04 Reactions and Stoichiometry

GUIDING QUESTIONS

- What is the significance of a balanced equation?
- How can the amount of reactants and products in a chemical reaction be determined?
- What are acids and bases?
- What models can be used to classify substances as acids and bases?

LEARNING OUTCOMES

Students should be able to:

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

6(a) define the terms *relative atomic, isotopic, molecular* and *formula mass* (Refer to Topic 1 Atomic Structure and Physical Periodicity for relative atomic and relative isotopic mass)

6(d) define the terms *empirical* and *molecular formula*

6(e) calculate empirical and molecular formulae using combustion data or composition by mass

6(f) write and/or construct balanced equations

6(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]

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

4(a) show understanding of, and apply the Arrhenius theory of acids and bases

4(b) show understanding of, and apply the Br∅nsted-Lowry theory of acids and bases, including the concept of conjugate acids and conjugate bases (Refer to Topic 15 Acid-Base Equilibria for concept of conjugate acids and conjugate bases).

4(c) show understanding of, and apply the Lewis theory of acids and bases (including non-aqueous system e.g. reaction between BF_3 and NH_3)

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

12(h) construct redox equations using the relevant half-equations

13(g) describe and explain the use of Fe^{3+}/Fe^{2+}, MnO_4^-/Mn^{2+} and $Cr_2O_7^{2-}/Cr^{3+}$ as examples of redox systems

REFERENCES

1. Peter Cann and Peter Hughes (2002), *Chemistry for Advanced Level*, John Murray, Chapters 1 & 7
2. Martin S. Silberberg (2006), *Chemistry: The Molecular Nature of Matter and Change*, 4th Edition, McGraw Hill, Chapters 3 & 4

LOOKING BACK

Chemistry is about the study of matter, its interactions and transformations. In the previous three topics, we have learnt about matter in the submicroscopic level: the atom and its electronic structure. Atoms interact and give rise to different types of bonding. We observe these interactions in our daily life at a macroscopic level, via the physical properties of elements, compounds and gases. In Topic 3 The Gaseous State, we have also learnt the concept of the mole. We shall now look at chemical transformations i.e. reactions, which involve the reorganisation or transfer of valence electrons among the reactants. In all reactions, matter and energy must be conserved. In this topic, we will apply the mole concept and key ideas of conservation of matter in the quantitative treatment of reactions – stoichiometry.

1 FORMULAE OF COMPOUNDS

1.1 Relative Masses of Compounds

In Topic 1 Atomic Structure, we learnt the definition of the relative mass of an atom and an isotope.

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

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

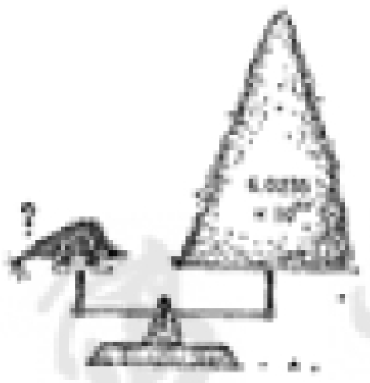
The definitions may be extended to relative masses of molecules and ionic compounds as follows:

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

$$\text{Relative formula mass} = \frac{\text{average mass of one formula unit of a substance}}{\frac{1}{12} \text{ x the mass of one atom of } ^{12}\text{C}}$$

Note:

- Due to the presence of isotopes in elements, the word "*average*" is necessary in the definitions.
- M_r = sum of A_r of all the atoms in the molecular formula
- All the above relative masses have no units, as they are ratios of two masses.
- Relative formula mass is used for ionic compounds.



Self-practice 1.1

Calculate the relative molecular / formula mass of the following substances, giving your answer to 1 decimal place.

(a) $Zn_3(PO_4)_2$ (b) $H_2C_2O_4$ (c) $C_6H_{12}O_6$ (d) $CuSO_4.5H_2O$

[Given A_r of H: 1.0; C: 12.0; O: 16.0; P: 31.0; S: 32.1; Cu: 63.5; Zn: 65.4]

[(a) 386.2, (b) 90.0, (c) 180.0, (d) 249.6]

1.2 Percentage Composition by Mass

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

Lecture Exercise 1.1

Which one of the following compounds, both used as fertilisers, contains the higher percentage by mass of phosphorus: $Ca_5(PO_4)_3F$ or $(NH_4)_2HPO_4$?

Self-Practice 1.2

1. The molecular formula of chlorophyll is $C_{55}H_{72}MgN_4O_5$. Calculate the percentage by mass of magnesium present in chlorophyll. **[2.72%]**

2. Haemoglobin, the oxygen-carrying protein in red blood cells, has four iron atoms per molecule and contains 0.34% iron by mass. Calculate the molar mass of haemoglobin.

[6.56×10^4 g mol^{-1}]

1.3 Empirical and Molecular Formulae

1.3.1 Definitions

*The **empirical formula** of a compound is the simplest formula which shows the **ratio** of the atoms of the different elements in the compound.*

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

For example,

compound	empirical formula	molecular formula
ethanoic acid	CH_2O	$C_2H_4O_2$
ethene	CH_2	C_2H_4

1.3.2 Derivation of Formulae using Composition by Mass

Lecture Exercise 1.2

1. Caproic acid (M_r = 116) occurs in goat's milk and has the following composition by mass: C, 62.1%; H, 10.3%; O, 27.6%. Determine the empirical formula and molecular formula of caproic acid.

2. A 0.4764 g sample of an oxide of iron was completely reduced by a stream of carbon monoxide to produce 0.3450 g of pure iron as the only iron-containing product. Find the empirical formula of the oxide.

Self-Practice 1.3

1. The formula of a complex salt **Z** is $NH_4[Cr(SCN)_x(NH_3)_y]$ and analysis produced the following composition by mass: Cr, 15.5%; S, 38.1%; N, 29.2%. Calculate the values of x and y in the formula for **Z**. **[x = 4, y = 2]**

2. On strong heating, 100 g of $CaSO_4 \bullet nH_2O$ is dehydrated and a constant mass of 79.09 g of anhydrous salt is obtained. Calculate n. **[2]**

1.3.3 Derivation of Formulae using Combustion Data

Organic compounds, on complete combustion with oxygen, form CO_2 and H_2O. By measuring and calculating the amount of the 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.

Lecture Exercise 1.3

Complete combustion of a hydrocarbon (a compound that contains hydrogen and carbon only) gave 0.352 g of carbon dioxide and 0.072 g of water. Calculate the empirical formula and its molecular formula, given that it has a molar mass of 104 g mol^{-1}.

Self-practice 1.4

X is an organic iron compound containing only Fe, C and H. When a 0.944 g sample of **X** was subjected to complete combustion, 2.23 g of CO_2 and 0.457 g of H_2O were formed.
What is the empirical formula of **X**? **[$FeC_{10}H_{10}$]**

2 REACTIONS AND STOICHIOMETRY

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

2.1 Law of Conservation of Matter

A chemical equation represents what happens during a chemical reaction. The law of conservation of matter is the fundamental principle governing the balancing of chemical equations.

When balancing chemical equations, we have to ensure that every atom of every element is accounted for since they are not destroyed or created, but rearranged. There must be the same number of atoms of each element on the right-hand side as there are on the left-hand side.

Self-Practice 2.1

Write balanced chemical equations for the following reactions.

1. lead + silver nitrate → lead nitrate + silver

2. iron(II) chloride + chlorine → iron(III) chloride

Similarly, when substances chemically react to form products, the sum of the masses of all the products is always found to be equal to the sum of the masses of the reactants.

Lecture Exercise 2.1

1. A mixture of $CuSO_4•5H_2O$ and $MgSO_4•7H_2O$ is heated until a mixture of the anhydrous salt is obtained. If 5.00 g of the mixture gives 3.00 g of the anhydrous salts, what is the percentage by mass of $CuSO_4•5H_2O$ in the mixture?

LAW OF CONSERVATION OF MASS

The Law of Conservation of Mass can be shown by the following experiment:

The following set-up is first done with lead(II) nitrate solution in the test tube and potassium iodide solution in the conical flask. The entire apparatus is then weighed.

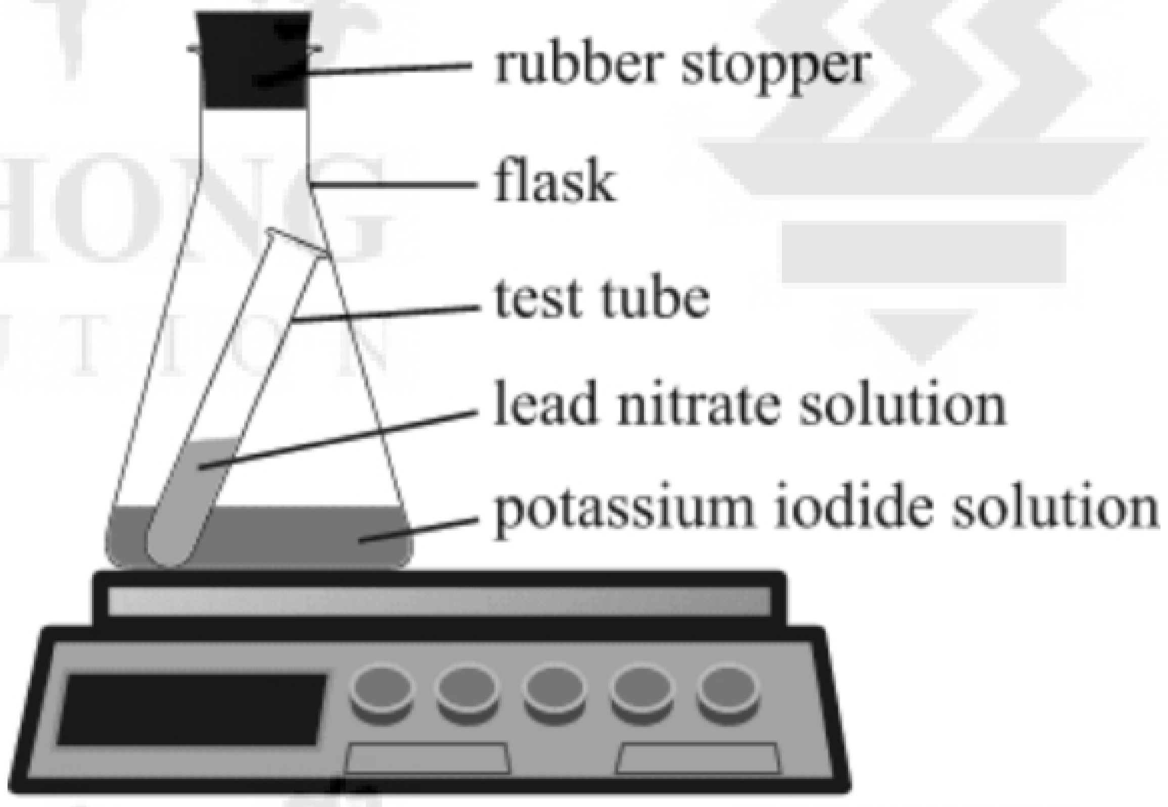


Figure 1. Experiment set-up to illustrate the Law of Conservation of Mass

When the conical flask is shaken to mix the contents, a precipitation reaction occurs (Refer to Section 2.2) forming yellow solid lead(II) iodide. On re-weighing the conical flask with its content, the mass should be the same as its initial mass.

2.2 Limiting Reactants and Percentage Yield

A balanced equation shows the **mole ratios** in which reactants react to give products, and the mole ratios in which the products are formed. It indicates that fixed proportions of reactants will react to give fixed proportions of products. It does *not*, however, represent the actual amount or proportion in which the reactants are present in a mixture. Hence, you should first determine whether there is a reactant in excess.

For example,

$$H_2(g) + ½O_2(g) \rightarrow H_2O(g)$$

The mole ratio (1 : ½ : 1), as shown by the **stoichiometric coefficients** in the balanced equation, tells us that 1 mole of H_2 must react with ½ mole of O_2 to give 1 mole of H_2O.

If 1 mole of H_2 is mixed with 1 mole of O_2, then ½ mole of O_2 must remain unreacted at the end of complete reaction. Reactants present **in excess** are not all consumed at the end of complete reaction. H_2, on the other hand, is the limiting reactant. **Limiting reactants** are completely consumed in the reaction and limits how much products can form.

Many reactions do not, however, go to completion and there may also be a loss of product in practice (e.g. after purification or separation). Hence, the **actual yield** is usually less than 100% of the **theoretical yield** that is calculated based on the limiting reactant.

$$\text{Percentage yield} = \frac{\text{Actual mass (or amount) of product formed}}{\text{Theoretical mass (or amount) of product}} \times 100\%$$

2.3 Types of Reactions

In Chemistry, there are several different types of chemical reactions and more than one way of classifying them. From this section onwards, we will classify the reactions into the following reaction types:

(a) Precipitation reaction

Precipitation reactions are reactions which involve the formation of an insoluble solid which is known as a precipitate, from the reaction of two solutions. The precipitate and the supernatant liquid can be separated by filtration or decanting. In calculations involving precipitation reaction, the mass of the solid will be obtained to find out the number of moles of the solid product formed.

Examples of precipitation reactions:

$$NaCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + NaNO_3(aq)$$

$$Na_2SO_4(aq) + Ba(NO_3)_2(aq) \rightarrow BaSO_4(s) + 2NaNO_3(aq)$$

(b) Thermal decomposition
Thermal decomposition is a chemical reaction caused by heat. In such reactions, a compound breaks down into two or more substances.

Examples of thermal decomposition:

$$2Mg(NO_3)_2(s) \rightarrow 2MgO(s) + 4NO_2(g) + O_2(g)$$

$$2HCl(g) \rightarrow H_2(g) + Cl_2(g)$$

(c) Acid-base reaction – Refer to Section 3

(d) Redox reactions – Refer to Section 4

Most of the reactions you learn at A-level fall into one or more categories. Remember that no classification is perfect and so it would be highly possible to find some reactions that do not fit nicely into any category.

In this section, we will classify the calculations according to:
(i) reacting masses (from formulae and equations)
(ii) volumes of gases (e.g. in the burning of hydrocarbons)
(iii) volumes and concentrations of solutions
However, it would be a good practice to try to identify the type of reactions taking place in each of the lecture exercises or self-practices given.

2.3.1 Calculation using Reacting Masses and Moles

Lecture Exercise 2.2

1. Solid aluminium sulfide reacts with water to give aluminium hydroxide and hydrogen sulfide gas. Write a balanced equation for this reaction. What is the maximum mass of H_2S that can form when 158 g of aluminium sulfide reacts with 131 g of water? Calculate the number of moles of the excess reagent remaining at the end of reaction.

2. When 41.5 g of tungsten(VI) oxide (WO_3) was reacted with excess hydrogen gas, metallic tungsten and 9.50 cm^3 of water was produced. Find the mass of tungsten obtained and its percentage yield, given that the density of water is 1.00 g cm^{-3}.

Self-practice 2.2

When 18.5 g of methane and 43.0 g of chlorine gas undergo a substitution reaction that has an 80.0% yield, what mass of chloromethane (CH_3Cl) is obtained (the other product is HCl)? **[24.5 g]**

2.3.2 Calculation using Volumes of Gases

In Topic 3 The Gaseous State, we learnt about the Avogadro's Law.

Avogadro's Law: *Equal volumes of all gases, under the same temperature and pressure, contain the same number of particles (atoms or molecules).*

Hence, for gases in a balanced equation, ***volume ratio = mole ratio***

For example, for a given equation: $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

The balanced equation tells us that **<u>20 cm^3</u>** of carbon monoxide will react with **<u>10 cm^3</u>** of oxygen to give **<u>20 cm^3</u>** of carbon dioxide.

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

The ***molar volume***, V_m, of any gas is the volume occupied by ***1 mole*** of the gas at a specified temperature and pressure. Thus,

$$\text{Volume of a gas, } V = n \times V_m$$

where n is the amount (in moles) of the gas

Table 1. Temperature, pressure and molar volume at s.t.p. and r.t.p.

condition	temperature	pressure	molar volume
standard temperature and pressure, s.t.p.	273 K (0 °C)	1 bar (100 kPa)	22.7 $dm^3\ mol^{-1}$
room temperature and pressure (room conditions), r.t.p.	293 K (20 °C)	1 atm (101 kPa)	24 $dm^3\ mol^{-1}$

Note: *Volumes of gases are dependent on temperature and pressure. Hence these conditions must be specified.*
The units for volume are cm^3, dm^3 and m^3; 1 dm^3 (1 litre) = 1000 cm^3; 1 m^3 = 10^6 cm^3

Lecture Exercise 2.3

1. A mixture of 10 cm^3 of methane, CH_4, and 10 cm^3 of ethane, C_2H_6, was sparked with an excess of oxygen. After cooling to room temperature, the residual gas was passed through aqueous potassium hydroxide. What volume of gas was absorbed by the alkali?

2. When 100 cm^3 of a gaseous hydrocarbon **W** is burnt in 500 cm^3 of oxygen, 50 cm^3 of oxygen is left unreacted while 300 cm^3 of carbon dioxide and 300 cm^3 of steam are formed. All gases are measured at 150°C and 1 atm. Deduce the balanced equation for the reaction and hence derive the molecular formula of **W**.

3. 10 cm^3 of a gaseous hydrocarbon was exploded with an excess of oxygen. A contraction of 20 cm^3 in volume occurs after the combustion. On passing the gaseous products through aqueous sodium hydroxide, a further contraction of 30 cm^3 occurs. Deduce the formula of the hydrocarbon. (All volumes were measured at r.t.p.)

Self-practice 2.3

1. In an experiment, 20 cm^3 of a gaseous organic compound was sparked with excess oxygen. 80 cm^3 of carbon dioxide and 80 cm^3 of water vapour were obtained. All gases are measured at the same temperature and pressure. Which of the following molecular formula fit the data?

1 $CH_3CH_2CH_2CH_3$
2 $CH_3CH_2CH_2CHO$
3 $CH_3CH_2CH_2CO_2H$ **[2 and 3 only]**

2. What volume of oxygen is required for the complete combustion of a mixture containing 5 cm^3 of methane and 10 cm^3 of ethene? **[40 cm^3]**

3. When 20 cm^3 of a gaseous hydrocarbon **Y** was exploded with 150 cm^3 of oxygen, the residual gases occupied 130 cm^3. After shaking the products with excess aqueous sodium hydroxide, the final volume was 90 cm^3. Deduce the molecular formula of **Y**. (All volumes were measured at room conditions.)

[C_2H_4]

4. 20 cm^3 of a gaseous hydrocarbon was mixed with 150 cm^3 of oxygen so that the hydrocarbon was completely burnt. The volume of gas remaining at the end of combustion was 100 cm^3. After passing over potassium hydroxide, this volume was reduced to 20 cm^3. All gases were measured at 20 °C and the same pressure. What is the formula of the hydrocarbon?

[C_4H_{10}]

2.3.3 Calculations using Concentrations

When a solute is dissolved in a solvent, a **solution** is formed.

If the solvent is water, an **aqueous solution** is formed.

The **concentration** of a solution shows the amount of solute dissolved in a given volume of solution.

Notation for concentration of solute X in a solution in terms of mol dm^{-3}: **[X]**

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

$$\text{Concentration of X (mol dm}^{-3}\text{)}, [\text{X}] = \frac{\text{amount of X (in mol)}}{\text{volume of solution, V (in dm}^{3}\text{)}}$$

No. of moles of solute, *n*

$$= \text{concentration of solute (mol dm}^{-3}\text{)} \times \text{volume (dm}^{3}\text{)}$$

$$= \frac{\text{mass of X (g)}}{\text{molar mass of X (g mol}^{-1}\text{)}}$$

Note: 1 dm^3 = 1000 cm^3 = 10^{-3} m^3 ; 1 cm^3 = 10^{-3} dm^3 = 10^{-6} m^3

Dilution

When a solution is diluted (by adding more solvent), the concentration of the solution decreases but the ***number of moles of the solute in the diluted solution remains unchanged***.

Lecture Exercise 2.4

14.3 g of hydrated sodium carbonate, $Na_2CO_3 \bullet 10H_2O$ (M_r = 286.0) were dissolved in water and the solution made up to 500 cm^3 using a volumetric flask. What is the concentration of sodium ions in the solution?

Self-practice 2.4

1. Calculate the volume, in cm^3, of a solution required to provide 0.85 g of ethanoic acid (CH_3CO_2H, $M_r = 60.0$) from a 0.30 mol dm^{-3} solution. **[47.2 cm^3]**

2. Agricultural biochemists often use 6-benzylaminopurine ($C_{12}H_{11}N_5$) in trace amounts as a plant growth regulator. In a typical application, 150 cm^3 of a solution contains 0.030 mg of the compound. What is the concentration of the solution? **[8.89×10^{-7} mol dm^{-3}]**

3. A sample of concentrated nitric acid solution has a density of 1.41 g cm^{-3} and contains 70.0% HNO_3 by mass. What is the concentration of the solution? **[15.7 mol dm^{-3}]**

Lecture Exercise 2.5

1. 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.

2. What would be the concentration of the final mixture made by combining 385 cm^3 of 0.725 mol dm^{-3} HCl and 525 cm^3 of 0.325 mol dm^{-3} HCl?

Self-practice 2.5

1. What is the volume of 0.0500 mol dm^{-3} $K_2Cr_2O_7$ solution required to prepare 500 cm^3 of 0.0200 mol dm^{-3} $K_2Cr_2O_7$ solution? **[200 cm^3]**

2. Calculate the concentration of Na^+ ions in a solution made by mixing 3.58 cm^3 of 0.288 mol dm^{-3} sodium chloride with 500 cm^3 of 6.51×10^{-3} mol dm^{-3} sodium sulfate. **[1.50×10^{-2} mol dm^{-3}]**

3. 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? **[243 cm^3]**

Generic procedure for preparing a solution from a solid

1. Using an electronic balance, **weigh** accurately about (mass) g of (solid) in a weighing bottle.
2. Transfer the solid into a 100 cm^3 beaker and **dissolve** the solid completely in some deionised water / (given solvent). **Reweigh** the weighing bottle to account for any remaining solid that is not transferred into the beaker.
3. **Transfer** the solution into a 250 cm^3 **volumetric flask**. Rinse the beaker a few times and transfer all washings into the volumetric flask.
4. **Top up to the mark** with deionised water / (given solvent).
5. **Stopper and shake well** to obtain a homogeneous solution.

volumetric flask

Note:

The beaker must be rinsed thoroughly (in step 3) to ensure complete transfer of solution. To prepare a standard solution by diluting a given solution, replace steps 1 to 3 with: "Using a burette (or pipette), place (volume) cm^3 of (solution) in a 250 cm^3 volumetric flask."

Table of recordings

mass of empty weighing bottle / g	
mass of weighing bottle and solid / g	
mass of weighing bottle and residual solid / g	
mass of solid used / g	

Preparing a series of solutions of different concentrations

To prepare a series of solutions of different concentrations, you need to mix the original solution of known concentration (sometimes called 'stock solution') with the solvent or another solution. Pipettes / burettes and volumetric flasks (100 cm^3 or 250 cm^3) are used for the accurate measurement of volumes of liquids.

$$\text{new concentration} = \text{original concentration} \times \frac{\textit{volume of original solution used for mixing}}{\textit{total volume after mixing}}$$

You need to decide the **range of concentrations** (it depends on the purpose of the experiment), and the **total volume** of each solution required. If your solution is required for a subsequent titration procedure, then the total volume must be sufficient for at least three titrations.

For example, your desired range is from 0 to 2.00 mol dm^{-3} at equal intervals of 0.5 mol dm^{-3}, and you need 100 cm^3 of each solution, you may present your plan in a table as shown:

solution	volume of original 2.00 mol dm^{-3} H_2SO_4 used / cm^3	total volume after dilution / cm^3	(new) $[H_2SO_4]$ / mol dm^{-3}
1	75.00	100	1.50
2	50.00	100	1.00
3	25.00	100	0.50

Generic procedure for preparing a series of solutions by dilution

1. Using a burette / pipette, add (volume) of the (original solution) to a 100 cm^3 (or 250 cm^3) volumetric flask.
2. Top up to the mark with (deionised water) .
3. Stopper and shake well to obtain a homogeneous solution.
4. Repeat steps 1 to 3, according to the volumes stated in the table above.

In the situation where you are required to prepare a very dilute solution, say 0.010 mol dm^{-3}, it would mean you measure 0.5 cm^3 of stock solution to top up to 100 cm^3, and this will give rise to a large measurement error. In this case, you may consider a **serial dilution method**, i.e. instead of adding water to the stock solution, you may add water to *successively diluted* solutions. This means that solution 2 is prepared from solution 1, solution 3 from solution 2, and so on.

solution	$[H_2SO_4]$ / mol dm^{-3}
1	2.00
2	1.00
3	1.00×10^{-1}
4	1.00×10^{-2}

Possible procedure:

1. Using a burette, add 50.0 cm^3 of solution 1 to a 100 cm^3 volumetric flask.
2. Top up to the mark with deionised water.
3. Stopper and shake well to obtain a homogeneous solution. Label this solution 2.
4. To prepare solutions 3 and 4, repeat steps 1 to 3 using 10.0 cm^3 of solutions 2 and 3 respectively instead of solution 1.

3 ACID-BASE REACTIONS

Acids and bases are important in many chemical processes that occur around us, from industrial processes to biological ones and from reactions in the laboratory to those in our environment.

The concept of acids and bases has broadened over time as chemists seek to propose a more comprehensive model to classify, rationalise and predict acid-base chemistry. The current understanding of acids and bases is primarily based on the historical contributions of chemists such as Svante Arrhenius, Johannes Bronsted, Thomas Lowry, and Gilbert Newton Lewis.

3.1 Definitions of Acids & Bases

3.1.1 Arrhenius Theory of Acids & Bases

- An acid is a substance that dissociates in water to produce $H_3O^+(aq)$.
  E.g. $HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

Note:
In aqueous solution, H^+ (a 'bare' proton) does not exist on its own. Instead, it forms a dative bond with a water molecule to form H_3O^+, called **hydronium or hydroxonium ion**. Chemists often use $H^+(aq)$ and $H_3O^+(aq)$ interchangeably to refer to the solvated H^+ ion.

- A base is a substance that dissociates in water to produce $OH^-(aq)$.
  E.g. $NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

- When an acid is added to a base, according to Arrhenius, the H^+ ion reacts with the OH^- ion to produce a molecule of water, and undergoes *neutralisation*.

  E.g. $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

  Ionic equation: $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

  The $Na^+(aq)$ and $Cl^-(aq)$ ions do not take part in the reaction. They are called '*spectator ions*'.

The limitation of this model is that it is restricted to aqueous solutions only. This limitation could be addressed through the introduction of the Bronsted-Lowry acid-base model.

3.1.2 Bronsted-Lowry Theory of Acids & Bases

- **An acid** is defined as any species which **donates a proton, H^+**.
  An acid must thus contain H in its formula. E.g. HNO_3 and $H_2PO_4^-$.

- **A base** is defined as any species which **accepts a proton, H^+**.
  A base must contain a lone pair of electrons to bind the H^+ ion. E.g. NH_3, CO_3^{2-}, F^- and OH^-.

A Bronsted-Lowry **acid-base reaction** involves the **transfer of a proton from an acid to a base**. Bronsted-Lowry acid-base reactions do not only occur in aqueous solutions. They can also occur between gases and non-aqueous systems. E.g. $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$.

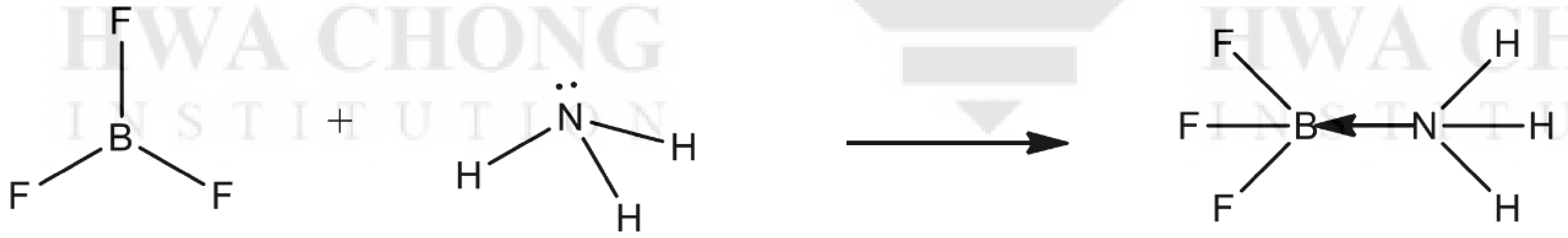
While the Bronsted-Lowry acid-base model is more inclusive than Arrhenius model, it still could not explain why substances such as BF_3 or $AlCl_3$ which do not contain any hydrogen atom but are yet known to behave as acids. This limitation is addressed through the introduction of the Lewis acid-base model.

3.1.3 Lewis Theory of Acids & Bases

- An acid is a species that accepts an electron pair, e.g. BF_3
- A base is a species that donates an electron pair, e.g. NH_3

A Lewis **acid-base reaction** can be viewed as a **transfer of a pair of electrons from the base to the acid**.

E.g. $BF_3 + NH_3 \rightarrow BF_3{\bullet}NH_3$



Recall in Topic 2 Chemical Bonding we learnt that BF_3 and NH_3 can react to form white solid NH_3BF_3. This can be considered an acid-base reaction according to the Lewis model. You will encounter more examples of Lewis acids and bases later in your A-Level course in organic chemistry.

Note:

The limitation of this theory is that it is too general. Thus, it is better to use the Bronsted-Lowry theory whenever possible for acid-base reactions, and apply Lewis theory only if the reaction does not involve proton transfer.

Lecture Exercise 3.1

Identify the Bronsted acid and base in each of the following (forward) reactions:

1. $HNO_3(aq) + NH_3(aq) \rightarrow NO_3^-(aq) + NH_4^+(aq)$

2. $HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$

3. $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$

4. $HNO_3(l) + H_2SO_4(l) \rightarrow H_2NO_3^+(aq) + HSO_4^-(aq)$

The three models of acids and bases can be used to interpret different acid-base systems. Bronsted-Lowry and Lewis theories are often used to describe specific acid-base reactions whereas Arrhenius theory is used to describe whether isolated substances are acids, bases or neither.

For example, in the case of nitric acid:

- Using Arrhenius model, nitric acid is an Arrhenius acid as it generates hydronium ions in the presence of water.

- Using Bronsted-Lowry model, nitric acid can be either Bronsted-Lowry acid or base, as seen in Lecture Exercise 3.1. It depends on what nitric acid reacts with. For instance, if it reacts with an alkali such as aqueous sodium hydroxide, it acts as a Bronsted-Lowry acid. If nitric acid reacts with a stronger acid such as sulfuric acid, it behaves like a Bronsted-Lowry base. (The concept of 'strength of acid' will be dealt with in Topic 15 Acid-Base Equilibria)

3.2 Titrations

Titration (or volumetric analysis) is a technique where a solution is gradually added from a burette to a fixed volume of another solution, i.e. the aliquot (measured with a pipette and placed in a conical flask), until the reactants in the two solutions have reacted completely. Titration is suitable for reactions in which the reactants react rapidly and completely.

It is used to obtain quantitative information such as the concentration of a solution or to establish the stoichiometry of a reaction. Usually one of the solutions used must be of an accurately known concentration, and this is called the **standard solution**.

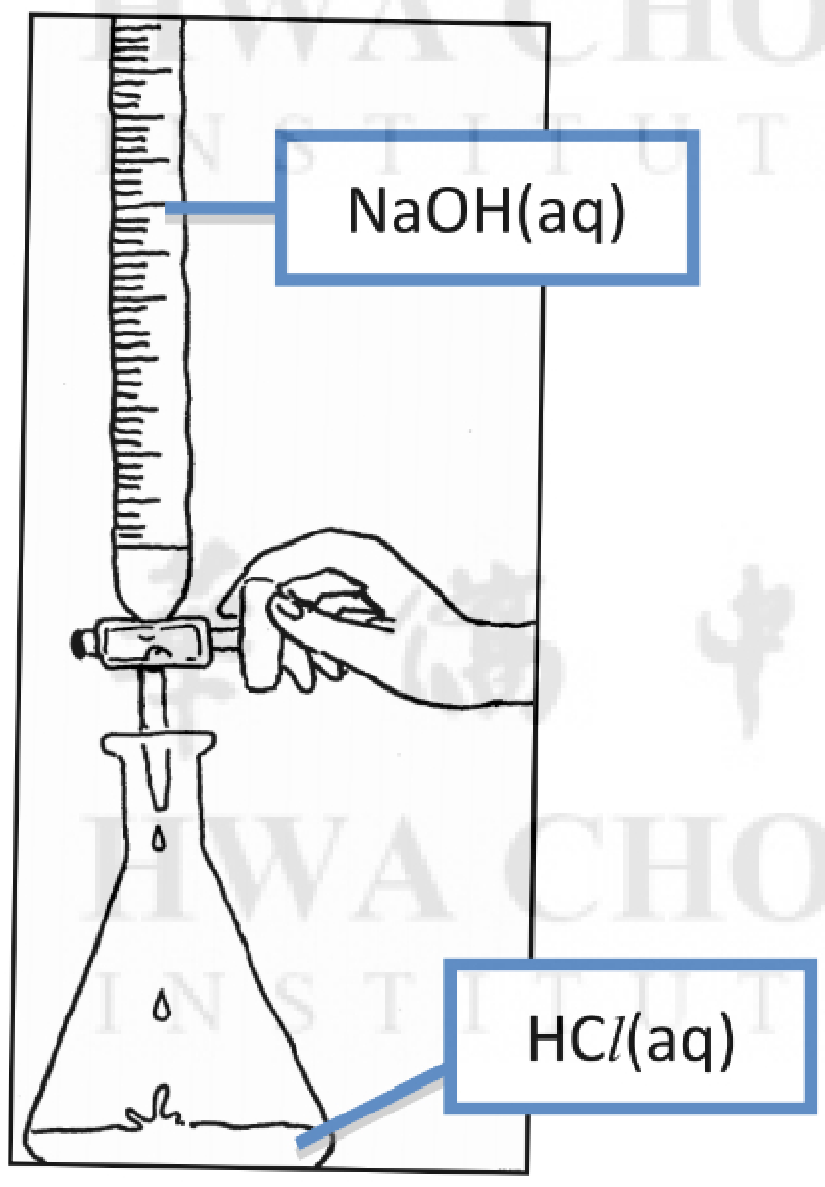
The **equivalence point** occurs when the reactants in the two solutions react according to the stoichiometry of the reaction. The volume of solution added from the burette is the **titre** volume.

For an acid-base titration, the completion of the reaction is often found by noting the colour change of an indicator added to the reaction flask. The point where the indicator changes colour is known as the **end point**.

Indicators for acid-base titration have distinct colours in the 'acid' and 'base' region as shown in Table 2. At certain pH, called the **working range**, the indicator will change its colour.

Table 2 – Some common indicators

indicators	pH working range	'acid' region	'base' region	colour at end point
methyl orange	3.1 – 4.4	red	yellow	orange
screened methyl orange	3.0 – 4.6	violet	green	grey
bromothymol blue	6.0 – 7.6	yellow	blue	green
phenolphthalein	8.0 – 9.6	colourless	pink	pink
thymol blue	8.0 – 9.6	yellow	blue	green



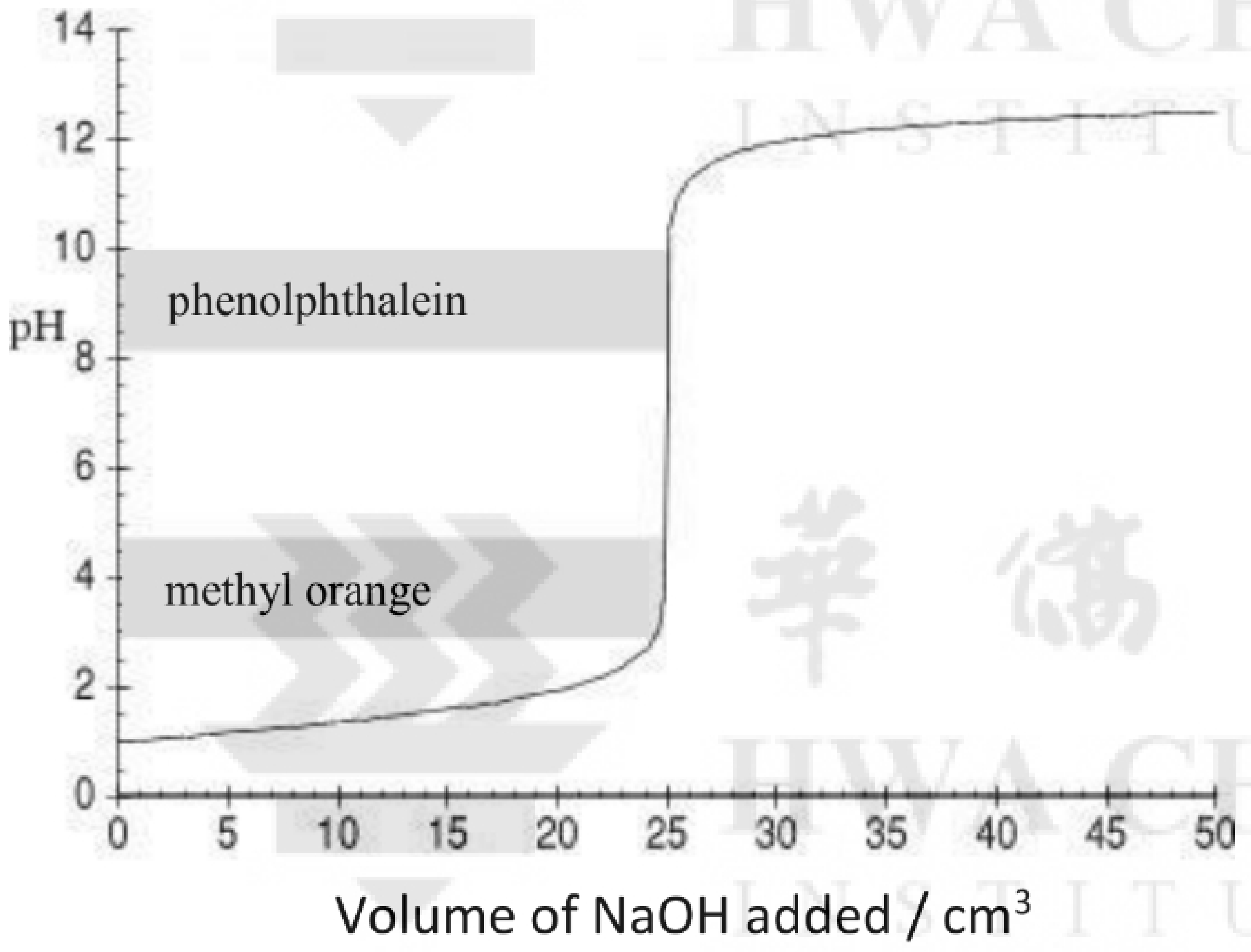


Figure 2. Titration curve of a strong acid-strong base titration. (Titration curves will be covered in Topic 15 Acid-Base Equilibria.)

Generic procedure for titration

1. **Pipette** (volume) cm^3 of (solution X) into a 250 cm^3 conical flask.
2. Add 2 to 3 drops of (suitable indicator) (for acid–base titration).
3. Fill a **burette** with (known concentration in mol dm^{-3}) (solution Y). Record the initial burette reading.
4. **Titrate** (solution X) against (solution Y) until the colour of the solution changes from (initial colour) to (colour at end-point). Record the final burette reading.
5. **Repeat titration until two consistent titres** within **±0.10 cm^3** are obtained.

Table of recordings

final burette reading / cm^3			
initial burette reading / cm^3			
volume of (solution Y) used / cm^3			

Note:

- For $KMnO_4$ titrations, replace step 2 with "Add (volume) cm^3 of dilute H_2SO_4 using a measuring cylinder". (To ensure that the acid is in excess. Normal laboratory concentration of H_2SO_4 is 1.0 mol dm^{-3}.) *{Refer to Section 4.4.1 Potassium manganate(VII) titration}*

- For I_2 / $S_2O_3^{2-}$ titrations, remove step 2, and replace step 4 with: Titrate the I_2 against $Na_2S_2O_3$(aq) until the solution changes (from brown) to pale yellow, then add 10 drops (or 1 cm^3) of starch solution which gives an intense dark blue-black colour, then continue titration until the blue-black colour just disappears. *{Refer to Section 4.4.2 Iodometric titrations – iodine / thiosulfate titration}*

Choice of indicators for titrations

type of titration	indicator	colour change
I_2 – thiosulfate (in burette)	starch solution (add 1 cm^3 or 10 drops when solution turns pale yellow)	blue-black to colourless
Fe(II) – $KMnO_4$ (in burette)	–	yellow to orange
strong acid – weak base (in burette)	methyl orange	red to orange
weak acid – strong base (in burette)	phenolphthalein	colourless to pink
weak acid – strong base (in burette)	thymol blue	yellow to green

Note:

- For acid-base titrations, the choice of indicators depends on the strength of the acid and base, i.e. whether the acid/base is strong/weak. This table shows the suitable indicator for different combinations of acid/base strengths.

- For $KMnO_4$ titrations, refer to Section 4.4.1.
- For $I_2/S_2O_3^{2-}$ titrations, refer to Section 4.4.2.

- For all procedures, state clearly when titration should be stopped, i.e. from ___(colour in conical flask at start of titration)___ to ___('midway' colour of indicator)___. For example, from strong acid-weak base (in burette), stop titration when methyl orange changes from red to orange (not yellow).

- If the positions of the reagents are reversed, e.g. strong acid (in burette) – weak base, the colour change is also reversed, i.e. methyl orange changes from yellow to orange (not red).

Lecture Exercise 3.2

A student was given solutions of HC*l* and NaOH with unknown concentrations. He carried out titrations and found that 27.50 cm^3 of the NaOH solution was required to completely react with 100 cm^3 of the HC*l* solution. In a separate experiment, he used 18.40 cm^3 of the NaOH solution to titrate completely 50.00 cm^3 of a 0.0782 mol dm^{-3} H_2SO_4. What are the concentrations of the given HC*l* and NaOH solutions?

Self-practice 3.1

27.82 g of hydrated sodium carbonate crystals with the formula $Na_2CO_3 \bullet nH_2O$ were dissolved in water and made up to 1.00 dm^3 aqueous solution. 25.0 cm^3 of this solution was neutralised by 48.80 cm^3 of 0.100 mol dm^{-3} dilute HC*l*. Find the value of *n*. **[10]**

3.3 Back Titration

In a back titration, a **known excess of one reagent A** is allowed to react with an **unknown amount of B**. The amount of **unreacted A** is then determined by **<u>titration</u> with a reagent C of known concentration**. From the titration results, the amount of unreacted **A** and the amount of **B** can be found by simple stoichiometric calculations.

In summary

$$\text{Total } \eta_A = \eta_A \text{ that reacted with } \mathbf{B} + \overbrace{\eta_A \text{ that reacted with } \mathbf{C}}^{\textit{amount of unreacted A found from titration results}}$$

General Steps:

1) Determine the amount of **C** required in the titration.
2) Using stoichiometry, find amount of **A** that reacted with **C** in the titration.
3) Note: amount of **A** that reacted with **C** in the titration
   = amount of **A** that did not react with **B** earlier
4) Therefore, amount of **A** that reacted with **B**
   = total amount (known excess) of **A** added – amount of **A** that did not react with **B** earlier
5) Knowing now the amount of **A** that reacted with **B**, using stoichiometry, the amount of **B** is found.

Lecture Exercise 3.3

1. A sample of impure magnesium was analysed by allowing it to react with excess HCl solution. After 1.32 g of the impure metal was treated with 100 cm^3 of 0.750 mol dm^{-3} HCl, the remaining solution required 50 cm^3 of a 0.250 mol dm^{-3} aqueous sodium hydroxide for complete neutralisation. Assuming the impurities do not react with the acid, what is the percentage by mass of Mg in the sample?

2. 1.60 g of a metallic oxide, MO, was dissolved in 100 cm^3 of 1.0 mol dm^{-3} HC*l*. The resulting liquid was made up to 500 cm^3 with distilled water. 25.0 cm^3 of this solution required 21.05 cm^3 of a 0.1020 mol dm^{-3} sodium hydroxide for neutralisation. Calculate:

(i) the mass of the oxide that reacts with 1 mole of HC*l*,

(ii) the relative formula mass of the oxide and the relative atomic mass of the metal.

Self-practice 3.2

A sample containing ammonium chloride was warmed with 100 cm^3 of 1.00 mol dm^{-3} sodium hydroxide. 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 neutralisation. What mass of ammonium chloride did the sample contain? **[4.01 g]**

4 REDOX REACTIONS

4.1 Definitions

Redox reaction: A reaction that involves **red**uction and **ox**idation simultaneously.

In 'O' Level, we have defined reduction and oxidation processes in terms of gain or loss of H or O. At 'A' Level, we shall further define these processes in terms of ***electron transfer*** and/or ***changes in oxidation number (oxidation state)***.

Reduction: A process whereby a substance **gains electrons**, resulting in a **decrease in oxidation number**.
e.g. $Cu^{2+} + 2e^{-} \rightarrow Cu$

Oxidation: A process whereby a substance **loses electrons**, resulting in an **increase in oxidation number**.
e.g. $Zn \rightarrow Zn^{2+} + 2e^{-}$ ☞ *Acronym: O I L R I G*

Reducing agent (reductant): A substance that **gives electrons** to another, **itself being oxidised** in the process.
e.g. Fe^{2+}, $C_2O_4^{2-}$, I^{-}, $S_2O_3^{2-}$

Oxidising agent (oxidant): A substance that **takes in electrons** from another, **itself being reduced** in the process.
e.g. MnO_4^{-}, $Cr_2O_7^{2-}$, H_2O_2, I_2

Disproportionation: A redox reaction in which the **same substance** is **both oxidised and reduced**.
e.g. $3Cl_2 + 6OH^{-} \rightarrow 5Cl^{-} + ClO_3^{-} + 3H_2O$

Oxidation number (oxidation state): The number of electrons to be added or subtracted from an atom in a combined state to convert it to elemental form.

- When writing the oxidation number (O.N.), the +/– signs **<u>must</u>** be stated before the number.
- For a covalent compound, the covalent bond is 'converted' to ionic by assigning the shared electrons to the more *electronegative* atom, such that the oxidation numbers of the atoms are therefore the 'charges' on the 'ions'.

4.2 Assigning Oxidation Number

	example
• For an atom in its elemental form, oxidation number = 0	O.N. of Na = 0, O.N. of O in O_2 = 0
• For a monoatomic ion, oxidation number = charge on the ion	O.N. of Mg in Mg^{2+} = +2 O.N. of I in I^- = –1
• For a polyatomic ion, sum of all the oxidation numbers = charge on the polyatomic ion	In MnO_4^-, (O.N. of Mn) + 4(O.N. of O) = –1 ∴ O.N. of Mn = +7
• For a neutral compound, sum of all the oxidation numbers = 0	In Fe_2O_3, 2(O.N. of Fe) + 3(O.N. of O) = 0
• For a compound, the more electronegative element is given the negative oxidation number.	In ClF, O.N. of F = –1; O.N. of Cl = +1 In HCl, O.N. of H = +1; O.N. of Cl = –1 In NaH, O.N. of H = –1

Some elements nearly always exhibit the same oxidation number in their compounds. Hence, they are used as reference points in assigning oxidation numbers to other elements. For example,

hydrogen, H	+1, except in metal hydrides (e.g. NaH) where O.N. is –1
oxygen, O	–2, except in peroxides (e.g. H_2O_2) where O.N. is –1
Group 1 metals: Li, Na, K, Rb, Cs, Fr	+1
Group 2 metals: Be, Mg, Ca, Sr, Ba, Ra	+2
aluminium, Al	+3
fluorine, F	–1

Self-practice 4.1

State the oxidation number of the underlined element in the following:

(i) $\underline{C}H_3OH$ (ii) $\underline{S}_8$ (iii) $\underline{Br}F_3$ (iv) $H\underline{N}O_2$ (v) $Ca(H\underline{C}O_3)_2$

[(i) –2, (ii) 0, (iii) +3, (iv) +3, (v) +4]

Lecture Exercise 4.1

Identify the type of reactions represented in the following equations.
Which are the reducing and oxidising agents for the redox reactions?

(i) $NO_3^-(aq) + 4Zn(s) + 7OH^-(aq) + 6H_2O(l) \rightarrow 4Zn(OH)_4^{2-}(aq) + NH_3(aq)$

(ii) $KCl(aq) + AgNO_3(aq) \rightarrow KNO_3(aq) + AgCl(s)$

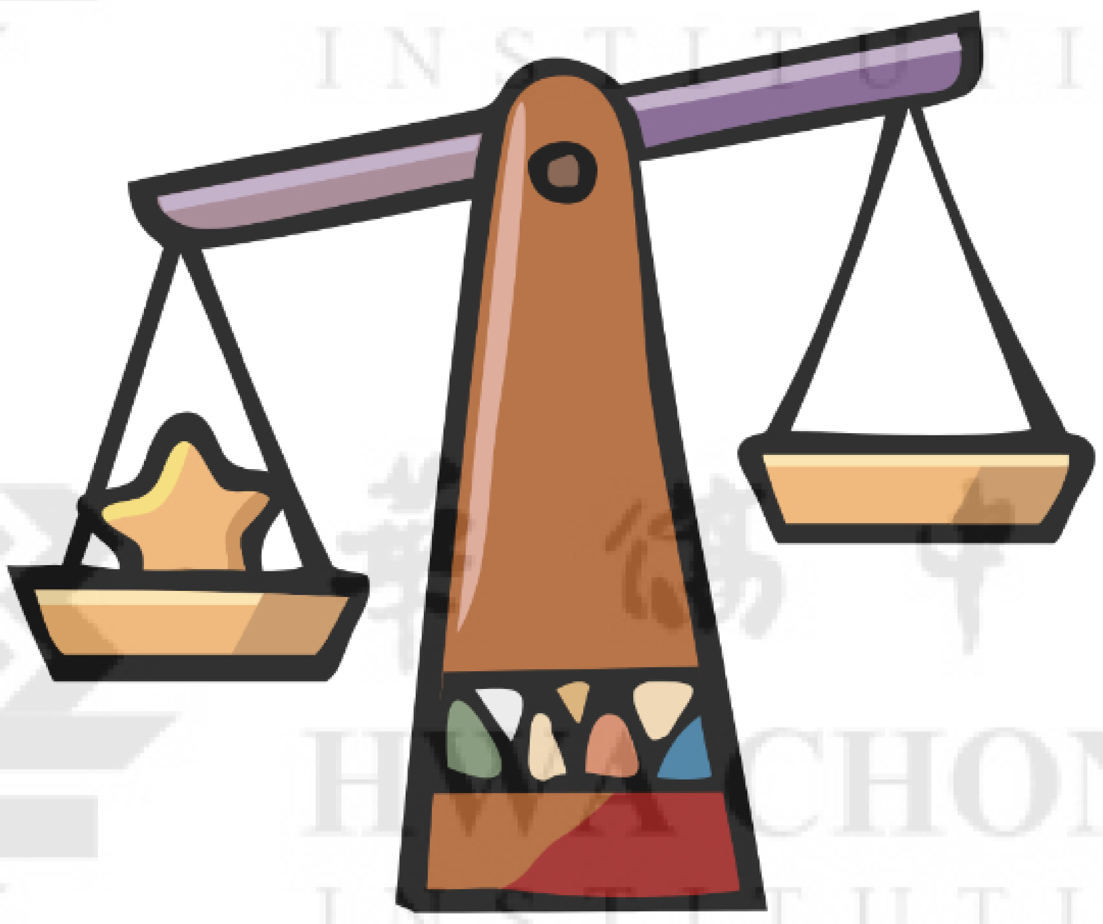
(iii) $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

(iv) $H_2O_2(aq) + 2Fe^{2+}(aq) + 2H^+(aq) \rightarrow 2Fe^{3+}(aq) + 2H_2O(l)$

4.3 Balancing Redox Equations

In a redox reaction, there is a transfer of electrons from the reducing agent (which loses electrons and is oxidised) to the oxidising agent (which gains electrons and is reduced).

Hence, in a balanced redox equation, the number of electrons lost by the reducing agent must be *equal* to the number of electrons gained by the oxidising agent, i.e. there are *no free electrons* in the overall balanced equation. Once again, the Law of Conservation of Mass applies here.



Here are two methods that can be used to balance redox equations:

Method 1

1. Divide the unbalanced ionic equation into two half-equations (*an oxidation half-equation and a reduction half-equation*).
2. For each half-equation,
   - Balance all atoms other than O and H.
   - Balance O by adding H_2O.
   - Balance H by adding H^+. For a redox reaction under **basic** conditions, additional steps to take include:
     i. add to both sides of the half-equation the same number of OH^- to neutralise the H^+ present,
     ii. combine H^+ and OH^- to form H_2O,
     iii. simplify the half-equation by cancelling any extra H_2O.
   - Balance the charges by adding electrons. (*The oxidation half-equation will have electrons on the right-hand side while the reduction half-equation will have electrons on the left-hand side.*)
3. Multiply each half-equation by an appropriate integer, if necessary, to make electrons lost = electrons gained (because number of electrons lost by reducing agent = number of electrons gained by oxidising agent).
4. Add the two half-equations (electrons on both sides must cancel out each other).
5. Simplify by cancelling any extra species appearing on both sides.
6. Make a final check that the redox equation is balanced in terms of atoms and charge.

Method 2 (by change in oxidation number)

1. Divide the unbalanced ionic equation into two half-equations (*an oxidation half-equation and a reduction half-equation*).
2. Balance each half-equation as follows:
    - Work out the oxidation number of the relevant elements in the reactant and product.
    - Balance the elements undergoing oxidation or reduction.
    - Add the appropriate number of electrons **according to the change in oxidation numbers** of elements, taking into account the number of each element in the formula unit.
    - Balance the charges on both sides of the half-equation by adding the appropriate number of H^+ (under acidic conditions) or OH^- (under alkaline conditions). Under neutral conditions, either H^+ or OH^- can be used.
    - Balance the O (or H) atoms by adding H_2O on the appropriate side.
    - Check the number of H (or O) atoms on both sides – it should be balanced.

Follow steps 3 – 6 of Method 1.

Lecture Exercise 4.2

Balance the following redox reactions.

(i) $Cr_2O_7^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}$ (acidic)

(ii) $Cl_2 \rightarrow Cl^- + ClO_3^-$ (basic)

Self-practice 4.2

Balance the following redox reaction.

$H_2O_2 + I^- \rightarrow I_2 + H_2O$ (acidic)

$TcO_4^- + As \rightarrow Tc + AsO_2^-$ (basic)

4.4 Redox Titrations

In a redox titration, a known concentration of oxidising agent is used to find an unknown concentration of reducing agent (or *vice versa*). Redox titrations are also used to establish the stoichiometry of redox reactions. The calculations involved are based on the mole concept, similar to acid-base titrations.

Table 3 – Common oxidising agents

oxidant	reaction medium	product
MnO_4^- (purple)	acidic	Mn^{2+} (colourless)
	alkaline	MnO_2 (dark brown solid / ppt)
$Cr_2O_7^{2-}$ (orange)	acidic	Cr^{3+} (green)
I_2 (brown in aqueous solution)	neutral	I^- (colourless)
H_2O_2 (colourless)	acidic	H_2O

Table 4 – Common reducing agents

reductant	reaction medium	product
Fe^{2+} (pale green)	acidic	Fe^{3+} (yellow)
I^- (colourless)	acidic/alkaline/neutral	I_2 (brown in aqueous solution)
$S_2O_3^{2-}$ (colourless)	neutral	$S_4O_6^{2-}$ (colourless)
H_2O_2 (colourless)	acidic	O_2
$C_2O_4^{2-}$ (colourless)	acidic	CO_2

4.4.1 Potassium Manganate(VII) titration

1. The $KMnO_4$ solution is usually placed in the burette and added into the conical flask containing the reductant (e.g. Fe^{2+} determination)

2. Typical reducing agents that can react with $KMnO_4$ are: Fe^{2+}, $C_2O_4^{2-}$, H_2O_2 and I^-

3. Manganate(VII) titrations are usually carried out in ***acidic*** conditions. The acid used is sulfuric acid (usually at 1 mol dm^{-3}) and added into the conical flask.
   Note: *Nitric acid and hydrochloric acid are both not suitable as nitric acid is itself an oxidising agent while hydrochloric acid can be oxidised by manganate(VII) ion to give chlorine.*

Relevant half-equation: $\mathbf{MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O}$

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

5. When all the reductant is used up, the first extra drop of $KMnO_4$ makes the solution in the conical flask turn permanently **pink**. This sharp colour change indicates that the end-point is reached. Hence no other indicator is required.

4.4.2 Iodometric titrations – iodine / thiosulfate titration

Iodine is often used to oxidise thiosulfate ions to tetrathionate ions, itself reduced to iodide.

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

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

2. During the titration, the thiosulfate is added from the burette into the flask and reduces brown iodine into colourless iodide ions. The solution gradually fades to pale yellow.

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

4. Titration then continues till all iodine is used up. Colour change at the end-point is from **blue-black to colourless**.

Points to note when conducting iodometric titration

a) The iodine solution should be titrated as soon as possible once it is prepared. Why?

Iodine is volatile and will vaporise easily at room temperature hence titration must be carried out as soon as possible. If this is not possible, cover all flasks containing iodine.

b) Why is the starch indicator added only towards the end of titration when the iodine solution is pale yellow, instead of right at the start?

Starch forms a blue-black water-soluble complex with iodine in which the iodine is trapped within the starch molecules. Hence, starch should not be added at the beginning of the titration when there is a high concentration of iodine since some iodine may remain trapped in the starch even at the equivalence point.

c) After titration is complete, a slow return of the blue colour is observed. Why is this so? Should we continue our titration?

This is due to atmospheric oxidation of I^- back to I_2.
Ignore any slow return of blue colour after the titration is done.

Iodometric back titrations are often used to analyse redox reactions involving some other oxidants (e.g. H_2O_2) that can oxidise iodide to iodine. This analysis takes place in two steps:

i. A known excess of potassium iodide solution is added to the oxidant (with unknown concentration) in a conical flask to liberate iodine. (*Note: Excess* I^- *ensures all the oxidant is reacted and serves to dissolve iodine in aqueous solution.*)
Example: $H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$

ii. The iodine liberated is then titrated with standard thiosulfate solution from a burette. From the titration results, the amount of iodine liberated, and hence the amount of oxidant can be determined.

Lecture Exercise 4.3

1. 27.50 cm^3 of a 0.0200 mol dm^{-3} solution of acidified potassium manganate(VII) was required to oxidise a 25.0 cm^3 solution of hydrogen peroxide. What was the concentration of hydrogen peroxide and the volume of oxygen (at *s.t.p.*) evolved during the titration?

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

Self-practice 4.3

Chlorine reacts with iodine to form a compound **T**, ICl_7. When dissolved in an excess of aqueous potassium iodide, **T** liberates iodine, I_2, which is the only iodine-containing product in the reaction.

$$\underset{\mathbf{T}}{ICl_7} + 7I^- \rightarrow 4I_2 + 7Cl^-$$

(i) Calculate the number of moles of iodine liberated when 1.00 g of **T** reacts with an excess of aqueous potassium iodide.

(ii) What volume of 1.00 mol dm^{-3} sodium thiosulfate would be required to react with all the iodine liberated in **(i)**?

[(i) 0.0107 mol, (ii) 21.3 cm^3]

4.5 Application of Oxidation Number and Electron Transfer

General Strategy:

To determine the change in oxidation number of **B** when a known amount of **A** reacts with stoichiometric amount of **B** in a redox reaction, the following steps can be taken:

1) Construct the half-equation for **A**, the reactant whose initial and final oxidation numbers are known.
2) Calculate the number of moles of electrons lost (or gained) using amount of **A**. Equate this to the number of moles of electrons gained (or lost) by the other reactant (**B**).
3) Determine the mole ratio of **B** and the electrons gained (or lost) by **B**. This gives the number of moles of electrons transferred for 1 mol of **B**.
4) Hence determine the new oxidation number of **B**.

Lecture Exercise 4.4

1. In an experiment, 50.0 cm^3 of a 0.10 mol dm^{-3} solution of a metallic salt reacted exactly with 25.00 cm^3 of a 0.1 mol dm^{-3} aqueous sodium sulfite. The half-equation for the oxidation of sulfite is shown below.

$$SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$$

If the original oxidation number of the metal in the salt was +3, what would be the new oxidation number of the metal?

2. 25.0 cm^3 of a solution of 0.0200 mol dm^{-3} potassium ethanedioate, $K_2C_2O_4$, reacted with 20.0 cm^3 of an acidified solution of 0.0100 mol dm^{-3} potassium manganate(VII).

Find the oxidation number of carbon in the product and hence suggest the identity of this product.

Self-practice 4.4

In a redox reaction, 1 mol of $S_2O_3^{2-}$ is oxidised by 4 mol of Cl_2. Which of the following is the sulfur-containing product of this reaction?
S , SO_2 , SO_3^{2-}, SO_4^{2-}, $S_4O_6^{2-}$

[SO_4^{2-}]

LOOKING AHEAD

The stoichiometry concepts learnt in this topic will be applicable in almost all future topics where you are required to write balanced equations for all reactions, and work out quantities of reagents to be used (e.g. in organic synthesis) etc. Our knowledge of redox reactions and acid-base reactions will also be expanded in the extension topics of electrochemistry and acid-base equilibria.