For interhalogen compounds: The more electronegative atom retains its O.N.

Substance	**More electronegative atom**	**O.N.**
IBr	Br	Br (–1), I (+1)
BrCl_3	C*l*	C*l* (–1), Br (+3)

- **Roman numerals** are used to state the oxidation state of the element within a compound
  E.g. CuO is named **copper(II) oxide** NOT copper(2) oxide
  (Oxidation number of Cu is +2).

Compound	Name	O.N. of iron
$FeSO_4$	Iron(II) sulfate	+2
$Fe_2(SO_4)_3$	Iron(III) sulfate	+3

Checkpoint 10

1. Calculate the oxidation number of the underlined element.

   (a) $\underline{O}_2F_2$ (b) $\underline{N}H_4^+$ (c) $H\underline{C}HO$

Let x be the oxidation number of the element to be calculated.

(a) 2(x) + 2(−1) = 0 ⇨ x =

(b) x + 4 (+1) = +1 ⇨ x =

(c)

2. Which one of the following pairs of ions contains two underlined elements having the same oxidation number?

A	$\underline{Cl}O_3^-$	$\underline{Cl}O_4^{2-}$
B	$\underline{Mn}O_4^-$	$\underline{Mn}O_4^{2-}$
C	$\underline{Cr}O_4^{2-}$	$\underline{Cr}_2O_7^{2-}$
D	$\underline{S}O_3^{2-}$	$\underline{S}O_4^{2-}$

Answer: _____

6.3 Oxidising and Reducing Agents

6.3.1 Oxidising Agents

- An oxidising agent **oxidises** another substance. In the process, it **gains or accepts electrons** from other substances and undergoes **reduction**.

- Oxidation number of an oxidising agent **decreases**.

Oxidising Agents	Products*
$\underline{Mn}O_4^-$ / H^+, (purple) manganate(VII) in acidic medium	$\underline{Mn}^{2+}$ (colourless)
$\underline{Mn}O_4^-$/ OH^- , (purple) manganate(VII) in basic medium	$\underline{Mn}O_2$ (Brown ppt)
$\underline{Cr}_2O_7^{2-}$ / H^+ , (orange) dichromate(VI) in acidic medium	$\underline{Cr}^{3+}$ (green)
Fe^{3+} (yellow) iron(III)	Fe^{2+} (pale green)
aqueous I_2 (brown)	I^- (colourless)
Br_2 (reddish brown gas / liquid)	Br^- (colourless)
Cl_2 (greenish yellow gas) aqueous Cl_2 (pale yellow)	Cl^- (colourless)
$\underline{S}O_4^{2-}$ (colourless) sulfate(VI)	$\underline{S}O_3^{2-}$ (colourless) sulfite
$H_2\underline{O}_2$ (colourless) hydrogen peroxide**	$H_2\underline{O}$

** may be obtained from the Data Booklet*

6.3.2 Reducing Agents

- A reducing agent **reduces** another substance. In the process, it **loses or donates electrons** to other substances and undergoes **oxidation**.
- Oxidation number of a reducing agent **increases**.

Reducing Agents	Products*
$\underline{S}_2O_3^{2-}$ (colourless) thiosulfate	$\underline{S}_4O_6^{2-}$ (colourless) tetrathionate
$\underline{C}_2O_4^{2-}$ (colourless) ethanedioate	$\underline{C}O_2$
Fe^{2+}, iron(II)	Fe^{3+}
Br^-	Br_2
I^-	I_2
S^{2-} (colourless) sulfide	S (yellow solid)
$\underline{S}O_3^{2-}$	$\underline{S}O_4^{2-}$
Metals, M	M^{n+}
H_2O_2 hydrogen peroxide**	O_2

** may be obtained from the Data Booklet*

6.3.3 Application of Oxidising and Reducing Agents

E.g.: Hydrogen Peroxide**

As a **reducing agent**	As an **oxidising agent**
In the **presence** of a **stronger** oxidising agent e.g. MnO_4^- / H^+	In the **absence** of a **stronger** oxidising agent.
Acts as **electron donor** and is **oxidised**: $\mathbf{H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-}$	Acts as **electron acceptor** and is **reduced:** $\mathbf{H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O}$

6.4 Redox reactions

*A **redox** reaction* is a process in which oxidation and reduction **occur simultaneously**.

It involves **electron transfer** from the reducing agent to oxidising agent. The transfer of electrons results in a **change in oxidation number** of the atoms involved.

> **No. of e^- lost from oxidation = no. of e^- gained for reduction**

Hence, redox reaction can be recognised by a change in the oxidation number of any atom in the reaction.

Special Cases:

1) Disproportionation is redox reaction in which the ***same** substance* is oxidised and reduced at the same time.

Example: $\underline{Cl}_2 + H_2O \rightarrow H\underline{Cl} + H\underline{Cl}O$

(0) (-1) (+1)

Cl_2 disproportionates to ClO^- and Cl^- as Cl_2 is reduced to Cl^- and oxidized to ClO^-.

2) Comproportionation is a redox reaction in which two reactants, each containing the same element of a different oxidation number, form a product in which the element involved reaches the same oxidation number.

It is the reverse reaction of a disproportionation reaction.

Example: $HCl + HClO \rightarrow Cl_2 + H_2O$

Checkpoint 11

By calculating relevant oxidation numbers, determine which species undergo oxidation, and which undergo reduction, during the following reactions.

(a) $2HNO_2 + 2HI \longrightarrow 2NO + I_2 + 2H_2O$

HNO_3 undergoes ______________ as the oxidation state of N decreases from _____ to _____.

HI undergoes _______________ as the oxidation state of I increases from _____ to _____.

(b) $NO_2 + NaClO_3 \longrightarrow NaNO_3 + ClO_2$

$NaClO_3$ undergoes ______________ as the oxidation state of Cl decreases from _____ to ____.

NO_2 undergoes _______________ as the oxidation state of N increases from _____ to _____.

6.5 Balancing Redox Equations

Three rules that must be observed when writing balanced redox equations:

1. Mass balance: The **number of atoms on left hand side of equation must equal to the number of atoms on right hand side of equation.**
2. Charge balance: The **sum of the charges on left hand side of equation must equal to the sum of the charges on right hand side of equation.**
3. **Number of electrons lost = number of electrons gained**

Two methods used to balance redox equations are the *oxidation number method* and the *half−equation* method.

6.5.1 The oxidation number method

- This method consists of five steps that use the changes in oxidation numbers to generate balancing coefficients.

Steps	Example *Use the oxidation number method to balance the following equation:* *$Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$*
1. Assign oxidation numbers to all elements in the reaction	$\overset{0}{Cu} + \overset{+1}{H}\underset{+5}{N}\overset{-2}{O_3} \rightarrow \overset{+2}{Cu}(\overset{+5}{N}\overset{-2}{O_3})_2 + \underset{+4}{N}\overset{-2}{O_2} + \overset{+1}{H_2}\overset{-2}{O}$
2. From the changes in oxidation numbers, identify the species being oxidised and reduced respectively	Cu was oxidised: the O.N. of Cu increased from 0 (in Cu metal) to +2 (in Cu^{2+}) HNO_3 was reduced: the O.N. of N decreased from +5 (in HNO_3) to +4 (in NO_2)
3. Compute the number of electrons lost in the oxidation and gained in the reduction from the oxidation number changes	loses $2e^-$ (Cu → $Cu(NO_3)_2$) $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$ gains $1e^-$ (HNO_3 → NO_2)
4. Multiply one or both of these numbers by appropriate factors to make the ***number of electrons lost equal the number of electrons gained***, and use the factors as balancing coefficients	Cu lost $2e^-$, so the $1e^-$ gained by N should be multiplied by 2. We put the coefficient 2 before NO_2 and HNO_3: $Cu + 2HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$
5. Complete the balancing by inspection, if necessary	Balancing N atoms requires a 4 in front of HNO_3 because two additional N atoms are in the NO_3^- ions in $Cu(NO_3)_2$: $Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$ Then, balancing H atoms requires a 2 in front of H_2O: $Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

Checkpoint 12

Use the oxidation number method to balance the following equations:

(a) __HNO_3 + __K_2CrO_4 + __$Fe(NO_3)_2$ → __KNO_3 + __$Fe(NO_3)_3$ + __$Cr(NO_3)_3$ + __H_2O

[Answer: 8:1:3:2:3:1:4]

(b) __$C_4H_8O_2$ + __H_2O → __CH_4 + __CO_2 [modified from N2017/III/4(a)(ii)]

[Answer: 2:2:5:3]

6.5.2 <u>The half−equation method</u>

The half−equation method divides the overall redox equation into oxidation and reduction half−equations.

- The steps to write a balanced half−equation are as follows:

Steps	Example
1. Write the skeletal equation showing only the oxidised and reduced forms of a species *If the oxidised form of a species is on the left side of the equation, the reduced form of that species is on the right, and vice versa.*	+7 MnO_4^- ⟶ +4 MnO_2 *oxidised form* *reduced form*
2. Balance **A**ll **El**ements other than O or H	Not applicable in this case
3. Balance **O** with H_2O	MnO_4^- ⟶ MnO_2 **+ 2 H_2O**
4. Balance **H** with H^+	MnO_4^- + **$4H^+$** ⟶ MnO_2 **+ 2 H_2O**
5. Balance charges with **e**lectrons (e^-)	MnO_4^- + $4H^+$ + **$3e^-$** ⟶ MnO_2 + 2 H_2O This is a <u>reduction</u> half−equation (<u>e^-</u> are <u>added</u> on <u>left</u> side of equation) in <u>acidic</u> medium.
6. For ***<u>basic medium only</u>*** H^+ ions are removed by adding OH^- on <u>both sides</u> of the equation to form H_2O Check to <u>cancel H_2O</u> on both sides of the overall equation.	MnO_4^- + 4 H^+ + $3e^-$ ⟶ MnO_2 + 2 H_2O ***+ 4 OH^-*** ***+ 4 OH^-*** = 4 H_2O Simplify to obtain the reduction half−equation in <u>basic/alkaline</u> medium: MnO_4^- + **$2H_2O$** + $3e^-$ ⟶ MnO_2 + $4OH^-$

Checkpoint 13

Write balanced half−equations for the following changes:
(a) the oxidation of $C_2O_4^{2-}$ to CO_2 in acid solution
(b) the reduction of H_2O_2 to water in acid solution
(c) the oxidation of H_2O_2 to oxygen in alkaline solution

(a)	$C_2O_4^{2-} \longrightarrow CO_2$
(b)	$H_2O_2 \longrightarrow H_2O$
(c)	$H_2O_2 \longrightarrow O_2$

6.5.3 <u>Writing Overall Redox Equation</u>

Step 1: Write separate balanced half−equations for the oxidation and reduction reactions
Step 2: If necessary, multiply one or both half−equations by an integer to make the **<u>number of electrons lost</u>** in the oxidation **<u>equals</u>** the **<u>number of electrons gained</u>** in the reduction
Step 3: Combine (add) the balanced half−equations to obtain the overall equation and cancel out the common terms. Include state symbols when necessary

Worked Example 16

Sulfur dioxide gas, SO_2, was bubbled into an acidified solution of potassium dichromate(VI), $K_2Cr_2O_7$. The SO_2 gas was oxidised to SO_4^{2-}. Construct the redox equation for this reaction with state symbols.

<u>**Step 1**: Write separate balanced half−equations for oxidation and reduction</u>

	Oxidation	Reduction
1. Write the skeletal equation showing only the oxidised and reduced forms of a species	$SO_2 \rightarrow SO_4^{2-}$	can be obtained from the *Data Booklet* $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ ––––––––– (2)
2. Balance **E**lements other than O or H	N.A	
3. Balance **O** with H_2O	$SO_2 + \mathbf{2H_2O} \rightarrow SO_4^{2-}$	
4. Balance **H** with H^+	$SO_2 + 2H_2O \rightarrow SO_4^{2-} + \mathbf{4H^+}$	
5. Balance charges with **el**ectrons (e^-)	$\underbrace{SO_2 + 2H_2O}_{0} \rightarrow \underbrace{SO_4^{2-} + 4H^+}_{-2+4=+2}$ $SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ \mathbf{+ 2e^-}$ ––––––––– (1)	

<u>**Step 2**: Multiply one or both half−equations by an integer (no. of e^- lost = no. of e^- gained)</u>

(1) x **3**: $\mathbf{3}SO_2 + \mathbf{6}H_2O \rightarrow \mathbf{3}SO_4^{2-} + \mathbf{12}H^+ + \mathbf{6}e^-$
(2) x **1**: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

<u>**Step 3**: Combine (add) the balanced half−equations and cancel out the common terms (include state symbols if question specifies)</u>

$3SO_2 + 6H_2O + Cr_2O_7^{2-} + 14H^+ \rightarrow 3SO_4^{2-} + 12H^+ + 2Cr^{3+} + 7H_2O$

Overall: $\mathbf{3SO_2\,(g) + Cr_2O_7^{2-}\,(aq) + 2H^+\,(aq) \rightarrow 3SO_4^{2-}\,(aq) + 2Cr^{3+}\,(aq) + H_2O\,(\mathit{l})}$

The overall redox equation **must** <u>**not**</u> contain the electron term.

Checkpoint 14

Hydrogen peroxide, H_2O_2 was reduced to water when it was added to an aqueous solution of Fe^{2+} in acidic medium. Fe^{2+} was oxidised to Fe^{3+}. Construct the redox equation for this reaction.

Oxidation:

------ **(1)** (From *Data Booklet*)

Since Fe^{2+} was oxidised, H_2O_2 will be reduced. Product is H_2O.

Reduction:

------ **(2)** (can be obtained from *Data Booklet)*

Overall redox equation:

7. Redox titrations

- A **redox titration** involves the **stoichiometric reaction** based on a **redox** reaction between the two solutions involved.

- Some redox titrations involving manganate(VII) and dichromate(VI) do not require the addition of an indicator to detect the end−point.

7.1 Manganate(VII) (MnO_4^-) Titration

- MnO_4^- is a very strong oxidising agent and is usually placed in the burette and added into the conical flask containing the reducing agent.

- Typical reducing agents that can react with MnO_4^- are Fe^{2+}, $C_2O_4^{2-}$, H_2O_2 and I^-.

- MnO_4^- titrations are usually carried out in **acidic** conditions. H_2SO_4 is suitable to acidify it.

$HCl(aq)$ and $HNO_3(aq)$ are not used to acidify MnO_4^- as both will interfere with the experiment. HCl will be oxidised by $KMnO_4$ to give chlorine and HNO_3 is an oxidising agent.

- Acidified MnO_4^- is used in the titration process. Alkaline or neutral MnO_4^- is seldom used as incomplete reduction of MnO_4^- occurs, causing precipitation of brown MnO_2.

- In **acidic medium**, the half−equation is

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

refer to Data Booklet

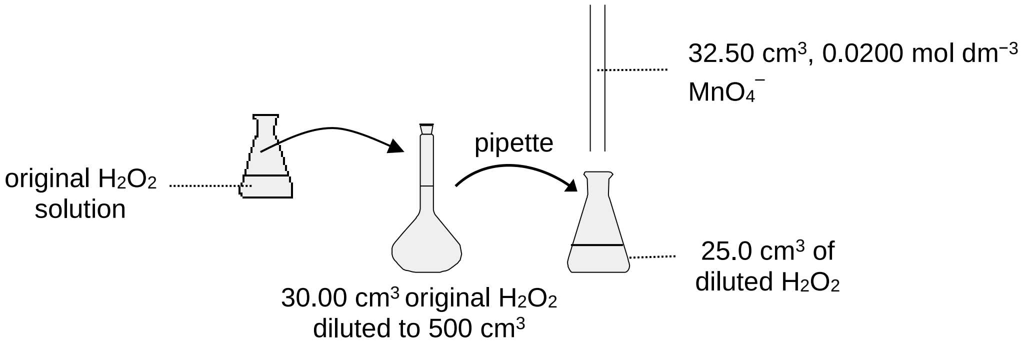
- No indicator is required for this titration because MnO_4^- itself acts as the indicator.

- During the titration, the purple MnO_4^- turns colourless as it is reduced to Mn^{2+} ions (colourless / pale pink)

- When all the reducing agent is used up, the first extra drop of MnO_4^- causes the solution in the conical flask to turn permanent pink (due to a slight excess of purple MnO_4^-). This sharp colour change indicates that the end−point is attained.

Worked Example 17

30.00 cm^3 of a given solution of hydrogen peroxide was diluted to 500 cm^3 with distilled water. 25.0 cm^3 of this diluted solution then required 32.50 cm^3 of 0.0200 mol dm^{-3} potassium manganate(VII) for titration in acidic conditions. Calculate the concentration of the original hydrogen peroxide solution in g dm^{-3}.



Oxidation: $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$ ----------- **(1)**

Reduction: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ ----------- **(2)**

Overall: {(1) x 5} + {(2) x 2}

$5H_2O_2\,(aq) + 2MnO_4^-\,(aq) + 6H^+\,(aq) \rightarrow 5O_2\,(g) + 2Mn^{2+}\,(aq) + 8H_2O\,(l)$

25.0 cm^3 **32.50 cm^3**
0.0200 mol dm^{-3}

Mole ratio: **$5H_2O_2 \equiv 2MnO_4^-$**

n(MnO_4^-) in 32.50 cm^3 = $\frac{32.50}{1000} \times 0.0200$
= 6.500×10^{-4} mol

n(H_2O_2) in 25.0 cm^3 = $\frac{5}{2} \times 6.500 \times 10^{-4}$
= 1.625×10^{-3} mol

n(H_2O_2) in 500 cm^3 = $\frac{500}{25} \times 1.625 \times 10^{-3}$
= 0.03250 mol

n(H_2O_2) in 30.00 cm^3 of original solution = 0.03250 mol

[H_2O_2] of original solution = $\frac{0.03250}{\frac{30.00}{1000}}$
= 1.083 mol dm^{-3}

Conc. of H_2O_2 in g dm^{-3} = 1.083×34.0 = 36.82 ≈ **36.8 g dm^{-3}**

7.2 Dichromate(VI) ($Cr_2O_7^{2-}$) Titration

- Acidified $Cr_2O_7^{2-}$ (usually $K_2Cr_2O_7$) is a strong oxidising agent but not as strong as MnO_4^-.
- H_2SO_4 is a suitable acid to acidify $Cr_2O_7^{2-}$.
- In **acidic medium**, the half−equation is

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ *refer to Data Booklet*

Worked Example 18

A 0.1576 g piece of iron wire was converted into Fe^{2+} ions and then titrated against acidified potassium dichromate(VI) solution of concentration 1.64 x 10^{-2} mol dm^{-3}. If 27.30 cm^3 of the oxidising agent was required, calculate the percentage purity of the iron wire.

Reduction: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
Oxidation: $Fe^{2+} \rightarrow Fe^{3+} + e^-$

Overall: $Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$

Mole ratio: $\mathbf{Cr_2O_7^{2-} \equiv 6Fe^{2+}}$

$n(Cr_2O_7^{2-})$ reacted $= \frac{27.30}{1000} \times 1.64 \times 10^{-2}$
$= 4.447 \times 10^{-4}$ mol

$n(Fe^{2+})$ reacted $= 6 \times 4.477 \times 10^{-4}$
$= 2.686 \times 10^{-3}$ mol

$n(Fe) = n(Fe^{2+})$ reacted $= 2.686 \times 10^{-3}$ mol

mass of pure Fe $= 2.686 \times 10^{-3} \times 55.8$
$= 0.1499$ g

% purity of wire = (0.1499 / 0.1576) x 100 %
= **95.1 %**

7.3 Iodometric Titration using Thiosulfate ($S_2O_3^{2-}$)

- This titration is used to determine the concentration of iodine or substances which liberate iodine from potassium iodide, KI, or potassium iodate(V), KIO_3.

- Half−equations:

  Oxidation: $2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$ (thiosulfate → tetrathionate) *refer to Data Booklet*

  Reduction: $I_2 + 2e^- \rightarrow 2I^-$ *refer to Data Booklet*

  Overall redox equation: $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

- The thiosulfate solution is usually placed in the burette and the brown iodine solution in the conical flask.

- During the titration, the thiosulfate added from the burette into the flask reduces the brown iodine (I_2) solution into colourless iodide (I^-) ions. The solution gradually fades to pale yellow.

- At this point, starch indicator is added into the flask. The solution turns blue−black as starch forms an intense blue-black complex with the remaining iodine.

- Titration then continues until all the iodine is used up and the colour changes from **blue−black** to **colourless**.

- **Note** :

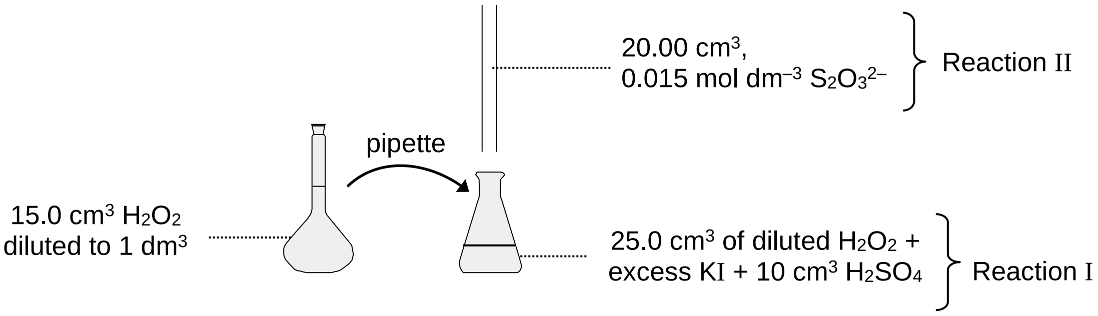
  - Iodine is volatile and will vaporise easily at room temperature hence titration must be conducted immediately. Otherwise, cover all flasks containing iodine.

  - Starch forms a blue−black water soluble complex with iodine where iodine is trapped within the starch molecules. Hence, it is important to only add starch at the end of the titration when there is a low concentration of iodine since some iodine may remain trapped in the starch even at the end−point.

  - Sometimes, the blue−black colour slowly reappears after the titration as some I^- ions are oxidised back to I_2.

Worked Example 19

A 15.0 cm^3 solution of H_2O_2 was diluted to 1 dm^3. 25.0 cm^3 of this solution was added to excess potassium iodide and 10 cm^3 of dilute sulfuric acid were added to the flask. The iodine liberated was titrated using sodium thiosulfate with starch as the indicator. The end−point was reached when 20.00 cm^3 of 0.015 mol dm^{-3} thiosulfate had been added.
What was the concentration of the original hydrogen peroxide solution?



<u>Reaction I between H_2O_2 and excess I^-</u>

Oxidation: $2I^- \rightarrow I_2 + 2e^-$

Reduction: $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$

Overall redox reaction: (1) + (2)

$H_2O_2\,(aq) + 2H^+\,(aq) + 2I^-\,(aq) \rightarrow I_2\,(aq) + 2H_2O\,(l)$

<u>Reaction II between I_2 and $S_2O_3^{2-}$</u>

$I_2\,(aq) + 2S_2O_3^{2-}\,(aq) \rightarrow S_4O_6^{2-}\,(aq) + 2I^-\,(aq)$

mole ratio: $\mathbf{H_2O_2} \equiv I_2 \equiv \mathbf{2\,S_2O_3^{2-}}$

n($S_2O_3^{2-}$) in 20.00 cm^3 = $\frac{20.00}{1000} \times 0.015 = 3.000 \times 10^{-4}$ mol

n(diluted H_2O_2) in 25.0 cm^3 = $\frac{3.000 \times 10^{-4}}{2} = 1.500 \times 10^{-4}$ mol

n(diluted H_2O_2) in 1 dm^3 (1000 cm^3) = $\frac{1000}{25} \times 1.500 \times 10^{-4}$

$= 6.000 \times 10^{-3}$ mol

n(original H_2O_2) in 15 cm^3 = 6.000×10^{-3} mol

[H_2O_2] in original solution = $\frac{6.000 \times 10^{-3}}{\frac{15.0}{1000}}$

= **<u>0.400 mol dm^{-3}</u>**

7.4 Determination of unknown oxidation number

At times, the initial or final oxidation number of one of the species is unknown. The unknown initial or final oxidation number of **B** can be determined when a known amount of **A** (whose final and initial O.N. are known) reacts in stoichiometric amount with **B** in a redox reaction.

Concept applied:

amount of electrons lost = amount of electrons gained

Worked Example 20

Thallium(III) ion, Tl^{3+} can oxidise iodide ions to I_2. In an experiment, 3.00×10^{-3} mol of aqueous Tl^{3+} was found to react with 30.00 cm^3 of 0.200 mol dm^{-3} aqueous potassium iodide, KI. What is the oxidation number of thallium at end−point?

(I^- is oxidised to I_2 while Tl^{3+} is reduced; final O.N. of T*l* is unknown)

Step 1: Calculate the amount (in moles) of each reactant

$n(Tl^{3+}) = 3.000 \times 10^{-3}$ mol (given)

$n(I^-)$ in 30.00 cm^3 = $\frac{30.00}{1000} \times 0.200 = 0.006000$ mol

METHOD 1 (PREFRRED METHOD)

Step 2: Calculate the amount (in moles) of e^- lost from oxidation

$2I^- \rightarrow I_2 + 2e^-$

$n(e^-)$ lost from oxidation = $n(I^-)$ = 0.006000 mol

$n(e^-)$ gained in reduction = $n(e^-)$ lost from oxidation = 0.006000 mol

Step 3: Derive mole ratio between e^- gained (or lost) and oxidising (or reducing) agent

mole ratio: $\frac{n(e^- \text{ gained})}{n(Tl^{3+})} = \frac{0.00600}{0.00300} = \frac{2}{1}$

Therefore, $Tl^{3+} + \mathbf{2e^-} \rightarrow Tl^{n+}$

n = 1, i.e. the final O.N. of T*l* is **+1.**

METHOD 2

Step 2: Derive mole ratio between oxidising and reducing agents

mole ratio: $\frac{n(I^-)}{n(Tl^{3+})} = \frac{0.00600}{0.00300} = \frac{2}{1}$

Mole ratio: $\mathbf{Tl^{3+} \equiv 2I^-}$

Since **2** mol of I^- **lost 2 mol of e^-** ($2I^- \rightarrow I_2 + 2e^-$), **1** mol of Tl^{3+} **gained 2 mol of e^-.**

Therefore, $Tl^{3+} + \mathbf{2e^-} \rightarrow Tl^{n+}$

n = 1, i.e. the final O.N. of T*l* is **+1**

<u>Summary</u>

- **Formulae to calculate number of moles**

No. of moles, n

From no. of particles: $n = \frac{N}{L}$

From volumes of gases: $n = \frac{V\,(dm^3)}{V_m\,(dm^3\ mol^{-1})}$

At s.t.p. (**273 K** (0 ^oC), 1 bar), molar volume of any gas = 22.7 dm^3

At r.t.p. (**293 K** (20 ^oC), 1 atm), molar volume of any gas = 24 dm^3

From masses of substances: $n = \frac{m}{M}$

From concentration and volume of solutions: $n = c\,V$

- **General strategy in performing mole concept calculations**

Steps in problem solving	**Concepts**
Analyse the question	• **acid−base titration; back titration; redox titration; gases** • **writing appropriate balance chemical equation**
Find amount (in moles) of reactant or product A	• $n = \frac{m}{M}$; $n = \frac{V}{V_m}$ (**Avogadro's Law**); $n = \frac{N}{L}$; $n = c\,V$
Ratio from balanced equation	• Applying to gases under same conditions **Avogadro's Hypothesis:** mole ratio = volume ratio • **Balancing equations:** Combustion equation, half−equations and overall equation • **Electron Transfer** in redox reactions **no. of electrons lost (oxidation) = no. of electrons gained (reduction)**
Find amount (in moles) of reactant or product B	• Use of ratio from balanced equation
Mass, volume of gas or volume (or concentration) of solution	• $n = \frac{m}{M}$; $n = \frac{V}{V_m}$ (**Avogadro's Law**); $n = \frac{N}{L}$; $n = c\,V$ • **dilution:** $(c_1 \times V_1)_{\text{before dilution}} = (c_2 \times V_2)_{\text{after dilution}}$ • **percentage yield, percentage purity:** $\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$ • **unit conversion, limiting reagent** • **scaling** • **units and decimal places/significant figures** A_r: no units, 1 d.p. M_r: no units, 1 d.p. Water of crystallisation: whole number • **calculations:** intermediate answers in working: 4 s.f final answer: 3 s.f.

Personal Checklist

<table>
<tr><th>S/N</th><th>Learning Outcomes

I am able to …</th><th>If you are able to solve the question, put a tick (√) in the box</th><th>Questions I wish to clarify</th></tr>
<tr><td>1.</td><td>calculate the relative atomic mass

In a sample of naturally occurring silicon analysed, a mixture of three isotopes, ^{28}Si, ^{29}Si and ^{30}Si, with relative abundance of 92.2%, 4.7% and 3.1% respectively was obtained. What is the relative atomic mass of silicon in this sample?
[Ans: 28.109]</td><td></td><td></td></tr>
<tr><td>2.</td><td>calculate empirical formulae (using combustion data)

When a hydrocarbon is burned in excess oxygen, 0.44 g of CO_2 and 0.27 g of H_2O is formed. Calculate the empirical formula of the hydrocarbon.
[Ans: CH_3]</td><td></td><td></td></tr>
<tr><td>3.</td><td>calculate molecular formulae (using composition by mass)

A compound, with molecular mass of 98.1, was found to contain 32.65% sulfur, 65.3% oxygen and 2.05% hydrogen. What is the molecular formula of the compound?
[Ans: H_2SO_4]</td><td></td><td></td></tr>
<tr><td>4.</td><td>understand concept of limiting reagent

$Cl_2 + 2NaOH \longrightarrow NaClO + NaCl + H_2O$

Identify the limiting reagent in an experiment where 30 cm^3 of 0.100 mol dm^{-3} NaOH was reacted with 0.350 g of Cl_2.
[Ans: NaOH]</td><td></td><td></td></tr>
<tr><td>5.</td><td>recognise the molar volumes at different conditions

Complete the table.
<table>
<tr><th></th><th>room temperature and pressure (r.t.p.) conditions</th><th>standard temperature and pressure (s.t.p.) conditions</th></tr>
<tr><td>temperature / K</td><td></td><td></td></tr>
<tr><td>pressure / Pa</td><td></td><td></td></tr>
<tr><td>molar volume / dm^3</td><td></td><td></td></tr>
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<table>
<tr><td>6.</td><td>understand the Arrhenius theory of acids and bases

Identify the Arrhenius acid and base in the following equation.

$CH_3CO_2H + NaOH \longrightarrow CH_3CO_2Na + H_2O$</td><td></td><td></td></tr>
<tr><td>7.</td><td>describe and explain redox processes

Define oxidation and reduction in terms of

<table><tr><th></th><th>oxidation</th><th>reduction</th></tr><tr><td>(a) electron transfer</td><td></td><td></td></tr><tr><td>(b) change in oxidation number</td><td></td><td></td></tr></table></td><td></td><td></td></tr>
<tr><td>8.</td><td>determine the oxidation number

Determine the oxidation number of the element underlined in each of the following compounds.

(a) $\underline{N}O_2^+$
(b) $\underline{Cl}O_4^-$
(c) $\underline{Mn}O_4^-$
(d) $\underline{Ni}O(OH)$</td><td></td><td></td></tr>
<tr><td>9.</td><td>construct half–equations

Construct half–equation for each of the following reactions.

(a) FeO_4^{2-} to Fe^{2+} in acidic medium
(b) HNO_3 to N_2O_3 in acidic medium
(c) $Fe(OH)_3$ to $Fe(OH)_2$ in basic medium
(d) MnO_2 to $MnO(OH)$ in basic medium</td><td></td><td></td></tr>
<tr><td>10.</td><td>construct balanced redox equations

Given the following half–equations,
(a) $Cl_2 + 2e \longrightarrow 2Cl^-$
$Cl_2 + 4OH^- \longrightarrow 2ClO^- + 2H_2O + 2e$

(b) $MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$
$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e$

(c) $H_2S \longrightarrow S + 2H^+ + 2e$
$2BrO_3^- + 12H^+ + 10e \longrightarrow Br_2 + 6H_2O$

Write a balanced equation for each of the reactions.</td><td></td><td></td></tr>
</table>