01 Atomic Structure & Physical Periodicity

GUIDING QUESTIONS

- What makes up an atom?
- How has the understanding of atomic structure developed and evolved?
- What is the evidence to show electrons in an atom exist in discrete energy levels?
- What do you understand by electronic configuration? How are the electrons arranged in the atoms of a given element?
- How is the arrangement of electrons of an element and its position in the Periodic Table related?
- What are the trends and variations in the physical properties in elements?
- How can the trends and variations in atomic and physical properties be explained?
- What are transition elements?
- Are there any trends/patterns in the properties of transition elements?

LEARNING OUTCOMES

Students should be able to:

1(a) identify and describe protons, neutrons and electrons in terms of their relative charges and relative masses

1(b) deduce the behaviour of beams of protons, neutrons and electrons in an electric field

1(c) describe the distribution of mass and charges within an atom

1(d) deduce the numbers of protons, neutrons and electrons present in both atoms and ions given proton and nucleon numbers (and charge)

1(e) **(i)** describe the contribution of protons and neutrons to atomic nuclei in terms of proton number and nucleon number

(ii) distinguish between isotopes on the basis of different numbers of neutrons present

1(f) describe the number and relative energies of the s, p and d orbitals for the principal quantum numbers 1, 2 and 3 and also the 4s and 4p orbitals

1(g) describe the shapes of s, p and d orbitals (Refer also to Topic 22 Chemistry of the Transition Elements) [knowledge of wave functions is **not** required]

1(h) state the electronic configuration of atoms and ions given the proton number (and charge)

1(i) explain the factors influencing the ionisation energies of the elements (see the *Data Booklet*)

1(j) deduce the electronic configurations of elements from successive ionisation energy data

1(k) interpret successive ionisation energy data of an element in terms of the position of that element within the Periodic Table

5(a) recognise variation in the electronic configurations across a Period and down a Group

5(b) describe and explain qualitatively the general trends and variations in atomic radius, ionic radius, first ionisation energy and electronegativity (Refer also to Topic 2 Chemical Bonding for more on electronegativity)

(i) across a Period in terms of shielding and nuclear charge,

(ii) down a Group in terms of increasing number of electronic shells, shielding and nuclear charge

6(a) define the terms *relative atomic*, *isotopic*, molecular and formula mass (Refer to Topic 4 Reactions and Stoichiometry for molecular and formula mass)

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6(c) calculate the relative atomic mass of an element given the relative abundances of its isotopes

13(a) explain what is meant by a transition element, in terms of d-block elements forming one or more stable ions with partially filled d subshells

13(b) state the electronic configuration of a first row transition element and its ion

13 (c) explain why atomic radii and first ionisation energies of the transition elements are relatively invariant

REFERENCES

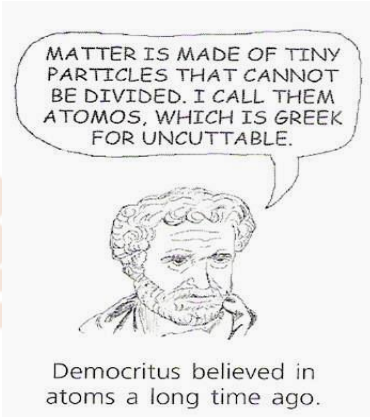
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1 THE STRUCTURE OF THE ATOM

1.1 The Discovery of the Subatomic Particles (Background Info)

The 5th century B.C. Greek philosopher *Democritus* proposed that one couldn't divide a piece of gold wire forever until there isn't any gold left as all matter consists of very small, indivisible particles. He called these particles *atomos*, meaning "uncuttable" or "indivisible". This concept remained undeveloped until nineteenth century.




Dalton's atomic theory may have been inspired by his favorite sport—lawn bowling.

In 1808, an English scientist and school teacher, *John Dalton* formulated the atomic theory that all matter is made up of atoms.

In 1897, *J.J. Thomson* proposed a model that described atoms as negatively charged electrons embedded in a sphere of positive charge, which was then known as the 'plum pudding' model.

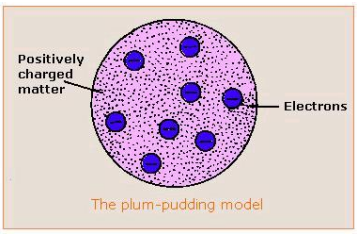


Figure 1. The plum-pudding model

In 1910, *Rutherford* observed that the majority of the α-particles passing through a thin sheet of gold foil went through with little deflection. But every now and then, he would observe great deflection. In some instances the particle actually bounced back. This surprising discovery led to the theory that the positive charge in the atom is concentrated into an incredibly small nucleus right in the middle of it. The diameter of the nucleus is less than 10^{-5} of the atom.

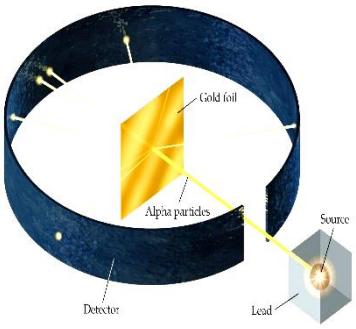


Figure 2. The gold foil experiment

Not until 1932 did the English physicist *James Chadwick* finally discover the neutron. He found it to be electrically neutral, having about the same mass as a proton. Together, the proton and neutron received the name "nucleon."

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1.2 Atoms and the Properties of the Three Subatomic Particles

LO 1(a): identify and describe protons, neutrons and electrons in terms of their relative charges and relative masses
LO 1(c): describe the distribution of mass and charges within an atom
LO 1(d): deduce the numbers of protons, neutrons and electrons present in both atoms and ions given proton and nucleon numbers (and charge)
LO 1(e)(i): describe the contribution of protons and neutrons to atomic nuclei in terms of proton number and nucleon number

An **atom** is the smallest component of an element having the chemical properties of the element.

All atoms are made up of the same three subatomic particles - the **electron**, the **proton** and the **neutron**.

The protons and neutrons make up the nucleus of the atom while the electrons surround the nucleus. The protons and neutrons are sometimes referred to as **nucleons**.

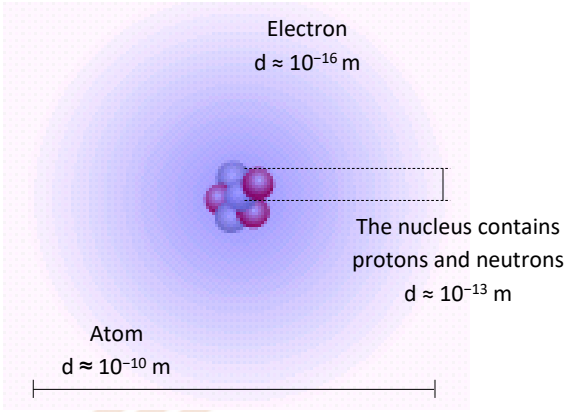


Figure 3. A schematic representation of an atom

The nucleus contains over 99.99% of the mass of an atom. This is due to the relatively large masses of the proton and neutron compared with the mass of the electron.

Table 1. Properties of the three subatomic particles.

property	proton	electron	neutron
relative charge	+1	−1	0
relative mass	1	$\frac{1}{1836}$	1

All atoms can be identified by the number of protons they contain. The chemical symbol is represented as

$${}^{A}_{Z}X$$

A Nucleon number
X Symbol for element
Z Proton number

E.g., ${}^{16}_{8}O$ has 8 protons, 8 electrons and 8 neutrons.

The ***proton number*** (**Z**) is the **number of protons in the nucleus of each atom** of an element.

In a neutral atom, the number of protons is equal to the number of electrons, so the proton number also indicates the number of electrons present in the atom. The chemical identity of an atom can be determined solely from its proton number.

The ***nucleon number*** (**A**), also called ***mass number***, is the **total number of neutrons and protons in the nucleus of an atom** of an element.

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1.3 Isotopes

LO 1(e)(ii): distinguish between isotopes on the basis of different numbers of neutrons present

Atoms of the same element do not all have the same mass. ***Isotopes*** are **atoms of an element that have the same proton number but different nucleon numbers** (or same number of protons but different number of neutrons).

Isotopes of an element have the **same** electronic configuration and chemical properties. They have **different** relative isotopic masses and physical properties.

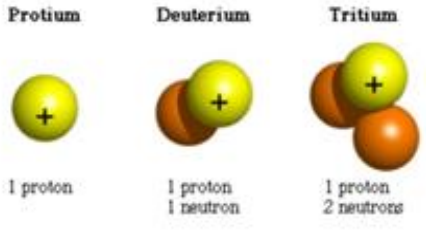


Figure 4. The nuclei of the three isotopes of hydrogen

Some common isotopes include: hydrogen (^{1}H, ^{2}H, ^{3}H), carbon (^{12}C, ^{13}C), oxygen (^{16}O, ^{18}O), sulfur (^{32}S, ^{34}S) and nitrogen (^{14}N, ^{15}N).

Isotopes may be stable or **unstable** (**radioactive**). E.g. the isotope ^{14}C decays by β-emission with a half-life of 5730 years.

When writing the chemical symbol for an element, it is not always necessary to write either or both the nucleon and proton numbers. E.g. $^{1}_{1}H$ may be written as ^{1}H or H. We assume the most abundant isotope is referred to when simply writing 'H' for example. However, when it is necessary to refer to a particular isotope of an element, the nucleon number as well as the proton number must be indicated e.g. if we want to refer to deuterium, then we should write $^{2}_{1}H$ for clarity's sake.

Exercise 1.1 (Worked Example)

Complete the following table with the no. of protons, neutrons and electrons for each particle.

		no. of protons	*no. of electrons*	*no. of neutrons*
(a)	$^{28}_{14}Si$			
(b)	$^{70}_{31}Ga^{3+}$			
(c)	$^{31}_{15}P^{3-}$			

Comments:

For each case, the subscript refers to the proton number (i.e. the number of protons present).

For (a), since it is a neutral atom, no. of protons = no. of electrons.
For (b), since it is positively charged, there should be 3 less electrons than protons. Hence, no. of electrons = 31 – 3 = 28.
For (c), since it is negatively charge, there should be 3 more electrons than protons. Hence, no. of electrons = 15 + 3 = 18.

The superscript refers to the nucleon number (i.e. the total number of protons and nucleons present). Thus, no. of neutrons = nucleon number – no. of protons.
For (a), no. of neutrons = 28 – 14 = 14
For (b), no. of neutrons = 70 – 31 = 39
For (c), no. of neutrons = 31 – 15 = 16

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Answer:

		no. of protons	*no. of electrons*	*no. of neutrons*
(a)	$^{28}_{14}Si$	**14**	**14**	**14**
(b)	$^{70}_{31}Ga^{3+}$	**31**	**28**	**39**
(c)	$^{31}_{15}P^{3-}$	**15**	**18**	**16**

Exercise 1.2

(a) Give the symbols of the elements (showing the nucleon numbers and charges) of the following three particles in the last column.

particle	protons	neutrons	electrons	*answer*
P	6	8	6	
Q	7	7	10	
R	8	7	7	

(b) Use the *Data Booklet* to identify which are not the usual isotopes of the elements concerned.

[J00/I/1b]

Exercise 1.3 (Worked Example)

In 1999 Russian chemists claimed to be the first to identify atoms of a new element of proton number 114. This was produced by bombarding atoms of plutonium, Pu, with atoms of an isotope of a Group 2 element, **X**. The reaction taking place is as shown below.

$$^{244}_{94}Pu + X \longrightarrow {}^{289}_{114}[\text{new element}] + 3 \text{ neutrons } (^{1}_{0}n)$$

What is **X**?

A Mg **B** Ca **C** Sr **D** Ba

[N03/I/4]

Answer: B

Comments:

Interpreting the numbers given for the atom of plutonium, $^{244}_{94}Pu$, we know that there are 94 protons (from the number at the bottom) and there are 150 neutrons.

If we look at the new element formed, we know that 20 protons (114 – 94) have been added into the new element. Referencing the periodic table, we can conclude that the element with proton number 20 is Calcium. The number of neutrons do not matter since the identity of an element is established by the number of protons.

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1.4 Ions and deflection of charged particles

LO 1(b): deduce the behaviour of beams of protons, neutrons and electrons in an electric field

A **negative** ion (**anion**) has **more** electrons than protons. It is represented by ${}^{A}_{Z}X^{n-}$ where the number of electrons = Z + n.

E.g., ${}^{16}_{8}O^{2-}$ has 8 + 2 = 10 electrons, 8 protons and 8 neutrons.

A **positive** ion (**cation**) has **fewer** electrons than protons. It is represented by ${}^{A}_{Z}X^{n+}$ where the number of electrons = Z – n.

E.g., ${}^{24}_{12}Mg^{2+}$ has 12 – 2 = 10 electrons, 12 protons and 12 neutrons.

Because of their relative masses and charges, protons, electrons and neutrons behave differently when placed in an electric field. Protons are deflected to the **negative** plate, electrons deflected to the **positive** plate, and neutrons being neutral **pass straight through**.

Similarly, **cations** are deflected to the **negative** plate and **anions** are deflected to the **positive** plate.

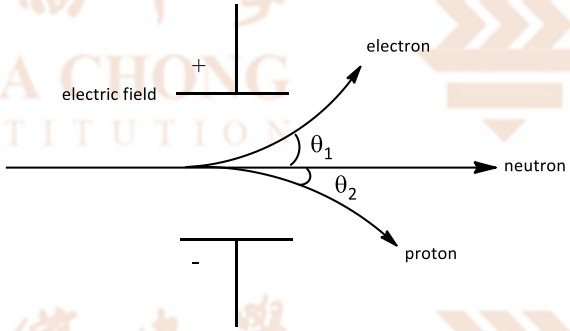


Figure 5. The behaviour of protons, neutrons and electrons in an electric field

In Figure 5, why is θ_1 greater than θ_2?

The electron has a much lower mass than the proton and is deflected to a much greater extent.

In general, we expect that the angle of deflection (θ) of a charged particle passing through an electric field to be directly proportional to the size of the charge (q), and inversely proportional to the mass (m).

$$\theta \propto \frac{q}{m}$$

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Exercise 1.4 (Worked Example)

In a particular experimental set-up, protons are deflected through an angle of +15°. Assuming an identical set of experimental conditions, by what angles will the following particles be deflected? (D is deuterium, ^2H, and T is tritium, ^3H)

- D^-
- T^+
- He^{2+}

[N12 /III/4(a)]

Strategy:

Since the angle of deflection is dependent on the $\frac{q}{m}$ ratio, you can present your answer in the form of a table, using the given angle of deflection of a proton as the reference point:

species	$\frac{q}{m}$ ratio	angle of deflection (θ)
proton, $^1H^+$	$\frac{q}{m}=\frac{+1}{1}$	θ = + 15° (given)
D^- (= $^2H^-$)		
T^+ (= $^3H^+$)		
He^{2+}		

Both D^- and He^{2+} have a $\frac{q}{m}$ ratio that is halved of that of $^1H^+$, thus the angle of deflection will be halved of that of $^1H^+$. However, as D^- is negatively charged, it will be deflected towards the positive plate (opposite to that of $^1H^+$). He^{2+} is positively charge and will be deflected towards the negative plate (similar to that of $^1H^+$).

T^+ has a $\frac{q}{m}$ ratio that is 1/3 of that of $^1H^+$, thus the angle of deflection will be 1/3 of that of $^1H^+$. Having a positive charge, it will be deflected to the negative plate.

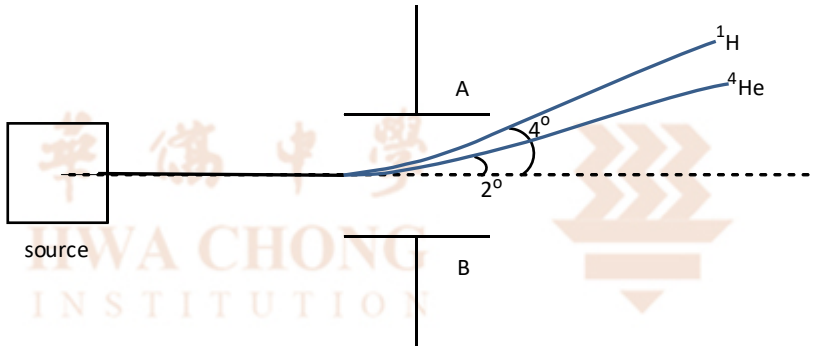
Answer:

species	$\frac{q}{m}$ ratio	angle of deflection (θ)
proton, $^1H^+$	$\frac{q}{m}=\frac{+1}{1}$	θ = + 15° (given)
D^- (= $^2H^-$)	$\frac{q}{m}=\frac{-1}{2}$	$\theta = -\frac{1}{2}\times 15 = -7.5^\circ$
T^+ (= $^3H^+$)	$\frac{q}{m}=\frac{+1}{3}$	$\theta = +\frac{1}{3}\times 15 = +5.0^\circ$
He^{2+}	$\frac{q}{m}=\frac{+2}{4}=+\frac{1}{2}$	$\theta = +\frac{1}{2}\times 15 = +7.5^\circ$

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Exercise 1.5

A plasma is a gaseous mixture in which the atoms have been completely stripped of their electrons, leaving bare nuclei. Because of possible use in controlled nuclear fusion reactions, plasma behaviour has been intensively studied. When passed between two plates carrying a certain electric charge, ^{1}H and ^{4}He nuclei are deflected as follows:



Giving reasons for your answers, suggest

(i) the polarity of plate **A**,

(ii) why ^{1}H is deflected twice as much as ^{4}He,

(iii) the angles of deflection (to 1 decimal place) of **I**: ^{2}H nuclei, **II**: ^{3}He nuclei.

[J00/I/1 (c)]

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2 QUANTIFYING THE MASSES OF ATOMS

In Section 1.2, we have looked at the composition of the atom. While the protons, neutrons and electrons have masses, they are so small such that it is impossible to weigh atoms individually except for highly specialised equipment. For day-to-day use in a laboratory, an easier way to quantify the masses of atoms is needed. And so we usually measure the *relative* masses of atoms, or how heavy one atom is compared to another atom.

2.1 Relative Masses of Atoms

LO 6(a)part: define the terms relative atomic, isotopic masses

We call this relative mass the relative atomic mass of an atom. We measure all relative masses against the mass of carbon-12, the most abundant isotope of carbon. Hence, the definition of relative atomic mass would look like the following:

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

Note that the word 'average' is used in the definition above as the atomic mass of an atom takes into account the relative abundance of all possible isotopes of that element. We will deal with the idea of relative abundance of isotopes in the next section.

In cases where we want to deal very specifically with the atomic mass of one of the possible isotopes of an element, then we would call this the relative isotopic mass. The definition would look like the following:

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

2.2 Relative Abundance of Isotopes

LO 6(c): calculate the relative atomic mass of an element given the relative abundances of its isotopes

Most elements consist of mixtures of isotopes. The abundance of each isotope in a mixture is called the ***isotopic abundance*** or the ***relative abundance***.

For instance, chlorine has two isotopes: ^{35}Cl and ^{37}Cl (note that isotopes of the same element have the same atomic number). Naturally occurring samples of chlorine are found to contain ^{35}Cl and ^{37}Cl in a ratio of 3:1. Hence, the relative abundance of ^{35}Cl is 75% and the relative abundance of ^{37}Cl is 25%.

The relative atomic mass of an element is also the sum of the relative isotopic masses of each isotope multiplied by their relative abundances.

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Using chlorine as an example,

Relative atomic mass, A_r of Cl = ∑ (relative isotopic mass x isotopic abundance)

= (35 x 0.75) + (37 x 0.25)

= 26.25 + 9.25

= 35.5 (1 d.p.)

17
Cl
chlorine
35.5

Exercise 2.1 (Worked Example)

The relative atomic mass of boron, which consists of the isotopes $^{10}_{5}B$ and $^{11}_{5}B$ is 10.8. What is the percentage of $^{11}_{5}B$ atoms in the isotopic mixture?

Solution:

Let a be the relative abundance of ^{11}B atoms.

∴ Relative abundance of ^{10}B atoms = $(1 - a)$

$a(11) + (1 - a)(10) = 10.8$

$11a + 10 - 10a = 10.8$

$\therefore a = 0.8$

∴ Percentage of ^{11}B atoms in the mixture = 80.0%

Comments:

The relative abundances of $^{10}_{5}B$ and $^{11}_{5}B$ should add up to 1.

The sum of the relative isotopic masses of each isotope multiplied by their relative abundances will give the relative atomic mass of 10.8.

Exercise 2.2

1. The five isotopes of krypton occur in the following abundances:

isotopic mass	% abundance
80	2
82	12
83	12
84	57
86	17

Use these data to calculate a value, to one decimal place, for the A_r of atmospheric krypton.

2. Naturally occurring gallium, Ga, is a mixture of two isotopes, gallium-69 and gallium-71. Use this information, together with the *Data Booklet*, to calculate the percentage abundance of each isotope.

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3 THE ARRANGEMENT OF THE ELECTRONS

LO 1(f): describe the number and relative energies of the s, p and d orbitals for the principal quantum numbers 1, 2 and 3 and also the 4s and 4p orbitals

3.1 Principal Quantum Shell

In order to understand chemical reactions, one must understand how electrons are arranged in atoms. Much about what we know of electrons comes from quantum theory, which states that electrons can be described by four *quantum numbers*. (The only one required in the A-level syllabus is the principal quantum number, *n*, of only integer value of 1, 2, 3, …)

The principal quantum number, n, describes the main energy level of an electron. It also indicates the relative size of the orbital and therefore relative distance of the electron from the nucleus. The larger the value of n, the higher the energy level and the further the electron is from the nucleus.

All atomic orbitals of the same value of ***n*** are said to be in the same quantum shell.

The **maximum** number of electrons that can occupy each principal quantum shell can be obtained by the formula $\mathbf{2}\boldsymbol{n}^{\mathbf{2}}$.

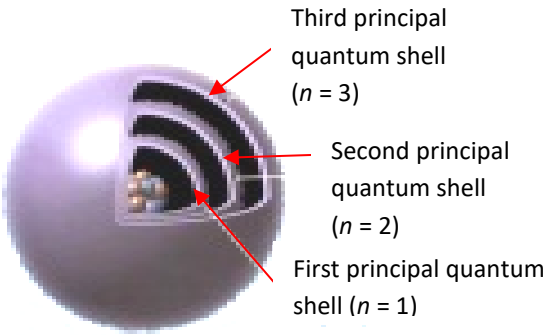


Figure 6. Principal quantum shells of an atom

Table 2 - Maximum number of electrons for each principal quantum shell.

principal quantum number (*n*)	**1**	**2**	**3**	**4**
maximum number of electrons ($2n^2$)	**2**	**8**	**18**	**32**

3.2 Subshells

Each principal quantum shell can be subdivided into one or more **subshells** (or sub levels). The number of subshells in a principal quantum shell is the same as its principal quantum number.

Table 3 - The subshells in each principal quantum shell

principal quantum number, *n*	**number of subshell**	**types of subshells**	**notation for subshells**
1	1	s	1s
2	2	s, p	2s , 2p
3	3	s, p, d	3s , 3p , 3d,
4	4	s, p, d, f	4s , 4p, 4d, 4f

Subshells within a given quantum shell differ slightly in energy, with the energy of the subshell increasing according to the following order: s, p, d, f, i.e., energy of 4s < 4p < 4d < 4f.

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3.3 Atomic Orbitals

Electrons are not randomly distributed in the region of space around the nucleus. They occupy specific volume regions, called **orbitals**, which have specific energies associated with them. According to the current quantum mechanical model of the atom, electrons in an atom **do not** remain in specific positions. They move in spaces defined by the Schrödinger's equation and Heisenberg's Uncertainty Principle (***NOT in A-level syllabus***). Instead of predicting the precise location for each electron in an atom, each electron is assigned to an energy level and orbital as it can only possess specific quantities of energy.

An atomic orbital is defined as the **region of space with a 90% probability (or more) of finding an electron**. This distribution of the probability of finding an electron at a certain position is the electron density.

- Each subshell (s, p, d, f) has one or more orbitals at the **same energy level** (**degenerate**) but **different orientations** in space.
- Each orbital can contain up to a **maximum of 2 electrons**. These electrons are of opposite spins.

Table 4.The number of orbitals and maximum number of electrons in each subshell

subshell	number of orbitals	maximum number of electrons in each subshell
s	1	2
p	3	6
d	5	10
f	7	14

The table below summarises the relationships among principal quantum shells, subshells, orbitals and number of electrons.

Table 5. Summary of the relationship between principal quantum shells, subshells and orbitals

principal quantum number, n	subshell	number of orbitals	maximum number of electrons in each principal quantum shell, $2n^2$
1	1s	1	2
2	2s 2p	1 3	8
3	3s 3p 3d	1 3 5	18
4	4s 4p 4d 4f	1 3 5 7	32

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*LO 1(g): describe the shapes of s, p and d orbitals (Refer also to Topic 22 Chemistry of the Transition Elements) [knowledge of wave functions is **not** required]*

3.3.1 The s Orbital

Each **s subshell** has **only one s orbital**. All s orbitals are **spherical** in shape with no nodal plane (region of zero electron density). The probability of finding an electron at a given distance from the nucleus is the same regardless of the direction from the nucleus. The size of s orbitals increases with the principal quantum number, i.e., 1s < 2s < 3s,…

Electron Density Plot **Schematic Representation**

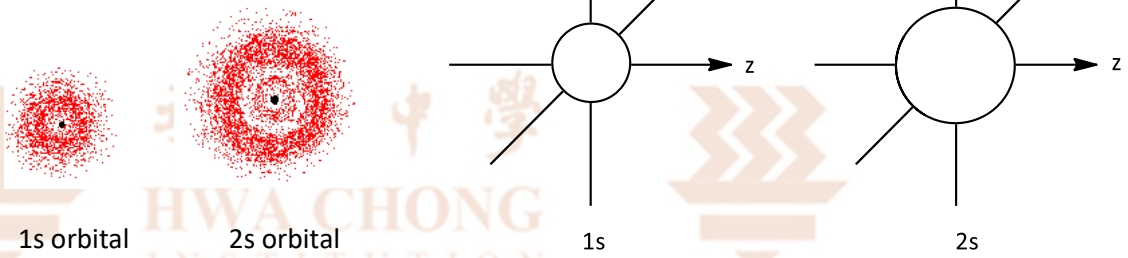


Figure 7. The s orbital

3.3.2 The p Orbital

Each **p subshell** has **three p orbitals.** Since each orbital can hold up to **2** electrons, each p **subshell** can hold up to **6** electrons. There are no p orbitals in the first quantum shell.

The **p orbital** is **dumb-bell** in shape. Each p orbital consists of two lobes with a region of zero electron density (node) between them centered on the nucleus.

The three p orbitals in a certain quantum shell are **identical** in **size** and **shape** but differ in their **spatial orientation**. The three p orbitals are represented as $\mathbf{p_x}$, $\mathbf{p_y}$, $\mathbf{p_z}$, where the subscripts denote the axes along which the orbitals are orientated. The three p orbitals are **degenerate**, i.e. at the same energy level. The size of p orbitals increases with the principal quantum number, i.e. 2p < 3p < 4p.

Electron Density Plot **Schematic Representation**

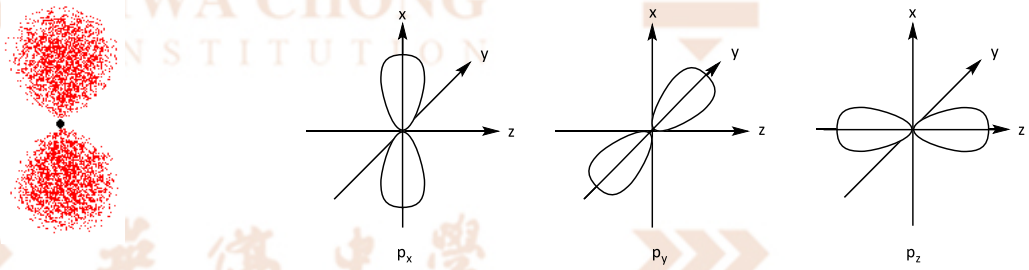


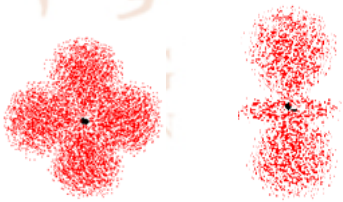
Figure 8. The p orbital

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3.3.3 The d Orbital

Each **d subshell** has **five d orbitals.** Since each orbital can hold **a maximum of 2** electrons, each d **subshell** can hold up to **10** electrons. There are **five** d orbitals: d_{xy}, d_{xz}, d_{yz}, d_z^2, $d_{x^2-y^2}$. The five d orbitals are also **degenerate**. The size of d orbitals increases with the principal quantum number, i.e. 3d < 4d < 5d …

Electron Density Plot



Schematic Representation

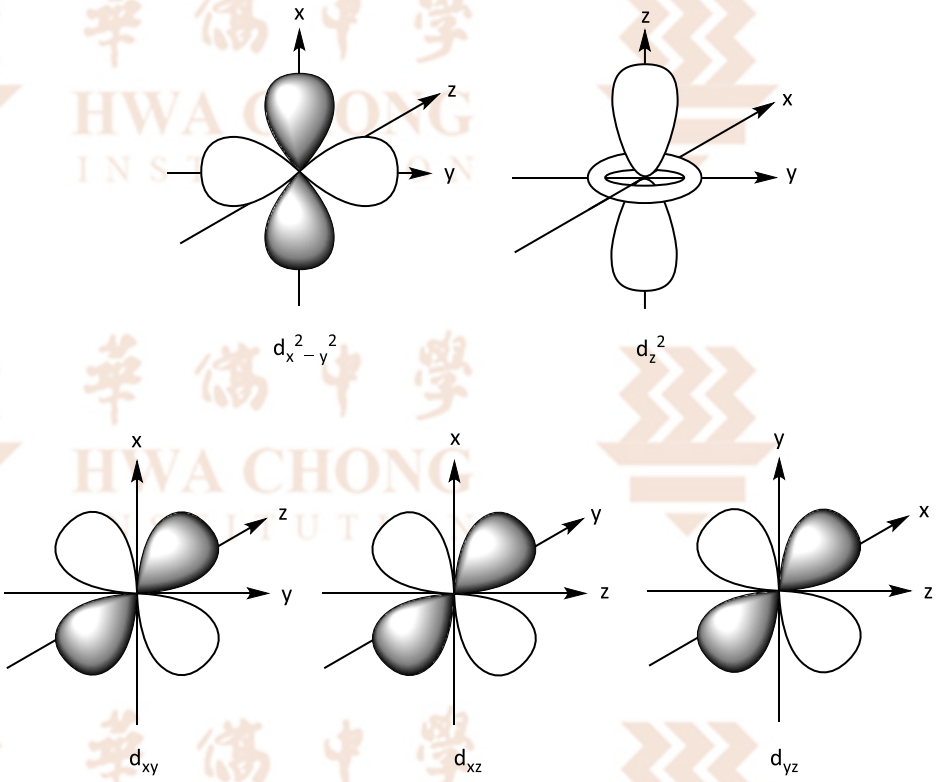


Figure 9. The d orbitals (Note: It is not necessary to colour/shade the orbitals)

Exercise 3.1

What kind of orbital must an electron with the principal quantum number *n* = 2 occupy?

A a spherically-shaped orbital
B either an s or p orbital
C the orbital closest to the nucleus
D a dumb-bell-shaped orbital *[N1995/IV/3; N2000/III/2]*

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3.4 Electronic Configuration

The electronic configuration of an atom shows the **distribution of electrons in various orbitals** in an atom.

Rule 1: The Aufbau or 'Building-up' Principle

Electrons in their ground states (i.e. when they are not excited) occupy orbitals **in order of energy levels**. The orbital with the **lowest** energy is always filled **first**.

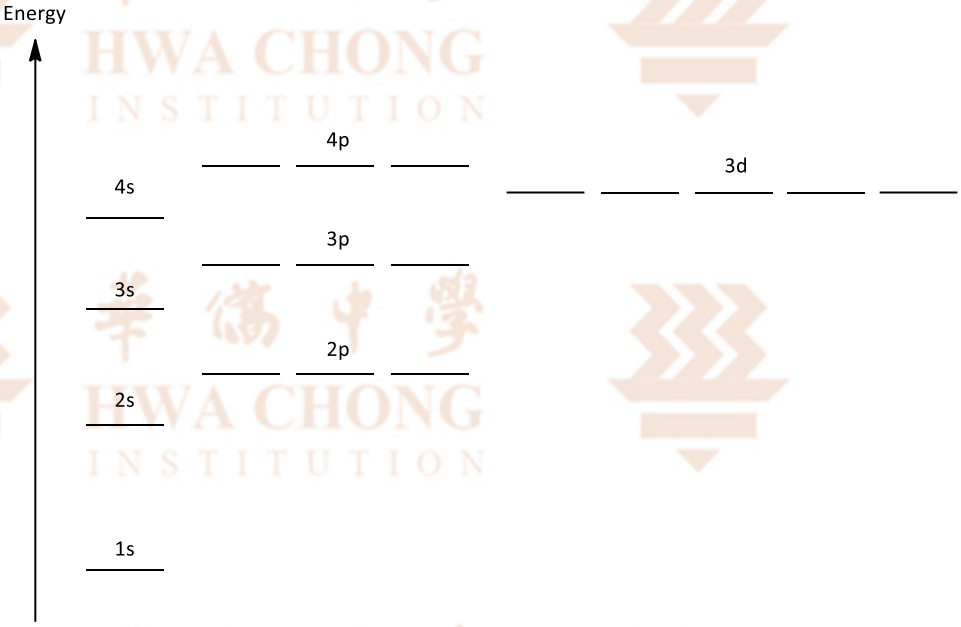


Figure 10. Relative energies of the orbitals for the first 20 elements

Figure 11 below shows the **sequence** in which the electron orbitals are populated with electrons in an atom as the proton number increases.

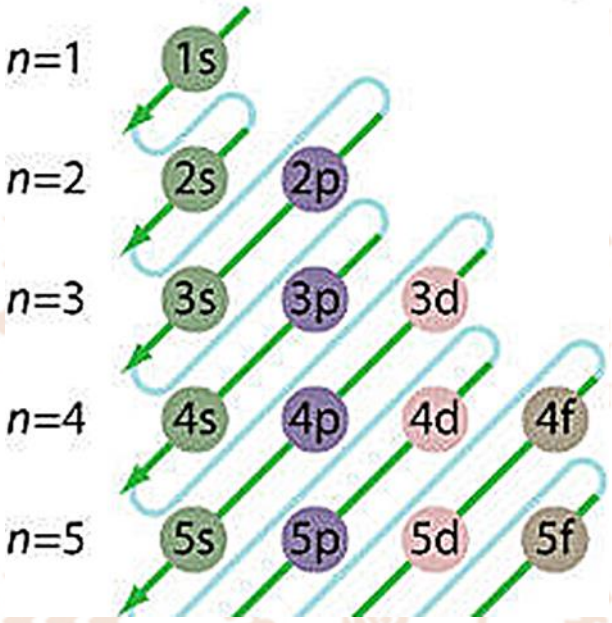


Figure 11. Mnemonic for the order of filling electrons into the orbitals

The 1s subshell is the first to be filled, then the 2s orbital, the 2p orbitals and then the 3s orbitals and so on. Electrons only enter higher energy levels after lower energy levels have been filled.

For example, nitrogen, N, with atomic number 7 will have 2 electrons in 1s orbital and 2 electrons in 2s orbital and 3 electrons in 2p orbitals.

The electronic configuration of N is represented as $1s^2\ 2s^2\ 2p^3$.

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Rule 2: Hund's Rule of Multiplicity

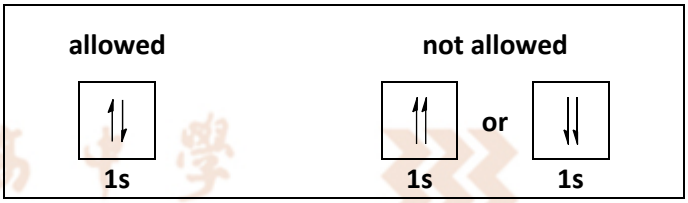
When filling subshells that contain more than one orbital with the same energy (p, d and f subshells), each orbital must be **singly occupied before electrons are paired**.

E.g. for $_7$N, each of the three 2p orbitals will be filled with 1 electron. To reflect this, we can write the electronic configuration of N as $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$.

Rule 3: Pauli Exclusion Principle

An orbital cannot hold more than two electrons and the two electrons sharing the same orbital must have **opposite spins**. This can be shown in an electron-in-box diagram where the **box** represents the **orbital** and the **arrows** within it represent the **electrons**. The direction of the arrow (up or down) indicates the spin of the electron.

Thus,



Exercise 3.2 (Worked Example)

Element	electronic configuration	electron-in-box diagram
$_6$C	$1s^2 2s^2 2p^2$	1s 2s 2p 2p 2p
$_8$O	$1s^2 2s^2 2p^4$	1s 2s 2p 2p 2p
$_{12}$Mg	$1s^2 2s^2 2p^6 3s^2$	1s 2s 2p 2p 2p 3s
$_{21}$Sc	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$	1s 2s 2p 2p 2p 3s 3p 3p 3p 3d 3d 3d 3d 3d 4s
$_{25}$Mn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$	1s 2s 2p 2p 2p 3s 3p 3p 3p 3d 3d 3d 3d 3d 4s
$_{24}$Cr*	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$	1s 2s 2p 2p 2p 3s 3p 3p 3p 3d 3d 3d 3d 3d 4s
$_{27}$Co	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$	1s 2s 2p 2p 2p 3s 3p 3p 3p 3d 3d 3d 3d 3d 4s
$_{29}$Cu*	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$	1s 2s 2p 2p 2p 3s 3p 3p 3p 3d 3d 3d 3d 3d 4s
$_{35}$Br	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$	1s 2s 2p 2p 2p 3s 3p 3p 3p 3d 3d 3d 3d 3d 4s 4p 4p 4p

Chromium and copper are two **exceptions** to this general pattern:

- Electronic configuration of Cr is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$ (not $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4\ 4s^2$)
- Electronic configuration of Cu is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$ (not $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9\ 4s^2$)

The explanation for these exceptions are not required in the A-level syllabus but they are a result of the effects of increasing nuclear charge on the 3d and 4s orbitals and the repulsions between electrons sharing the same orbital. *For a full explanation with references to the published papers, please refer to 'Inorganic Chemistry, 3rd Ed, G.L. Miessler & D.A. Tarr, Pearson, Prentice Hall, Chapter 2, sections 2.2.3 & 2.2.4, pgs 34 to 43.*

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LO 1(h): state the electronic configuration of atoms and ions given the proton number (and charge)

When writing the electronic configuration of a **cation**:

- first write the electronic configuration of the atom,
- then **remove** the number of electrons equal to the positive charge, starting from the highest energy (outermost) subshell.
- From Scandium onwards, the 4s electrons are removed first in the formation of positive ions.

E.g., the electronic configuration of $_{29}Cu$ is **$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^1$** while that of $_{29}Cu^{2+}$ is **$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^9$**.

When writing the electronic configuration of an **anion**:

- first write the electronic configuration of the atom,
- then **add** number of electrons equal to the negative charge, starting from orbitals of lowest energy available.

E.g., the electronic configuration of $_{16}S$ is $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^4$, while that of $_{16}S^{2-}$ is **$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$**.

Exercise 3.3 (Worked Example)
Complete the table below.

ion	electronic configuration of atom	electronic configuration of ion
$_{11}Na^+$		
$_{26}Fe^{2+}$		
$_{17}Cl^-$		

Comments:
The electronic configurations of the atoms and ions can be obtained by applying the rules stated above.

For Na^+ and Fe^{2+}, remove 1 and 2 electrons respectively from the highest energy subshell. One 3s electron will be removed from Na and two 4s electrons will be removed from Fe.

Answer:

ion	electronic configuration of atom	electronic configuration of ion
$_{11}Na^+$	$1s^2 2s^2 2p^6 3s^1$	$1s^2 2s^2 2p^6$
$_{26}Fe^{2+}$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$
$_{17}Cl^-$	$1s^2 2s^2 2p^6 3s^2 3p^5$	$1s^2 2s^2 2p^6 3s^2 3p^6$

Exercise 3.4
Which of the following particles would, **on losing an electron**, have a half-filled set of p orbitals?

A C^- **B** N^- **C** O^+ **D** O^-

[J93/IV/2]

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3.5 Electronic Configuration and Periodicity

LO 5(a): recognise variation in the electronic configurations across a Period and down a Group

In the Periodic Table, the arrangement of the elements was proposed according to their electronic configurations. It is divided into the s-block, the d-block and the p-block. The electronic configurations of elements will affect their physical and chemical properties.

Table 6(a). The valence electronic configuration of each group in the periodic table

group Number	valence shell electronic configuration	block
1	ns^1	s-block
2	ns^2	
13	ns^2np^1	p-block
14	ns^2np^2	
15	ns^2np^3	
16	ns^2np^4	
17	ns^2np^5	
18	ns^2np^6	

Table 6(b). The valence electronic configuration for elements in Periods 2 & 3

Period 2	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
	$[He]2s^1$	$[He]2s^2$	$[He]2s^22p^1$	$[He]2s^22p^2$	$[He]2s^22p^3$	$[He]2s^22p^4$	$[He]2s^22p^5$	$[He]2s^22p^6$
Period 3	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
	$[Ne]3s^1$	$[Ne]3s^2$	$[Ne]3s^23p^1$	$[Ne]3s^23p^2$	$[Ne]3s^23p^3$	$[Ne]3s^23p^4$	$[Ne]3s^23p^5$	$[Ne]3s^23p^6$

Note: For simplicity, [He] and [Ne] are used to represent the configuration $1s^2$ and $1s^22s^22p^6$ respectively. Do not use these symbols when asked to write electronic configuration in examinations.

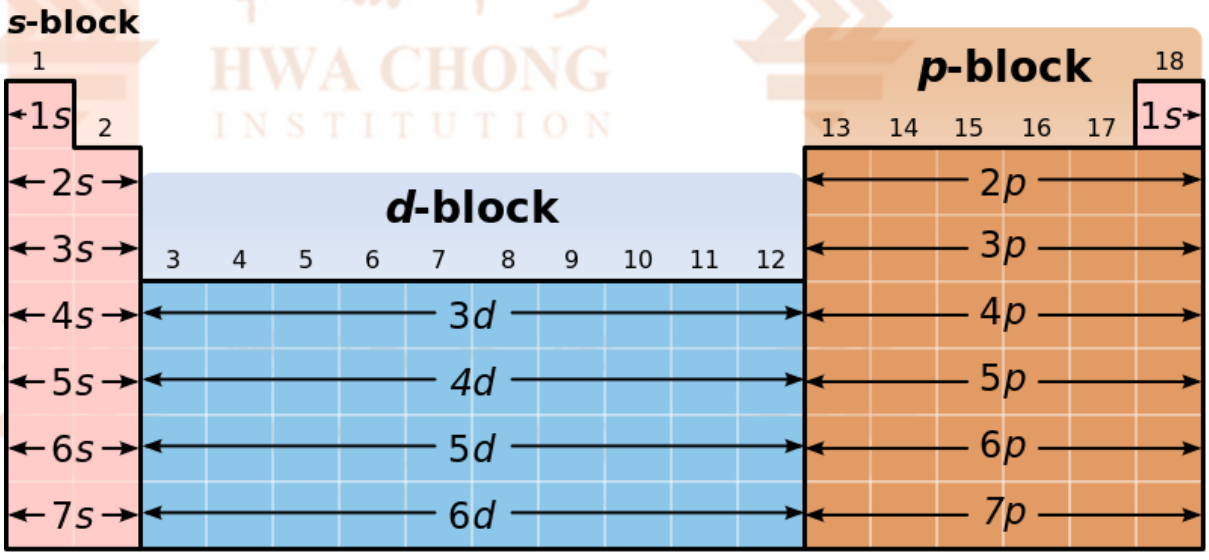


Figure 12. Periodic table illustrating how elements are grouped according to their valence subshells

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LO 13(a): explain what is meant by a transition element, in terms of d-block elements forming one or more stable ions with partially filled d subshells
LO 13(b): state the electronic configuration of a first row transition element and its ion

By definition,

A **transition metal** is a *d*-block element that form one or more stable ions with a partially-filled *d*-subshell.

As a result, *d*-block elements such as scandium and zinc are not considered to be transition elements because:

- scandium forms only the Sc^{3+} which has the $3d^0$ configuration
- zinc forms only Zn^{2+} ion which has $3d^{10}$ configuration

Exercise 3.5
Which of the following corresponds to the configuration of the three electrons of highest energy for the ground state of an element in Group 13?

A $1s^2\ 2s^1$ **B** $2s^1\ 2p^2$ **C** $3p^3$ **D** $4s^2\ 4p^1$

[N1985/III/3; J1989/III/3]

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4 PERIODIC TRENDS IN ATOMIC AND IONIC RADII

LO 5(b)part: describe and explain qualitatively the general trends and variations in atomic radius, ionic radius, first ionisation energy
(i) across a Period in terms of shielding and nuclear charge,
(ii) down a Group in terms of increasing number of electronic shells, shielding and nuclear charge

In explaining periodic trends in atomic and ionic radii, two fundamental considerations are important:

(i) number of quantum shells

The **number of quantum shells** determine how far the outermost electron is from the nucleus. The further the outermost electron is from the nucleus, the weaker the attraction between the outermost electron and the nucleus.

(ii) effective nuclear charge

The **effective nuclear charge**, Z_{eff}, is the **net nuclear charge** experienced by an **outer electron**. It is dependent on:

(a) **Nuclear charge (Z)**: The nuclear charge is dependent on the number of protons. The larger the number of protons, the greater the nuclear charge and the attraction for the outermost electrons by the nucleus.

(b) **Shielding** or **screening effect (S)**: Presence of inner-shell electrons reduces the electrostatic attraction between the outermost electrons and the nucleus.

Hence, $\mathbf{Z_{eff} = Z - S}$

Electrons in the **same** quantum shell do exert **some** shielding effect on each other.*
**For example, shielding of p electrons by s or p electrons in the same quantum shell does occur. However this shielding effect is small compared to that by the inner core electrons.*
**Order of shielding effect by electrons in the same quantum shell: s > p > d > f.*

4.1 Trend in Atomic Radius

<u>Down the Group</u>:

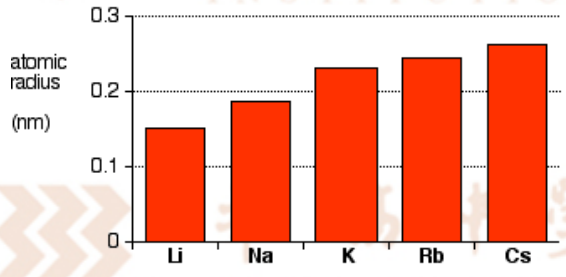


Figure 13. Atomic radii of Group 1 elements

General Trend:
Atomic radius increases down the group.

Reason:

- As the number of quantum shells **increases** the outermost **electrons are further away** from the nucleus, hence the atomic radius **increases**. Both the **nuclear charge** and **shielding effect** increase down the group, hence the **effective nuclear charge** differs little down the group.

  Hence the number of quantum shells is the more important factor.

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Across Periods 2 and 3:

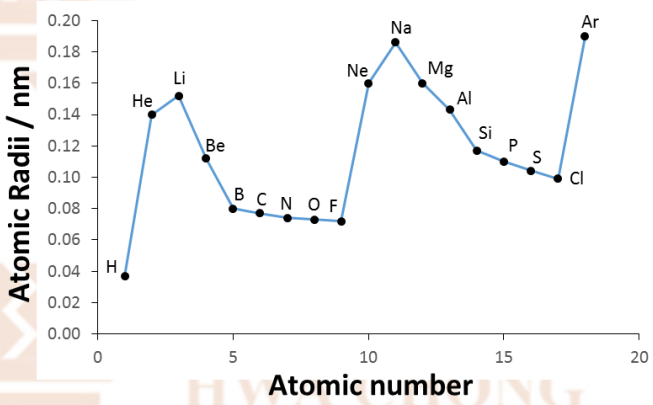


Figure 14. Atomic radii of period 2 & 3 elements

Why are the atomic radii of the noble gases so large?

The term atomic radius does not mean the same thing for every element. The atomic radii given for He, Ne and Ar in the *Data Booklet* are labelled van der Waals' radii, rather than covalent radii (see Chapter 02 Section 4.2 for explanation). Ar, for instance, does not form compounds, so it will not have a covalent radius. The van der Waals' radius of an atom is always larger than the covalent radius, which explains the anomalously high atomic radii of the noble gases in the graph above.

General Trend:

Atomic radius decreases across the period.

Reason:

- **nuclear charge increases** due to the **increase** in the **number of protons** in the nucleus
- **shielding effect remains relatively constant** (as the electrons are added to the same outermost shell)
- **effective nuclear charge increases**, resulting in stronger electrostatic forces of attraction between the nucleus and the outermost electron
- **outermost electrons are pulled closer to the nucleus** and hence a **decrease** in the atomic radius

Across the First Row Transition Elements:

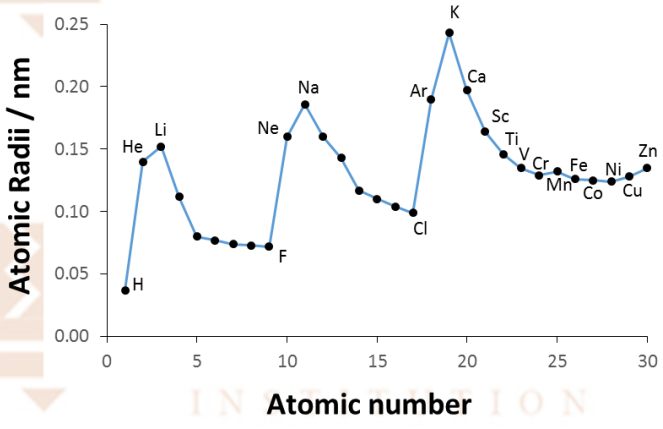


Figure 15. Atomic radii across periods 2, 3 and the first row transition elements

General Trend:

Atomic radius is relatively invariant.

Reason:

- **nuclear charge increases** due to increasing number of protons
- **electrons are added** to the **inner 3d subshell**, which **contributes** to the **shielding effect**
- shielding effect increases thereby **nullifying, to a considerable extent,** the **influence of each additional proton** in the nucleus
- **effective nuclear charge** remains almost c**onstant**

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4.2 Trend in Ionic Radius

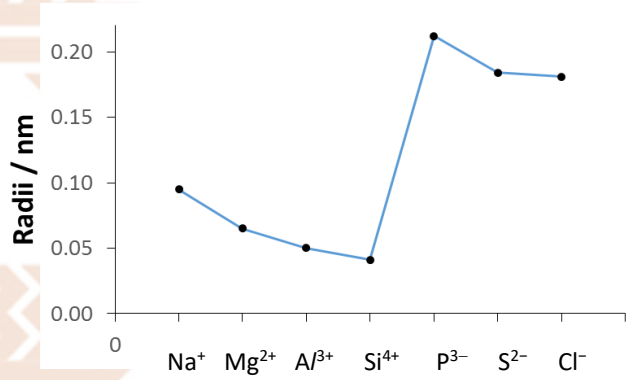


Figure 16. Ionic Radii across Period 3

Ionic radius of cations:

$Na^+ > Mg^{2+} > Al^{3+} > Si^{4+}$

Ionic radius of anions:

$P^{3-} > S^{2-} > Cl^-$

The ions, Na^+, Mg^{2+}, Al^{3+} and Si^{4+} are said to be **isoelectronic** as they have the **same number of electrons**, which is 10. Similarly P^{3-}, S^{2-} and Cl^- are **isoelectronic** as they have 18 electrons each. Across the two isoelectronic series (Na^+ to Si^{4+} and P^{3-} to Cl^-), nuclear charge **increases** and **shielding effect** is the same (due to same number of electrons).

This results in an **increase** in the effective nuclear charge and a stronger attraction between the outermost electrons and the nucleus, hence a **decrease** in ionic size across each series.

There is a **sharp increase in ionic radius from the cationic series of Na^+ to Si^{4+} to the anionic series of P^{3-} to Cl^-**, because the **anions have one more quantum shell of electrons than the cations**.

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5 Ionisation Energy (IE)

5.1 Definitions

First ionisation energy is the energy needed to remove 1 mole of electrons from 1 mole of gaseous atoms to form 1 mole of unipositively charged gaseous ions.

$X(g) \rightarrow X^+(g) + e^-$ **1st IE**

Examples:

$Na(g) \rightarrow Na^+(g) + e^-$ 1st IE of Na

$Fe(g) \rightarrow Fe^+(g) + e^-$ 1st IE of Fe

Second ionisation energy is the energy required to remove 1 mole of electrons from 1 mole of unipositively charged gaseous ions to form 1 mole of gaseous ions with double positive charge.

$X^+(g) \rightarrow X^{2+}(g) + e^-$ **2nd IE**

Examples:

$Na^+(g) \rightarrow Na^{2+}(g) + e^-$ 2nd IE of Na

$Fe^+(g) \rightarrow Fe^{2+}(g) + e^-$ 2nd IE of Fe

Similarly, nth **ionisation energy** is the energy needed to remove 1 mole of electrons from 1 mole of gaseous ions with (n–1)+ charge to form 1 mole of gaseous ions with n^+ charge.

$X^{(n-1)+}(g) \rightarrow X^{n+}(g) + e^-$ **nth IE**

Factors affecting ionisation energy of an atom:

- number of quantum shells
  The larger the number of quantum shells in an atom, the further the electron is from the nucleus and hence experiences weaker nuclear attraction and is easier to remove, hence the lower the ionisation energy.
- effective nuclear charge, Z_{eff}
  The higher the effective nuclear charge, the stronger the attractive forces between the nucleus and the electrons to be removed, hence the greater the ionisation energy.

5.2 Trend in the Successive Ionisation Energies of the Same Element

For the same element, ionisation energies always increase in the following order:

$IE_1 < IE_2 < IE_3 < IE_4 < \ldots$

Reason:

When an electron is removed from a neutral atom, the number of protons that exert an attraction for the remaining electrons remains the same. However, the shielding effect (or mutual electrostatic repulsion) among the remaining electrons in the outermost shell is reduced since there is now one less electron. Hence effective nuclear charge increases. More energy is needed to remove another electron from the more positively charged ion, and hence a higher ionisation energy.

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Application of successive ionisation energy values

LO 1(j): deduce the electronic configurations of elements from successive ionisation energy data
LO 1(k): interpret successive ionisation energy data of an element in terms of the position of that element within the Periodic Table

Successive ionisation energy values can be used to determine the electronic configuration of atoms and hence the identity of the element.

E.g., the ground state electronic configuration of magnesium is $1s^2\ 2s^2\ 2p^6\ 3s^2$.

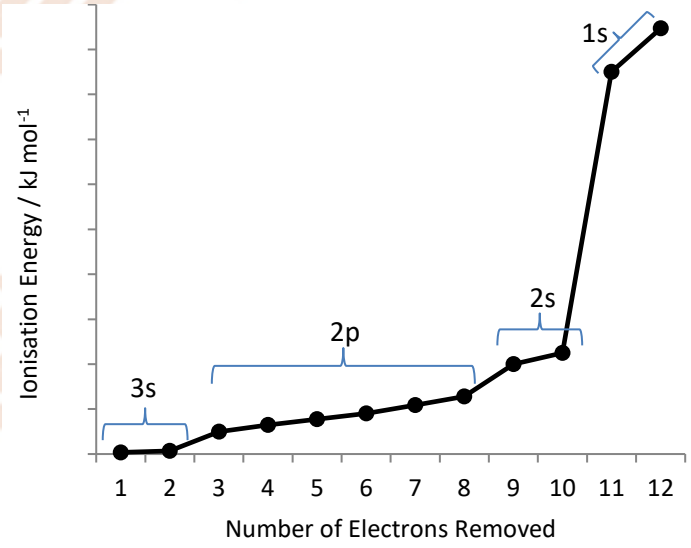


Figure 17. Successive ionisation energies of magnesium

- the **first big** increase from the **2nd** to **3rd** ionisation energies:

  - implies that the **third** electron is in an **inner** quantum shell, and thus there are **two** electrons in the outermost or valence 3s subshell.

  Conclusion: **Mg** is a **Group 2** element.

- the **gradual increase** from the **3rd** to **10th** ionisation energies:

  - implies that the next 8 electrons are removed from the second quantum shell.

  - a **slightly greater increase** from the **8th** to **9th** ionisation energies as more energy is required to remove the **2s** electrons, which are closer to the nucleus compared to the **2p** electrons.

- the **second big** increase from the **10th** to **11th** ionisation energies

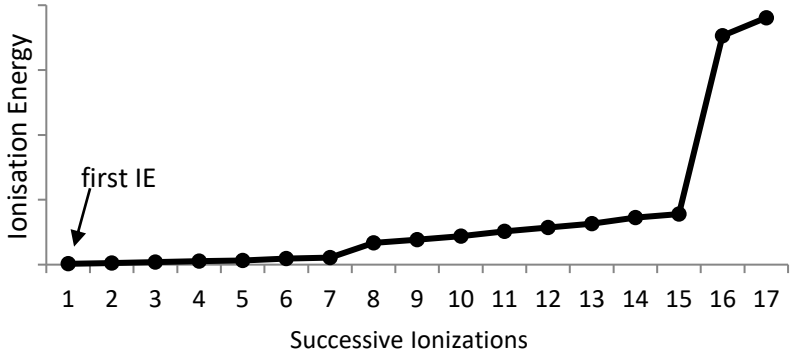
  - implies that the **last** two electrons are in the first (**inner most**) quantum shell.

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Exercise 5.1 (Worked Example)

Identify the group number of the element for each set of ionisation energies.

(i) **A:**



(ii) **B**: successive ionisation energies (in kJ mol^{-1}): 1060, 1900, 2920, 4960, 6280, 21 200

(iii) **C**: successive ionisation energies (in kJ mol^{-1}): 687, 1577, 3232, 4355, 16 091, 19 784.

Answers:

(i) **A: Group 17**
(ii) **B: Group 15**
(iii) **C: Group 14**

Comments:

For this question, look for the first big increase in ionisation energy which would signal that there is a change in quantum shell.

In (i), the first big increase in ionisation energy between electron 7 and 8, indicating that there are 7 electrons in the outer most shell of **A**.

For (ii) and (iii) find the difference between each successive ionisation.
For (ii), the biggest increase in ionisation energy occurs between electron 5 and 6. This shows that there are 5 electrons in the outermost quantum shell.
Similarly for (iii), there are 4 electrons in the outermost quantum shell.

Exercise 5.2

The use of the Data Booklet is relevant to this question.

The successive ionisation energies, in kJ mol^{-1}, of an element **X** are given below:

870 1800 3000 3600 5800 7000 13200

What is **X**?

A $_{33}As$ **B** $_{40}Zr$ **C** $_{52}Te$ **D** $_{53}I$

[J92/IV/4; N2002/I/14; J2003/I/4]

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5.3 Trend in the First Ionisation Energies of Different Elements

LO 1(i): explain the factors influencing the ionisation energies of the elements (see the Data Booklet)

Down the Group:

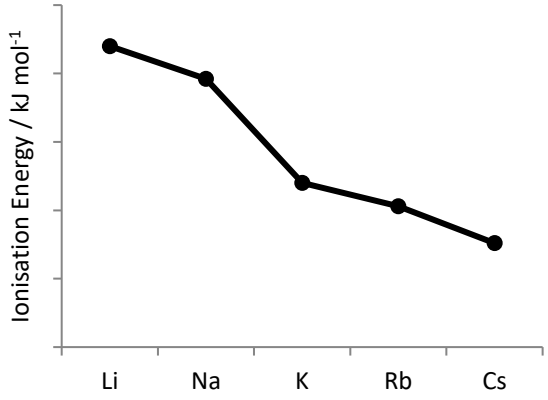


Figure 18. First ionisation energy trend down a group

General Trend:

In general, **first ionisation energy** of elements **decreases** down a group.

Reason:

Down the group, the number of quantum shells of electrons increases, hence the outermost electrons are further from the nucleus. Therefore, the electrostatic forces of attraction between the nucleus and the outermost electron is weaker and less energy is required to remove this electron.

Both the **nuclear charge** and **shielding effect** increase down the group, so the **effective nuclear charge** differs little down the group. Hence, the number of quantum shells is the more important factor.

Across Periods 2 and 3:

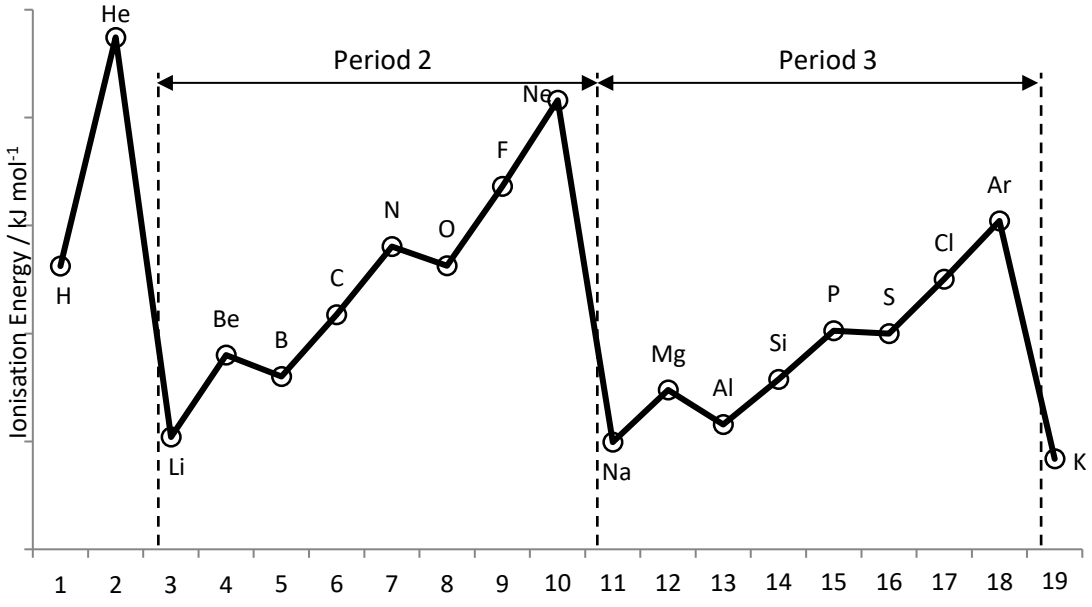


Figure 19. First ionisation energy trend across Periods 2 & 3

General Trend:

In general, **first ionisation energy** of elements **increases** across a period.

Reason:

Across the period, nuclear charge **increases** and shielding effect remains **relatively the same**. Hence the effective nuclear charge **increases** and the electrostatic forces of attraction between the outermost electrons and the nucleus **become stronger**, so more energy is required to remove the outermost electron.

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Two Anomalies:

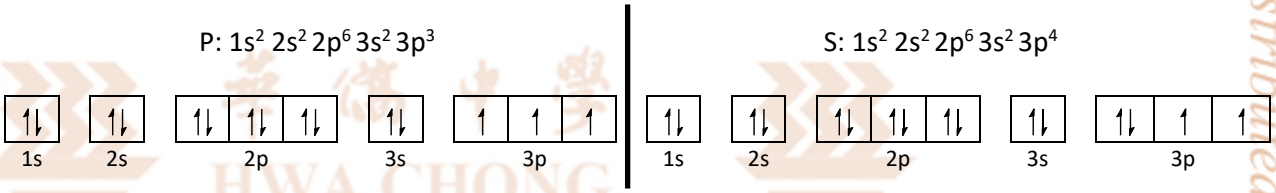
- **Small dip between Group 2 and Group 13 elements**
  A*l* has lower 1st ionisation energy than Mg.

  Mg: $1s^2\ 2s^2\ 2p^6\ 3s^2$ A*l*: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

  The 3p subshell of A*l* is **further away** from the nucleus than the 3s subshell. There is weaker attraction between the nucleus and the outermost electron. Hence less energy is required to remove the 3p electron from A*l*, resulting in a lower ionisation energy for A*l.*

- **Small dip between Group 15 and Group 16 elements**
  S has lower 1st IE than P.

  Consider the electronic configurations of P and S.



All the 3p electrons in P are **unpaired**. In S, two of the 3p electrons are **paired**. There is some **inter-electronic repulsion** between the paired electrons in the 3p subshell in S. Thus, less energy than expected is required to remove one of these paired electrons from S.

<u>Across Transition Elements:</u>

LO 13(c): explain why atomic radii and first ionisation energies of the transition elements are relatively invariant

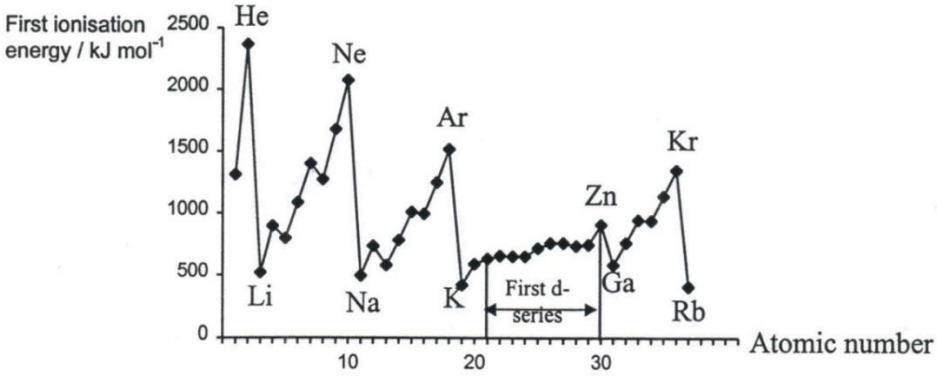


Figure 20: First ionisation energy trend across the first transition elements series

General Trend:

First ionisation energy remains relatively invariant.

Reason:

- 1st ionisation energy involves removal of a 4s electron
- The nuclear charge increases due to increasing number of protons while additional electrons are added to the inner 3d subshell, which contributes to the shielding effect. The shielding effect increases thereby nullifying, to a considerable extent, the influence of each additional proton in the nucleus

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- Effective nuclear charge remains almost constant. Thus, energy required to remove the outermost electron of each succeeding element remains relatively invariant

Exercise 5.3 (Worked Example)

The diagram shows part of the Periodic Table.

						H											He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr

Which element in the diagram has the largest atomic radii?

A Br **B** K **C** Kr **D** Sc

[N10/I/1]

Answer: B

Comments:

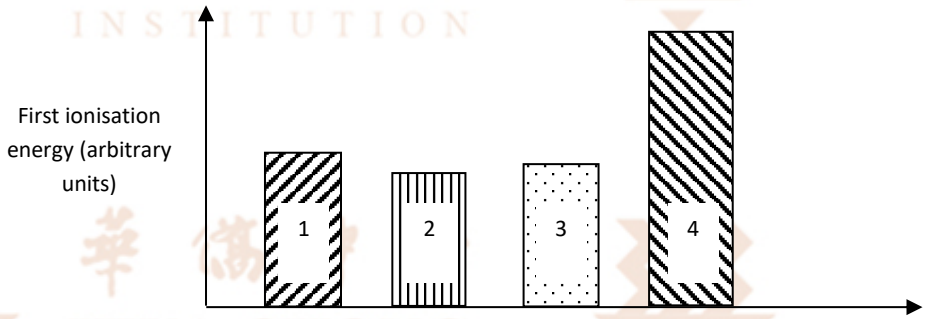
The atomic radius of an atom decreases across the period due to the increasing effective nuclear charge. K is the only group 1 element here, thus the answer is B.

Exercise 5.4

Use of the *Data Booklet* is relevant to this question.

The bar chart gives some information about the first ionisation energies of elements, numbering from 1 to 4.

The elements are adjacent to one another in the Periodic Table with increasing proton number either across a period from left to right, or down a group.



What could these elements be?

A B, C, N, O
B Co, Ni, Cu, Zn
C Mg, Ca, Sr, Ba
D Si, P, S, Cl

[N09/I/17]

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LOOKING AHEAD

In this topic, we have looked at the structure of the atoms, the shapes and energies of the atomic orbitals, as well as the energies associated with removal of electrons from isolated gaseous atoms. In the following topic, we will be applying these concepts to help us understand how atoms interact to form chemical bonds.

A particularly important and useful concept is that of effective nuclear charge. We have used this concept of effective nuclear charge quite extensively in this last section of Topic 1. So far, we have only considered isolated gaseous atoms and discussed the impact of the effective nuclear charge on removing electrons from these atoms. In reality, the electrostatic forces due to the effective nuclear charge of the atom extend beyond its outermost electron.

When two atoms are in proximity, the nucleus of each atom exerts an attractive force on its own electrons as well as the electrons of the other atom. The same nucleus also exerts a repulsive force on the nucleus of the other atom. This attraction and repulsion on the electrons and nucleus of the other atom by the first atom result in a net attractive force on the electrons of the other atom. It is quite clear then that the effective nuclear charge of the first atom would play a significant role in attracting the electrons of the other atom.

This attraction was first referred to as 'oxygenicity' in 1809 by Avogadro and Bezelius adopted the term 'electronegativity' in 1811. The concept of 'electronegativity' was finally defined and quantified by Linus Pauling in 1932. (Interesting fact: Linus Pauling is the only person to be awarded two unshared Nobel Prizes.)

Electronegativity quantifies the attractive force one atom exerts on the electrons of another atom in a chemical bond. A larger number implies a larger force of attraction towards the electrons. We will have a more thorough discussion of the concept of electronegativity when we deal with chemical bonding in Topic 2.

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02 Chemical Bonding

GUIDING QUESTIONS

- What holds particles together?
- What are the different models that describe the forces that hold particles together?
- How do these models explain the properties of matter?
- How do we determine the shapes of molecules?
- What are the trends and variations in physical properties in compounds?
- How can the trends and variations in physical properties be explained?

LEARNING OUTCOMES

Students should be able to:

2(a) show understanding that all chemical bonds are electrostatic in nature and describe:
- **(i)** ionic bond as the electrostatic attraction between oppositely charged ions
- **(ii)** covalent bond as the electrostatic attraction between a shared pair of electrons and positively charged nuclei
- **(iii)** metallic bond as the electrostatic attraction between a lattice of positive ions and delocalized electrons

2(b) describe, including the use of 'dot-and-cross' diagrams:
- **(i)** ionic bonding as in sodium chloride and magnesium oxide
- **(ii)** covalent bonding as in hydrogen; oxygen; nitrogen; chlorine; hydrogen chloride; carbon dioxide; methane; ethene
- **(iii)** co-ordinate (dative covalent) bonding, as in formation of the ammonium ion and in the Al_2Cl_6 molecule

7(e) explain, in qualitative terms, the effect of ionic charge and of ionic radius on the numerical magnitude of a lattice energy (Refer to Topic 5 Chemical Energetics)

2(c) describe covalent bonding in terms of orbital overlap *(limited to s and p orbitals only)*, giving σ and π bonds

2(d) explain the shapes of, and bond angles in, molecules such as BF_3 (trigonal planar); CO_2 (linear); CH_4 (tetrahedral); NH_3 (trigonal pyramidal); H_2O (bent); SF_6 (octahedral) by using the Valence Shell Electron Pair Repulsion theory

2(e) predict the shapes of, and bond angles in, molecules analogous to those specified in (d)

2(f) explain and deduce bond polarity using the concept of electronegativity [quantitative treatment of electronegativity is not required]

2(g) deduce the polarity of a molecule using bond polarity and its molecular shape (analogous to those specified in (d));

2(h) describe the following forces of attraction (electrostatic in nature):
- **(i)** intermolecular forces, based on permanent and induced dipoles, as in $CHCl_3(l)$; $Br_2(l)$ and the liquid noble gases
- **(ii)** hydrogen bonding, using ammonia and water as examples of molecules containing –NH and –OH groups

2(i) outline the importance of hydrogen bonding to the physical properties of substances, including ice and water

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2(j) explain the terms bond energy and bond length for covalent bonds

2(k) compare the reactivities of covalent bonds in terms of bond energy, bond length and bond polarity

2(l) describe, in simple terms, the lattice structure of a crystalline solid which is:

- **(i)** ionic, as in sodium chloride, magnesium oxide
- **(ii)** simple molecular, as in iodine
- **(iii)** giant molecular, as in graphite; diamond
- **(iv)** hydrogen-bonded, as in ice
- **(v)** metallic, as in copper

[the concept of the 'unit cell' is **not** required]

2(m) describe, interpret and/or predict the effect of different types of structure and bonding on the physical properties of substances

2(n) suggest the type of structure and bonding present in a substance from given information

5(b) describe and explain qualitatively the general trends and variations in atomic radius, ionic radius, first ionization energy and electronegativity,

- **(i)** across a Period in terms of shielding and nuclear charge,
- **(ii)** down a Group in terms of increasing number of electronic shells, shielding and nuclear charge

(Refer to Topic 1 Atomic Structure & Physical Periodicity for trends and variations in atomic and ionic radii, and first ionization energy.)

5(c) interpret the variation in melting point and in electrical conductivity across a Period in terms of structure and bonding in the elements (metallic, giant molecular, or simple molecular) (Refer to Topic 21 Chemical Periodicity)

5(d) describe and explain the trend in volatility of the Group 17 elements in terms of instantaneous dipole-induced dipole attraction (Refer to Topic 21 Chemical Periodicity)

11.1(d) describe sp^3 hybridisation, as in ethane molecule, sp^2 hybridisation, as in ethene and benzene molecules, and *sp* hybridisation, as in ethyne molecule (Refer to Topic 12 Arenes with regards to benzene)

11.1(e) explain the shapes of, and bond angles in, the ethane, ethene, benzene and ethyne molecules in relation to σ and π carbon-carbon bonds (Refer to Topic 12 Arenes with regards to benzene)

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1. Peter Cann and Peter Hughes, Chemistry for Advanced Level, 1st Edition, John Murray (Publishers) Ltd, Chapters 3 & 4.
2. Martin S. Silberberg, Chemistry: The Molecular Nature of Matter and Change, Global Edition, Chapter 9 to 12.
3. http://www.chemguide.co.uk/index.html

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1 INTRODUCTION

LOOKING BACK

The discovery of electrons by J. J. Thomson and the development of the atomic model, led to the development of the concept of a chemical bond. As you uncover the nature of the chemical bond, consider the following questions:

- Which parts of the atom is responsible for chemical bonding?
- How does the structure of the atom affect the chemical bonding it participates in?

1.1 Nature of a Chemical Bond

LO 2(a): show understanding that all chemical bonds are electrostatic in nature

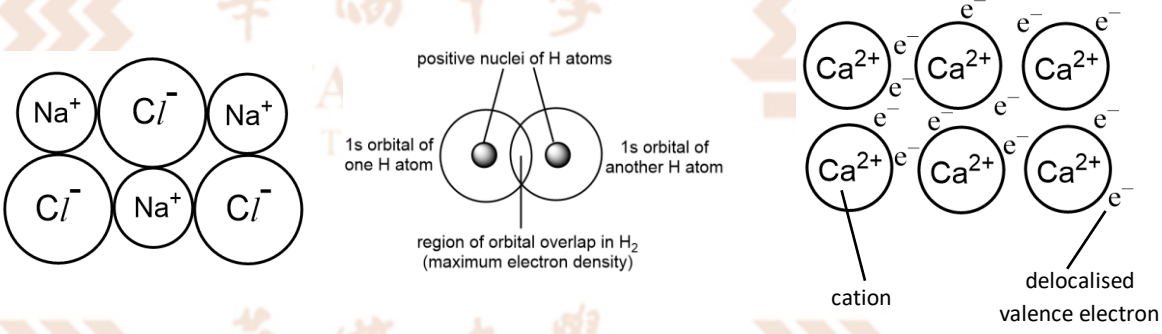
(i) *ionic bond as the electrostatic attraction between oppositely charged ions*

(ii) *covalent bond as the electrostatic attraction between a shared pair of electrons and positively charged nuclei*

(iii) *metallic bond as the electrostatic attraction between a lattice of positive ions and delocalized electrons*

All **chemical bonding** arises from **electrostatic attractions between positive and negative charges**. Electrostatic attraction is present in the three major types of bonding – ionic, covalent and metallic.

Types of chemical bonding	Lecture Notes
Ionic bond is the **electrostatic forces of attraction** between **oppositely charged ions**. In sodium chloride, the Na^+ cations and the Cl^- anions are held by ionic bonds.	Section 3
Covalent bond is the **electrostatic forces of attraction** between the **positively charged nuclei** (of both bonded atoms) and their **shared electrons**. In the hydrogen molecule (H_2), the two shared negatively charged electrons are attracted by the positive nuclei of both hydrogen atoms.	Section 4
Metallic bond is the **electrostatic forces of attraction** between the **metal cations** and the **sea of delocalised electrons**. In calcium, the Ca^{2+} cations and delocalised electrons are held by metallic bonds.	Section 2



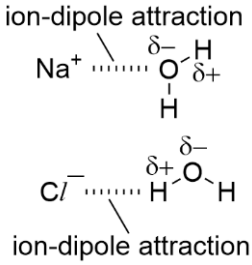
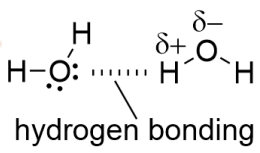
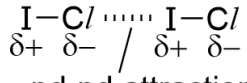
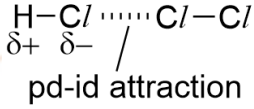
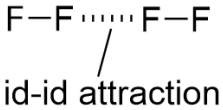
(a) ionic bonding in NaCl (b) covalent bonding in H_2 (c) metallic bonding in Ca

Figure 1. Ionic, covalent and metallic bonding are all electrostatic in nature

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In addition to ionic, covalent and metallic bonding, we will also be looking at other forces of attractions summarised in Table 1.

Table 1. Comparison of the different types of chemical bonding

Types of chemical bonding	Basis of attraction	Energy /kJ mol^{-1}	Example
ionic	cation – anion	400 – 4000	NaCl
covalent	nuclei – shared electrons	150 – 1100	H–H
metallic	cations – delocalised electrons	75 – 1000	Mg
ion-dipole attraction	ion charge – dipole charge	40 – 600	
hydrogen bonding	Between lone pair on F or O or N and H on F or O or N	10 – 40	
permanent dipole-permanent dipole (pd-pd) attraction	dipole charges	5 – 25	
permanent dipole-induced dipole (pd-id) attraction	dipole charge – polarisable electron cloud	2 – 10	
instantaneous dipole-induced dipole (id-id) attraction **also called dispersion forces**	polarisable electron clouds	0.05 – 40	

1.2 Electronegativity

Electronegativity of an atom is a measure of its **ability to attract the electrons** in a **covalent bond** to itself.

In the hydrogen molecule (Figure 1b), the bonding electrons are **equally shared** between the two hydrogen atoms as they have the **same** electronegativity.

When the covalent bond is formed by two different atoms of **different** electronegativities, the bonding electrons are **not shared equally**. For example in hydrogen chloride molecule (HCl), electron density is pulled closer to the more electronegative Cl atom.

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LO 5(b)part: describe and explain qualitatively the general trends and variations in electronegativity, (i) across a Period in terms of shielding and nuclear charge, (ii) down a Group in terms of increasing number of electronic shells, shielding and nuclear charge

Factors affecting electronegativity (same as those that affect ionisation energy)

- **Across the Period**

  Nuclear charge increases while shielding effect remains relatively constant.
  Effective nuclear charge increases, hence electronegativity **increases** across the period.

- **Down the Group**

  Elements in the same group experience **roughly the same effective nuclear charge** as both nuclear charge and shielding effect increase down the group.
  However, as the **number of quantum shells increases**, atomic radius increases. Hence, electronegativity **decreases** down the group.

Pauling's Electronegativity Scale (Background info)

Electronegativity is a concept introduced by Linus Pauling which quantifies attractive force one atom exerts on the electrons of another atom in close proximity. He assigned numerical values to the elements on a scale of 0 to 4 and a larger number implies a larger force of attraction towards electrons.

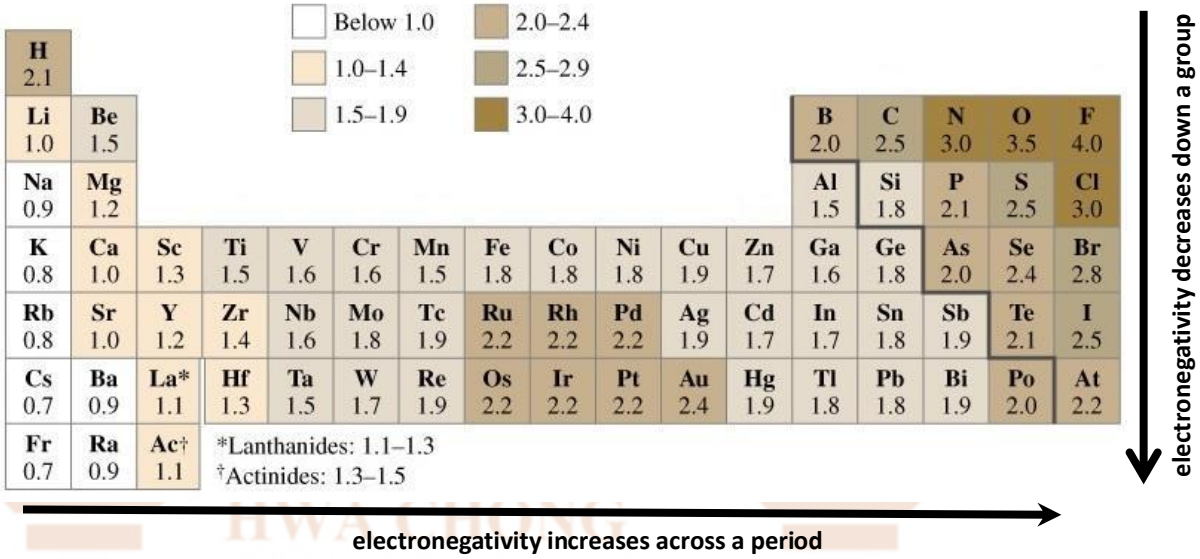


Figure 2. Electronegativity values for the elements; to which group of elements do you think Pauling assigned an electronegativity value of zero?

You are **not** required to memorise the electronegativity values!

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1.3 Electronegativity and Types of Chemical Bonding

The **difference in electronegativity** between two atoms can be used to **predict the type of bond formed** between them.

similar electronegativity between atoms	→	electron sharing	→	**covalent** bonding
large difference in electronegativity between atoms	→	electron transfer	→	**ionic** bonding

In general,

- **Covalent bonds** are formed between atoms of **non-metals** of **similar electronegativity**.
- **Ionic bonding** occurs between a **metal and non-metal** with a **large difference in electronegativity**.

Table 2. Some trends in Period 3 elements

Element	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
	metal			**metalloid**	**non-metal**			
Group	1	2	13	14	15	16	17	18
Electronic structure	[Ne] $3s^1$	[Ne] $3s^2$	[Ne] $3s^2\,3p^1$	[Ne] $3s^2\,3p^2$	[Ne] $3s^2\,3p^3$	[Ne] $3s^2\,3p^4$	[Ne] $3s^2 3p^5$	[Ne] $3s^2\,3p^6$
No. of valence electrons	1	2	3	4	5	6	7	8
Types of structure	**giant metallic**			**giant molecular**	**simple molecular**			**simple atomic**
Electrical conductivity	good conductors			semi-conductor	non-conductors			

Exercise 1.1

Identify the type of chemical bonding in the following

a) barium, Ba **b)** oxygen, O_2

c) barium oxide, BaO **d)** nitrogen dioxide, NO_2

However, it is possible for a metal and non-metal to form covalent bonds (rather than ionic bonds). For example, the bonds in $AlCl_3$ are considered covalent.

Most chemical bonds are neither purely covalent nor purely ionic but have characteristics of both ionic and covalent bonding (see section 7).

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2 METALLIC BONDING & PHYSICAL PROPERTIES OF METALS

2.1 Metallic Lattice

*LO 2(l) part: describe, in simple terms, the lattice structure of a crystalline solid which is: **(v)** metallic, as in copper*

Metals in the solid state have a **giant metallic lattice structure** which is a lattice of **metal cations** and the **sea of delocalised electrons** held together by metallic bonding.

Figure 3 shows the structure and bonding in calcium metal.

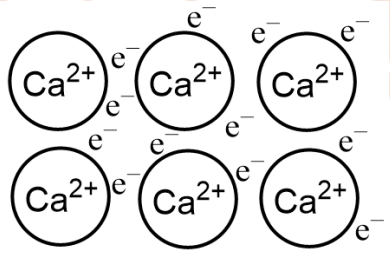


Figure 3. Structure and bonding in calcium metal

In solid calcium, Ca^{2+} cations are arranged in a **regular** manner. Each Ca atom contributes **two valence electrons** into the **sea of delocalised electrons**. These delocalised electrons are no longer attracted to only one specific atom but can **move freely** throughout the lattice. These delocalised electrons are responsible for the characteristic physical properties of metals such as good electrical and thermal conductivity.

Note: The metal is electrically neutral as the number of positive and negative charges **balance** out.

2.2 Strength of Metallic Bonding

The strength of the attraction between the metal cations and the delocalised electrons depends on:

- **number of valence electrons contributed per metal atom**
  The larger the number of valence electrons contributed per atom, the greater the number of delocalised electrons, the stronger the metallic bonding.

- **charge and radius of the metal cation**
  The higher the charge and the smaller the radius of the metal cation, the higher its **charge density***, and the stronger the metallic bonding.

  *Charge density of an ion, sometimes called surface charge density, is the amount of charge per unit surface area of that ion. For simplicity, we can compare the charge densities of two ions by comparing their $\frac{\text{ionic charge}}{\text{ionic radius}}$ ratio.

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2.3 Physical properties of metals

LO 2(m): describe, interpret and/or predict the effect of different types of structure and bonding on the physical properties of substances
LO 2(n): suggest the type of structure and bonding present in a substance from given information

2.3.1 High melting and boiling points

Metals have **high** melting and boiling points as a large amount of energy is needed to overcome the strong attraction between the metal cations and the delocalised electrons.

The **stronger** the metallic bonding, **more** energy is needed to overcome the metallic bonding, the **higher** the melting and boiling points.

Exercise 2.1 (Worked Example)
Explain why the melting point of Mg (650 °C) is higher than that of Na (98 °C), quoting relevant data from the *Data Booklet*.

Answer:
Each Mg atom has two valence electrons while each Na atom has one valence electron. Hence, magnesium has a **larger number of delocalised electrons**.
Mg^{2+} (0.065 nm) has a **larger charge** and **smaller ionic radius** than Na^{+} (0.095 nm). Mg^{2+} has a **higher charge density** than Na^{+}.
More energy is needed to overcome the **stronger metallic bonding** in magnesium than that in sodium.

Strategy:
- *compare the no. of valence electron*
- *compare the charge and radius*
- *compare strength of metallic bond & energy needed*

(Useful information)
When a solid metal *melts*, the closely packed cations become further apart but the metallic bonding is *not completely broken*, unlike during boiling. Hence, the boiling point is a better indicator of the strength of metallic bonding than the melting point.

2.3.2 Good electrical and thermal conductivity

In order for a material to conduct electricity, it must have **mobile charge carriers** which are typically electron or ions. Metals are good electrical conductors because the delocalised electrons act as mobile charge carriers.

The delocalised electrons also explain why metals are good conductors of heat. Thermal energy causes the electrons to move more quickly. The energy is then transferred to the other parts of the metal by the mobile electrons.

Exercise 2.2
Why does copper wire conduct electricity when a potential difference is applied?

A Bonding electrons in the crystal lattice move.
B Copper(II) ions move to the cathode.
C The atoms of copper become ionised.
D The crystal lattice breaks down. *[J2002/I/5]*

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2.3.3 Malleable and ductile

Metals are usually malleable (easily beaten or rolled into sheets) and ductile (easily drawn into rods, wires and tubes). When a large stress (e.g. hammering) is applied to a piece of solid metal, the layers of ions will slide over one another into new positions. The overall shape of the metal changes (the metal deforms) but it does not break apart because the 'sea' of delocalised electrons prevents repulsion between the cations as they move past one another, and metallic bonding remains intact.

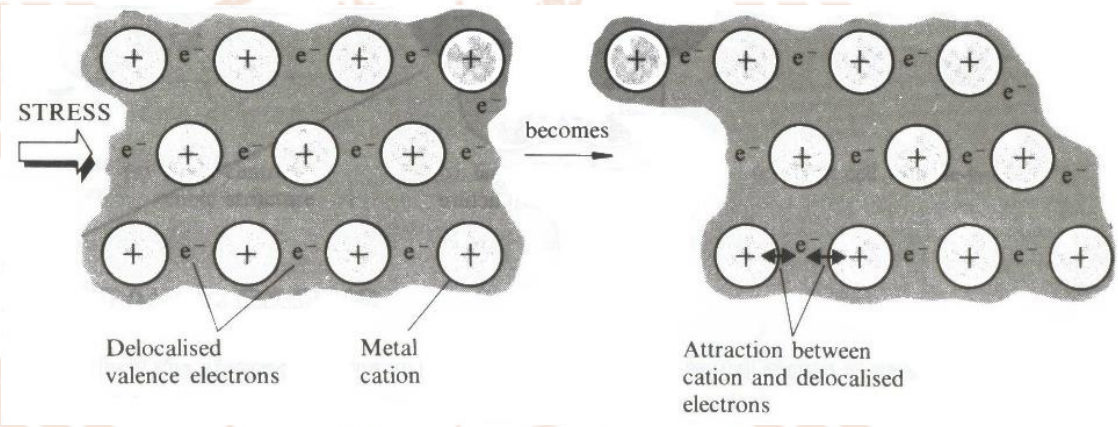


Figure 4. The metallic lattice when subjected to shear stress

2.3.4 Hardness

The hardness of a solid material depends on how easily we can move the particles from their fixed positions in the solid lattice. In metals, this depends on the strength of metallic bonding.

Metals are usually hard, although the Group 1 and 2 metals are soft. Iron is hard and does nor deform easily while sodium can be easily cut with a pen knife.

Alloys & their uses (Application example)

Most metals used in practical applications such as aluminium aircraft frames are in the form of an alloy instead of the pure metal.

Alloys are mixtures of metals involving incorporation of small quantities of other element(s) into the pure metal. Alloying makes metals harder. This is because atoms of the added element(s) have a different size. This will disrupt the orderly arrangement of the main metal atoms such that they can no longer slide over each other easily when a force is applied. This increases the hardness and strength of the alloy compared to the pure metal.

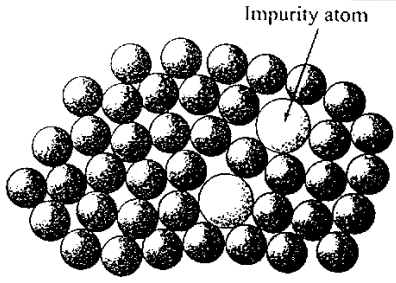


Figure 5. Arrangement of atoms in an alloy

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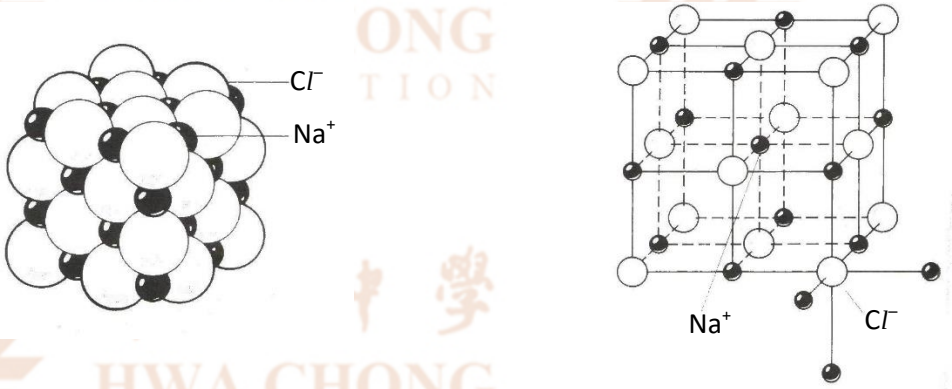
3 IONIC BONDING & PHYSICAL PROPERTIES OF IONIC COMPOUNDS

3.1 Ionic Lattice

*LO 2(l) part: describe, in simple terms, the lattice structure of a crystalline solid which is: **(i)** ionic, as in sodium chloride, magnesium oxide*

Ionic compounds in the solid state have a **giant ionic lattice structure** which is a lattice of **cations and anions** held together by ionic bonding.

Figure 6 shows the structure and bonding in sodium chloride.



space-filling model expanded model

Figure 6. Models of the NaCl lattice. The space-filling model illustrates the close packing of ionic solids while the expanded model shows the coordination number of each ion and the orderly arrangement within the giant ionic lattice.

Ionic bonding exists between *any two* adjacent ions of opposite charge. Ionic bonding is *non-directional* and extends indefinitely in all directions while a covalent bond is *directional* as one covalent bond can only be formed between *two specific* atoms.

Coordination number (Background info)

The number of ions that surround another ion of the **opposite charge** in an ionic lattice is called the **coordination number** of that central ion.

For example, in sodium chloride, one Na^+ cation is surrounded by six Cl^- anions and vice-versa so the coordination number is six (see Figure 6).

Table 3. Coordination number of an ion in an ionic lattice depends on relative sizes and charges of cation and anion

compound	cation radius /nm	anion radius /nm	$\frac{\text{anion radius}}{\text{cation radius}}$	coordination number of cation	coordination number of anion
ZnS	0.08	0.19	2.4	4	4
NaCl	0.10	0.18	1.8	6	6
MgO	0.07	0.14	2.0	6	6
CsCl	0.17	0.18	1.1	8	8
CaF_2	0.10	0.13	1.3	8	4

You are **not** required to memorise the coordination numbers in Table 3.

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Coordination number depends on:

- Relative sizes – a small ion typically has a lower coordination number as there will be less space for ions of the opposite charge to surround it;
- Relative charges – e.g. a cation with +2 charge needs twice as many anions with –1 charge, compared to a cation with +1 charge, to gain charge neutrality.

3.2 Strength of Ionic Bonding

LO 7(e): explain, in qualitative terms, the effect of ionic charge and of ionic radius on the numerical magnitude of a lattice energy

Lattice energy is defined as the heat evolved when 1 mole of a pure ionic solid is formed from its constituent gaseous ions.

We can compare the strength of ionic bonding using lattice energy – the **larger** the magnitude of lattice energy, the **more** heat is given out when the ionic bonds are formed, the **stronger** the ionic bonding.

The magnitude of lattice energy depends on the **charge of the ions**, and their **radii**.

$$\textbf{lattice energy} \propto \frac{q_+ \times q_-}{r_+ + r_-}$$

where q_+ = charge on cation, q_- = charge on anion

r_+ = radius of cation, r_- = radius of anion

The higher the charge and the smaller the radii of the ions, the **larger** the magnitude of lattice energy, the **stronger** the ionic bonding.

3.3 Physical Properties of Ionic Compounds

LO 2(n): describe, interpret and/or predict the effect of different types of structure and bonding on the physical properties of substances

LO 2(o): suggest the type of structure and bonding present in a substance from given information

3.3.1 High melting and boiling points

Ionic solids have **high** melting and boiling points as a large amount of energy is needed to overcome the strong electrostatic attractions between oppositely charged ions.

The **stronger** the ionic bonding, **more** energy is needed to overcome the ionic bonding, the **higher** the melting and boiling points.

Table 4. Small, highly charged ions bond strongly, leading to high melting points.

compound	cation radius /nm	anion radius /nm	cation charge	anion charge	m.p. /°C
NaCl	0.10	0.18	+1	–1	801
NaF	0.10	0.13	+1	–1	993
MgF_2	0.07	0.13	+2	–1	1261
MgO	0.07	0.14	+2	–2	2852

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Exercise 3.1 (Worked Example)

Explain why magnesium oxide has a higher melting point than sodium chloride, quoting relevant data from the *Data Booklet*.

Answer:

From Data Booklet,

	Mg^{2+}	O^{2-}	Na^{+}	Cl^{-}
Ionic radii/nm	0.065	0.140	0.095	0.181

Mg^{2+} has a **smaller radius** than Na^{+} while O^{2-} has a **smaller radius** than Cl^{-}.

Mg^{2+} and O^{2-} have **higher charges** than Na^{+} and Cl^{-}, respectively.

Lattice energy $\alpha \frac{q_+ \times q_-}{r_+ + r_-}$

Lattice energy of MgO is **larger** in magnitude.

More energy is needed to overcome the **stronger** ionic bonding in MgO.

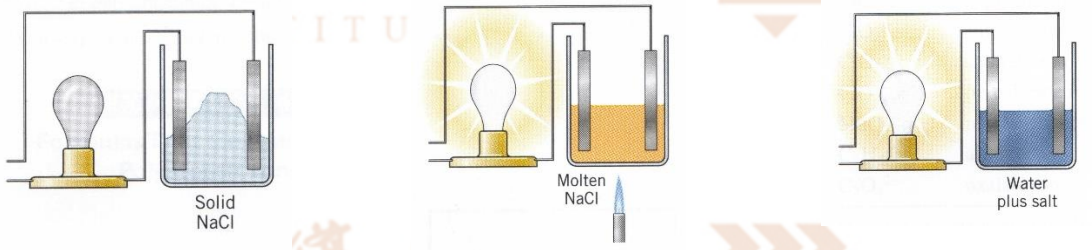
Strategy:

- *quote ionic radii from Data Booklet*
- *compare ionic charges*
- *quote LE formula & compare magnitude of lattice energy, strength of ionic bond & energy needed*

3.3.2 Good electrical conductivity

In the solid state, ionic compounds do not conduct electricity as the ions are in fixed positions and are not free to move.

In the **molten or aqueous** state, ionic compounds are good electrical conductors because the ions can act as **mobile charge carriers**.



Lamp unlit Lamp lights up Lamp lights up

Figure 7. Ionic compounds do not conduct electricity in the solid state but do so when molten or dissolved in aq. solution

The electrical conductivity of an aqueous solution of an ionic compound increases as its concentration increases, because there are more ions to carry the charge.

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3.3.3 Hard and rigid but brittle

In an ionic lattice, oppositely charged ions are held in fixed positions throughout the crystal lattice by **strong** ionic bonding. Moving the ions out of position requires **large amounts of energy** to overcome these bonds. Ionic lattices are therefore quite **hard** (do not dent or deform easily) and **rigid** (do not bend easily).

If a strong enough force (e.g. by cutting or knocking) is applied, it will force ions of like charges to move next to each other. **Repulsion** between ions of **like** charges will cause the lattice to shatter. Ionic lattices are therefore brittle (crack without deforming).

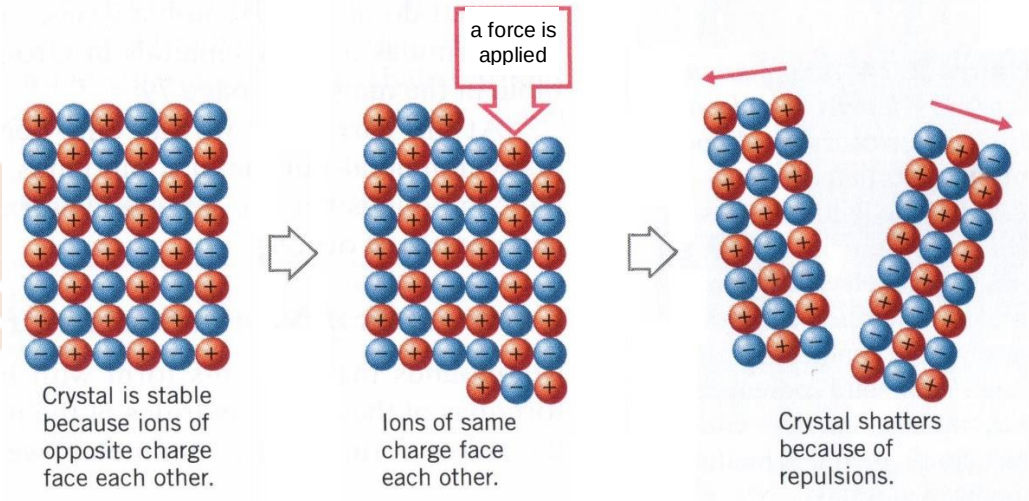


Figure 8. A shearing force will shatter an ionic crystal

3.3.4 Solubility

Ionic compounds are usually soluble in water, e.g. NaC*l*, KBr and BaCl_2. However, there are examples of insoluble ionic compounds as well, e.g. AgC*l*. See Section 12 for the explanation on the solubility of ionic compounds.

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4 FORMATION AND STRENGTH OF COVALENT BONDING

4.1 Covalent Bonding and Orbital Overlap

LO 2(c): describe covalent bonding in terms of orbital overlap (limited to s and p orbitals only), giving σ and π bonds

A covalent bond is formed when two atoms share a pair of electrons which are found in the valence orbitals of the atoms.

In order for the bond to be formed, the **orbitals of the two atoms must overlap**. The shared electrons or bond pairs occupy the region between the two nuclei formed by the overlap.

There are two types of orbital overlap:

- **sigma (σ) bond** is formed by **'head-on' overlap** of two orbitals.

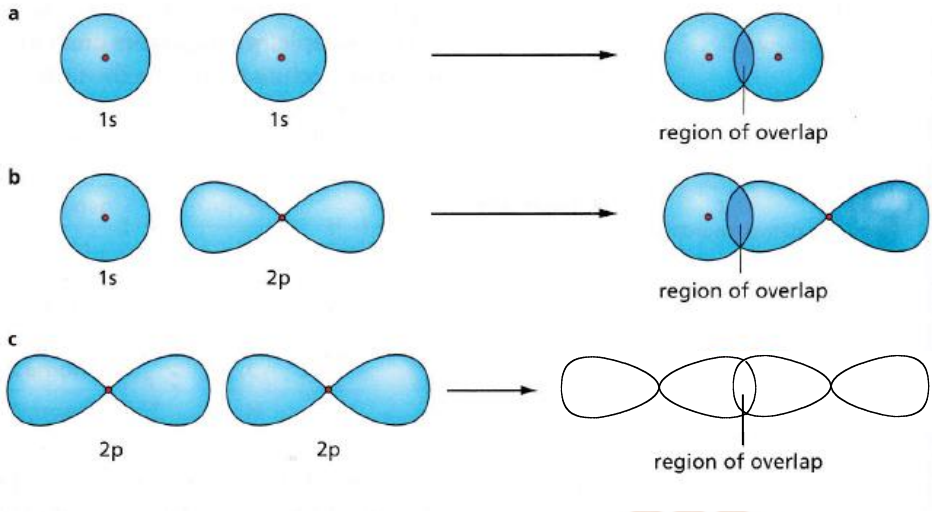


*Figure 9. Examples of head-on overlaps **(a)** σ bond formed by s-s overlap (e.g. H–H bond); **(b)** σ bond formed by s-p overlap (e.g. H–F bond); **(c)** σ bond formed by p-p overlap (e.g. F–F bond)*

- **pi (π) bond** is formed by **'side-on' overlap** of two orbitals.

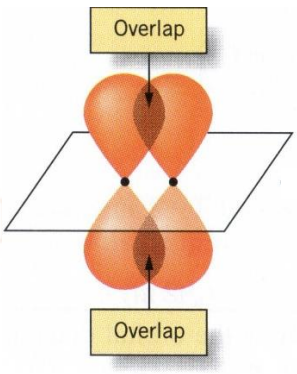


Figure 10. Side-on overlap between two p orbitals to form a π bond.

While p orbitals can overlap both head-on and side-on, s orbitals can only overlap head-on to form sigma bonds; they are unable to overlap side-on to form pi bonds.

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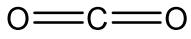
Side-on overlap for a π bond is **poorer** than head-on overlap for a σ bond, as the degree of overlap is smaller for the former. Hence, a π bond is **weaker** than a σ bond.

Between two atoms, there **can only be one σ bond** as it is **not** possible for a second pair of orbitals to overlap head-on as well. Also, for a π bond to form, a σ bond must first be formed. Hence,

- a **single** bond consists of a **σ bond** (the two atoms share one pair of electrons);
- a **double** bond consists of **one σ bond and one π bond** (the two atoms share four electrons);
- a **triple** bond consists of **one σ bond and two π bonds** (the two atoms share six electrons).

Exercise 4.1

(a) State the number of σ bonds and π bonds present in a CO_2 molecule, given the structure below.



(b) Draw a diagram to illustrate how the atomic orbitals overlap for each of the following.

(i) σ bond in the H_2 molecule **(ii)** π bond in the CO_2 molecule

4.2 Strength of Covalent Bonding

LO 2(j): explain the terms bond energy and bond length for covalent bonds

Bond strength depends on the **degree of orbital overlap** between the two bonded atoms and also **how strongly the electrons in the overlap region are attracted** to the nuclei of the atoms.

Bond energy is the average amount of energy required to **break** 1 mole of a covalent bond in the gaseous state to form gaseous atoms.

We can compare the strength of covalent bonding using bond energies – the **larger** the bond energy, the more heat is needed to break the bond, the **stronger** the covalent bonding.

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Bond energy, hence strength of covalent bonding, depends on:

- **bond length** i.e. the distance between the nuclei of the two bonded atoms

  Smaller atoms form **shorter** and **stronger** bonds, as the overlap between orbitals is more effective.

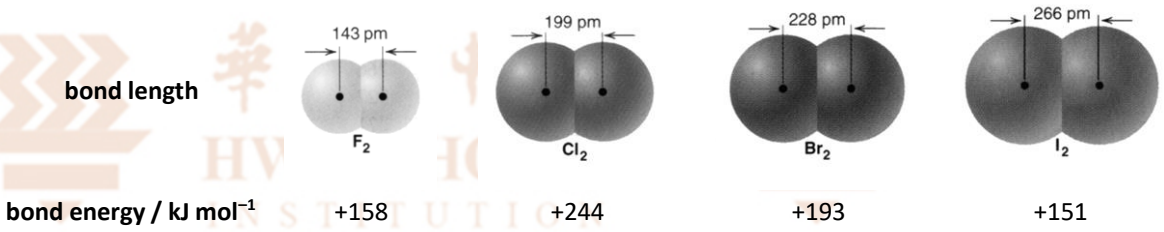


Figure 11. Bond length and bond energy in the diatomic halogen molecules.

  Exception: The F–F bond is shorter *but* weaker than the C*l*–C*l* bond. This is possibly due to the repulsion between the lone pairs on the fluorine atoms which are in close proximity.

- **bond order** i.e. the number of covalent bonds between a pair of atoms

  Multiple bonds are **shorter** and **stronger** than single bonds. When more electrons are being shared, the attraction between the two positively charged nuclei and the shared electrons is stronger.

Table 5. Multiple bonds are stronger and shorter than single bonds

bond	bond length /pm	bond energy / kJ mol^{-1}	bond	bond length /pm	bond energy / kJ mol^{-1}
C–C	154	+350	C–O	143	+360
C=C	134	+610	C=O	123	+740
C≡C	121	+840	C≡O	113	+1080

LO 2(k) part: compare the reactivities of covalent bonds in terms of bond energy, bond length

In general, a **longer** bond is **weaker** so it is usually broken more easily and **reacts more readily**. For example, the H-I bond is weaker than the H-C*l* bond. Hydrogen iodide undergoes decomposition readily; hydrogen chloride does not decompose on heating. N_2 is unreactive due to the strong N≡N triple bond.

Exercise 4.2

Suggest, in terms of orbital overlap, why the bond energy of C=C bond (+610 kJ mol^{-1}) is less than twice the bond energy of C-C bond (+350 kJ mol^{-1}).

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Bond Length, Covalent Radius and van der Waals Radius – Useful Information

Iodine exists as a diatomic molecule, I_2. When we measure the distances between the nuclei of two bonded iodine atoms in iodine solid, we obtain two different values.

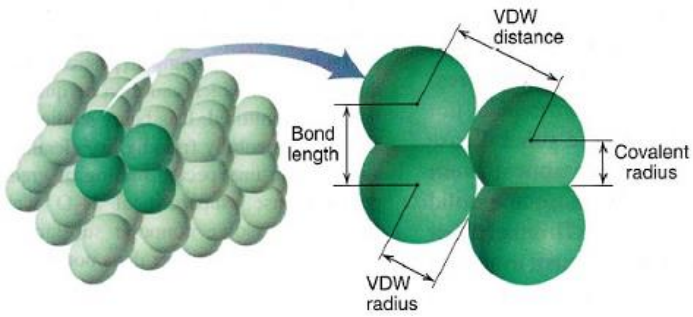


Figure 12. Covalent radius and van der Waals radius of iodine

The shorter distance is between **two bonded atoms** in the same molecule. This is called the **bond length** and half of this distance is called the **covalent radius** (referred to as 'single covalent' in the *Data Booklet*).

The longer distance is between **two non-bonded atoms** in adjacent molecules. Half of this distance is called the **van der Waals radius**. The van der Waals radius of an atom is always larger than its covalent radius. In the *Data Booklet*, the radii listed for the noble gases are the van der Waals radii since they do not form compounds.

Both covalent radii and van der Waals radii decreases across a period and increases down a group. It is important to compare radii of the same type when comparing sizes of atoms. In Topic 1 Figure 14, the van der Waals radii of He, Ne and Ar were plotted with the covalent radii of the other elements. This explains why the atomic radii increase from Group 17 to Group 18.

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5 DOT-AND-CROSS DIAGRAMS

The dot-and-cross diagram is used to represent the type of bond (ionic or covalent) and the valence electrons of the interacting atoms. The element's symbol represents the nucleus and the inner shell electrons, while the dots and crosses represent the valence electrons.

When an ionic bond is formed, electron transfer occurs. When a covalent bond is formed, electron sharing occurs. In many cases (though not always), the atoms lose, gain or share electrons to attain a filled outer electron shell of eight electrons (i.e. octet or noble gas configuration $ns^2\ np^6$). This is known as the **octet rule** (see section 5.2.1 for exceptions to octet rule).

5.1 Dot-and-Cross Diagrams for Ionic Compounds

LO 2(b)(i): describe, including the use of 'dot-and-cross' diagrams: ionic bonding as in sodium chloride and magnesium oxide

Figure 13 shows the dot-and-cross diagrams for sodium chloride and magnesium chloride. Electron(s) are transferred from the metal (sodium and magnesium) to the non-metal (chlorine). Each atom forms an ion with an octet electronic configuration. The resulting ions combine in the correct proportions such that the compound is electrically neutral.



Figure 13. Dot-and-cross diagrams for sodium chloride and magnesium chloride. When the cation is formed, the valence electron(s) are lost so we do not draw any dots or crosses around the metal.

Exercise 5.1

(a) Draw the dot-and-cross diagrams for the following ionic compounds.

(i) magnesium oxide (MgO)

(ii) sodium oxide (Na_2O)

(b) Explain why the oxide of sodium has this formula Na_2O.

[N2006/III/4(a) modified]

Each Na at… forming Na…

Each O at… (from tw…

Na is need… to … charg… ra…

Therefore…

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5.2 Dot-and-Cross Diagrams for Covalent Compounds

LO 2(b)(ii): describe, including the use of 'dot-and-cross' diagrams: covalent bonding as in hydrogen; oxygen; nitrogen; chlorine; hydrogen chloride; carbon dioxide; methane; ethene

Figure 14 shows the dot-and-cross diagrams for the hydrogen, oxygen and nitrogen molecules. Between any two bonded atoms, use different electron symbols (• and × only; do not use other symbols e.g. circles, triangles unless otherwise stated).

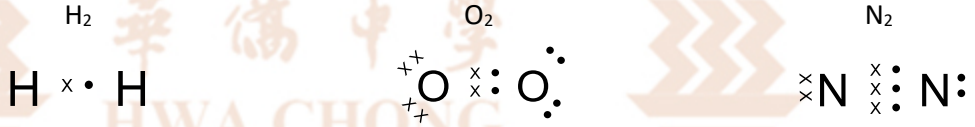


Figure 14. Dot-and-cross diagrams for hydrogen, oxygen and nitrogen

The hydrogen atom has one valence electron, so it forms one bond. The oxygen atom has six valence electrons. It needs two more electrons to attain an octet configuration so it forms two bonds. Similarly, nitrogen has five valence electrons and forms three bonds. Both oxygen and nitrogen obey the octet rule; each has eight electrons after sharing electrons. Hydrogen does not follow the octet rule since it is in Period 1 and its valence shell (1s) can only accommodate two electrons.

Exercise 5.2

Draw the dot-and-cross diagrams for the following molecules.

(a) HC*l* **(b)** CO_2 **(c)** CH_4

5.2.1 Exceptions to the octet rule

The octet rule is based on empirical observations. We can use the rule to identify structures which are likely to be stable but it **cannot** be used to explain the stability of substances.

While the octet rule is obeyed by nearly all the Period 2 elements (such as C, N, O, F), there are several exceptions.

- **Molecule whose central atom has fewer than 8 electrons**
  In beryllium chloride and boron fluoride, the central atoms (Be and B) have fewer than 8 electrons in their valence shell. Beryllium chloride and boron fluoride are **electron deficient** species.



Figure 15. Dot-and-cross diagrams for beryllium chloride and boron fluoride

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Exercise 5.3

Draw the dot-and-cross diagrams for the following molecules.

(a) aluminium chloride, $AlCl_3$ **(b)** boron hydride, BH_3

- **Molecule whose central atom has <u>more</u> than 8 electrons**

  In phosphorus pentachloride, PCl_5, the central phosphorus atom has 10 electrons in its valence shell. Phosphorus (in **Period 3**) can form **more than 4 bonds** by using its **d orbitals** to accommodate additional electrons (i.e. one 3s + three 3p + one 3d). We say phosphorus (and other elements **from Period 3 and higher**) can **<u>expand its octet</u>** by using **<u>energetically accessible d orbitals</u>**.

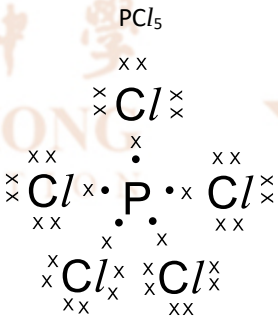


Figure 16. Dot-and-cross diagram for phosphorus pentachloride

Period 2 elements (e.g. nitrogen) have only four orbitals in their valence shells (2s, $2p_x$, $2p_y$ and $2p_z$). Their 3d orbitals are not energetically accessible, because they are in an outer quantum shell which is at a much higher energy level. Thus, elements in Period 2 cannot accommodate more than four pairs of electrons in their valence shells. The number of covalent bonds formed is restricted by an overall maximum of eight electrons, since every new bond brings another electron into the valence shell.

Exercise 5.4 (Worked Example)

(a) Oxygen and sulfur are both Group 16 elements. Oxygen forms OF_2 with fluorine but not OF_4 or OF_6. Sulfur forms SF_2, SF_4 as well as SF_6. Give reasoning for this observation.

Answer:

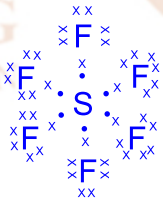
Both oxygen and sulfur have <u>six valence electrons</u> so they use two valence electrons to <u>form two bonds</u> (in OF_2 and SF_2) to attain octet.

Unlike oxygen in Period 2, sulfur in Period 3 is able to use its <u>energetically accessible 3d orbitals</u> to <u>accommodate more than 8 electrons</u>. Hence, sulfur can use four or six valence electrons in bonding with fluorine to form SF_4 and SF_6 respectively.

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(b) Draw the dot-and-cross diagrams for OF_2 and SF_6.

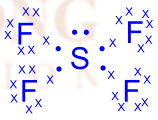




(c) State the number of electrons around the sulfur atom in SF_4.

Answer:
There are 10 electrons around the sulfur atom in SF_4

Comment: *"electrons around the sulfur atom" here refers only to valence electrons, whether lone pairs or bonding electrons. FYI, SF_4 is*



Besides phosphorus and sulfur, the chlorine atom can also expand its octet to form ClF_3 and ClF_5 but not ClF_4 and ClF_6 because this will result in an unpaired valence electron. It is not able to form ClF_7 because the Cl atom is too small to accommodate seven fluorine atoms around it.

- **Molecule with <u>unpaired</u> electrons**
  In some molecules (with odd total number of electrons), the central atom (usually a Group 15 or Group 17 element) has unpaired electrons in the valence shell. **Species with unpaired electrons** are called **<u>radicals</u>**. Radicals are very reactive.

NO



ClO_2

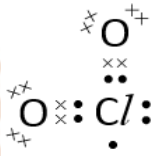


Figure 17. Dot-and-cross diagrams for nitrogen monoxide and chlorine dioxide

5.3 Further Dot-and-Cross Diagrams

Some dot-and-cross diagrams are less straight forward to draw, for example, C_2H_4 (ethene), and polyatomic ions such as NH_4^+, SO_4^{2-} and NO_3^-.

General guidelines

1. Decide on the **<u>central atom</u>**, and the terminal atoms. The central atom is usually the one with the lowest electronegativity (e.g. sulfur in SO_4^{2-}) or the one that can form more covalent bonds (e.g. carbon in C_2H_4 and nitrogen in NH_4^+); H forms one bond so it cannot be a central atom.

2. For polyatomic ions:
   For each (–) charge, **add** one electron to the **more** electronegative atom. E.g. oxygen is assigned the extra electrons in SO_4^{2-}
   For each (+) charge, **remove** one electron from the **less** electronegative atom. E.g. the electron is removed from hydrogen, in NH_4^+

   Draw **square brackets** around the ion and write its **charge** as a superscript outside the bracket.

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3. Make **terminal atoms** achieve **octet** by assigning single, double or triple bonds accordingly. The number of bonds is equal to the number of electrons needed to achieve octet.
   E.g. in SO_4^{2-}, the oxygen which is assigned the 'extra electron' has 7 electrons so it forms a single bond while the oxygen with 6 valence electrons forms a double bond or 2 single bonds.

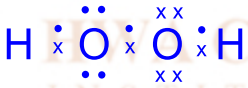
   Draw in the remaining valence electrons of all atoms in pairs.

4. Check the **central atom**.
   - Elements in **Period 2** (e.g. C, N, O) can accommodate **maximum 8 electrons**; if there are more than 8 electrons, change a double bond to a **co-ordinate (dative) bond** (see section 5.4).
   - Elements in **Period 3 or higher** (e.g. P, S, Cl) can accommodate **more than 8 electrons**.
   - Elements in Group 2 (e.g. Be) and Group 13 (e.g. B, Al) may be **electron deficient**.
   - Elements in Group 15 (e.g. N) and Group 17 (e.g. Cl) may have **unpaired electrons**.

Exercise 5.5

Draw the dot-and-cross diagrams for the following molecules, ions or compounds.

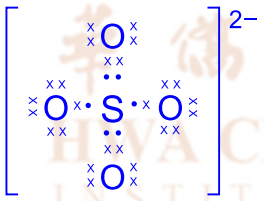
(a) hydrogen peroxide, H_2O_2 **(Worked Example)**



- *The name 'peroxide' means two oxygen atoms are linked together by a single covalent bond.*
- *Oxygen is in **Period 2**; do **not** place > 8 electrons around it.*

(b) barium peroxide, BaO_2 (contains one cation and one anion)

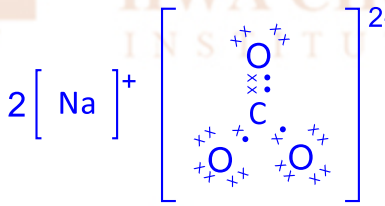
(c) SO_4^{2-} **(Worked Example)**



- *S is the central atom. It is less electronegative than O.*
- *Two negative charges ⇒ add 1 electron each to two of the O atoms. These O atoms form a single bond with S atom. The O atoms with 6 valence electrons form a double bond.*
- *S is in **Period 3** so it can accommodate > 8 electrons i.e. **expand** its **octet**.*
- *Draw square brackets around the ion and write the charge outside the bracket.*

(d) PCl_4^+

(e) Na_2CO_3 **(Worked Example)**



- *Two negative charges ⇒ add 1 electron each to two of the O atoms (**more electronegative** than than C).*
- *Ratio of Na^+ to CO_3^{2-} is 2:1 so that the compound is **electrically neutral**.*

(f) NaClO (contains one cation and one anion)

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5.4 Co-ordinate Bonding (also called dative bonding)

LO 2(b)(iii): describe, including the use of 'dot-and-cross' diagrams: co-ordinate (dative covalent) bonding, as in formation of the ammonium ion and in the Al_2Cl_6 molecule

So far, we have looked at covalent bonds in which each atom provides one electron to form the bond. If **both** bonding electrons come from one atom, the bond is called **co-ordinate bond** or **dative bond**. A co-ordinate bond, once formed, is no different from any other covalent bond.

To form a co-ordinate bond, the **donor atom** must have a **lone pair** (valence electron pair not involved in bonding) while the **acceptor atom** must contain an **empty orbital in its valence shell**. We represent a co-ordinate bond with an arrow from the donor atom to the acceptor atom. In dot-and-cross diagrams, a co-ordinate bond is represented using two dots or two crosses.

Example 1: NH_3BF_3

When gaseous NH_3 and gaseous BF_3 react together, white solid NH_3BF_3 forms.

The **nitrogen** atom in NH_3 has a **lone pair**. The **boron** atom in BF_3 has only 6 electrons in its valence shell and is **electron deficient**. It has an **empty 2p orbital** which can accept the lone pair from nitrogen.

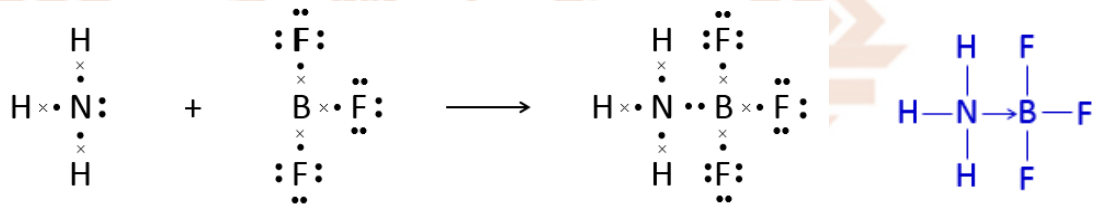


Figure 18. Dot-and-cross diagrams for NH_3, BF_3, and NH_3BF_3

Example 2: Al_2Cl_6

Just below its melting point, aluminium chloride exists as the Al_2Cl_6 dimer.

In the monomer $AlCl_3$, the **aluminium** atom has 6 electrons in its valence shell and is **electron deficient**. It has an **empty 3p orbital** which can accept the **lone pair** from the **chlorine** atom of another $AlCl_3$ monomer.

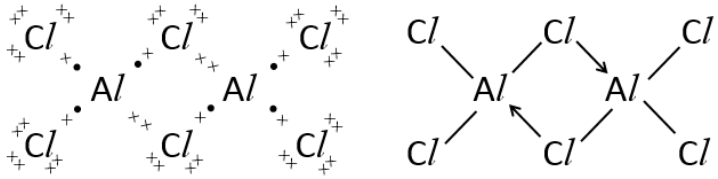


Figure 19. Dot-and-cross diagram and structure of Al_2Cl_6 dimer. The co-ordinate bonds are broken above 800 °C.

Example 3: The ammonium cation, NH_4^+

When gaseous NH_3 and gaseous HCl react together, the H–Cl bond breaks to give H^+ and Cl^-. **The lone pair** on the **nitrogen** atom forms a co-ordinate bond with **H^+**, which has an **empty 1s orbital**, to form NH_4^+.

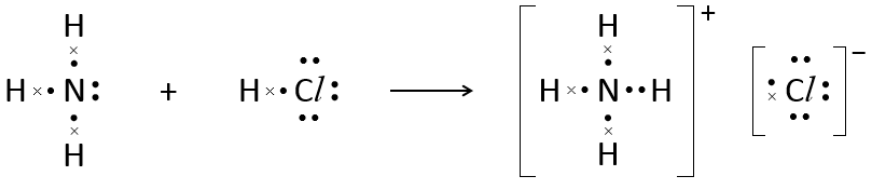


Figure 20. Dot-and-cross diagrams for NH_3, HCl and NH_4Cl

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Exercise 5.6

Draw the dot-and-cross diagrams for the following molecules, ions or compounds.

(a) NO_2 **(Worked Example)**



- *Nitrogen and oxygen are in **Period 2**; do **not** place > 8 electrons around them. Hence, N does not form 2 N=O bonds (N will have 9 electrons around it); change one N=O bond to a co-ordinate bond.*
- *N atom has an **unpaired** electron; NO_2 is a radical.*

(b) CO

(c) ClF_4^-

(d) $Mg(NO_3)_2$

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6 SHAPES OF MOLECULES AND POLYATOMIC IONS

LO 2(d): explain the shapes of, and bond angles in, molecules such as BF_3 (trigonal planar); CO_2 (linear); CH_4 (tetrahedral); NH_3 (trigonal pyramidal); H_2O (bent); SF_6 (octahedral) by using the Valence Shell Electron Pair Repulsion theory
LO 2(e): predict the shapes of, and bond angles in, molecules analogous to those specified in (d)

The shapes of molecules and polyatomic ions refer to the geometrical figure that results if the nuclei of the bonded atoms are joined by straight lines.

The shapes, as well as bond angles, of molecules and polyatomic ions are determined by the arrangement of the electrons pairs around each atom. There are two types of electron pairs:

- An electron pair that is shared between bonded atoms is called a **bond pair**.
- An electron pair that is in the valence shell but not shared with another atom is called a **lone pair**.

6.1 Valence Shell Electron Pair Repulsion (VSEPR) Theory

The two main principles of the VSEPR theory are:

- The electron pairs (or electron groups) around the central atom of a molecule (or ion) arrange themselves **as far apart as possible** so as to minimise their mutual repulsion.

- The repulsion between **lone pair and lone pair > lone pair and bond pair > bond pair and bond pair**.

  A lone pair is attracted by only one nucleus while a bond pair is attracted by two nuclei. The electron cloud of a lone pair is less 'elongated' than a bond pair. A lone pair of a central atom takes up more space around the atom. It is **closer** to the central atom so it repels other electron pairs around it more than a bond pair would.

We can use the VSEPR theory to predict the shapes of, and bond angles in a molecule or ion.

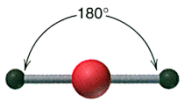
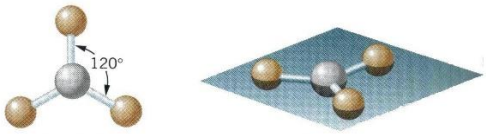
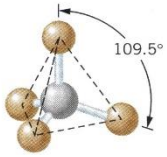
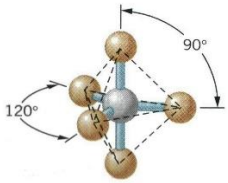
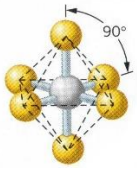
1. Determine the **number of electron pairs** (i.e. total number of bond pairs and lone pairs) around the central atom. This may be done by drawing the dot-and-cross diagram.

   A double bond or triple bond is counted as <u>one group</u> of electrons.

2. Arrange the electron pairs (or electron groups) such that they are **as far apart as possible** (see Table 6).

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Table 6. Arrangement of electron pairs around a central atom

number of electron pairs	arrangement of electron pairs	description
2		linear
3		trigonal planar
4		tetrahedral
5		trigonal bipyramidal
6		octahedral

Although they are important in determining the shape of a molecule or ion, lone pairs are **not** included when describing the shape. **The <u>shape</u> is named based on the positions of the <u>atoms</u>**.

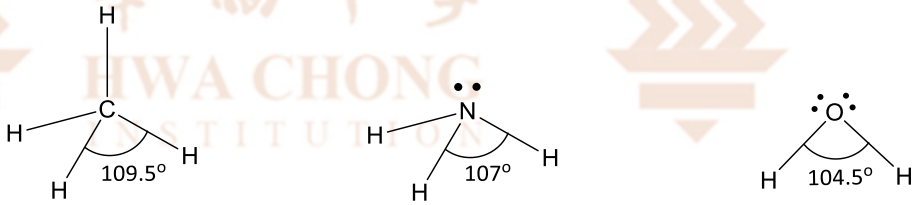


Figure 21. The shapes of CH_4 (tetrahedral), NH_3 (trigonal pyramidal) and H_2O (bent).

Consider CH_4, NH_3 and H_2O. All three molecules have four electron pairs around the central atom but only the methane molecule has a tetrahedral shape. Ammonia is trigonal pyramidal (it has 3 bond pairs and 1 lone pair), and water has a bent shape (it has 2 bond pairs and 2 lone pairs).

The drawings in Figure 21 are examples of **Lewis structures**. Lines are drawn between bonded atoms ('–', '=' and '≡' to represent single, double and triple bonds respectively). An arrow → can be used to represent a co-ordinate (dative) bond.

A lone pair on the central atom is indicated as two dots or drawn like an 'electron cloud'. When **<u>drawing structures</u>** to illustrate the shapes of molecules, we **<u>must include the lone pairs on the central atom</u>**. The lone pairs of terminal atoms (if any) can be omitted since these are not considered in the determination of the shapes.

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Table 7. The shapes of molecules and ions depends on the number of bond pairs and lone pairs. The shape is named based on the positions of the atoms.

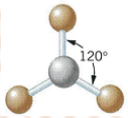
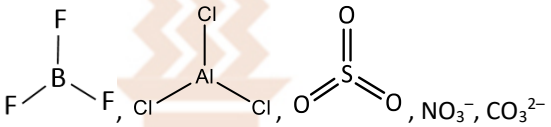
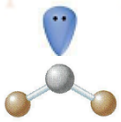
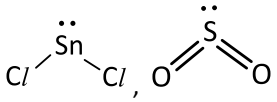
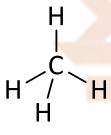
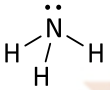
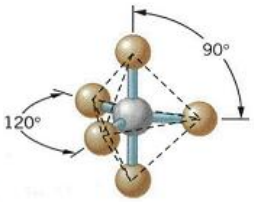
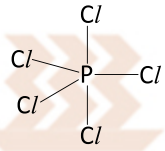
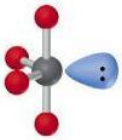
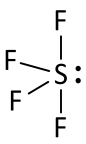
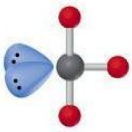
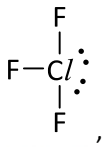
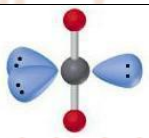
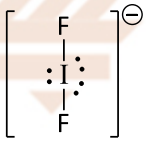
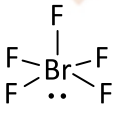
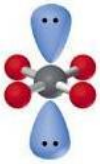
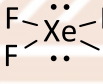
number of			shape and bond angle	examples
electron pairs	bond pairs	lone pairs		
2	2	0	 linear 180°	Cl—Be—Cl , O=C=O , H—C≡N
3	3	0	 trigonal planar 120°	 , NO_3^-, CO_3^{2-}
	2	1	 bent e.g. 118°	 , $PbCl_2$, NO_2^-, O_3
4	4	0	 tetrahedral 109.5°	 , CCl_4, $SiCl_4$, NH_4^+, SO_4^{2-}, ClO_4^-
	3	1	 trigonal pyramidal 107°	 , NF_3, PH_3, PCl_3, PF_3, ClO_3^-, H_3O^+
	2	2	 bent 104.5°	 , H_2S, OF_2, SF_2, SCl_2
5	5	0	 trigonal bipyramidal	 , AsF_5, SF_5^+
	4	1	 see saw	

Table continues next page

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number of			shape and bond angle	examples
electron pairs	bond pairs	lone pairs		
5 (cont'd)	3	2	 T-shape See Useful Information on page 57	 , BrF_3, ICl_3
	2	3	 linear 180°	 , I_3^-, XeF_2
6	6	0	 octahedral 90°	 , PCl_6^-, IF_6^+
	5	1	 square pyramidal	 , IF_5, SF_5^-, $SbCl_5^{2-}$
	4	2	 square planar 90°	 , ICl_4^-, ClF_4^-

In the above examples, there is only one central atom in the molecule or ion. If there are more than one central atom (e.g. H_2SO_4, H_2O_2, C_2H_4), we state the shape **with respect to each central atom** to be unambiguous.

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Useful Information

In ClF_3, the central atom is surrounded by five pairs of electrons (three bond pairs and two lone pairs). There are three ways to arrange these five pairs of electrons.

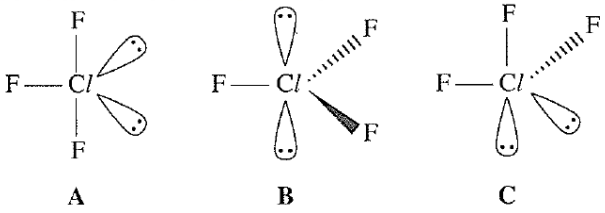


Figure 22. Three different molecular arrangements of ClF_3

C is the least stable as the 2 lone pairs are only 90° apart so lone pair-lone pair repulsion is the greatest. **B** is less stable than **A** as **B** has more significant lone pair-bond pair repulsions. Although the 2 lone pairs in **B** are 180° apart, the 3 bond pairs are perpendicular to the lone pairs, i.e. 90° apart, resulting in significant lone pair-bond pair repulsions. In **A**, there are only 2 bond pairs at 90° to the lone pairs. Hence, ClF_3 molecule has a T-shape.

3. **Bond angle** is the angle **between two bond pairs**.

The second principle of the VSEPR theory – repulsion between **lone pair and lone pair > lone pair and bond pair > bond pair and bond pair** is used to explain the bond angles in molecules such as CH_4, NH_3 and H_2O.

Although each molecule have four electron pairs around the central atom, only the CH_4 molecule has a bond angle of 109.5°. NH_3 and H_2O contain one and two **lone pairs** respectively, which **exert a stronger repulsion** than the bond pairs. The bond pairs in NH_3 and H_2O are pushed closer together resulting in slightly **smaller bond angles**, 107° and 104.5° respectively (see Figure 21).

Compare SO_3 and SO_2. Both molecules have three groups of electron around the central atom (see Table 7). SO_3 is trigonal planar with a bond angle of 120°. SO_2 has one lone pair so it has a bent shape and a bond angle of about 118°.

Useful Information

Repulsion between electron pairs also depends on the electronegativity of both the central and terminal atoms. For example, O is more electronegative than S. The bond pairs are closer to the central atom in H_2O than in H_2S resulting in greater repulsion and larger angle.

F is more electronegative than H. The bond pairs are closer to the central atom in NH_3 than in NF_3 resulting in greater repulsion and a larger angle.



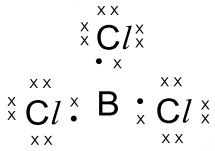
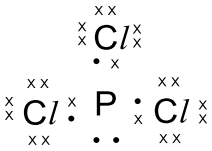
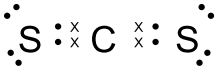
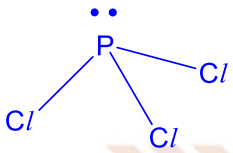
The bond pairs are closer to O than to S. *The bond pairs are closer to N in NH_3 than in NF_3.*

Figure 23. H_2O and H_2S are both bent but have different bond angles.
NH_3 and NF_3 are both trigonal pyramidal but have different bond angles.

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Exercise 6.1

Predict the shapes and bond angles of the following.

	BCl_3	PCl_3 **(Worked Example)**	CS_2
dot-and-cross diagram			
no. of bond pairs around central atom		3	
no. of lone pairs around central atom		1	
arrangement of electron pairs (to minimise repulsion)			
shape		trigonal pyramidal	
bond angle		107° *(between two P–Cl bonds)*	

Exercise 6.2

Predict the shapes and bond angles of the following.

(a) XeF_2 **(Worked Example)**

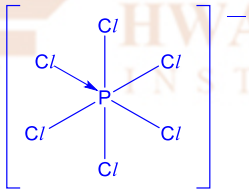


linear, 180°

- *Xe is in **Period 5** so it can **expand** its **octet** and accommodate > 8 electrons around it*
- *2 bond pairs & 3 lone pairs around central Xe atom ⇒ linear*
- *Bond angle between two Xe–F bonds is 180°*

(b) PCl_5

(c) PCl_6^- **(Worked Example)**



octahedral, 90°

- *One negative charge ⇒ add 1 electron to one of the Cl atoms (**more electronegative** than P atom)*
- *6 bond pairs & no lone pair around P atom ⇒ octahedral*
- ***Four equatorial Cl atoms** and the P atom form a **square plane**; the other **two** Cl atoms are **axial Cl atoms.***

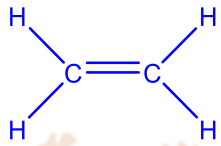
(d) ClF_4^-

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(e) IF_5 (bond angle not required)

(g) ClO_4^-

(g) C_2H_4 **(Worked Example)**



trigonal planar around each C atom, 120°

- *3 bond 'pairs' (or group of electrons) & no lone pair around **each** central atom ⇒ trigonal planar around **each** C atom*
- *Bond angles between C–H bond and C=C bond and between two C–H bonds are 120°*

(h) H_2O_2

6.2 Hybridisation of Atomic Orbitals

LO 11.1(d): describe sp^3 hybridisation, as in ethane molecule, sp^2 hybridisation, as in ethene and benzene molecules, and sp hybridisation, as in ethyne molecule (Refer to Topic 12 Arenes with regards to benzene)
LO 11.1(e): explain the shapes of, and bond angles in, the ethane, ethene, benzene, and ethyne molecules in relation to σ and π carbon-carbon bonds (Refer to Topic 12 Arenes with regards to benzene)

The hybridisation theory (Background Info)

To account for the bonding in diatomic molecules like HF, we picture the direct overlap of s and p orbitals of isolated H and F atoms.

But how can we account for the shapes of so many molecules and polyatomic ions through the overlap of spherical s orbitals, dumbbell-shaped p orbitals and cloverleaf-shaped d orbitals?

For example, consider the methane molecule, CH_4, which has a tetrahedral shape and a bond angle of 109.5°. Its tetrahedral shape suggests that its C atom should 'provide' four orbitals oriented in a tetrahedral geometry, each containing one electron, and each orbital forms a σ bond with the 1s orbital of a H atom via head-on overlap (Figure 24).

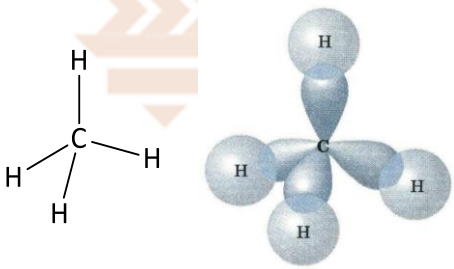


Figure 24. CH_4 molecule and expected orientation of orbitals around the C atom (each orbital forms a σ bond with the 1s orbital of a H atom)

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Now look at an isolated ground-state carbon atom's valence shell electronic configuration ($2s^2\ 2p^2$), and the shapes of its 2s and 2p orbitals:

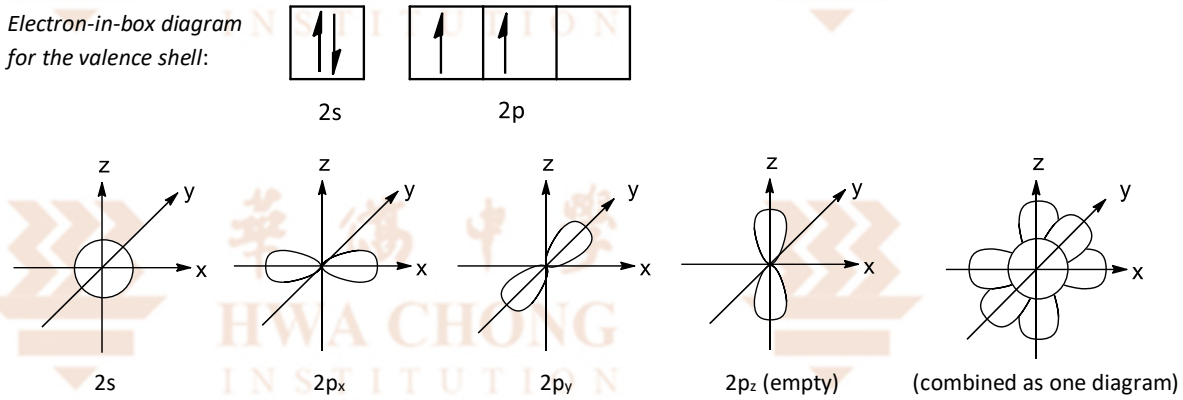


Figure 25. Electron-in-box diagram and shapes of valence atomic orbitals of an isolated ground-state C atom

There is a mismatch between the expected orientation (tetrahedral) of the orbitals involved in bonding for the C atom in CH_4, compared to those of an isolated C atom (perpendicular 2p orbitals); and also in terms of the numbers of single unpaired electrons that can be used for σ bonding.

Linus Pauling proposed that valence atomic orbitals of atoms in a molecule are *different* from those of isolated atoms. In his **hybridisation theory**, **atomic orbitals (s and p, and sometimes d) mix to form new orbitals called hybrid orbitals** which may then involve in σ bonding. Using this theory, we can explain **how molecular shapes arise from the arrangements of hybrid orbitals**. In the example of the methane molecule, one 2s orbital and three 2p orbitals are mixed to give four sp^3 hybrid orbitals which are oriented 109.5° to each other so as to minimise repulsion with one another. All four hybrid orbitals are identical in energy, so the four valence electrons of carbon occupy each hybrid orbital singly.

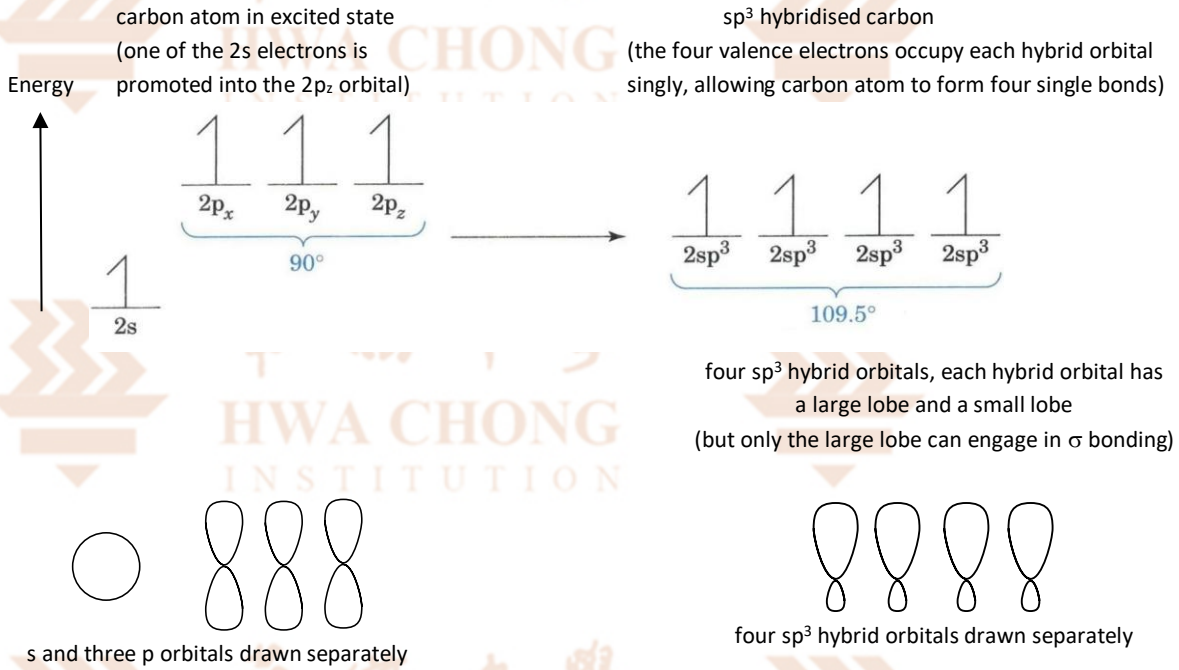


Figure 26. Mixing of an s orbital and three p orbitals to form four sp^3 hybrid orbitals for a carbon atom

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Each of the four C–H bonds is an s-sp^3 σ bond, which is formed via a head-on overlap between the 1s orbital of a H atom and one sp^3 hybrid orbital of the C atom.

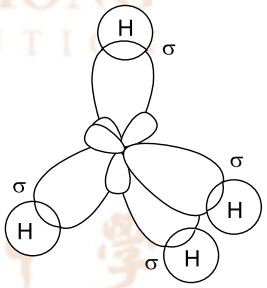
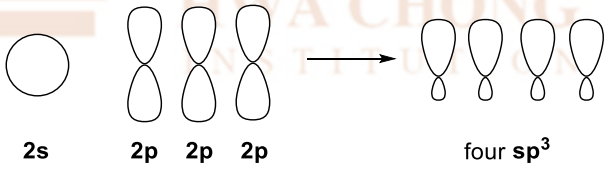


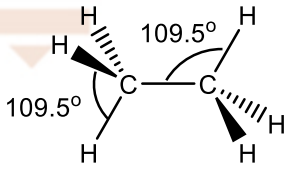
Figure 27. Overlapping of orbitals in methane, CH_4

6.2.1 The bonding in ethane, CH_3CH_3 and sp^3 hybridisation of carbon

Similar to methane, both carbon atoms in ethane are **sp^3 hybridised**. Each carbon atom in ethane shares four electrons (one with each of three hydrogen atoms, and one with the other carbon atom), forming **four σ bonds**. Mutual repulsion of the electrons in the four σ bonds around each carbon atom tends to place them as far apart as possible. Hence, the shape about each carbon atom is **tetrahedral** and the bond angles are **109.5°**.



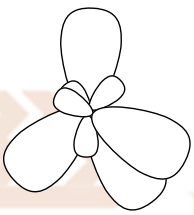
i. mixing of atomic orbitals to form hybrid orbitals for a carbon atom



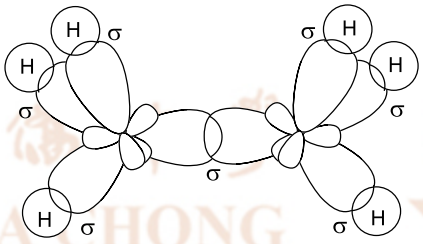
ii. geometry in ethane

Figure 28a. Bonding in ethane, CH_3CH_3

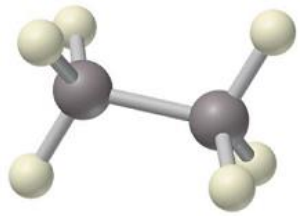
For each carbon, the **four** sp^3 hybrid orbitals, obtained by mixing **one s orbital and three p orbitals**, are arranged in a **tetrahedral** geometry as shown in Figure 28b(i). The C–C bond is an sp^3–sp^3 σ bond, formed from head-on overlap of two sp^3 hybrid orbitals from adjacent C atoms. There are six C–H bonds, each bond is s–sp^3 σ bond, formed from a head-on overlap of the 1s atomic orbital of H and the sp^3 hybrid orbital of C.



*i. arrangement of sp^3 hybrid orbitals around **each carbon***



ii. overlapping of orbitals in ethane



iii. ball & stick model

Figure 28b. Bonding in ethane, CH_3CH_3

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6.2.2 The bonding in ethene, $CH_2=CH_2$ and sp^2 hybridisation of carbon

Each carbon atom shares three electrons (one with each of two hydrogen atoms, and one with the other carbon atom), forming **three σ bonds**. The fourth electron on each carbon atom occupies a 2p orbital which overlaps side-on to form the **π bond**.

Mutual repulsion of the three groups of electrons around each carbon atom tends to place them as far apart as possible. Hence, the shape about each carbon atom is **trigonal planar** and the bond angles are **120°**.

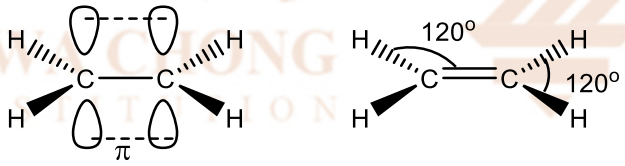


Figure 29a. Bonding in ethene, $CH_2=CH_2$

Both carbon atoms in ethene, $CH_2=CH_2$, are **sp^2 hybridised**. Mixing **one s orbital and two p orbitals** gives three **sp^2 hybrid orbitals**.

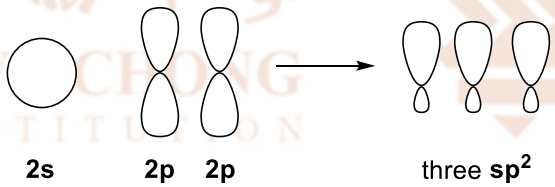
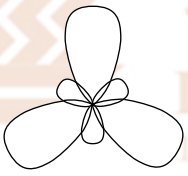


Figure 29b. Bonding in ethene, $CH_2=CH_2$

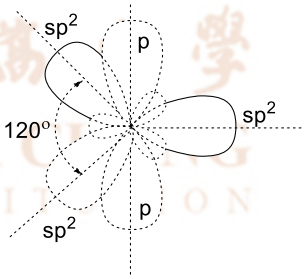
For each carbon, the **three** sp^2 hybrid orbitals are arranged in a **trigonal planar** geometry as shown in Figure 29c(i). **One p orbital remains unhybridised**, and this p orbital is arranged perpendicular to the three sp^2 hybrid orbitals as shown in Figure 29c(ii).

The C=C double bond consists of one sp^2–sp^2 σ bond formed by head-on overlap of two sp^2 hybrid orbitals, and one p-p π bond formed by side-on overlap of the unhybridised p orbitals.

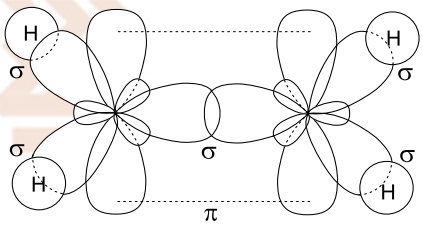
There are four C–H bonds, each of which is an s–sp^2 σ bond formed from head-on overlap of the 1s atomic orbital of H and the sp^2 hybrid orbital of C.



*i. arrangement of sp^2 hybrid orbitals around **each carbon***



*ii. around **each carbon**, unhybridised p orbital is **perpendicular** to the hybrid orbitals*



iii. *overlapping of orbitals in ethene*

Figure 29c. Bonding in ethene, $CH_2=CH_2$

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6.2.3 The bonding in ethyne, C_2H_2 and sp hybridisation of carbon

Each carbon atom shares two electrons (one with each hydrogen atom, and one with the other carbon atom), forming **two σ bonds**. The remaining two electrons on each carbon atom occupies a 2p orbital each which overlaps side-on to form the **two π bonds**.

Mutual repulsion of the two groups of electrons around each carbon atom tends to place them as far apart as possible. Hence, the shape about each carbon atom is **linear** and the bond angles are **180°**.

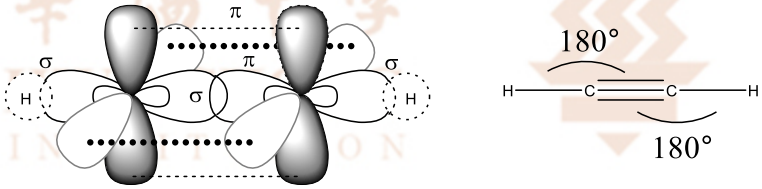


Figure 30a. Bonding in ethyne, H–C≡C–H

Both carbon atoms in ethyne, H–C≡C–H, are **sp hybridised**. Mixing **one s orbital and one p orbital** gives two **sp hybrid orbitals**.

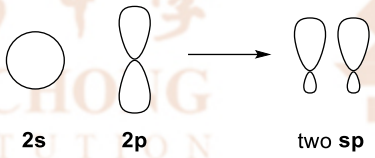
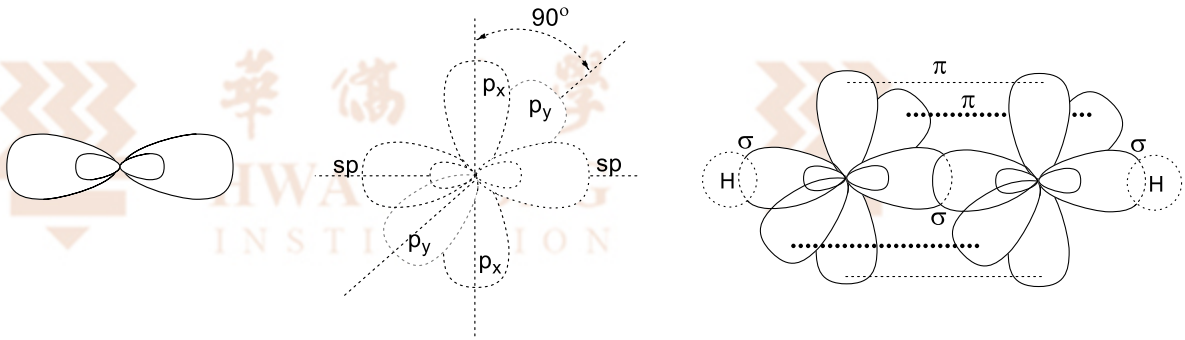


Figure 30b. Bonding in ethyne, H–C≡C–H

For each carbon, the **two** sp hybrid orbitals are arranged in a **linear** geometry as shown in Figure 30c(i). **Two p orbitals remain unhybridised**, and these p orbitals are arranged perpendicular to the two sp hybrid orbitals as shown in Figure 30c(ii).

The C≡C triple bond consists of one sp–sp σ bond formed by head-on overlap of two sp hybrid orbitals, and two p–p π bonds formed by side-on overlap of the unhybridised p orbitals.

Each C–H bond is an s–sp σ bond formed from head-on overlap of the 1s atomic orbital of H and the sp hybrid orbital of C.



*i. arrangement of sp hybrid orbitals around **each carbon***

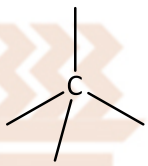
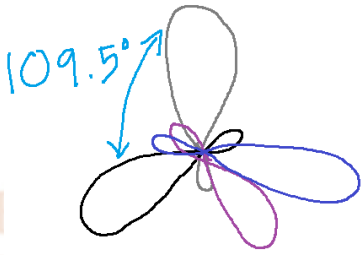
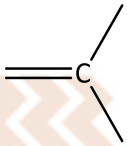
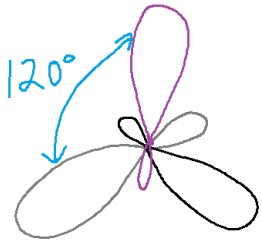
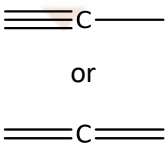
*ii. arrangement of hybrid orbitals and unhybridised p orbitals around **each carbon***

iii. *overlapping of orbitals in ethyne*

Figure 30c. Bonding in ethyne, H–C≡C–H

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Table 8. Summary of the orbital hybridisation of carbon

Geometry of the carbon atom	Type of hybrid orbitals for that carbon atom	A diagram to illustrate the relative orientation of hybrid orbitals for that carbon atom
tetrahedral 	sp^3	 The molecule is **tetrahedral** around this carbon atom, bond angle is **109.5°** around this carbon atom.
trigonal planar 	sp^2	 The molecule is **trigonal planar** around this carbon atom, bond angle is **120°** around this carbon atom.
linear  or	sp	 The molecule is **linear** around this carbon atom, bond angle is **180°** around this carbon atom.

6.2.4 Hybridisation and strength of covalent bond

Each type of hybrid orbital (sp^3 vs. sp^2 vs. sp) has different characteristics depending on what atomic orbitals it originates from. A p orbital is more elongated as compared to a spherical s orbital. Hence, a hybrid orbital that has more p character, i.e. p orbitals make up a larger fraction of the hybrid orbital, tends to form a longer and weaker bond.

hybrid orbital	ratio of s:p orbitals	% s character	% p character
sp^3	1:3	25%	75%
sp^2	1:2	33.3%	66.6%
sp	1:1	50%	50%

Hence the bond formed by an sp^3 hybrid orbital is actually longer and weaker than a bond formed by an sp hybrid orbital as it has a higher percentage of the characteristic of a p orbital.

Thus, the C–C single bond in ethane, $H_3C–CH_3$, which is formed by a sp^3–sp^3 overlap, is longer and weaker than the C–C single bond in propyne, $H–C{\equiv}C–CH_3$, which is formed by a sp–sp^3 overlap.

[See **N2010/I/19** and **N2008/I/19**]

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7 POLAR COVALENT BONDS and IONIC BONDING WITH COVALENT CHARACTER

Most chemical bonds are neither purely covalent nor purely ionic but have characteristics of both ionic and covalent bonding.

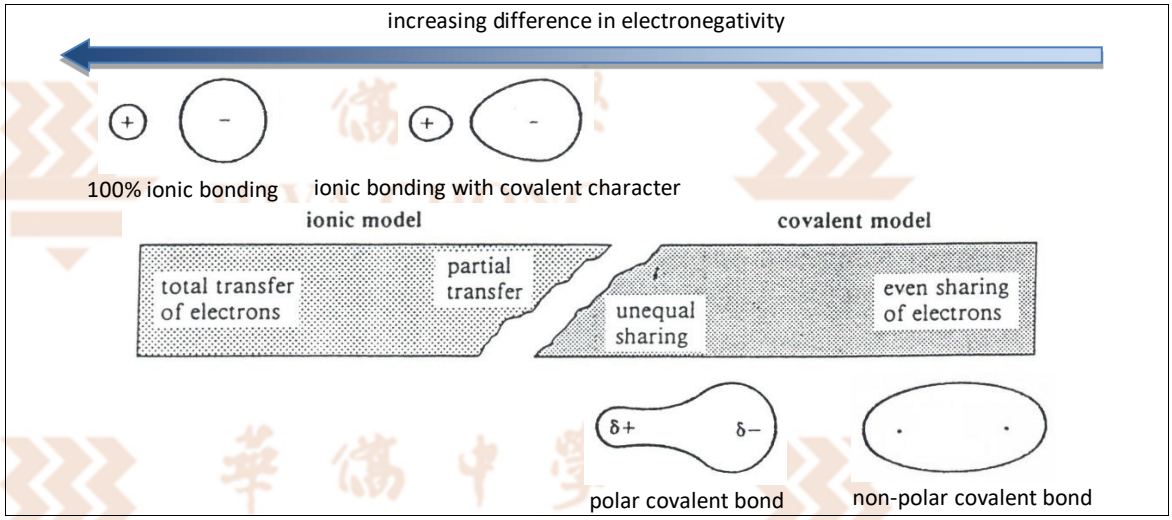
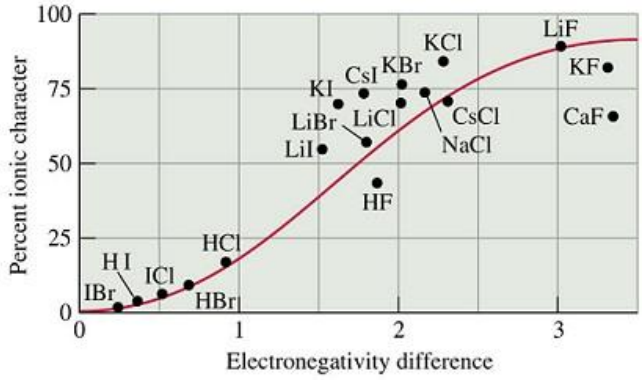


Figure 31. The classification of ionic and covalent bonds is on a continuum

The difference in electronegativity between two atoms can be used to predict the type of bond formed between them.



General guidelines (not required to memorise):			
Electronegativity difference	0 – 0.5	0.5 – 2.0	> 2.0
Nature of bond	non-polar covalent	polar covalent	ionic
Examples	H–H *Cl*–*Cl* C–H	H–*Cl*	Na^+ Cl^-

Figure 32. The electronegativity difference suggests whether a covalent or ionic bonding forms between two atoms

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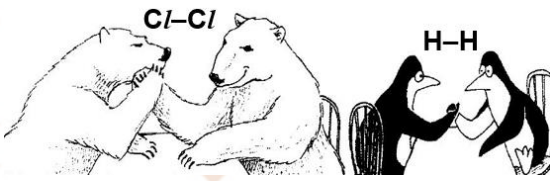
7.1 Polar covalent bonds

*LO 2(f): explain and deduce bond polarity using the concept of electronegativity [quantitative treatment of electronegativity is **not** required]*

In the hydrogen molecule, the bonding electrons are **equally shared** between the two hydrogen atoms as they have the **same electronegativity**. The H–H bond is a **non-polar** covalent bond. Other non-polar bonds include the C*l*–C*l* bond and O=O bond.

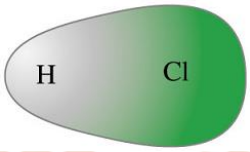


Figure 33. Bonding electrons are shared equally in a non-polar bond.

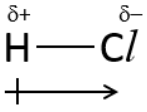


When the covalent bond is formed by two different atoms, e.g. hydrogen atom and chlorine atom, the bonding electrons are **not shared equally** as the atoms have **different electronegativities**. The H–C*l* bond is a **polar** covalent bond.

The C*l* atom is more electronegative than the H atom. The bonding electrons will be found, on average, nearer to C*l* than to H, resulting in a **partial charge separation** or **dipole**. C*l* acquires a partial negative charge (**δ–**) while H acquires a partial positive charge (**δ+**). The 'cross-and-arrow' symbol can also be used to show the **dipole moment** or the direction in which the electrons are more strongly attracted.



(a)



(b)

Figure 34. (a) Unequal sharing of the bonding electrons in a polar bond (b) Partial charge separation in a polar bond

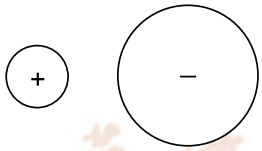
If the electron-attracting strength is *unequal*, the bond will be polar…



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7.2 Ionic bonding with covalent character

In *ideal* ionic bonding, there is *complete* electron transfer. The nucleus of the cation and that of the anion only attracts its own electrons. The electron cloud of each ion is spherical (see Figure 35a).



(a) ideal ionic bonding leads to spherical electron cloud



(b) polarisation of anion leads to covalent character in the ionic bonding

Figure 35. Ideal ionic bonding vs. ionic bonding with covalent character

However, in many cases, the cation tends to attract the electrons of the anion causing the electron cloud to be polarised or distorted, resulting in covalent character in the ionic bonding (see Figure 35b). The **degree of covalent character** depends on:

- **polarising power of the cation**

Cations that are small and highly charge have **high charge densities** (see section 2.2) and **high polarising power**. These cations have a high tendency to distort the anion's electron cloud, resulting in **greater covalent character** in the ionic bonding.

Table 9. Relative charge/radii ratio of cations.

cation	charge	radius / nm	relative charge/radii ratio
K^+	+1	0.133	1/0.133 = 7.5
Li^+	+1	0.078	1/0.078 = 12.8
Ba^{2+}	+2	0.135	2/0.135 = 14.8
Mg^{2+}	+2	0.065	2/0.065 = 30.8
Al^{3+}	**+3**	**0.050**	**3/0.050 = 60.0**
Be^{2+}	**+2**	**0.031**	**2/0.031 = 64.5**

- **polarisability of the anion**

Anions that are relatively **large** have **high polarisability**. Their valence electrons are further from and less strongly attracted by the nucleus so the electron cloud is easily distorted by a cation, resulting in **greater covalent character** in the ionic bonding.

The bonding in caesium fluoride is said to be predominantly ionic (with little covalent character). Cs^+ ion has a low charge density and low polarising power while F^- ion has a low polarisability. The electron cloud of F^- ion is only slightly polarised by Cs^+ ion.

The bonding in aluminium oxide is ionic with significant covalent character. Al^{3+} ion is highly polarising due to the high charge density so it is able to distort the electron cloud of the oxide anion. In Topic 21 Chemical Periodicity, we will look at how the covalent character in the ionic bond affects the properties of aluminium oxide. We will also look at how covalent character in ionic bond affects the magnitude of lattice energy in Topic 5 Chemical Energetics.

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***Summary** of the concept of 'ionic bonding with covalent character'*

compound formed from a **metal** and a **non-metal**

↓

metal cation has high charge and small radius ⇒ high charge density ⇒ high polarising power

anion has large radius ⇒ high polarisability

↓

cation attracts outermost electrons or electron cloud of anion

cation distorts or polarises electron cloud of anion

↓

partial sharing of electrons, or even a high degree of that in some cases

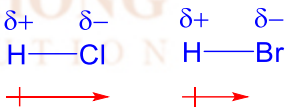
↓

ionic bonding with covalent character or even a covalent molecule

Exercise 7.1 (Worked Example)

Which of the bond is more polar, the bond in hydrogen chloride or in hydrogen bromide? With the aid of diagrams, explain your answer.

Answer:



Cl is more electronegative than Br. The difference in electronegative between Cl and H is larger than that between Br and H. Hence, the H-Cl bond is more polar (*use a longer 'arrow' to represent the larger dipole moment*).

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8 POLARITY OF MOLECULES

LO 2(g): deduce the polarity of a molecule using bond polarity and its molecular shape (analogous to those specified in (d))

In section 7.1, we said that when two bonded atoms have different electronegativities, the covalent bond is polar and has a dipole associated with it.

Depending on the **shape** of the molecule, the individual dipoles may or may not cancel each other completely. If the **overall dipole** or **net dipole** is **zero**, the molecule is **non-polar**. Figure 36 shows some examples of non-polar molecules.



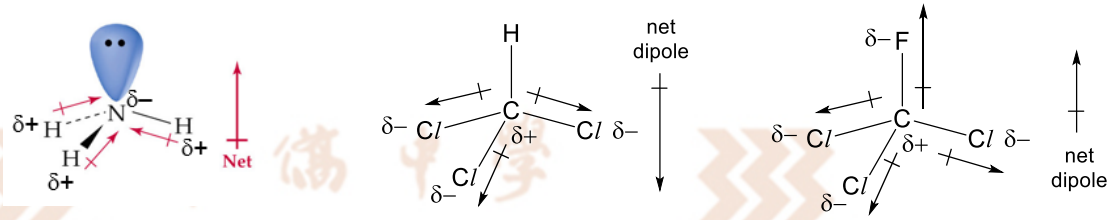
(a) molecules such as Cl_2, O_2, N_2 and CH_4 are non-polar as the **bonds are non-polar** (note the C–H bond is considered non-polar)

(b) CO_2 is non-polar; the two C=O **bonds** are **polar but** the individual **dipoles cancel each other** due to the linear shape

(c) CCl_4 is non-polar; the C–Cl **bonds** are **polar but** the individual **dipoles cancel each other** due to the tetrahedral shape

Figure 36. Non-polar molecules do not have polar bonds or the net dipole is zero

If the sum of all individual bond dipoles is **not zero**, the molecule is **polar**. Figure 37 shows some examples of polar molecules.



(a) NH_3 is polar as the N–H **bonds** are **polar** and the **net dipole is not zero**

(b) $CHCl_3$ is polar; the C–Cl **bonds** are **polar** but the individual **dipoles do not cancel each other**

(c) $CFCl_3$ is polar; the C–Cl and C–F **bonds** are **polar** but the individual **dipoles do not cancel each other**

*Figure 37. Polar molecules have polar bonds and the net dipole is **not** zero*

Fluorine is more electronegativity than chlorine so the C–F bond is more polar than the C–Cl bond. The individual dipoles in $CFCl_3$ do not cancel each other so the net dipole is **not** zero.

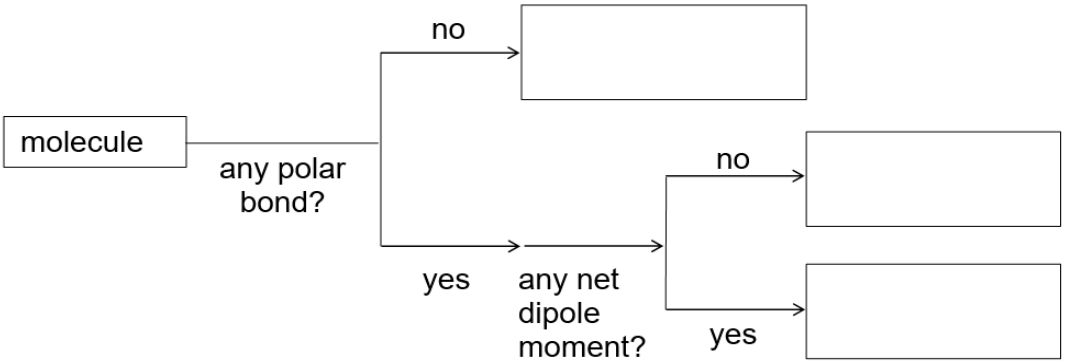
***Summary** of the concepts of 'polar covalent bonds' and 'polar vs. non-polar simple covalent molecules'*

a simple covalent molecule in which there's a difference in electronegativity between bonded atoms
↓
unequal sharing of bonding electrons in covalent bond(s)
↓
polar covalent bond(s) in this molecule
↓
any net dipole moment? (shape of molecule must be considered)
↓*yes* polar molecule ↓*no* non-polar molecule

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Exercise 8.1

The presence or absence of polar bonds, and the shape of the molecule determine its polarity. Complete the flowchart by filling the boxes with 'polar molecule' or 'non-polar molecule'.



Exercise 8.2

Deduce if each of the following molecules is polar or non-polar. Explain your answer with suitable diagrams.

(a) BF_3 **(b)** H_2O

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9 INTERMOLECULAR FORCES OF ATTRACTIONS

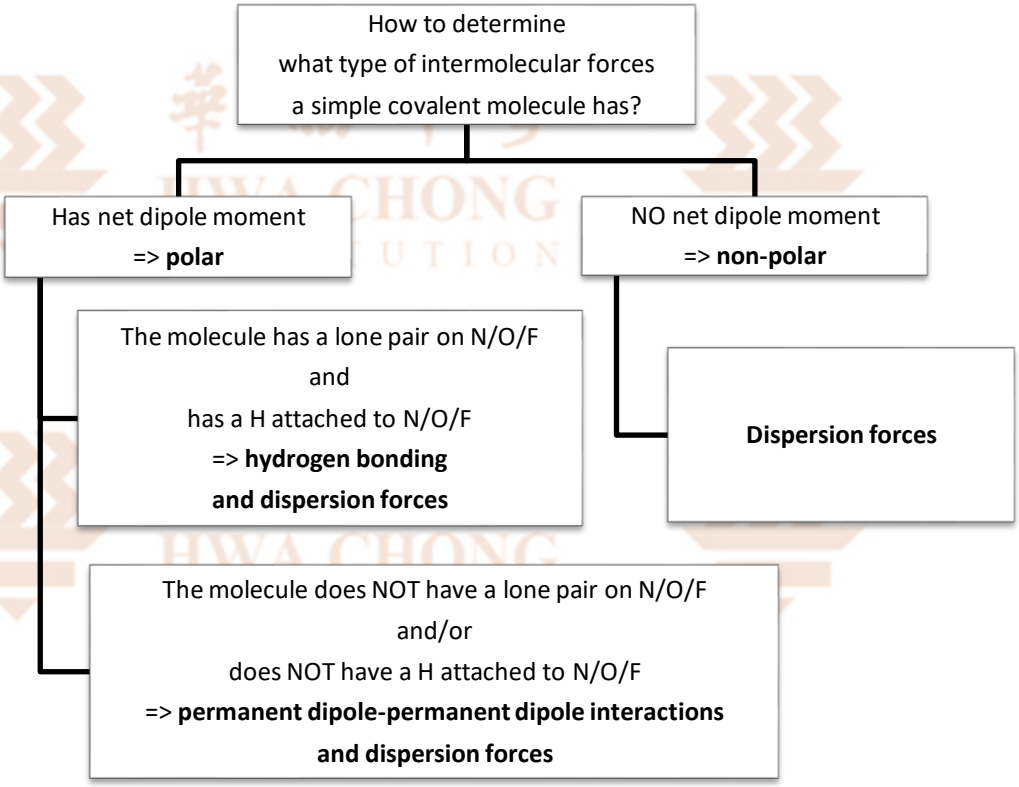
LO 2(h): describe the following forces of attraction (electrostatic in nature): (i) intermolecular forces, based on permanent and induced dipoles, as in $CHCl_3(l)$; $Br_2(l)$ and the noble gases; (ii) hydrogen bonding, using ammonia and water as examples of molecules containing –NH and –OH groups

There are three types of **intermolecular** forces (attractions **between** molecules):

- instantaneous dipole-induced dipole attractions (also called dispersion forces)
- permanent dipole-permanent dipole attractions
- hydrogen bonding

These intermolecular forces are attractions between partial charges and are electrostatic in nature. They are generally **weaker** and require **less** thermal energy to overcome resulting in low melting points and low boiling points.

***Summary** of how to determine the type of intermolecular forces of a simple covalent molecule*



9.1 Instantaneous Dipole-Induced Dipole Attractions (Dispersion Forces)

Dispersion forces exist between **all** molecules or between noble gas atoms. Between non-polar molecules such as H_2 and CH_4 and between atoms of noble gases such as Ne and Ar, it is the only intermolecular forces of attraction.

The electrons in a molecule are constantly moving. **Fluctuations** (or distortions) **in electron distribution** can cause an **instantaneous dipole** in one molecule, which **induces** a dipole in a nearby molecule. An attraction arises between the two molecules. This 'short-lived' and generally weak attraction is called **instantaneous dipole-induced dipole (id-id) attraction** or **dispersion forces** (see Figure 38).

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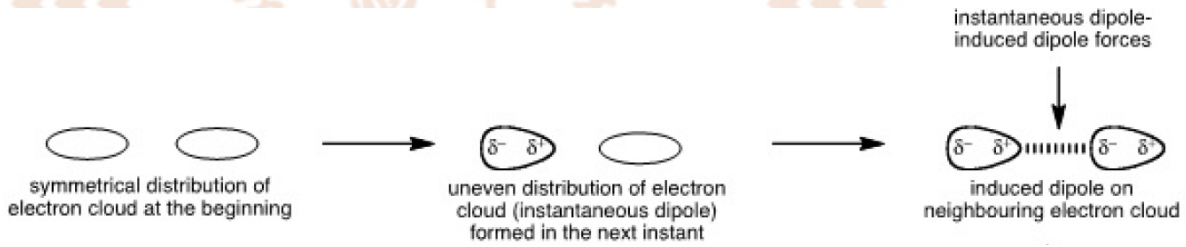


Figure 38. Dispersion forces arise due to fluctuations in electron densities

9.1.1 Strength of dispersion forces

The strength of dispersion forces depends on:

- **the number of electrons in the molecule**
  The **larger** the number of electrons, the **more polarisable** the electron cloud, the **stronger** the dispersion forces.

  For example, the dispersion forces between H_2 molecules (two electrons) is much weaker than those between Br_2 molecules (70 electrons).

- **the surface area of contact between adjacent molecules**
  The **larger** the surface area of contact, the more easily induced dipoles are formed, the **stronger** the dispersion forces.

  The surface area of contact between molecules depends on the overall **shape** of the molecules. Consider pentane and 2,2-dimethylpropane. These isomers (same molecular formula but different structural formula) have the same number of electrons. Pentane has an elongated shape and a larger surface area than 2,2-dimethylpropane which has a spherical shape. Hence, the dispersion forces between pentane molecules are stronger.

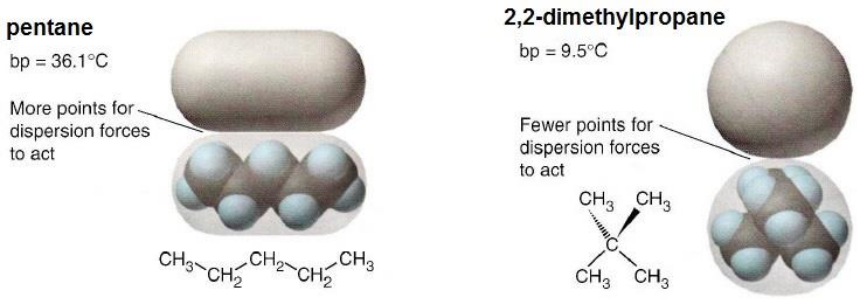


Figure 39. Strength of dispersion forces depends on the surface area of contact

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LO 5(d): describe and explain the trend in volatility of the Group 17 elements in terms of instantaneous dipole-induced dipole attraction

Exercise 9.1 (Worked Example)

Group 17 elements exist as diatomic molecules. At room temperature and pressure, F_2 and Cl_2 are gases, Br_2 is a liquid and I_2 is a solid. Explain the trend in volatility of the Group 17 elements.

Answer:

Group 17 elements are non-polar simple covalent molecules. As the number of electrons **increases**, the instantaneous dipole-induced dipole attractions (or dispersion forces) between the molecules* become **stronger**. **More energy** is needed to overcome the stronger intermolecular* dispersion forces so volatility of the elements decreases.

Strategy:

- *Identify the type of IMF and consider what affects the strength; in this case, the number of electrons increases from 18 in F_2 to 34 in Cl_2 to 70 in Br_2 and 106 in I_2.*
- *Compare the strength of IMF & energy needed; *key words "between the molecules" or "intermolecular".*

9.2 Permanent Dipole-Permanent Dipole Attractions

Polar molecules have a permanent dipole, with an uneven electron distribution. The attraction between the oppositely-charged ends (δ+ and δ–) of two polar molecules is called **permanent dipole-permanent dipole (pd-pd) attractions**.

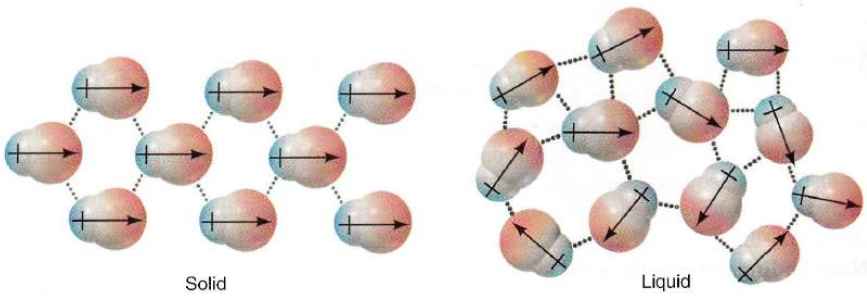


Figure 40. Permanent dipole-permanent dipole attractions

9.3 Hydrogen Bonding

Hydrogen bonding exists between certain polar molecules. For hydrogen bonding to occur,

- the molecule must contain a **hydrogen atom bonded to** a highly electronegative atom (**F, O, N**),
- there must be an **atom (F, O, N) with a lone pair of electrons**.

Hydrogen bonding exists between HF molecules, between H_2O molecules and between NH_3 molecules.

Take HF as an example. The bonding electrons in H–F bond are pulled strongly towards the **highly electronegative** fluorine atom. The hydrogen atom (which has no inner electrons is practically left with its nucleus with one proton) is **highly electron deficient** (carries a significant δ+ charge). The **lone pairs** on F, found in 2p orbitals which are small, is able to attract the electron deficient H atom strongly. This particularly strong attraction between adjacent HF molecules is called **hydrogen bonding**.

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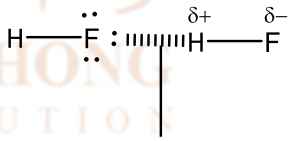


Figure 41. Hydrogen bonding between HF molecules

When asked to draw a diagram to illustrate hydrogen bonding:

- **label the dipole** for the covalent bond (F–H, O–H or N–H) carrying the acceptor hydrogen atom with 'δ^+' symbol on H and 'δ^-' symbol on the more electronegative F or O or N atom
- **draw the lone pair** of electrons for the fluorine, oxygen or nitrogen atom involved in the hydrogen bonding
- **Indicate the hydrogen bonding** using a dotted/dashed line together with a label

Exercise 9.2
Draw diagrams to illustrate the hydrogen bonding

(a) between two H_2O molecules **(b)** between one H_2O molecule and one NH_3 molecule

9.3.1 Strength and extent of hydrogen bonding

- The **electronegativity** of the atom that H atom is bonded to affects the **strength** of the hydrogen bonding. For example, F is **more electronegative** than N. The δ+ charge on H in HF is larger than that in NH_3 hence the hydrogen bonding between HF molecules is **stronger**.

- The **extent** of hydrogen bonding depends on the **number of H atom** bonded to F, O or N and the **number of lone pairs** available.

  The hydrogen bonding in H_2O is **more extensive** than that in HF or NH_3. H_2O has two lone pairs of electrons and two electron deficient hydrogen atoms. H_2O can form on **average two hydrogen bonds per molecule**. On the other hand, NH_3 has only one lone pair (despite having three hydrogen atoms); HF has only one electron deficient hydrogen atom (despite having three lone pairs). NH_3 and HF can only form **one hydrogen bond per molecule**.

The effect of strength and extent of hydrogen bonding on boiling points are discussed in section 9.3.2.

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9.3.2 Effect of hydrogen bonding on some properties

LO 2(i): outline the importance of hydrogen bonding to the physical properties of substances, including ice and water
*LO 2(l) part: describe, in simple terms, the lattice structure of a crystalline solid which is: **(iv)** hydrogen-bonded, as in ice*

- **Considerably high boiling points of NH_3, H_2O and HF**

  Figure 42 shows the boiling points of the hydrides (compound formed between hydrogen and another element).

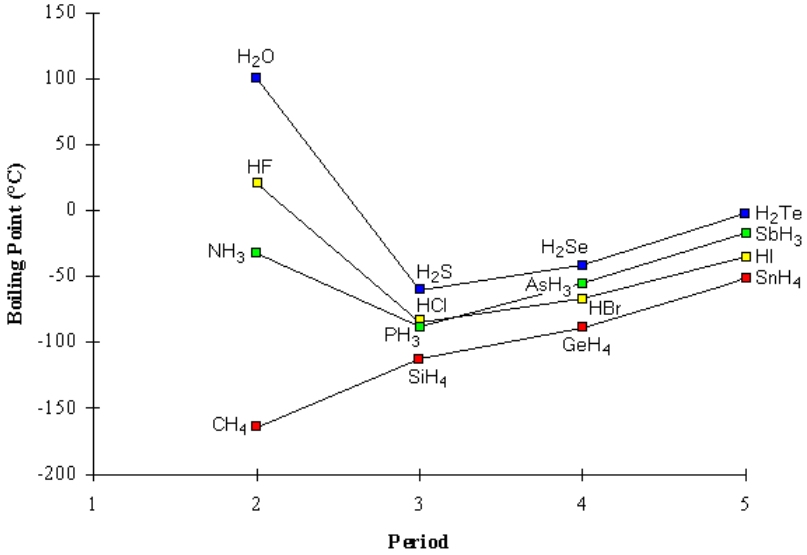


Figure 42. Boiling points of NH_3, H_2O and HF compared to CH_4 and other hydrides in their respective groups

  CH_4, NH_3, H_2O and HF have the same number of electrons (hence similar dispersion forces). However, the boiling points of NH_3, H_2O and HF are considerably higher than that of CH_4. The **hydrogen bonding** in NH_3, H_2O and HF are **stronger than** the **dispersion forces** in CH_4.

  Similarly, the boiling points of NH_3, H_2O and HF are also considerably higher than those of other hydrides in their respective groups (Groups 15, 16 and 17).

- **Boiling point: HF > NH_3** (see Figure 42 and section 9.3.1)

  F is **more electronegative** than N, the **electronegativity difference** between F and H is **larger** than that between N and H, hence the $\delta+$ charge on H in HF is **larger** than that in NH_3. **More** energy is needed to overcome the **<u>stronger</u> hydrogen bonding between HF molecules** than that between NH_3 molecules hence HF has a higher boiling point.

- **Boiling point: H_2O > NH_3 and H_2O > HF** (see Figure 42 and section 9.3.1)

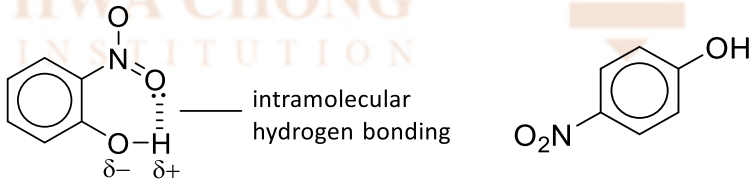
  H_2O has two lone pairs of electrons and two electron deficient hydrogen atoms hence H_2O can form on **average two hydrogen bonds per molecule**. On the other hand, NH_3 has only one lone pair while HF has only one electron deficient hydrogen atom, hence NH_3 and HF can only form **one hydrogen bond per molecule**. **More** energy is needed to overcome the **<u>more extensive</u> hydrogen bonding** in H_2O than that in NH_3 and HF hence H_2O has a higher boiling point.

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- **Intermolecular and intramolecular hydrogen bonding**

Intramolecular hydrogen bonding occurs when the electron deficient H atom in a molecule is in close proximity to the lone pairs on atoms (F, O, N) in the **same** molecule.

2-nitrophenol is able to form **intra**molecular hydrogen bonding so the **inter**molecular **hydrogen bonding is less extensive**. Its isomer 4-nitrophenol is only able to form intermolecular hydrogen bonding. **Less** energy is needed to break the less extensive **inter**molecular hydrogen bonding in 2-nitrophenol hence it has a lower boiling point.



2-nitrophenol
boiling point 214 °C

4-nitrophenol
boiling point 290 °C

*Figure 43. **Intra**molecular hydrogen bonding in 2-nitrophenol is **not** broken during boiling.*

- **Dimerisation of carboxylic acids in non-polar solvent**

In water, ethanoic acid (CH_3CO_2H) forms hydrogen bonds with H_2O molecules. However, in non-polar solvent such as benzene (unable to form hydrogen bonding), the acid molecules form dimers via hydrogen bonding. Hence, the observed M_r is 120 instead of 60 (expected value for CH_3CO_2H).

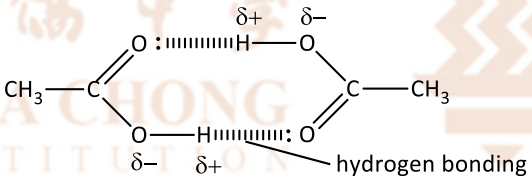


Figure 44. Dimer of CH_3CO_2H

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- **Ice is less dense** than liquid water

  In ice, each H_2O molecule is hydrogen bonded to four other molecules in a roughly **tetrahedral arrangement**. This produces an **open lattice**, with empty spaces between the H_2O molecules. The **more random arrangement** of hydrogen bonding in liquid water **takes up less space** as the H_2O molecules are **closer** together.

  For the same mass, the lattice structure of ice occupies a larger volume, hence the lower density.

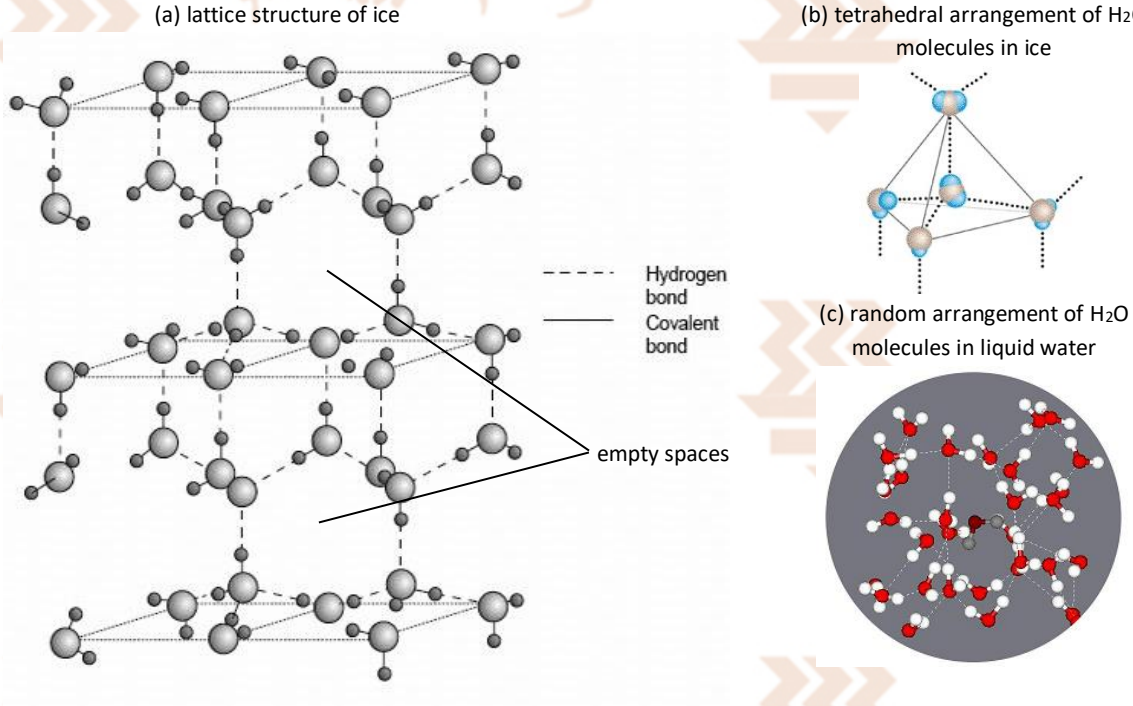


Figure 45. Tetrahedral arrangement in ice vs random arrangement in liquid water

- Liquid water has **high surface tension** (defined as the amount of force required to break the layer of water molecules on its surface)

  The hydrogen-bonded H_2O molecules form an array across the surface of water, allowing objects which you might expect to sink in water, such as pond skaters and even small coins (if you are careful), to 'float' on water.

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10 COVALENT LATTICES AND PHYSICAL PROPERTIES

LO 2(m): describe, interpret and/or predict the effect of different types of structure and bonding on the physical properties of substances

A lattice consists of particles that are arranged in a regular three-dimensional pattern. In sections 2 and 3, we described the metallic and ionic lattices respectively.

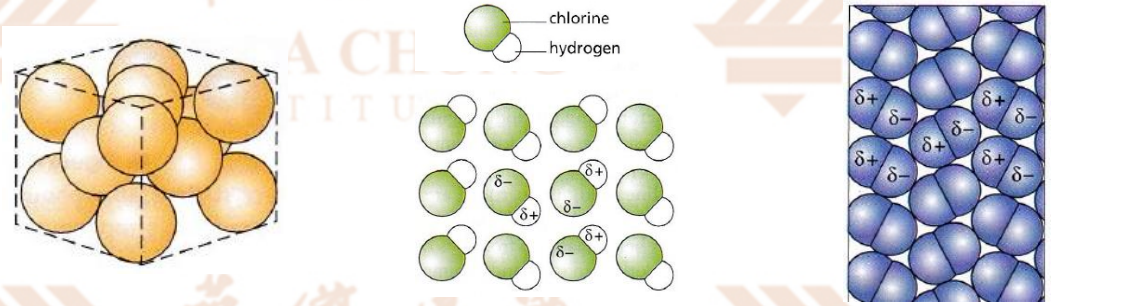
Covalent lattices can be giant molecular (as in graphite and diamond) or simple molecular (as in iodine and ice). We will describe and explain the physical properties of these substances in terms of their structure and bonding in the following sections.

10.1 Simple Molecular (or Simple Covalent) Lattices

*LO 2(l) part: describe, in simple terms, the lattice structure of a crystalline solid which is: **(ii)** simple molecular, as in iodine*

In simple molecular lattices, the particles are held by comparatively weak intermolecular forces (see section 9).

Figure 46 shows examples of simple atomic and simple molecular lattices.



(a) simple atomic lattice of solid argon (id-id attraction between atoms)

(b) simple molecular lattice of solid hydrogen chloride (pd-pd attraction between molecules)

(c) simple molecular lattice of solid iodine (id-id attraction between molecules)

Figure 46. Lattice structures of solid Ar, solid HCl and solid I_2

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10.1.1 Physical properties of substances with simple molecular lattices

Physical properties of simple molecular substances depends on the strength of the **intermolecular forces**. In general, substances with simple molecular lattice structures have **low melting points and low boiling points** as the **weak intermolecular forces between molecules** require **little thermal energy** to overcome. For example, boiling water breaks the weak hydrogen bonding holding the molecules together. The strong covalent bonds holding the hydrogen and oxygen atoms together are not broken; the H_2O molecules remain intact!

Many simple molecular compounds are soluble in **organic solvents** like propanone (CH_3COCH_3), tetrachloromethane (CCl_4) and benzene (C_6H_6). Some (e.g. ethanol, ethanoic acid, glucose) are soluble in water due to their ability to form hydrogen bonds with water. See section 12 for more discussions on solubility.

Simple molecular substances are **unable to conduct electricity** as there are no mobile charge carriers. However, some simple covalent substances are able to react with water to give aqueous ions. This allows the resulting solution to conduct electricity, for example: $HCl(g) + H_2O(l) \rightarrow Cl^-(aq) + H_3O^+(aq)$.

Exercise 10.1 (Worked Example)

Explain in terms of structure and bonding the following:

(a) Argon has a lower boiling point than hydrogen chloride.

Answer:

Argon has a **simple atomic structure** while hydrogen chloride has a **simple molecular structure**.
Stronger permanent dipole-permanent dipole attractions (and dispersion forces) exist between polar HCl molecules*.
Less energy is needed to overcome the **weaker** dispersion forces between argon atoms* so it has a lower boiling point.

Strategy:

- *State the structures*
- *Identify the type of attractions broken during boiling; keywords "between HCl molecules", "between Ar atoms"*
- *Compare the strength of relevant attractions (pd-pd vs dispersion forces; HCl & Ar have comparable dispersion forces due to the same no. of electrons) & energy needed*

(b) Hydrogen iodide has a higher boiling point than hydrogen bromide.

Answer:

Both hydrogen iodide and hydrogen bromide are **polar simple covalent molecules**.
Permanent dipole-permanent dipole attractions and dispersion forces exist between the molecules.
HI molecules have **more** electrons so **more** energy is needed to overcome the **stronger** dispersion forces between the molecules. Hence, HI has a higher boiling point than HBr.

Strategy:

- *State the structures*
- *Identify the type of attractions broken during boiling; keywords "between molecules" or "intermolecular"*
- *Compare the strength of relevant attractions (in this case dispersion forces; pd-pd attraction is "irrelevant" as H–Br bond is more polar than H–I bond so pd-pd between HBr molecules is stronger which would result in a higher, rather than a lower, boiling point for HBr) & energy needed.*

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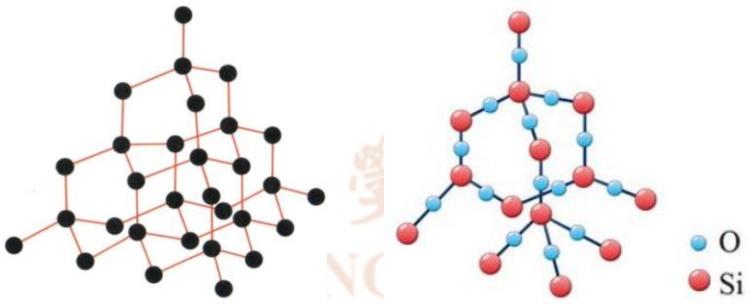
10.2 Giant Molecular (or Giant Covalent) Lattices

*LO 2(l) part: describe, in simple terms, the lattice structure of a crystalline solid which is: **(iii)** giant molecular, as in graphite; diamond*

Giant molecular lattices consist of three-dimensional arrays of atoms, held together by strong covalent bonds. Figure 47 shows examples of giant molecular lattices.

In **diamond** (figure 47a), each (sp^3 hybridised) C atom is covalently bonded to four other C atoms, in a tetrahedral arrangement.

In **silicon(IV) oxide (also known as quartz)**, each Si atom is covalently bonded to four O atoms, and each O atom is bonded to two Si atoms. The formula SiO_2 is an empirical formula. (Refer to figure 47b)

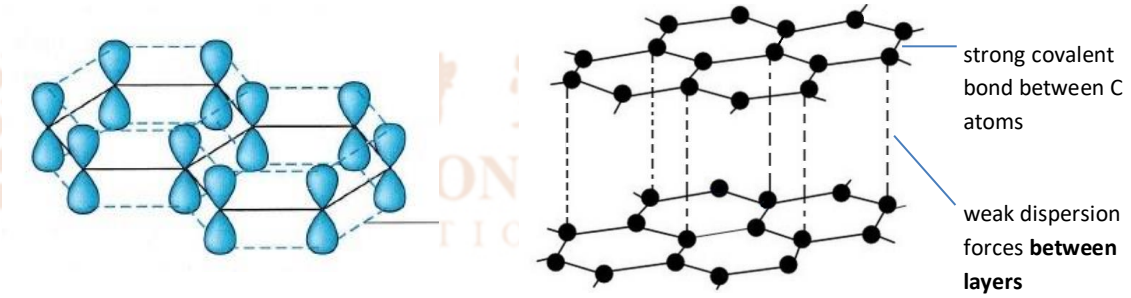


(a) diamond lattice (b) silicon(IV) oxide lattice

Figure 47. Lattice structures of diamond and silicon(IV) oxide

Diamond and graphite are allotropes of carbon – different forms of carbon, in which the atoms are arranged in different ways.

In g**raphite**, each (sp^2 hybridised) C atom is covalently bonded to three other C atoms, forming a two-dimensional layer of hexagonal carbon rings. Each C atom in graphite has a 2p orbital containing one electron (not used in forming the C–C σ bonds). Within each layer, the 2p orbitals side-on overlap with each other to form a **delocalised π bonding system** (similar to the delocalisation of π electrons in benzene, refer to Topic 12 Arenes!). Between the layers of carbon atoms, there is (significant) **dispersion forces** due to the large surface area. (Refer to figure 48)



(a) **Within each layer:** each C atom has a 2p orbital (containing one electron) which can overlap with one another

(b) **Each 2D layer** consists of covalently bonded C atoms arranged hexagonally

Figure 48. Structure of graphite

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10.2.1 Properties of substances with giant molecular lattices

Unlike simple covalent compounds, substances with giant molecular lattice have very **high melting points** and very **high boiling points** as a lot of energy is needed to break the **strong covalent bonds** between the atoms.

Table 10. The structure and bonding, and some physical properties of diamond, graphite and quartz

Property	Diamond	Graphite	Quartz also silicon(IV) oxide
structure and bonding	giant molecular each C atom is covalently bonded to four other C atoms, in a tetrahedral arrangement.	giant molecular **within each layer** each C atom is covalently bonded to three other C atoms, forming a 2D layer of hexagonal carbon rings. Overlap of 2p orbitals (of each C atom) give rise to delocalised π bonding system. **between layers** dispersion forces hold 2D layers together	giant molecular each Si atom is covalently bonded to four O atoms, and each O atom is bonded to two Si atoms. Si : O ratio = 1 : 2
melting point / °C	3550	3730	1610
boiling point / °C	4827	-	2230
electrical conductivity	poor	good along the layers	-
hardness	very hard	soft and slippery	hard
solubility in solvents	insoluble	insoluble	insoluble

Diamond is **unable to conduct electricity** as there are no mobile charge carriers. All the valence electrons are held between the atoms and are not free to move. Graphite is a **good conductor of electricity** (and heat) as the **delocalised electrons are free to move along the layers** – graphite is used in batteries and electrolysis. The delocalised electrons are unable to jump from one layer to the next so graphite does not conduct electricity in the direction at right angles to the layers.

Diamonds are very hard (the hardest natural substance known)**, strong and non-malleable** because of the rigid structure, held together by strong covalent bonds – diamonds are used for cutting tools and oil rig drills. **Graphite is soft** (over 500 times softer than diamond) **and slippery** as the layers can slide over each other due to the dispersion forces between them – graphite is used as a lubricant and in pencils.

Both diamond and graphite are **insoluble** in water and organic solvents. Attractions between the solvent molecules and carbon atoms are not strong enough to overcome the strong covalent bonds between the carbon atoms.

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11 PHYSICAL PERIODICITY

LO 5(c) part: interpret the variation in melting point across a Period in terms of structure and bonding in the elements (metallic, giant molecular, or simple molecular)

Figure 49 shows the variation in melting point for the period 3 elements, sodium to argon.

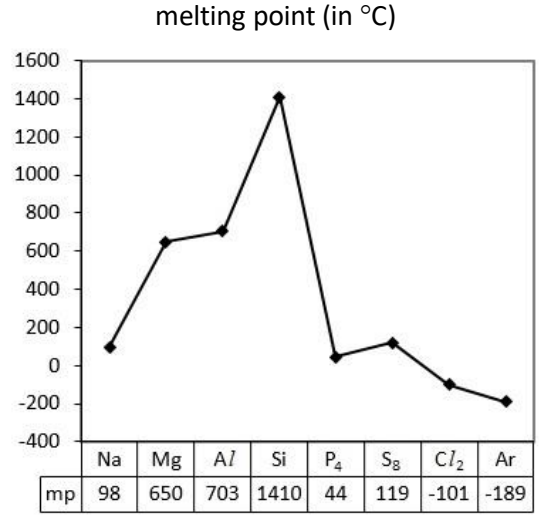
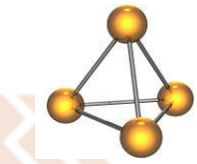
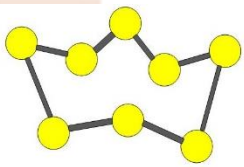


Figure 49. Variation in m.p. for period 3 elements



P_4 molecule



S_8 molecule

Figure 50. Structure of phosphorus and sulfur

Na, Mg and A*l* have **giant metallic structures** and relatively high melting points due to the **strong metallic bonding between cations and the sea of delocalised valence electrons**.

From Na to A*l*, melting point increases as **more** energy is needed to overcome the **stronger** metallic bonding due to

- the increase in **number of valence electrons** contributed per atom
- and the increase in **charge density of the cation** (due to increasing charge and decreasing ionic radius/cationic size).

Table 11. Factors affecting strength of metallic bonding in Na, Mg and Al (refer also to section 2.2)

	Na	Mg	A*l*
No. of valence e contributed per atom	1	2	3
Charge of cation	+1	+2	+3
Ionic radius of cation / nm	0.095	0.065	0.050

Si has a **giant molecular structure** and a very high melting point as a lot of energy is needed to overcome the **many strong covalent bonds** between the Si atoms during melting.

Non-polar P_4, S_8, and Cl_2 have **simple molecular structures**. Ar has simple atomic structure. Little energy is needed to overcome the **weak dispersion forces between the molecules or between argon atoms** hence the low melting points.

The **number of electrons*** and hence **strength of dispersion forces** decreases from S_8 to P_4 to Cl_2 to Ar. Hence, **energy** needed to overcome the dispersion forces during melting and the resulting melting point decreases in the same order.

*from *Data Booklet*, no. of electrons in S_8 (128) > P_4 (60) > Cl_2 (34) > Ar (18)

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LO 5(c) part: interpret the variation in electrical conductivity across a Period in terms of structure and bonding in the elements (metallic, giant molecular, or simple molecular)

Figure 51 shows the variation in electrical conductivity for the period 3 elements, sodium to argon.

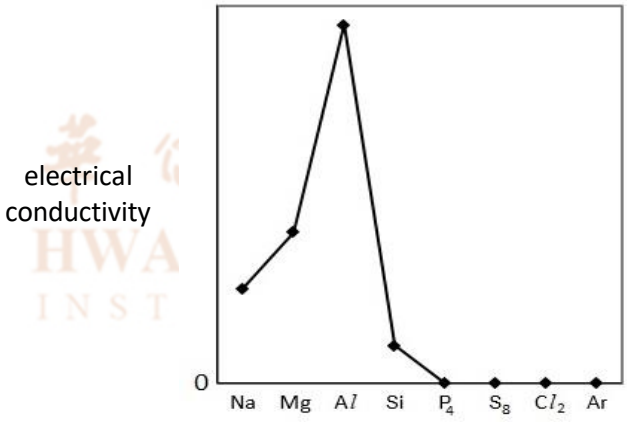


Figure 51. Variation in electrical conductivity for period 3 elements

Na, Mg and A*l* have **giant metallic structures** with **strong metallic bonding between cations and the sea of delocalised valence electrons**. Metals are good electrical conductors because the delocalised electrons are able to act as mobile charge carriers.

From Na to A*l*, the **number of valence electrons** contributed per atom increases. Therefore, electrical conductivity increases.

Si has a **giant molecular structure** with **covalent bonds between atoms**. As a metalloid (an element with properties of metals and non-metals), it is a semiconductor.

P_4, S_8, and Cl_2 have **simple molecular structures**. Ar has simple atomic structure. In P_4, S_8 and Cl_2, the valence electrons are held strongly in covalent bonds. There are **no mobile charge carriers** in these molecules as well as in argon atoms so they do not conduct electricity.

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Exercise 11.1

Using the data provided below, describe the various forces responsible for keeping the particles together in the element or compound. Account for the melting point of each substance in terms of its structure and bonding.

substance	formula	melting point / °C
neon	Ne	–248
argon	Ar	–189
water	H_2O	0
sodium fluoride	NaF	993
graphite	C	3948

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12 SOLUBILITY OF A SUBSTANCE IN A GIVEN SOLVENT

LO 2(m): describe, interpret and/or predict the effect of different types of structure and bonding on the physical properties of substances

When a solute dissolves in a solvent, the interactions between the solute particles (solute-solute interaction) and between the solvent particles (solvent-solvent interaction) must be overcome. The solute particles and solvent particles then need to form favourable solute-solvent interactions with each other such that the particles are able to mix freely with each other.

In terms of energy changes, a solute is **soluble** in a solvent if
the energy released from **solute-solvent** interactions is **greater than or comparable** to the energy needed to overcome **solute-solute** interactions and **solvent-solvent** interactions.

Hence, when explaining the solubility (or miscibility) of two substances, it is helpful to:

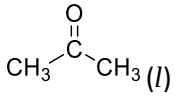
- identify the **type** of interactions holding **solute** particles together,
- identify the **type** of interactions holding **solvent** particles together,
- identify the **type** of interaction that can occur between the **solute** and the **solvent** particles,
- compare the **strength** of the **new** interactions (solute-solvent) with the **existing** interactions (solute-solute and solvent-solvent)

Table 12. Tips on how to identify types of solute-solvent interactions

Types of chemical bonding	How to identify?
Ion-dipole interaction	Between a cation and a partial negatively charged atom on a polar molecule Between an anion and a partial positively charged atom on a polar molecule
Hydrogen bonding	Between one molecule that has a lone pair on N/O/F and another molecule with a H on N/O/F
Permanent dipole-permanent dipole interaction	Between two polar molecules that cannot form hydrogen bonding
Permanent dipole-induced dipole interaction	Between a polar molecule and a non-polar molecule
Instantaneous dipole-induced dipole interaction (also called dispersion forces)	Between two non-polar molecules/atoms But also occurs between • two polar molecules • a polar molecule and a non-polar molecule

Exercise 12.1 (Worked Example)

Identify the type of solute-solvent interaction present in the following:

	solute	solvent	solute-solvent interaction
(a)	NaCl (s)	H_2O (*l*)	NaCl(s) is ionic; H_2O is a polar molecule ⇒ ion-dipole interaction between Na^+ and H_2O; ion-dipole interaction between Cl^- and H_2O
(b)	Br_2 (*l*)	CCl_4 (*l*)	Both molecules are non-polar ⇒ dispersion forces
(c)	 (*l*)	CH_2Cl_2 (*l*)	Both molecules are polar ⇒ permanent dipole-permanent dipole interactions
(d)	ICl (*l*)	$CH_3(CH_2)_4CH_3$ (*l*)	ICl (*l*) is a polar molecule; hydrocarbons are considered non-polar ⇒ permanent dipole-induced dipole interactions
(e)	CH_3CH_2OH (*l*)	H_2O (*l*)	Both molecules are able to form hydrogen bonding ⇒ hydrogen bonding

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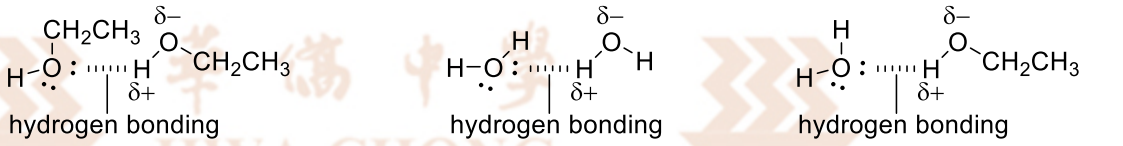
12.1 Solubility of substances in water

Water molecules are held together by hydrogen bonding. Depending on the solute, the interactions formed by water and a solute include:

- **hydrogen bonding** with polar molecules such as ethanol (CH_3CH_2OH), propanone (CH_3COCH_3)
- **permanent dipole-induced dipole interactions** with non-polar molecules such as iodine, hexane ($CH_3(CH_2)_4CH_3$)
- **ion-dipole attractions** with cations or anions (from ionic solids)

Example 1: Ethanol dissolves in water

The energy released when forming **hydrogen bonds** between ethanol and water molecules is comparable to the energy needed to overcome the existing hydrogen bonding between ethanol molecules and the existing hydrogen bonding between water molecules.



(a) *between ethanol molecules* (b) *between water molecules* (c) *between ethanol and water molecules*

Figure 52. Diagrams to illustrate hydrogen bonding

Example 2: Hexane, $CH_3(CH_2)_4CH_3$, is insoluble in water

The energy released when forming **weak permanent dipole-induced dipole** interactions between polar water and non-polar hexane molecules is insufficient to overcome the dispersion forces between hexane molecules and the **stronger hydrogen bonding** between water molecules.

Example 3: Sodium chloride, Na*Cl*, dissolves in water

Sodium chloride is an ionic compound. Both Na^+ and Cl^- ions are able to form ion-dipole attractions with water molecules. The ion-dipole attractions are relatively strong and very extensive. The energy released when forming **ion-dipole interactions** between Na^+ and H_2O and between Cl^- and H_2O is comparable to the energy required to overcome the **hydrogen bonding** between water molecules and **ionic bonding** between Na^+ and Cl^- ions in Na*Cl*.



(a) between Na^+ and H_2O (b) between Cl^- and H_2O

Figure 53. Diagrams to illustrate ion-dipole interactions

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Figure 54 illustrates the 'microscopic' processes that occur when sodium chloride dissolves in water.

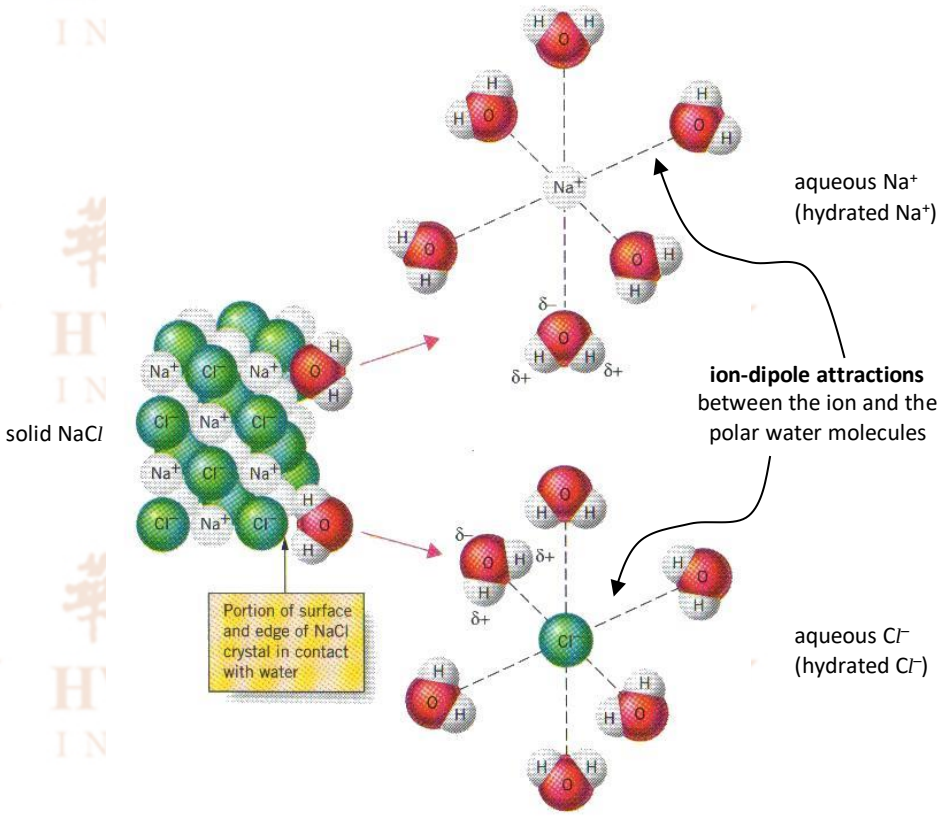


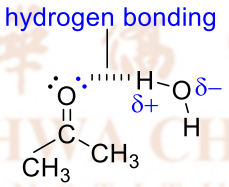
Figure 54. Water molecules form ion-dipole attractions with ions on the crystal's surface, forming solvated aqueous ions

The energy released from ion-dipole interactions depends on the charge densities of the ions (see Topic 5 *Chemical Energetics*). Ions with lower charge densities (e.g. Ag^+, Cl^-) form weaker ion-dipole interactions so less energy is released. This explains why some ionic compounds e.g. silver chloride are insoluble in water.

Exercise 12.2 (Worked Example)

Propanone (CH_3COCH_3) and water are miscible. Explain this with a suitable diagram to show the interactions formed between propanone and water.

Answer:

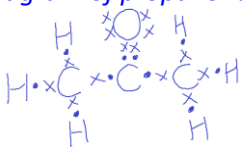


CH_3COCH_3 forms hydrogen bonding with water.

The energy released is able to compensate the energy needed to overcome the weaker permanent dipole-permanent dipole interactions between CH_3COCH_3 molecules, and the hydrogen bonding between water molecules.

Strategy:

For your info, dot-and-cross diagram of propanone:



- *identify the solute-solvent interactions*
- *compare strength of solute-solvent interactions to solute-solute and solvent-solvent interactions*

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12.2 Solubility of substances in organic solvents

Organic solvents can be **non-polar** (e.g. hexane, benzene (C_6H_6), tetrachloromethane (CCl_4)) or **polar** (e.g. propanone, ethanol). The interactions formed between the solvent and the solute depends on the specific substances involved.

Exercise 12.3 (Worked Example)
Explain why solid iodine is soluble in an organic solvent such as CCl_4 but insoluble in water.

Answer:
Both I_2 and CCl_4 are non-polar simple molecules. The energy released when forming **dispersion forces** between I_2 and CCl_4 molecules is **comparable to** the energy needed to overcome existing **dispersion forces** between I_2 molecules and between CCl_4 molecules. Hence, I_2 is soluble in CCl_4.

Water exists as polar simple molecules. The energy released when forming **permanent dipole-induced dipole interactions** between polar water and non-polar I_2 molecules is **insufficient** to overcome the dispersion forces between I_2 molecules and the **stronger hydrogen bonding** between water molecules. Hence, I_2 is **in**soluble in water.

LOOKING AHEAD
The study of chemical bonding, the structure of elements and compounds, as well as the interactions present explains their physical properties. These ideas will be pertinent when discussing the properties of aqueous and gaseous systems, as well as the concept of chemical changes or reactions. In preparation for the coming topics, consider the following questions:

- How does chemical bonding influence the movement of gaseous particles?
- How does chemical bonding influence chemical changes?
- How is energy related to chemical bonding?
- How can we measure the strength of a chemical bond?

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03 The Gaseous State

GUIDING QUESTIONS

- What is a mole? Why is it important in Chemistry?
- What is an ideal gas? What conditions are needed for a gas to behave ideally?
- What is the relationship between pressure, volume, temperature and amount of a gas?
- How do the individual components of a gas mixture contribute to the pressure of the mixture?

LEARNING OUTCOMES

Students should be able to:

3(a) state the basic assumptions of the kinetic theory as applied to an ideal gas

3(b) explain qualitatively in terms of intermolecular forces and molecular size:

(i) the conditions necessary for a gas to approach ideal behaviour

(ii) the limitations of ideality at very high pressures and very low temperatures

3(c) state and use the general gas equation PV = nRT in calculations, including the determination of M_r

3(d) use Dalton's Law to determine partial pressures of gases in a mixture

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

6(b) define the term *mole* in terms of Avogadro's constant

REFERENCES

1. Peter Cann, Peter Hughes, *Chemistry*, 1st Edition, Hodder Education, Chapter 4
2. Silberberg, *Chemistry: The Molecular Nature of Matter and Change*, 3rd Edition, McGraw-Hill, Chapter 5
3. Burrows, Holman, Parsons, Pilling, Price, *Chemistry: Introducing inorganic, organic and physical chemistry*
4. http://www.chemguide.co.uk/physical/ktmenu.html#top

LOOKING BACK

In the gaseous state, the particles are far apart as compared to solid and liquid states and are in constant random motion. An element or compound that exists as a gas at room temperature generally have weak interactions between its particles. You should keep in mind how the structure and bonding of a substance impact on its physical properties such as melting and boiling points.

Early experiments on the macroscopic properties of gases led to an understanding of the laws that govern the macroscopic properties of gases and the development of the mole concept. In preparation for this chapter, you should recall the basics of mole concept that you have learnt previously (e.g. what is 1 mole of particles?).

You may watch the lecture recording via https://youtu.be/2TI-b-9nXAo. You may click on the time stamp to skip to the relevant sub-sections.

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1 GASES

1.1 Development of Mole Concept through Gas Experiments (Background info)

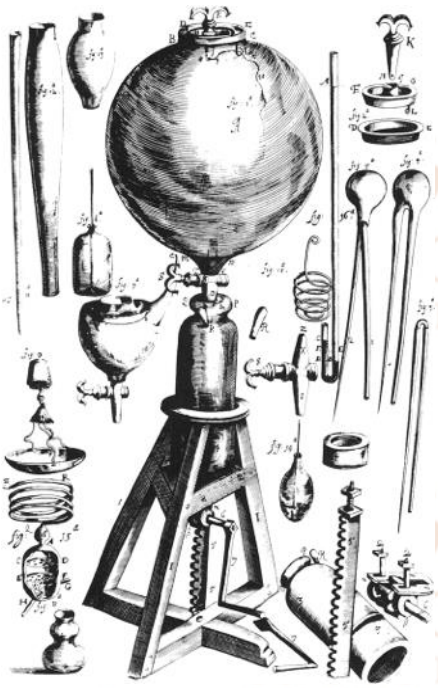


Figure 1. Some apparatus used by Robert Boyle

Some of the earliest scientific investigations concerning matter were performed by scientists trying to understand the physical and chemical properties of gases. It was these studies (~1650–1800 AD) that helped establish chemistry as a scientific discipline. The experiments of scientists such as Robert Boyle (1627 - 1691), Jacques Charles (1746-1823), and Gay-Lussac (1778-1850) led to our understanding of laws that govern the macroscopic properties of gases and we will learn these gas laws in *Section 3*.

Joseph Louis Gay-Lussac was a French chemist who studied how different volumes of gases combined during chemical reactions to make products. He determined that when different gases reacted, they would always do so in small whole number ratios (e.g., two volumes of hydrogen would react with one volume of oxygen in forming water) – the "Law of Combining Volumes of Gases". This was one of the greatest advancements of its time and helped form the basis for later atomic theory and how chemical reactions occur.

Amadeo Avogadro, an Italian physics professor, hypothesised the **Avogadro's Law** to explain Gay-Lussac's data.

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

LO 6(b): define the term mole in terms of Avogadro's constant

One ***mole*** contains exactly 6.02×10^{23} (or Avogadro constant, L) elementary entities. (notation: η, unit: **mol**)

LO 6(a): define the terms relative atomic, isotopic, molecular and formula mass

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

Note:

- Due to the presence of isotopes, the word "*average*" is necessary in definition of M_r
- M_r = sum of A_r of all the atoms in the molecular formula
- M_r has no units as it is a ratio of two masses



Exam tip

You are not required to remember the history of the development of mole concept for the examinations. However, you will need to define the important terms used in mole concept (those given in boxes above). The use of these terms in calculation will be covered in *Topic 4: "Reactions and Stoichiometry".*

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1.2 Units of Pressure

Pressure is defined as force exerted per unit area. Gas pressure is a gauge of the frequency and force of collisions between gas particles and the walls of the container that hold them. It is measured in a number of different units. One of the units is the millimetre of mercury, mmHg, which originates from measuring atmospheric pressure (760 mmHg) with a mercury barometer.

The SI units of pressure is the pascal, Pa, defined as 1 newton, N, per square metre. This is a very common unit used in the A-level syllabus.

$$1 \text{ Pa} = 1 \text{ N m}^{-2}$$

It is a much smaller unit of pressure than the standard atmosphere (**atm**) and the **bar**, which are approximated to the following values for calculations:

1 atm = 101,325 Pa

1 bar = 100,000 Pa

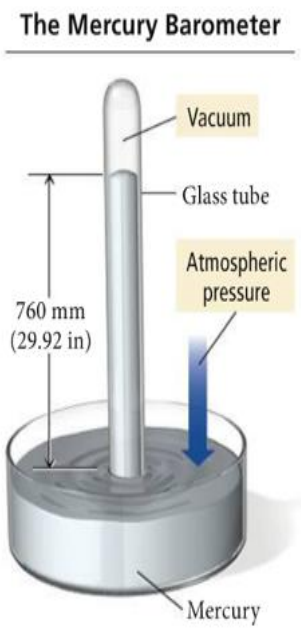


Figure 2. A mercury barometer at sea level

1.3 Measuring standards for gas samples

Because the physical properties of a gas sample can vary greatly depending on several factors, we often have to specify the conditions under which the measurements were made.

Molar volume, V_m, of any gas is the volume occupied by 1 mole of the gas at a specified temperature and pressure. The common conditions used for gas measurements and molar volumes are summarised in the table below.

Table 1. Molar volume and measurement conditions for gas samples

	Measurement conditions used		
	Pressure	Temperature	Molar volume (V_m)
Standard temperature and pressure (s.t.p.)	1 bar (100,000 Pa)	273 K (0 °C)	22.7 dm^3 mol^{-1}
Room temperature and pressure (r.t.p.)	1 atm (101,325 Pa)	293 K (20 °C)	24 dm^3 mol^{-1}

the Data book

You do not need to memorise the conditions and molar volumes for s.t.p. and r.t.p as they are listed on the first page of the Data Booklet!

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2 THE SIMPLE GAS LAWS AND IDEAL GAS LAW

Because most gases are difficult to observe directly, they are described through the use of four macroscopic properties.

- Pressure (**P**)
- Volume (**V**)
- Temperature (**T**)
- Number of moles of gas (**n**)

Simple gas laws are formulated to describe the relationship between pairs of the properties and hold to good approximations for all gases.

2.1 Simple Gas Laws

The simple gas laws describe the relationships between pairs of the above variables, when the other two variables are held constant.

In the early 1660s, the English scientist Robert Boyle found that at constant temperature, the volume of a fixed mass of gas (i.e. for n is constant) is *inversely proportional* to its pressure. The mathematical and graphical relationships of **Boyle's Law** are given below:

Mathematical relationship

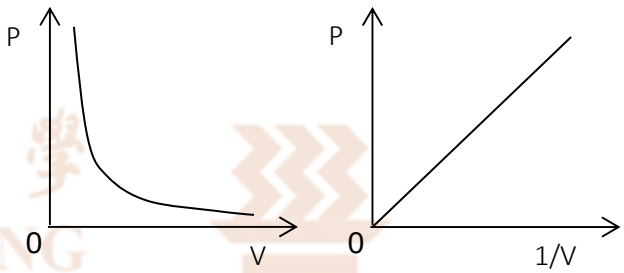
For n is constant and T is constant,

$$V \propto \frac{1}{P}$$

or

$$P \propto \frac{1}{V}$$

Graphical representation



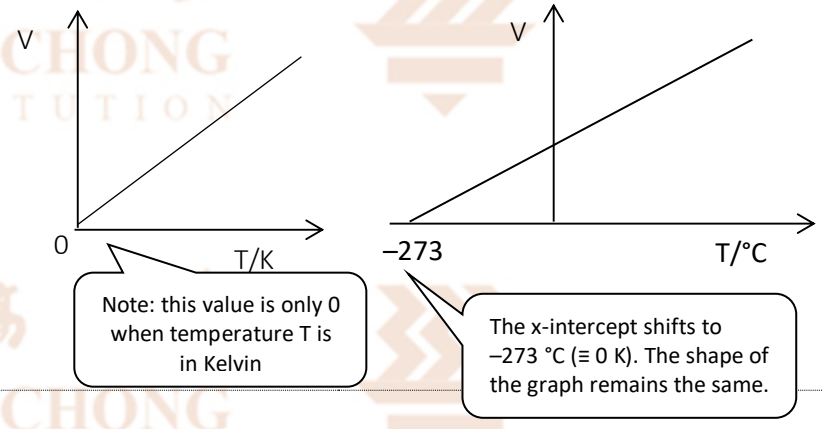
Later, in 1787, the French physicist Jacques Charles found that at constant pressure, the volume of a fixed mass of gas is *directly proportional* to its absolute temperature (measured in K). The mathematical and graphical relationships of **Charles' Law** are given below:

Mathematical relationship

For n is constant and P is constant,

$$V \propto T$$

Graphical representation



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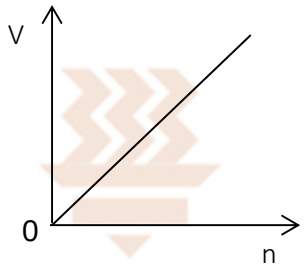
In 1811, Amadeo Avogadro proposed that at constant temperature and pressure, the volume of a gas is *directly proportional* to the number of molecules (or number of moles of gas) present. The mathematical and graphical relationships of **Avogadro's Law** are given below:

Mathematical relationship

For T is constant and P is constant,

$V \propto n$

Graphical representation



Take note that at constant temperature and volume, the pressure of a gas is also *directly proportional* to the number of moles present.

Exercise 2.1

Which of the simple gas laws is at work in each of the following examples?

(i) The bubbles exhaled by a scuba diver grow in size as the bubbles approach the surface of the ocean.

(ii) On collision, airbags in cars inflate rapidly. A sensor triggers the ignition of sodium nitride according to the following equation: $2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$

(iii) The print head of a bubble jet printer contains 64 or 128 tiny nozzles. The tip of the nozzle is filled with ink which is then heated by an electronic heater. This vaporizes the ink and a bubble of vapor ink is then published on the paper. This bubble when published acts as a dot, of a letter or image.

Review your answers here: (timestamp 16:52)

2.2 The Ideal Gas Equation

LO 3(c): state and use the general gas equation PV = nRT in calculations, including the determination of M_r

By combining the three relationships given above, we get $P \propto \frac{nT}{V}$

We can replace the proportionality sign by incorporating a proportionality constant known as the *molar gas constant* (R):

$$P = R\left(\frac{nT}{V}\right) \xrightarrow{\text{Rearrange}} \boxed{PV = nRT}$$

This equation is known as the **ideal gas equation**. It expresses the relationship among the four variables P, V, T and n for an **ideal gas**. An **ideal gas** is one which follows this equation exactly, under all conditions of pressure, volume and temperature. Refer to Section 4 for more information on the assumptions of the kinetic theory as applied to an ideal gas.

Using the ideal gas equation in calculations

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We can use the ideal gas equation to determine the value of any one of the four variables given the other three.

When using **R = 8.31 J K^{-1} mol^{-1}** (*Data Booklet*), P, V, n and T must be in **SI units**:

- P must be in Pa (≡ N m^{-2})
- V must be in m^3
- n must be in moles
- T must be in K

Table 2. Table showing possible units of the four measurable variables when substituted in the ideal gas equation

Variable	Symbol	SI units	Other Units	Conversions
Pressure	P	Pa (pascal) or N m^{-2}	atm , bar	1 atm = 101325 Pa 1 bar = 100000 Pa
Volume	V	m^3	cm^3 ; dm^3	1 cm^3 = 1 × 10^{-6} m^3 1 dm^3 = 1000 cm^3 = 1 × 10^{-3} m^3
Temperature	T	K (kelvin)	*–nil–*	Absolute temperature (in K) = temperature (in °C) + 273 0 K = −273 °C (absolute zero)
Amount	n	mol	*–nil–*	

Exercise 2.2 (Worked Example)

On the surface of Venus, the temperature is 470 °C and the pressure is 1.00 atm. What is the volume occupied by 1.00 mol of an ideal gas under these conditions?

Working and solution:

Use PV = nRT and convert all variables to SI units (Pressure from atm to Pa, Temperature from °C to K).

V = (1.00)(8.31)(470+273)/ 101325 = 0.0609 m^3

(You may also review the explanation via timestamp 25:47)

2.3 Using the Ideal Gas Equation to determine M_r

$$n = \left(\frac{\text{mass}}{\text{molar mass}}\right) = \frac{m}{M_r}$$

$$\therefore \text{PV} = \left(\frac{m}{M_r}\right)\text{RT}$$

Exercise 2.3

In a syringe experiment, 0.10 g of a gas is found to occupy 83.1 cm^3 measured at standard temperature and pressure. What is the relative molecular mass of the gas?

Review your answers here: (timestamp 27:31)

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Exercise 2.4

A sample of *m g* of an organic compound is vaporised in a gas syringe and occupies *V* cm^3 at *T* K and *P* bar. What is the relative molecular mass of the compound, M_r? (*N00/III/6*)

A $M_r = \dfrac{m \times 22700 \times T}{P \times V \times 273}$ **B** $M_r = \dfrac{m \times 22700 \times (T + 273)}{P \times V \times 273}$

C $M_r = \dfrac{m \times 22700 \times 273 \times P}{V \times T}$ **D** $M_r = \dfrac{m \times 22700 \times 273 \times P}{V \times (T + 273)}$

Review your answers here: (timestamp 30:30)

2.4 Combined Gas Equation

The combined gas equation is useful for changes to gas systems where the **amount of the gas, n, is kept constant**.

Since n and R are constants,

$$\frac{PV}{T} = nR \quad \Longrightarrow \quad \frac{PV}{T} = \text{constant}$$

$$\frac{P_1V_1}{T_1} = \text{constant} = \frac{P_2V_2}{T_2}$$

$$\boxed{\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}}$$

where P_1, V_1 and T_1 relate to the gas in its initial condition, and P_2, V_2 and T_2 relate to the gas in its final condition. Temperature values must **only be in K** for the expression to be valid.

The combined gas equation can be further reduced to:

$P_1V_1 = P_2V_2$	if temperature is constant
$P_1 / T_1 = P_2 / T_2$	if volume is constant and
$V_1 / T_1 = V_2 / T_2$	if pressure is constant

Useful tip:

- Because these relationships do not make use of the gas constant R, it is possible to use *any units of pressure or volume*, as long as they are consistently used for initial and final values.

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Exercise 2.5 (Worked Example)

An air bubble rises from the bottom of the sea, where the temperature is 6.0 °C and pressure is 8.4 atm, to the water surface. The water surface has a temperature of 24.0 °C at 1.0 atm. Calculate the volume of the bubble in cm^3, to 2 decimal places, if its initial volume is 0.030 cm^3.

Working and solution:

The variables mentioned in the question stem are summarised below:

$T_1 = 273 + 6.0 = 279$ K $P_1 = (8.4 \times 101325)$ Pa $V_1 = (0.030 \times 10^{-6})$ m^3

$T_2 = 273 + 24.0 = 297$ K $P_2 = (1.0 \times 101325)$ Pa $V_2 = ?$

Since the air bubble contains a fixed amount of gas,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$V_2 = \frac{(8.4 \times 101325) \times (0.030 \times 10^{-6}) \times 297}{(1.0 \times 101325) \times 279} = 0.27 \text{ cm}^3$$

(Note: As the conversion to SI units for pressure and volume term involves multiplying a constant, once you are experienced enough, it need not be written out in your working as it'll be cancelled off).

(You may also review the explanation via timestamp 40:59)

Exercise 2.6

A 400 cm^3 mixture of petrol vapour and air is taken into the cylinder of a car engine at 200 °C and a pressure of 100 kPa. The piston compresses this gaseous mixture to 50.0 cm^3.
Find the pressure of the compressed gas if temperature is constant. [Assume that the gases do not react]

Review your answers here: (timestamp 44:19)

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2.5 Graphical Relationships for Ideal Gases

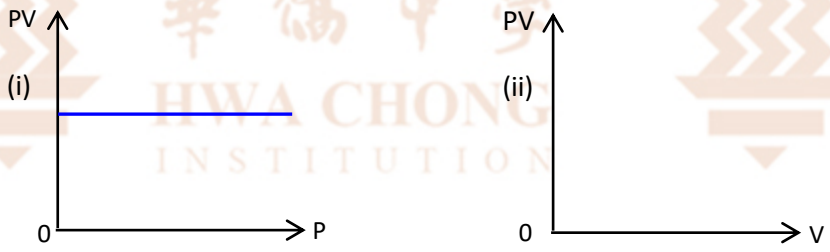
The graphical relationships for simple gas laws are introduced in *section 2.1*. In this section, we will attempt to predict the graphical relationship between other variables, based on manipulation of the ideal gas equation **PV = nRT**. Figure out which of the four variables are constants, and rearrange this equation in the form $y = mx + c$.

Exercise 2.7 (Worked Example)

Watch the video review here: (timestamp 46:41)

Situation 1

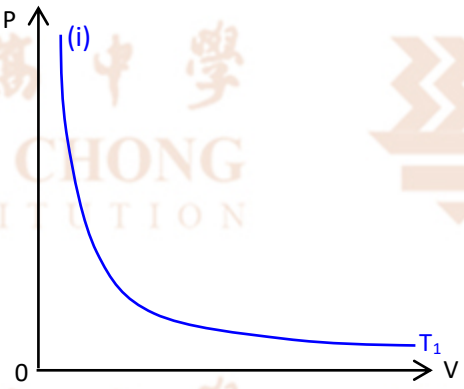
For a fixed amount of gas kept at a constant temperature, sketch a graph of
(i) PV against P **(Worked Example)** and
(ii) PV against V.



Since n and T are both constant,
PV = nRT = constant
$\Longrightarrow$ PV $= k$, which is a constant. Hence a horizontal line is obtained as PV remains constant even if P changes.

Situation 2 (Extension of Boyle's Law)

For a fixed amount of gas at two different temperatures (T_1 and T_2), sketch on the same axes, a graph of P against V for
(i) T_1 **(Worked Example)**
(ii) T_2 ($T_2 > T_1$)



PV = nRT $\Rightarrow$ P = (nRT)$(\frac{1}{V})$

(nRT) is constant for a fixed amount of a gas at one temperature, hence $P \propto \frac{1}{V}$

The graph of P against V would be like the asymptote graph shown above.

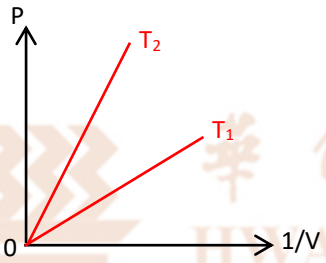
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Interpreting graphs

Each of the following graphs represents plots for an ideal gas at two different conditions. In each case, you should be able to identify the variable with the higher value by using either of the following two strategies:

1. Consider for a given value of a variable (taken to be the x-axis variable for consistency) by drawing a vertical line. Then compare how the other variable would change under the two different conditions given by looking at where the line you've drawn cuts the graphs.
2. (This works best for straight line graphs) Rearrange PV = nRT to fit the variable given by the y- and x-axes. Check how the changing variable affects the steepness of the gradient.

Which temperature is higher, T_1 or T_2?



Rearrange PV = nRT and make P the subject of the equation, we will get P = (nRT)(1/V).

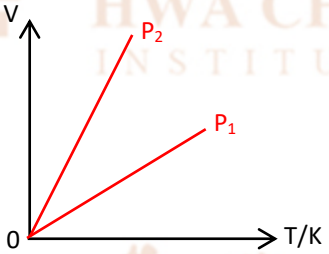
Therefore, plotting P against 1/V will give us a straight line that passes through the origin with gradient = nRT.:

Since the graph with T_2 is a steeper line than that of T_1, that means $nRT_2 > nRT_1$. This is only possible if $T_2 > T_1$. Hence T_2 has a higher temperature than T_1.

Exercise 2.8

Review your answers here: (timestamp 54:38)

(a) Which pressure is higher, P_1 or P_2? **(Worked Example)**



Strategy:

Rearrange PV = nRT and make V the subject of the equation, we will get V = (nR/P)T.

Therefore, plotting V against T will give us a straight line that passes through the origin with gradient = nR/P.

Since the graph with P_2 is a steeper line than that of P_1, that means $nR/P_2 > nR/P_1$. This is only possible if $P_2 < P_1$. Hence P_1 has a higher pressure than P_2.

(b) Which temperature is higher, T_1 or T_2?



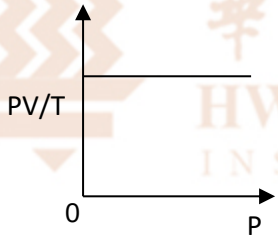
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Exercise 2.9

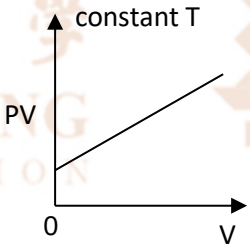
Review your answers here: (timestamp 56:51)

Which graph correctly describes the behaviour of a fixed mass of an ideal gas?

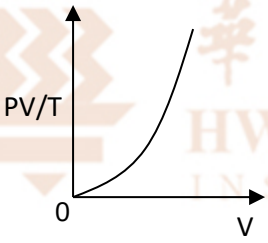
A



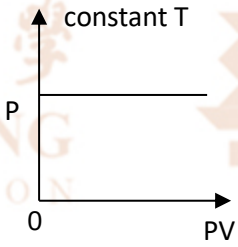
B



C



D



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3 GAS MIXTURES AND PARTIAL PRESSURES

LO 3(d) use Dalton's Law to determine the partial pressures of gases in a mixture

If a mixture of non-reacting gases is confined in a container, each gas occupies the volume (V) of the container and exerts its own pressure (P) on the walls of the container as if it alone were present. This observation is known as **Dalton's law of partial pressures**, and the pressure exerted by a particular gas in a mixture is referred to as its **partial pressure**.

If we let P_{total} be the total pressure of a gas mixture, we can write Dalton's law of partial pressures as:

$$P_{total} = P_a + P_b + P_c + \cdots$$

where P_a, P_b, P_c... are the partial pressures of the individual gases *a*, *b*, *c*... respectively.

Since T and V are constant, the partial pressure of each component is directly dependent on (and proportional to) the amount of each gas in the mixture. So, for gases *a, b, c, etc…*

$$P_a = n_a\left(\frac{RT}{V}\right) \qquad P_b = n_b\left(\frac{RT}{V}\right) \qquad P_c = n_c\left(\frac{RT}{V}\right) \qquad \text{… and so on}$$

Combining these into the expression for P_{total}, we get:

$$\begin{aligned} P_{total} &= n_a\left(\frac{RT}{V}\right) + n_b\left(\frac{RT}{V}\right) + n_c\left(\frac{RT}{V}\right) + \cdots \\ &= (n_a + n_b + n_c + \cdots)\left(\frac{RT}{V}\right) \\ &= n_{total}\left(\frac{RT}{V}\right) \end{aligned}$$

Dividing the expression for P_a by that for P_{total}, and rearranging:

$$P_a = \left(\frac{n_a}{n_{total}}\right) P_{total}$$

where $\left(\frac{n_a}{n_{total}}\right)$ is called the **mole fraction**, sometimes represented by the Greek letter *chi*, χ, or:

$$P_a = \chi_a P_{total}$$

Thus, in a gas mixture, the **partial pressure of any individual gas is directly proportional to its mole fraction** in the mixture.

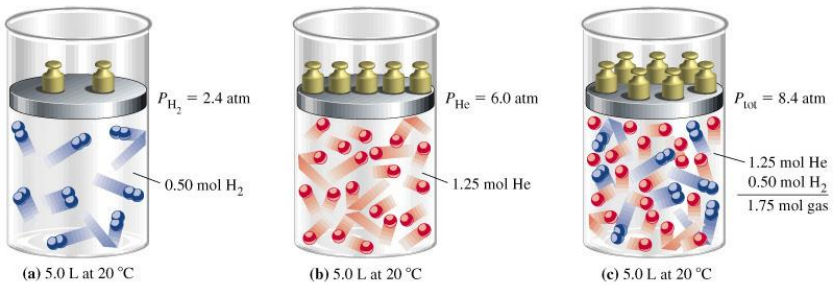


Figure 3. Illustration of Dalton's Law of Partial Pressures

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Exercise 3.1 (Worked Example)

Two moles of oxygen and one mole of nitrogen are contained in a cylinder with a volume of 10.0 dm^3 at 298 K. What is the total pressure? What is the partial pressure of oxygen?

Working and solution:

As oxygen and nitrogen do not react under the given conditions, the total pressure will simply be dependent on the total number of moles of gas. The ideal gas equation can be used to calculate the total pressure.

$$P_{total} = \frac{\eta_{total}RT}{V} = \frac{(2+1)(8.31)(298)}{10.0 \times 10^{-3}} = 742914 \text{ Pa} = 743 \text{ kPa}$$

$$P_{O_2} = \frac{\eta_{O_2}}{\eta_{total}} \times P_{total} = \frac{2}{3} \times 742914 = 495 \text{ kPa}$$

(You may also review the explanation via timestamp 1:01:37)

Exercise 3.2

Flask **Q** contains 1.00 dm^3 of helium at a pressure of 2.00 kPa and flask **R** contains 2.00 dm^3 of neon at a pressure of 3.00 kPa. If the flasks are connected at constant temperature, what is the final pressure of the system?

Review your answers here: (timestamp 1:03:17)

Exercise 3.3

A 12.5 dm^3 scuba diving tank is filled with a heliox mixture containing 24.2 g of He and 4.32 g of O_2 at 298 K. Calculate the total pressure and the partial pressures of helium and oxygen in the mixture.

Review your answers here: (timestamp 1:07:23)

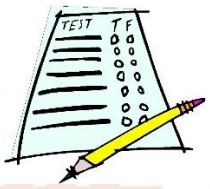
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4 ASSUMPTIONS ABOUT IDEAL GASES

LO 3(a): state the basic assumptions of the kinetic theory as applied to an ideal gas

The kinetic theory of gases is a model used to describe the microscopic behaviour of gas particles and their interactions. This theory was developed in reference to **ideal gases** (refer to *section 2.2*), though it can be applied reasonably well to real gases. The following assumptions are about ideal gases:

1. The size of the gas particles is so small compared to the space between them that we can assume that the particles themselves have negligible volume. In other words, **the gas particles have negligible volume compared to the volume of the container**.
2. The **intermolecular forces of attraction** between gas particles are **negligible**.
3. **Collisions** between gas particles, and their collisions with the walls of the container, are **perfectly elastic;** i.e. there is no net loss or gain of kinetic energy during collision.



Exam tip

In the A-level examinations, you may be asked to recall the assumptions of the Kinetic Molecular Theory as applied to ideal gases. Assumptions 1 and 2 are the most important ones, particularly for the discussion on how real gases deviate from ideal behaviour.

If you are required to state more than 2 assumptions, assumption 3 can be included.

Exercise 4.1 (Worked Example)

Argon exists in the atmosphere as a monoatomic inert gas.

(a) Using the Data Booklet, calculate the volume of an argon atom, indicating the units clearly. [Given: volume of a sphere is $^4/_3\,\pi r^3$, where r is its radius]

(b) Calculate the total combined volume of one mole of argon atoms.

(c) If the gas volume of 1 mole of argon is 24 dm^3 at room temperature and pressure, calculate the percentage of the total volume occupied by the argon atoms themselves.

(d) Based on your answer in (c), comment on whether it is justified to assume that argon at room conditions behaves ideally. State the relevant assumption applied to an ideal gas.

Working and solutions:

(a) Check data booklet for atomic radius of Ar (convert nm to m)
Volume of a sphere = $^4/_3\,\pi(0.190 \times 10^{-9})^3 = 2.87 \times 10^{-29}\ m^3$

(b) One mole of atoms contains Avogadro's number of particles.
Total volume of one mole of argon atoms $= 2.87 \times 10^{-29} \times 6.02 \times 10^{23}$
$= 1.73 \times 10^{-5}\ m^3$

(c) Molar volume at rtp = 24 $dm^3 = 24 \times 10^{-3}\ m^3$
% of total volume occupied by the argon atoms at rtp = $1.73 \times 10^{-5}\ m^3 / 24 \times 10^{-3} \times 100\%$
$= 0.0721\%$

(d) Yes. The assumption is that the gas particles have negligible volume compared to the volume of the container.

(You may also review the explanation via timestamp 1:14:13)

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4.1 Conditions for real gases to behave ideally

LO 3(b)(i): explain qualitatively in terms of intermolecular forces and molecular size: the conditions necessary for a gas to approach ideal behaviour

- At **low pressures**, the gaseous molecules are relatively far apart. The volume of the molecules themselves is negligible compared to the volume of the container. Thus, real gas molecules at low pressure can be approximated to have negligible volume. Also, intermolecular forces are negligible as the particles are far apart. Hence their behaviour at low pressures would approach that of ideal gases.

- At **high temperatures**, gas particles have enough kinetic energy to overcome intermolecular forces, which can thus be considered insignificant. As such, the behavior of real gases approach ideal gas behavior at high temperatures.

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5 REAL GASES AND DEVIATION FROM IDEAL BEHAVIOUR

LO 3(b)(ii): explain qualitatively in terms of intermolecular forces and molecular size: the limitations of ideality at very high pressures and very low temperatures

Based on the reasons given in Section 4.1, real gases would therefore deviate from ideal behaviour at high pressures and low temperatures.

Under these conditions, the following two assumptions about ideal gases are no longer valid, namely:

1) The gas particles have negligible volume compared to the volume of the container; and
2) The intermolecular forces of attraction between gas particles are negligible.

Figure 4 shows a plot of PV/RT against pressure for some real gases compared with that of an ideal gas. For 1 mol of an ideal gas, the ratio PV/RT is equal to 1 at any pressure. In general, deviations from ideal behaviour become greater at higher pressures.

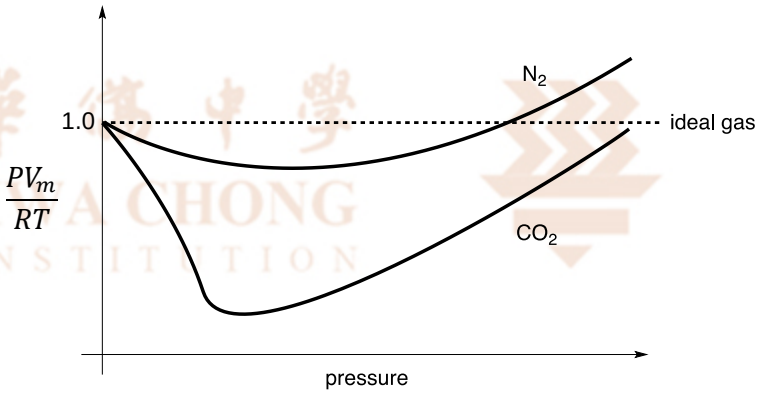


Figure 4. Effect of pressure on the behaviour of several real gases at 300 K

Figure 4 also shows how different gases deviate differently from ideal behaviour. Molecules with stronger intermolecular forces will violate assumption 2 and show greater deviation. For example, CO_2 has a larger electron cloud and hence stronger dispersion forces than N_2, hence CO_2 deviates more from ideal behaviour.

For molecules with similar electron cloud size, e.g. NH_3 (M_r = 17.0) versus CH_4 (M_r = 16.0), other intermolecular forces besides dispersion forces need to be considered. NH_3, with stronger hydrogen bonding, should deviate more from ideal behaviour than CH_4, with only intermolecular dispersion forces.

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Interesting to note



Liquefaction is a key property of real gases that is not predicted by the kinetic molecular theory of gases, as it requires the action of intermolecular forces (which the theory assumes to be negligible) in order to occur. In other words, ideal gases never condense into liquids!

Figure 5 shows how one mol of nitrogen behaves as a result of changing the temperature. The deviation is greatest at low temperatures.

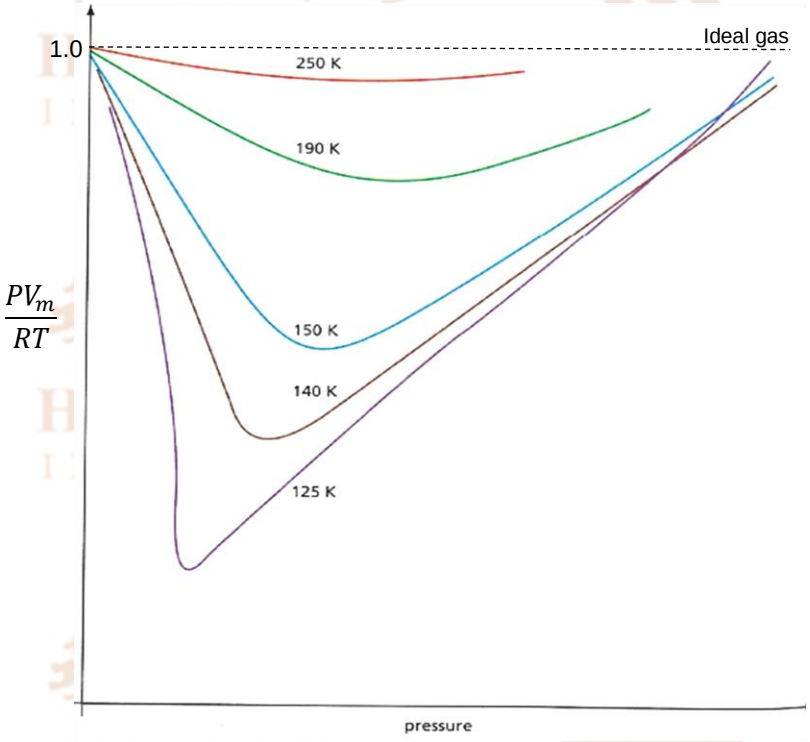


Figure 5. Effect of temperature on the behaviour of nitrogen gas

Conclusion: Real gases do not obey the ideal gas law, especially at high pressures and/or low temperatures.

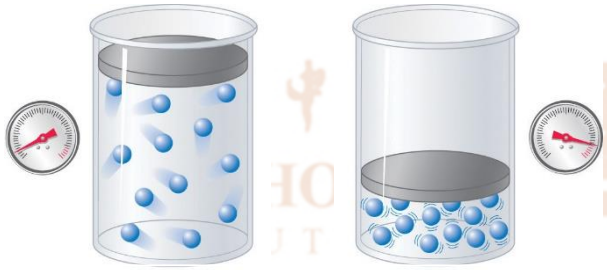
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5.1 Explaining deviations at high pressures

- The gas particles can no longer be considered to have negligible volume compared to the volume of the container.

At high pressures, the volume of the container decreases. The molecules are pushed closely together and take up a significant portion of the container volume, resulting in less space in which the molecules can move. Thus, it is no longer valid to assume that its volume is negligible compared to the container volume, and so the gas deviates from ideal behaviour. (In fact, the total volume occupied by a real gas is actually greater than the volume predicted by the ideal gas equation.)

Also, since the gas particles are close together, they tend to interact with one another, hence intermolecular attractions are not negligible.



a) Low pressure b) High pressure

Figure 6. Illustration of effect of non-zero particle size at low and high pressures

5.2 Explaining deviations at low temperatures

- The intermolecular forces between gas particles become significant.

As temperature is lowered, the kinetic energy of the gas particles decreases, causing them to move more slowly and intermolecular forces to become more significant. This also causes collisions to become inelastic (such that assumption 3 is no longer valid either). Eventually, it reaches a point where the particles can no longer overcome the intermolecular forces, at which point real gases liquefy (condense to form a liquid) when cooled to below its boiling point.

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Did you notice?

Increasing the pressure on a real gas has opposite effects on the value of the product P × V. It increases the observed V, while decreasing the observed P. This effect is summarized in Figure 7 below:

- where the value of PV deviates below that of ideal gas, the effect of intermolecular forces dominates. As pressure increases, the gas molecules are closer together, resulting in stronger intermolecular forces, decreasing the observed P. The **stronger the intermolecular forces present, the greater the extent of deviation**.
- At higher pressures, where the value of PV deviates above that of ideal gas, the gas particles can no longer be considered to have negligible volume compared to the volume of the container, increasing the observed V.

As the pressure increases, the strength of the intermolecular forces increases at a greater rate than the increase in the volume, hence the PV value decreases leading to the minimum point seen in the graph of PV against pressure applied for some gases.

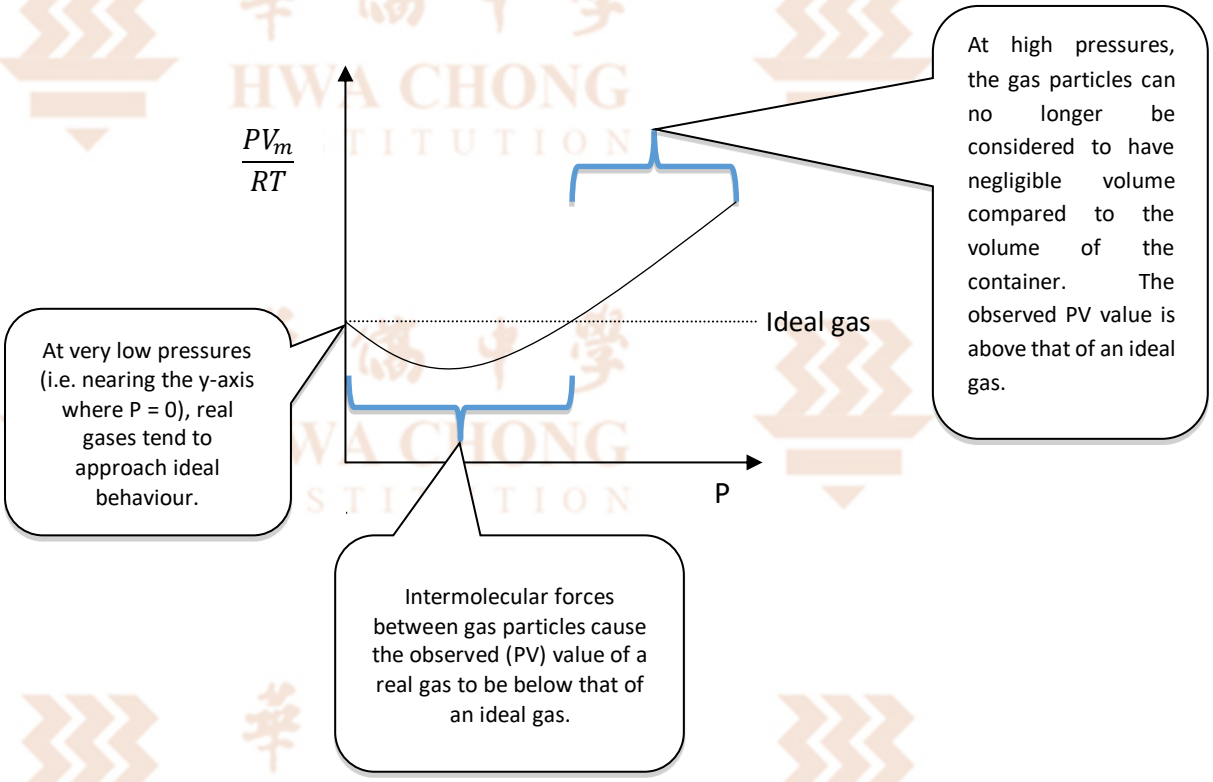


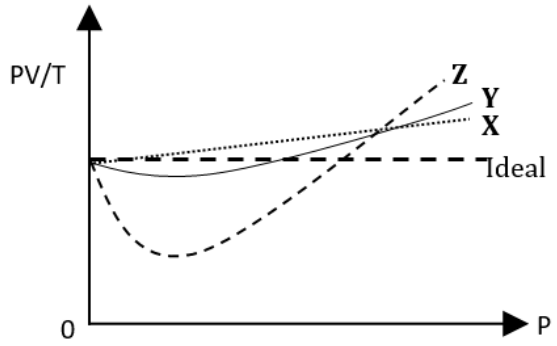
Figure 7. Understanding the shape of a non-ideal gas curve

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Exercise 5.1 (Worked Example)

Interpreting real gas behaviour from a plot PV/RT versus P

The following curves represent the behaviour for equal amounts of three real gases and an ideal gas at a fixed temperature. Among the options given, what could the possible identities of real gases **X**, **Y** and **Z** be?



	X	Y	Z
A	NH_3	N_2	H_2
B	H_2	NH_3	N_2
C	N_2	H_2	NH_3
D	H_2	N_2	NH_3

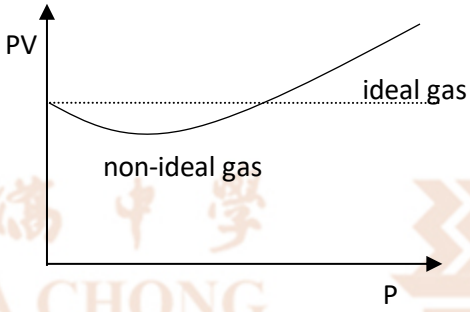
Working and solution:

- The question mentions that 'equal amounts' of all gases are plotted – we therefore expect n to be the same, and thus their PV/T (which is = nR) values should also be the same when behaving ideally.
- Line Z has the greatest deviation below the ideal line and should represent the gas that has the strongest intermolecular forces, i.e. NH_3 (hydrogen bonding).
- Between the two remaining options, N_2 should show greater deviation (line Y) than H_2 (line X) as it has larger electron cloud (stronger dispersion forces)
- Option **D**

(You may also review the explanation via timestamp 1:30:13)

Exercise 5.2

The value of PV is plotted against P for two gases, an ideal gas and a non-ideal gas, where P is the pressure and V is the volume of the gas.



Which gas shows the greatest deviation from ideality?

A ammonia
B ethene
C methane
D nitrogen

[N2010/I/7]

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6 DISTRIBUTION OF MOLECULAR SPEEDS

The **average kinetic energy** of the gas particles is **directly proportional** to the **absolute temperature**. So at a particular temperature, all types of gaseous particles have the same average kinetic energy.

Although collectively the molecules in a gas sample have the **same *average* kinetic energy**, the individual molecules are moving at **different speeds**. There exists a distribution of speeds among the particles in a sample of gas. At a given temperature, heavier gases travel slower while lighter gases travel faster (recall: KE = ½mv^2). Figure 8 shows how the speed distribution varies with the molar mass of the gas for different gas samples at the same temperature.

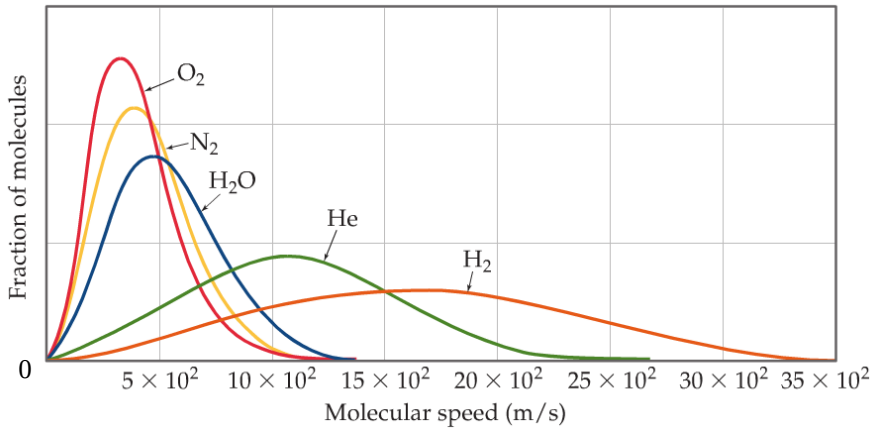


Figure 8. Variation of speed distribution with molar mass at a given T

For a gas sample at **different temperatures** as shown in Figure 9, the speed distribution of the molecules shifts toward higher speeds and becomes less sharply peaked as the temperature of the gas sample is increased. Even at low temperatures, a small number of molecules have high speed and kinetic energy. This number of molecules increases with temperature, while the number of molecules with low speed and kinetic energy becomes smaller but does not vanish.

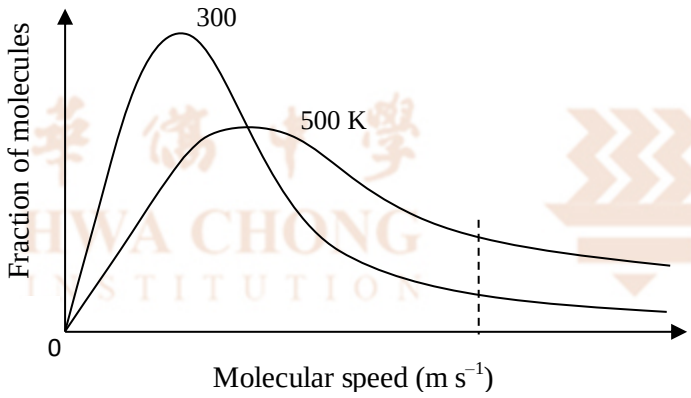


Figure 9. Variation of speed distribution with T for a given gas sample

The above speed distributions are referred to as **Maxwell-Boltzmann distribution curves**, or simply, the **Boltzmann distribution curve**.

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Note the following about Maxwell-Boltzmann distribution curves:

1. The examples above use speed on the horizontal axis. However, since kinetic energy of a molecule is proportional to the square of its speed, the graph would have the same shape if kinetic energy were used on the x-axis instead.

2. Common labels for the vertical axis include number of (gas) particles (or molecules), proportion of particles, or fraction of particles.

3. The *area under the curve* generally represents the **total number of particles** in the sample. So for a fixed amount of sample at different temperatures, the area should remain the same even as the curve shifts.

4. The *peak* of each curve represents the **most probable speed** (or most probable kinetic energy, depending on the x-axis label). As the temperature increases, the peak decreases in height and shifts to the right as the distribution of molecular speeds becomes more spread out.

5. All curves start at the *origin* (0,0) because in a gas sample **there are no particles with zero speed** (or zero kinetic energy). In other words, all gas particles must be moving.
   [The only exception is at 0 K, absolute zero, which is the theoretical lowest possible temperature, one at which all particles have zero kinetic energy and particle motion stops.]

6. The curves **do not show a maximum speed** (or kinetic energy) value and run asymptotically along the x-axis – i.e. the curves do not intersect the x-axis again as there is theoretically no limit to the amount of speed (or energy) a particle can have.

LOOKING AHEAD

In this topic, you have learnt to describe the behaviour of a gas in macroscopic terms of pressure, volume, temperature and number of moles (ideal gas equation). This will set the foundation for your learning in subsequent topics so keep in mind the following questions:

1. How to calculate partial pressures of gaseous species in reactions? (This will be especially useful for Topic 7 Chemical Equilibria)
2. How do you use the principles of mole concept in stoichiometric calculations involving reacting masses, volumes of gases and concentrations of solutions? (Topic 4 Reactions and Stoichiometry)

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PLANNING FOR AN EXPERIMENT THAT INVOLVES GAS COLLECTION

The volume of a gas produced in a reaction can be measured through a variety of experiments to determine *concentration*, *percentage purity*, *rate of reaction* etc.

Common reactions which can produce a gas are:

- Acid + metal $\rightarrow H_2$
- Acid + carbonate $\rightarrow CO_2$
- Catalysed decomposition of $H_2O_2 \rightarrow O_2$
- H_2O_2 + oxidising agent $\rightarrow O_2$
- Decomposition of solids (e.g. Group 2 carbonate $\rightarrow CO_2$)

- You may be required to suggest the mass and/or volume of chemicals to react. These can be calculated based on your chosen capacity of your gas collection container (e.g. gas syringe, burette). Volume of container must be reflected in diagram or written clearly in the procedure.

– The total volume of the reaction mixture should not exceed the capacity of your chosen reaction flask e.g. a 250 cm^3 conical flask.

– Ensure your proposed setup is a **closed** system (no loss of gas) and the chemicals are separated, ready to mix.

– The method of gas collection depends mainly on the solubility of the gas in water.

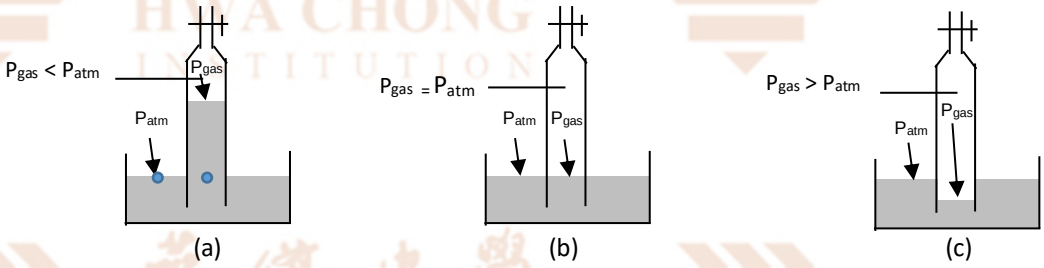
- **Graduated gas syringe**: suitable for all gases. Typical capacity of gas syringe: 50 cm^3, 100 cm^3. The syringe must be graduated (draw markings in your diagram, or label *'graduated gas syringe'*).
- **Downward-displacement of water** in an inverted burette (50 cm^3) or measuring cylinder (50 cm^3, 100 cm^3): suitable for gases that are sparingly soluble in water, e.g. H_2, O_2. A burette is more precise for measuring small volumes.

Sources of error:

➢ This method of collection is only appropriate for gases that have low solubility in water, e.g. H_2, O_2.

➢ When a gas is collected over water, some water in the burette will vapourise and gets mixed with the gas collected. The water vapour will exert its own pressure as well. Hence, the total pressure of the gas in the burette is due to both the partial pressure of the gas collected and the partial pressure of the water vapour.

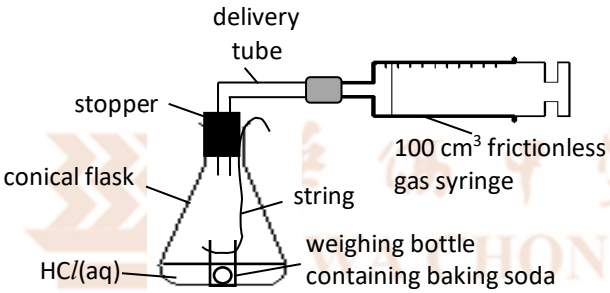
➢ Pressure is the same at all points on the same horizontal level within a liquid. Since the water column will also exert its own pressure, in (a) taking the water level as reference, $P_{atm} = P_{gas} + P_{water\ vapour} + P_{water\ column}$. As the water level inside the inverted burette changes, the pressure of the gas will also change. This limitation has an impact on the accuracy of the volume of gas measured.



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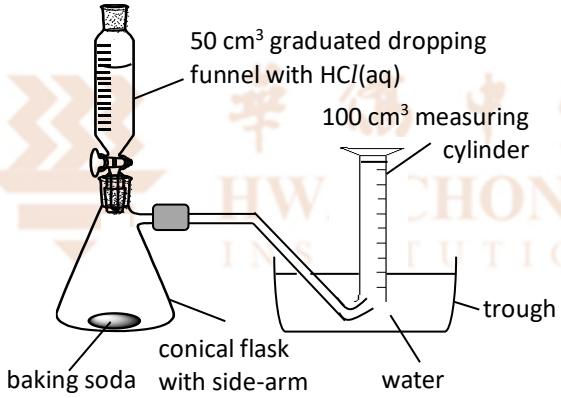
Set-up

A) Set–up with suspended test-tube and gas syringe



One reactant is added into the test-tube (or small vial) and lowered into the flask. The other reactant is added directly into the flask. *Care must be taken to ensure the two reactant* ***do not*** *come into contact at this stage.* To start the reaction, the flask is shaken/swirled to mix the two reactants. Gas produced is collected without loss.

B) Set-up with dropping funnel and downward displacement of water



The liquid reactant (e.g. aqueous acid) is placed into the dropping funnel with the tap closed. The other reactant (e.g. Na_2CO_3 solid) is placed into the reaction flask. To start the reaction, the tap is opened to release the liquid reactant and closed when the desired volume of liquid is added. Gas produced is collected without loss. There will however be a volume of air displaced into the measuring cylinder by the liquid reactant when the liquid is added. This needs to be subtracted from the total volume of gases collected.

Generic Procedure for (A)

1. Using an electronic balance, weigh accurately about (mass) of (solid reactant) in a weighing bottle.
2. Using a measuring cylinder, transfer (volume) of (aqueous reactant) into a 250 cm^3 conical flask.
3. Carefully lower the weighing bottle containing (solid reactant) into the conical flask, ensuring the reactants do not mix. Insert the stopper to ensure a closed set-up.
4. Set up the apparatus as shown in the diagram (A).
5. Record the initial reading, x cm^3, on the gas syringe.
6. Shake the conical flask to topple the weighing bottle, and continue swirling the conical flask to thoroughly mix the reactants.
7. When the volume reading has remained constant for a period of time, record the final reading, y cm^3, on the gas syringe (or if it's for a kinetics experiment, "record volume of gas at appropriate time intervals"). The volume of gas collected is $(y - x)$ cm^3.

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Generic Procedure for (B)

1. Using an electronic balance, weigh accurately about (mass) of (solid reactant) in a weighing bottle. Transfer the solid into a conical flask with side-arm. Reweigh the weighing bottle to account for any residual solid.

2. Set up the apparatus as shown in the diagram (B).

3. Fill a 50.0 cm^3 graduated dropping funnel with (aqueous reactant).

4. Record the initial reading, x cm^3, on the (measuring cylinder/burette).

5. Take note of the initial reading on the graduated dropping funnel. Open the tap of the dropping funnel to add the (aqueous reactant) to the solid. When (volume) of (aqueous reactant) has been added, close the tap. Swirl the flask to thoroughly mix the reactants. (Note: There will be a corresponding volume of air displaced by the added liquid)

6. When bubbling through the (measuring cylinder/burette) has stopped, record the final reading, y cm^3, on the (measuring cylinder/burette). The volume of gas collected is ($y - x - V_{displaced\ air}$) cm^3.

Note:

- It may sometimes be necessary to allow the set-up to equilibrate to room conditions, for example, if the reaction is highly exothermic. However, in a kinetics experiment where the volume of gas needs to be read at appropriate time intervals, it would not be possible to allow the set-up to equilibrate to room conditions (Refer to planning section in Topic 6 Reaction Kinetics.)

- If the reaction produces effervescence, it is possible to tell the reaction has stopped when no more effervescence is observed.

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PLANNING FOR AN EXPERIMENT THAT INVOLVES HEATING OR DRYING TO CONSTANT MASS (GRAVIMETRY)

Gravimetry (or gravimetric analysis) refers to the quantitative determination of an analyte (i.e. the substance being analysed) based on the mass of a solid.

It may involve heating hydrated salts (e.g. $Na_2CO_3 \cdot 10H_2O$), or heating to decompose a solid (e.g. $MgCO_3$) or mixing two solutions to form a precipitate (e.g. $BaSO_4$ or AgCl), followed by filtering, drying, and weighing of the precipitate.

The **principle of heating (or drying) to constant mass** is applicable in this method.

Generic Procedure for Heating to Constant Mass

Using an electronic balance, **weigh** accurately __(mass)__ g of __(solid)__ in a dry empty **crucible** (or boiling tube). Record mass of empty crucible, mass of crucible and solid, and mass of solid collected.

1. **Heat** the crucible and its contents gently first for 1 min then strongly for about 5 min.
2. Allow the crucible and its contents to **cool** on a wire gauze.
3. **Re–weigh** the crucible with its contents.
4. **Repeat heating, cooling and re–weighing until there is no further change in mass**.

Heating to constant mass ensures that the solid is **completely** decomposed (or in the case of heating hydrated salts, water of crystallization has been **completely** driven off). The mass lost (or mass of residue) can then be used for stoichiometric calculations.

*Why must the crucible (or boiling tube) be **dry**?*
Any water present will contribute to the mass lost determined, leading to inaccurate calculations.

*Why do we need to allow the crucible and contents to **cool** after every heating?*
This is to prevent fluctuations of the mass readings on the electronic balance. Hot objects generate convection currents in the air that causes the readings to fluctuate.

Heating Techniques

- **Safety**: Eye protection must be worn for all heating experiments.



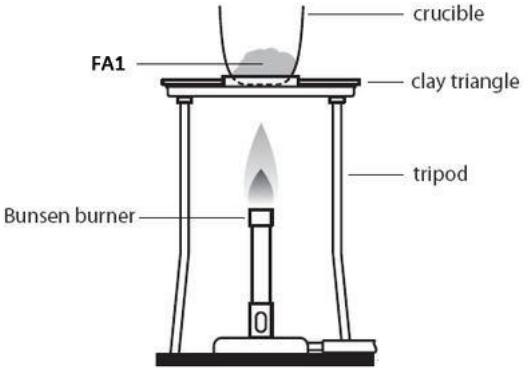
How to arrange the crucible on clay triangle on tripod stand



Where to place the Bunsen burner to heat strongly using hottest part of the flame

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- A common experimental set-up for heating:



- A boiling tube may also be used for heating solids.
- Use a **dry** crucible (or boiling tube) for heating.
- Heat **gently at first** to prevent 'spitting' of solid.
- Gradually increase the heat to maximum and then heat strongly.
- Do not overheat as the residue of some solid may decompose or vessel may crack.
- Heat the solid **evenly** and **thoroughly** (e.g. spread out the solid in the crucible instead of a heap, gently agitate the solid by tapping the boiling tube on the wire gauze).
- Place the vessel on the heat-proof mat to cool **before** weighing.

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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 Brønsted-Lowry theory of acids and bases, including the concept of conjugate acids and conjugate bases (Refer to Topic 14 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 (2015), *Chemistry*, Hodder Education, Chapters 1 & 7
2. Martin S. Silberberg (2009), *Chemistry: The Molecular Nature of Matter and Change*, 5th Edition, McGraw Hill, Chapters 3 & 4

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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

LO 6(a): define the terms relative atomic, isotopic, molecular and formula mass

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.

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Exercise 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]

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.

Exercise 1.2 (Worked example)

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

M_r of $Ca_5(PO_4)_3F$ = 5(40.1) + 3(31.0 + 4(16.0)) + 19.0 = 504.5

$\therefore$ Percentage by mass of P = $\frac{3(31.0)}{504.5} \times 100\%$ = 18.4%

M_r of $(NH_4)_2HPO_4$ = 2(14.0 + 4(1.0)) + 1.0 + 31.0 + 4(16.0) = 132.0

$\therefore$ Percentage by mass of P = $\frac{31.0}{132.0} \times 100\%$ = 23.5%

$\therefore$ $(NH_4)_2HPO_4$ contains higher percentage by mass of P.

Exercise 1.3 (Worked example)

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

M_r of chlorophyll = 55(12.0) + 72(1.0) + 24.3 + 4(14.0) + 5(16.0) = 892.3

Percentage by mass of Mg = $\frac{24.3}{892.3} \times 100\%$ = 2.72% (3 sf)

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.

Let M_r of haemoglobin be m,

$$\frac{0.34}{100} m = 4(55.8)$$

$$m = 6.56 \times 10^4 \text{ g mol}^{-1}$$

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1.3 Empirical and Molecular Formulae

LO 6(d): define the terms empirical and molecular formula

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

Exercise 1.4 (Worked example)

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.

	C	H	O
mass in 100 g / g	**62.1**	**10.3**	**27.6**
no. of moles	**62.1 / 12.0 = 5.175**	**10.3 / 1.0 = 10.3**	**27.6 / 16.0 =1.725**
mole ratio	**5.175 / 1.725 = 3**	**10.3 / 1.725 = 6**	**1.725 / 1.725 = 1**

∴ Empirical formula of caproic acid is C_3H_6O.

Let molecular formula of caproic acid be $(C_3H_6O)_n$.
$n(3(12.0) + 6(1.0) + 16.0) = 116$
∴ $n = 116 / 58 = 2$
∴ Molecular formula of caproic acid is $C_6H_{12}O_2$.

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.

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Thinking process: Since iron was the only iron-containing product formed, the mass of iron present in the oxide must have been 0.3450 g. The mass of oxygen present in the oxide can hence be found.

	Fe	O
mass / g	**0.3450**	**0.4764 – 0.3450 = 0.1314**
no. of moles	**0.3450 / 55.8 = 6.183×10^{-3}**	**0.1314 / 16.0 = 8.213×10^{-3}**
mole ratio	**6.183×10^{-3} / 6.183×10^{-3} = 1**	**8.213×10^{-3} / 6.183×10^{-3} = 1.33**
simplest ratio	**3**	**4**

∴ Empirical formula of the oxide is Fe_3O_4.

Exercise 1.5

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**.

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.

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1.3.3 Derivation of Formulae using Combustion Data

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

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.

Exercise 1.6 (Worked example)

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}.

(Thinking process: Since the reactants of this reaction are the hydrocarbon and oxygen only, the carbon present in CO_2 and the hydrogen present in H_2O must have come from the hydrocarbon. Hence, the mass of carbon present in the hydrocarbon is equal to the mass of carbon present in CO_2, while the mass of hydrogen atoms present in the hydrocarbon is equal to the mass of hydrogen atoms present in H_2O. This is an application of Law of Conservation of Matter – Refer to Section 2.1.)

Mass of C in 0.352 g of CO_2 = $\frac{12.0}{44.0} \times 0.352$ = 0.096 g

Mass of H in 0.072 g of H_2O = $\frac{2(1.0)}{18.0} \times 0.072$ = 0.008 g

	C	H
mass / g	0.096	0.008
no. of moles	0.096 / 12.0 = 0.008	0.008 / 1 = 0.008
mole ratio	1	1

Empirical formula of the hydrocarbon is $\underline{CH}$.

Let the molecular formula of the hydrocarbon be $(CH)_n$.

$n(12.0 + 1.0) = 104 \Rightarrow n = 104 / 13.0 = 8$

$\therefore$ Molecular formula of the hydrocarbon is $\underline{C_8H_8}$.

Exercise 1.7

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**?

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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 (Background info)

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.

Exercise 2.1

Write balanced chemical equations for the following reactions.

1. lead + silver nitrate → lead nitrate + silver **(Worked example)**

$\mathbf{Pb + 2AgNO_3 \rightarrow Pb(NO_3)_2 + 2Ag}$

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.

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Exercise 2.2 (Worked example)

A mixture of $CuSO_4 \bullet 5H_2O$ and $MgSO_4 \bullet 7H_2O$ 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 $CuSO_4 \bullet 5H_2O$ in the mixture?

(Thinking process: The hydrated $CuSO_4 \bullet 5H_2O$ and $MgSO_4 \bullet 7H_2O$ are heated to give $CuSO_4$ and $MgSO_4$ respectively. 1 mol of each of the hydrated salt should give 1 mol of the corresponding anhydrous salt. By relating the no. of moles of each anhydrous salt left to their total mass, the initial mass of $CuSO_4 \bullet 5H_2O$ can be found.)

Let mass of $CuSO_4 \bullet 5H_2O$ present in the mixture be x g.

$\therefore$ Mass of $MgSO_4 \bullet 7H_2O$ = (5.00 – x) g

$$\eta_{CuSO_4.5H_2O} = \frac{x}{249.6} \text{ mol} \Rightarrow \eta_{CuSO_4} = \frac{x}{249.6} \text{ mol}$$

$$\eta_{MgSO_4.7H_2O} = \frac{5.00-x}{246.4} \text{ mol} \Rightarrow \eta_{MgSO_4} = \frac{5.00-x}{246.4} \text{ mol}$$

$$\text{Mass of } CuSO_4 \text{ left} = \left(\frac{x}{249.6} \times 159.6\right) \text{ g}$$

$$\text{Mass of } MgSO_4 \text{ left} = \left(\frac{5.00-x}{246.4} \times 120.4\right) \text{ g}$$

$$\left(\frac{x}{249.6} \times 159.6\right) + \left(\frac{5.00-x}{246.4} \times 120.4\right) = 3.00$$

$\therefore$ x = 3.69

$\therefore$ Percentage by mass of $CuSO_4.5H_2O$ in the mixture = $\frac{3.693}{5.00} \times 100\%$ = **73.8 %**

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LAW OF CONSERVATION OF MASS (Background info)

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.

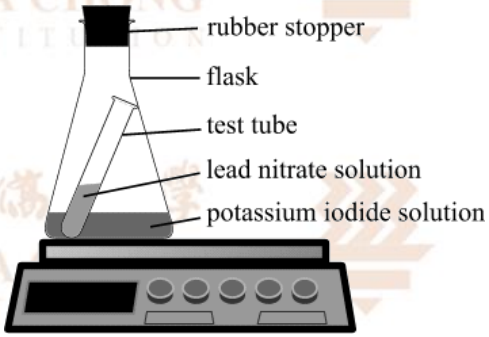


Figure 1. Experiment set-up to illustrate the Law of Conservation of Mass

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 (Background info)

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,

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g)$$

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.

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

2.3 Types of Reactions (Background info)

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 the following sections, we will see calculations involving the use of:

(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 exercises given.

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2.4 Calculation using Reacting Masses and Moles

LO 6(g)part: perform calculations, including use of the mole concept, involving: (iv) reacting masses (from formulae and equations)

Exercise 2.3 (Worked example)

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.

$Al_2S_3(s) + 6H_2O(l) \rightarrow 2Al(OH)_3(s) + 3H_2S(g)$

$\eta_{Al_2S_3} = \dfrac{158}{2(27.0)+3(32.1)} = 1.051$ mol

$\eta_{H_2O} = \dfrac{131}{18.0} = 7.278$ mol

No. of moles of H_2O required to react with 1.051 mol of $Al_2S_3 = 1.051 \times 6 = 6.306$ mol

$\therefore Al_2S_3$ is the limiting reagent.

η_{H_2S} formed $= 1.051 \times 3 = 3.153$ mol

$\therefore$ Maximum mass of H_2S that can form $= 3.153 \times (2(1.0) + 32.1) =$ <u>108 g (3.s.f)</u>

No. of moles of excess $H_2O = 7.278 - 6.306 =$ <u>0.972 mol</u>

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}.

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

Amount of H_2O formed $= 9.50 \times 1.00 / 18.0 = 0.5278$ mol

Actual amount of tungsten obtained $= 0.5278 / 3 = 0.1759$ mol

Actual mass of tungsten obtained $= 0.1759 \times 184 = 32.37$ g = <u>32.4 g (3 sf)</u>

$\eta_{WO_3} = \dfrac{41.5}{184+3(16.0)} = 0.1789$ mol = Theoretical amount of tungsten formed

Theoretical mass of tungsten formed

$= 0.1789 \times 184 = 32.92$ g

Percentage yield

$= 32.37/32.92 \times 100\% =$ <u>98.3%</u>

OR

Percentage yield $= \dfrac{0.1759}{0.1789} \times 100\% =$ <u>98.3 %</u>

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Exercise 2.4

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)?

2.5 Calculation using Volumes of Gases

LO 6(g)part: perform calculations, including use of the mole concept, involving: (v) volumes of gases (e.g. in the burning of hydrocarbons)

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 **20 cm^3** of carbon monoxide will react with **10 cm^3** of oxygen to give **20 cm^3** of carbon dioxide.

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

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

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Exercise 2.5 (Worked example)

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?

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$C_2H_6 + 7/2O_2 \rightarrow 2CO_2 + 3H_2O$

Volume of CO_2 produced from complete combustion of 10 cm^3 of methane = 10 cm^3

Volume of CO_2 produced from complete combustion of 10 cm^3 of ethane

$= 10 \times 2 = 20$ cm^3

$\therefore$ Total volume of CO_2 absorbed by the alkali = 10 + 20 = <u>30 cm^3</u>

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**.

	$C_xH_y(g)$	+ $\left(x+\frac{y}{4}\right)O_2(g)$	$\rightarrow$ $xCO_2(g)$	+ $\frac{y}{2}H_2O(g)$
initial vol. / cm^3	100	500	–	–
final vol. / cm^3	0	50	300	300
	100 reacted	450 reacted	300 produced	300 produced
mole ratio	1	4.5	3	3

$\therefore x = 3/1 = 3$

$\therefore y/2 = 3/1 = 3 \Rightarrow y = 6$

Balanced equation: <u>$C_3H_6 + 9/2O_2 \rightarrow 3CO_2 + 3H_2O$</u>

Molecular formula of W is <u>C_3H_6</u>.

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.)

Let a be the initial volume of oxygen, and a' be the final volume of oxygen remaining in cm^3

	$C_xH_y(g)$	+ $\left(x+\frac{y}{4}\right)O_2(g)$	$\rightarrow$ $xCO_2(g)$	+ $\frac{y}{2}H_2O(l)$
initial vol. / cm^3	10	a	–	–
final vol. / cm^3	0	a'	30	–
	10 reacted	a–a' reacted	30 produced	–

Mole ratio of $C_xH_y : CO_2 = 1 : x = 10 : 30 \Rightarrow x = 30/10 = 3$

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Total initial volume – total final volume = 20 cm^3

(10 + a) – (a' + 30) = 20

a – a' = 40

Based on vol ratio, volume O_2 reacted = $10\left(3+\frac{y}{4}\right)$ = a – a' = 40

∴ y = 4

∴ Molecular formula of the hydrocarbon is C_3H_4.

Exercise 2.6

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. 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?

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.)

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?

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2.6 Calculations using Concentrations

LO 6(g)part: perform calculations, including use of the mole concept, involving: (vi) volumes and concentrations of solutions

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.

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

No. of moles of solute, *n*
= concentration of solute (mol dm^{-3}) × volume (dm^3)
$$= \frac{\text{mass of X (g)}}{\text{molar mass of X (g mol}^{-1}\text{)}}$$

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***.

Exercise 2.7 (Worked example)

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?

$$\eta_{Na_2CO_3 \bullet 10H_2O} \text{ in 500 cm}^3 = \frac{14.3}{286.0} = 0.05 \text{ mol}$$

$$\therefore \eta_{Na^+} \text{ in 500 cm}^3 = 0.05 \times 2 = 0.10 \text{ mol}$$

$$\therefore [Na^+] = \frac{0.10}{500 \times 10^{-3}} = \underline{0.200 \text{ mol dm}^{-3}}$$

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Exercise 2.8

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.

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?

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?

Exercise 2.9 (Worked example)

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.

$\eta_{H_2SO_4}$ = 0.300 × 2.00 = 0.600 mol

∴ Volume of 18.0 mol dm^{-3} H_2SO_4 required = $\frac{0.600}{18.0}$ = 0.0333 dm^3 = <u>33.3 cm^3</u>

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

Total η_{HCl} in the mixture = $\left(\frac{385}{1000}\times 0.725\right)+\left(\frac{525}{1000}\times 0.325\right)$ = 0.4498 mol

Total volume of mixture = 385 + 525 = 910 cm^3

∴ [HC*l*] in the final mixture = $\frac{0.4497}{910\times 10^{-3}}$ = <u>0.494 mol dm^{-3}</u>

Exercise 2.10

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?

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.

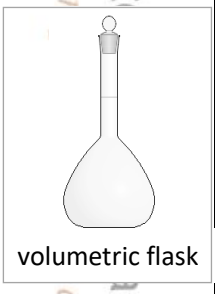
3. What is the volume of water that must be added to 150 cm^3 of 0.0262 mol dm^{-3} NaOH to obtain a 0.0100 mol dm^{-3} NaOH solution?

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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 transf
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	

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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.

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

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.

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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

LO4(a): show understanding of, and apply the Arrhenius theory of acids and 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 coordinate 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. $NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$

- 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.

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3.1.2 Bronsted-Lowry Theory of Acids & Bases

LO4(b): show understanding of, and apply the Brønsted-Lowry theory of acids and bases, including the concept of conjugate acids and conjugate 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.

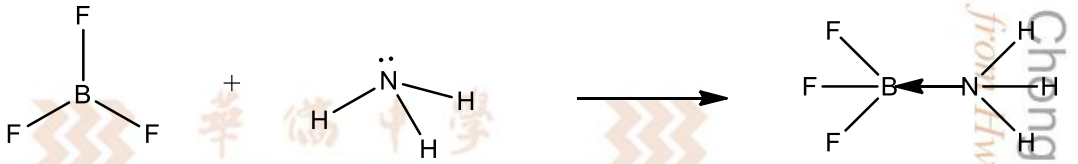
3.1.3 Lewis Theory of Acids & Bases

LO4(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)

- 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.

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Exercise 3.1

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

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

acid **base**

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

acid **base**

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

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

Note: H_2O is amphoteric (can act as an acid or base, depending on the other substance present)

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 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 14 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.

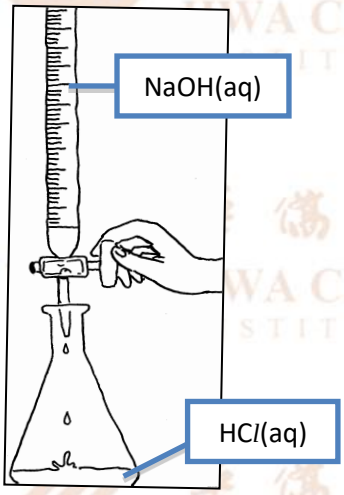
For an acid-base titration, the completion of the reaction is often found by noting the colour change of an indicator added to the reaction flask. The point where the indicator changes colour is known as the **end point**.

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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



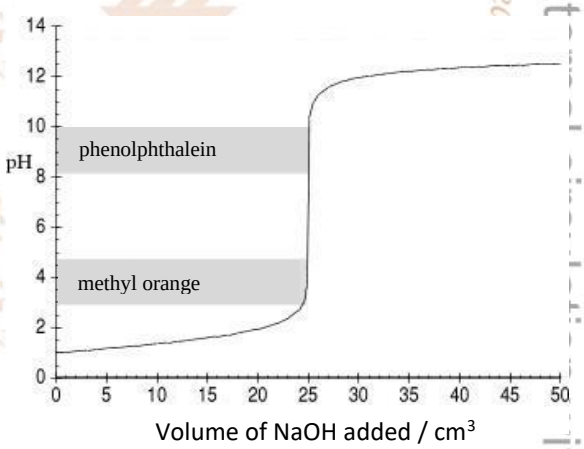


Figure 2. Titration curve of a strong acid-strong base titration. (Titration curves will be covered in Topic 14 Acid-Base Equilibria.)

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			

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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).

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Exercise 3.2 (Worked example)

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?

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

$\eta_{H_2SO_4}$ used in titration = $\frac{50}{1000} \times 0.0782 = 0.00391$ mol *(note: the H_2SO_4 is the standard solution)*

η_{NaOH} reacted with $H_2SO_4 = 0.00391 \times 2 = 0.00782$ mol

$[NaOH] = \frac{0.00782}{18.40 \times 10^{-3}} = \underline{0.425 \text{ mol dm}^{-3}}$

$NaOH + HCl \rightarrow NaCl + H_2O$

η_{NaOH} reacted with HC*l* = $\frac{27.50}{1000} \times 0.425 = 0.01169$ mol

η_{HCl} in 100 cm^3 = 0.01169 mol

$\therefore [HCl] = \frac{0.01169}{100 \times 10^{-3}} = \underline{0.117 \text{ mol dm}^{-3}}$

Exercise 3.3 (Worked example)

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*.

$2HCl + Na_2CO_3 \rightarrow 2NaCl + CO_2 + H_2O$

$2HCl \equiv Na_2CO_3$

In 25.0 cm^3 of solution, amount of $Na_2CO_3 = \frac{1}{2} \times \frac{48.80}{1000} \times 0.100 = 0.00244$ mol

In 1.00 dm^3 of solution, amount of $Na_2CO_3 = 0.00244 \times \frac{1000}{25} = 0.0976$ mol

$Na_2CO_3.nH_2O \equiv Na_2CO_3 \equiv nH_2O$

$\frac{27.82}{106 + 18n} = 0.0976$ mol

$n \approx 10$

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3.3 Back Titration (Application Example)

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 **titration 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

amount of unreacted A found from titration results

Total η_A = η_A that reacted with **B** + η_A that reacted with **C**

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.

Exercise 3.4 (Worked example)

1. A sample of impure magnesium was analysed by allowing it to react with excess HC*l* solution. After 1.32 g of the impure metal was treated with 100 cm^3 of 0.750 mol dm^{-3} HC*l*, 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?

$Mg + 2HCl \rightarrow MgCl_2 + H_2$

$HCl + NaOH \rightarrow NaCl + H_2O$

η_{NaOH} used to react with remaining HC*l* = $\frac{50}{1000} \times 0.250 = 0.0125$ mol

η_{HCl} remaining after reaction with Mg = 0.0125 mol

Initial η_{HCl} used = $\frac{100}{1000} \times 0.750 = 0.0750$ mol

$\therefore \eta_{HCl}$ reacted with Mg = 0.0750 – 0.0125 = 0.0625 mol

$\therefore \eta_{Mg}$ present = 0.0625 ÷ 2 = 0.03125 mol

$\therefore$ Mass of Mg present = 0.03125 × 24.3 = 0.759 g

$\therefore$ Percentage by mass of Mg = $\frac{0.759}{1.32} \times 100\% = 57.5\ \%$

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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.

$MO + 2HCl \rightarrow MCl_2 + H_2O$

$HCl + NaOH \rightarrow NaCl + H_2O$

η_{NaOH} used to react with remaining HC*l* $= \frac{21.05}{1000} \times 0.1020 = 2.147 \times 10^{-3}$ mol

$\therefore \eta_{HCl}$ in 25.0 $cm^3 = 2.147 \times 10^{-3}$ mol

$\therefore \eta_{HCl}$ in 500 $cm^3 = 2.147 \times 10^{-3} \times \frac{500}{25.0} = 0.04294$ mol

$= \eta_{HCl}$ remaining after reaction with MO

Initial η_{HCl} used $= \frac{100}{1000} \times 1.0 = 0.100$ mol

$\therefore \eta_{HCl}$ reacted with MO = 0.100 – 0.04294 = 0.05706 mol

(i) Mass of MO that reacted with 1 mole of HC*l* $= \frac{1.60}{0.05706} =$ <u>28.0 g</u> (3.s.f)

(ii) M_r of MO $= \frac{28.0}{0.5} =$ <u>56.1</u> (3.s.f)

$\therefore A_r$ of M = 56.1 – 16.0 = <u>40.1</u> ($\Rightarrow$ M is calcium)

Exercise 3.5

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?

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4 REDOX REACTIONS

LO12(a): describe and explain redox processes in terms of electron transfer and/or of changes in oxidation number (oxidation state)

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)***.

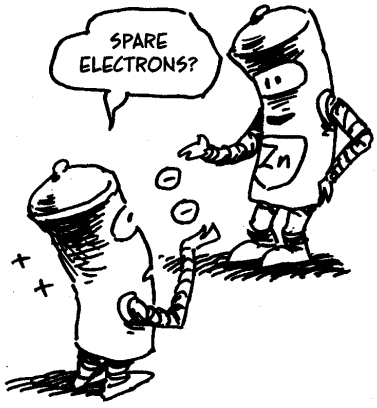
Reduction: A process whereby a substance **gains electrons**, resulting in a **decrease in oxidation number**.
e.g. $Cu^{2+} + 2e^- \rightarrow Cu$

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. $3Cl_2 + 6OH^- \rightarrow 5Cl^- + ClO_3^- + 3H_2O$



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Oxidation number (oxidation state): The total number of electrons that an atom either gains or loses in order to form a chemical bond with another atom.

An oxidation number is a number that is assigned to an atom in a substance. The oxidation number could be positive, negative, or zero, and it indicates if electrons are lost or gained. In other words, the oxidation number is a number that helps us keep track of electrons in an atom (so called its 'electron environment').

The calculation of oxidation state by first principle is based on one simple assumption – a perfect ionic model, i.e. what is the charge that an atom would have if the more electronegative element takes all the electrons.

Two examples are used below, H_2O and H_2O_2. The dot-and-cross diagrams of both compounds are drawn and a boundary (represented using dotted lines) is drawn to show what happens if the more electronegative element takes all the electrons. If the same element is bonded next to each other, then each element 'will take back their own'.



For the oxygen atom in H_2O, after drawing the boundary, a quick count reveals 8 electrons. Originally, oxygen has 6 electrons around it; the oxidation state of oxygen in H_2O is –2.

Similarly, for H_2O_2, a quick count reveals 7 electrons. Therefore, the oxidation state of oxygen in H_2O_2 is –1.

4.2 Assigning Oxidation Number

- When writing the oxidation number (O.N.), the +/– signs **must** 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'.
- Here are the most important rules and exceptions to remember when assigning oxidation numbers:

	example
1. For an atom in its elemental form, oxidation number = 0	O.N. of Na = 0, O.N. of O in O_2 = 0
2. 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
3. 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

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4. 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
5. For a compound, the more electronegative element is given the negative oxidation number.	In C*l*F, O.N. of F = −1; O.N. of C*l*= +1 In HC*l*, O.N. of H = +1; O.N. of C*l*= −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, A*l*	+3
fluorine, F	–1

For elements other than these reference elements, the oxidation number can be calculated using the equations in rules (3) or (4), as shown above for Mn in MnO_4^-, and Fe in Fe_2O_3. Note that when applying these equations, the oxidation number obtained is the **average oxidation number** because you are assuming that all the atoms of the element has the same electron environment (i.e. the atoms are bonded in the same way to the other atoms). This is not always be the case, as you will see in the example below.

Using first principle, calculate the oxidation state of each carbon atom individually in the compound, ethanol.

- CH_3CH_2OH

You find that because the two C atoms have are bonded to different atoms (i.e. have different 'electron environments'), they have different oxidation numbers: the oxidation no of the first C is –3, while that for the second C is –1. On the other hand, if you use rule (4), you obtain the oxidation no of –2, which is the average oxidation no.

In most applications, you will use the five rules to assign the (average) oxidation number. You seldom need to calculate the oxidation number individually from first principles, unless when dealing with how atoms in different electron environments will react specifically in a given reaction.

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Exercise 4.1 (Worked example)

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) HNO_2 (v) $Ca(H\underline{C}O_3)_2$

(i) C + 3 – 1 = 0 ⇒ C = –2
(ii) 8(S) = 0 ⇒ S = 0
(iii) Br – 3 = 0 ⇒ Br = +3
(iv) 1 + N + 2(–2) = 0 ⇒ N = +3
(v) 2 + 2(1 + C + 3(–2)) = 0 ⇒ C = +4

Exercise 4.2

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

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

5 0 +2 –3

Type of reaction: redox reaction

Oxidising agent: NO_3^- Reducing agent: Zn

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

Type of reaction: Precipitation

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

Type of reaction: acid-base reaction / neutralisation

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

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4.3 Balancing Redox Equations

LO12(h): construct redox equations using the relevant half-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.

When you are balancing an ionic equation, besides balancing the atoms, you also need to balance the charges as well.

Balancing redox equations using half equations (ion-electron method)

In the ion-electron method (also called the half-equation method), the redox equation is separated into two half-equations - one for oxidation and one for reduction. Each of these half-reactions is balanced separately and then combined to give the balanced redox equation.

1. Divide the unbalanced redox equation into two half-equations (*an oxidation half-equation and a reduction half-equation*). If the equation is written in the molecular form, re-write it as an ionic equation before splitting it into half-equations.
2. Balance each half-equation as follows:
   - Balance the element undergoing oxidation or reduction in the reactant and product.
   - Work out the oxidation number of the relevant elements.
   - 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.
3. Multiply each balanced half-equation by an appropriate integer, if necessary, to make electrons lost = electrons gained (i.e. **total number of electrons lost by reducing agent = total number of electrons gained by oxidising agent**).
4. Add the half-equations together (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.

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Exercise 4.3 (Worked example)

Balance the following redox reactions.

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

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

Oxidation: $\mathbf{Fe^{2+} \rightarrow Fe^{3+} + e^-}$

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

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

Reduction: $\mathbf{Cl_2 + 2e^- \rightarrow 2Cl^-}$

Oxidation: $\mathbf{Cl_2 + 12OH^- \rightarrow 2ClO_3^- + 6H_2O + 10e^-}$

Overall: $\mathbf{3Cl_2 + 6OH^- \rightarrow 5Cl^- + ClO_3^- + 3H_2O}$ **(basic)**

This is a disproportionation reaction where the same species (Cl_2 in this case) undergoes both oxidation and reduction.

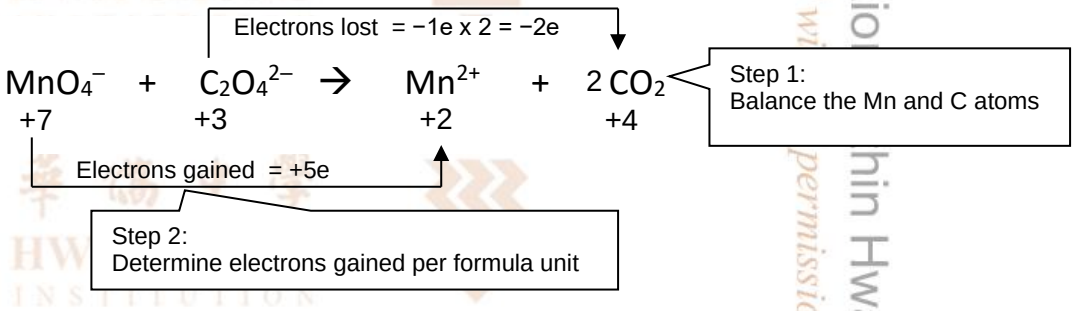
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Balancing redox equations without splitting into half equations

Where it is not required to work with half equations, you may balance a redox equation without splitting into half equations, using the same principles as in the ion-electron method.

1. Write the unbalanced redox equation with the two reactants and their corresponding products on the same line (with some spaces on top and below for working). Balance the element undergoing oxidation or reduction in the reactant and product.
2. Determine the number of electrons gained / lost by each element undergoing reduction / oxidation, **according to the change in oxidation number of the element**, and then determine the number of electrons gained / lost per formula unit of the two reactants, **taking into account the number of each element in the formula unit**.
3. Determine the correct mole ratio of the two reactants, such that electrons lost = electrons gained (i.e. **total number of electrons lost by reducing agent = total number of electrons gained by oxidising agent**).
4. Complete the balancing of charges and O (or H) as in the ion-electron method.
5. Make a final check that the redox equation is balanced in terms of atoms and charge.

These steps are illustrated below for the example below.



Step 3: Determine mole ratio such that electrons lost = electrons gained

$2\ MnO_4^- + 5\ C_2O_4^{2-} \rightarrow 2\ Mn^{2+} + 10\ CO_2$

Step 4: Balance charges and O / H atoms

$2\ MnO_4^- + 5\ C_2O_4^{2-} + 16\ H^+ \rightarrow 2\ Mn^{2+} + 10\ CO_2 + 8\ H_2O$

Step 5: Check atoms and charges are balanced

Exercise 4.4 (Worked example)

Review your answers here: (timestamp 3:43:03)

Balance the following redox reaction.

$H_2O_2 + I^- \rightarrow I_2 + H_2O$ (acidic) **$2H^+ + H_2O_2 + 2I^- \rightarrow I_2 + 2H_2O$**

$TcO_4^- + As \rightarrow Tc + AsO_2^-$ (basic) **$3TcO_4^- + 7As + 4OH^- \rightarrow 3Tc + 7AsO_2^- + 2H_2O$**

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4.4 Redox Titrations

LO13(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

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).

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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:

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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.

Exercise 4.5 (Worked example)

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?

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

Oxidation: $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$

Overall: $2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$

$\eta_{MnO_4^-}$ **used** $= \frac{27.50}{1000} \times 0.0200 = 5.50 \times 10^{-4}$ **mol**

$\eta_{H_2O_2}$ **present** $= 5.50 \times 10^{-4} \times 5/2 = 1.375 \times 10^{-3}$ **mol**

$\therefore [H_2O_2] = \frac{1.375 \times 10^{-3}}{25.0 \times 10^{-3}} =$ **0.0550 mol dm^{-3}**

η_{O_2} **evolved** $= 1.375 \times 10^{-3}$ **mol**

Volume of O_2 evolved $= 1.375 \times 10^{-3} \times 22.7 =$ **0.0312 dm^3**

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.

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

Oxidation: $Fe^{2+} \rightarrow Fe^{3+} + e^-$

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

$\eta_{Cr_2O_7^{2-}}$ **used** $= \frac{27.30}{1000} \times 1.64 \times 10^{-2} = 4.477 \times 10^{-4}$ **mol**

$\eta_{Fe^{2+}}$ **present** $= 4.477 \times 10^{-4} \times 6 = 2.686 \times 10^{-3}$ **mol** $= \eta_{Fe}$ **present in the wire**

Mass of Fe in the wire $= 2.686 \times 10^{-3} \times 55.8 = 0.1499$ **g**

Percentage purity of the iron wire $= \frac{0.1499}{0.1576} \times 100\% =$ **95.1%**

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Exercise 4.6 (Worked example)

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.

$\mathbf{T \equiv 4I_2}$

Amount of $\mathbf{I_2}$ liberated = $4 \times \frac{1.00}{375.4}$ = 0.01066 mol ≈ 0.0107 mol (3sf)

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

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

$2\ S_2O_3^{2-} \equiv I_2$

Amount of $S_2O_3^{2-}$ required = 2 × 0.01066 = 0.02132 mol

Volume of solution required = 0.02132 ÷ 1.00 = 0.2132 dm^3 = 21.3 cm^3 (3 sf)

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4.5 Application of Oxidation Number and Electron Transfer (Application Example)

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**.

Exercise 4.7 (Worked example)

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?

$\eta_{SO_3^{2-}}$ **reacted** $= \frac{25.00}{1000} \times 0.1 = 0.0025$ **mol**

η_{e^-} **lost by** $SO_3^{2-} = 0.0025 \times 2 = 0.0050$ **mol =** η_{e^-} **gained by** M^{3+}

$\eta_{M^{3+}}$ **reacted** $= \frac{50.0}{1000} \times 0.10 = 0.0050$ **mol**

$\therefore \eta_{M^{3+}} : \eta_{e^-}$ **gained** $= 0.0050 : 0.0050 = 1 : 1$

Each mole of M^{3+} **gains 1 mole of electrons.**

$\therefore$ **New oxidation number of the metal =** $+3 - 1 = +2$

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.

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

$\eta_{MnO_4^-}$ reacted = $\frac{20.0}{1000} \times 0.0100 = 0.0002$ mol

η_{e^-} gained by MnO_4^- = $0.0002 \times 5 = 0.0010$ mol = η_{e^-} lost by $C_2O_4^{2-}$

$\eta_{C_2O_4^{2-}}$ reacted = $\frac{25.0}{1000} \times 0.0200 = 0.0005$ mol

$\eta_{C_2O_4^{2-}} : \eta_{e^-}$ lost = 0.0005 : 0.0010 = 1 : 2

Each mole of $C_2O_4^{2-}$ loses 2 moles of electrons.

There are 2 C atoms in each $C_2O_4^{2-}$

∴ Each C loses 1 electron.

The oxidation state of C in $C_2O_4^{2-}$ is +3.

Exercise 4.8

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-}, $S_4O_6^{2-}$

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.

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05 Chemical Energetics: Thermochemistry & Thermodynamics

GUIDING QUESTIONS

- What are the energy changes in a chemical or physical process?
- Why do some chemical or physical processes take place spontaneously? How can we predict if a process is spontaneous?
- How can we measure or find out the energy change in a chemical or physical process?

LEARNING OUTCOMES

Students should be able to:

7(a) explain that most chemical reactions are accompanied by energy changes, principally in the form of heat usually associated with the breaking and forming of chemical bonds; the reaction can be exothermic (ΔH negative) or endothermic (ΔH positive)

7(b) construct and interpret an energy profile diagram, in terms of the enthalpy change of the reaction and of the activation energy (Refer to Topic 6 Reaction Kinetics)

7(c) explain and use the terms:

- **(i)** enthalpy change of reaction and standard conditions, with particular reference to: formation; combustion; hydration; solution; neutralisation; atomisation
- **(ii)** bond energy (ΔH positive, i.e. bond breaking) (Refer to Topic 2 Chemical Bonding)
- **(iii)** lattice energy (ΔH negative, i.e. gaseous ions to solid lattice)

7(d) calculate enthalpy changes from appropriate experimental results, including the use of the relationship: heat change = $mc\Delta T$

7(e) explain, in qualitative terms, the effect of ionic charge and of ionic radius on the numerical magnitude of a lattice energy (Refer to Topic 2 Chemical Bonding)

7(f) apply Hess' Law to construct simple energy cycles, e.g. Born-Haber cycle, and carry out calculations involving such cycles and relevant energy terms (including ionisation energy and electron affinity), with particular reference to:

- **(i)** determining enthalpy changes that cannot be found by direct experiment, e.g. an enthalpy change of formation from enthalpy change of combustion
- **(ii)** the formation of a simple ionic solid and of its aqueous solution
- **(iii)** average bond energies

7(g) explain and use the term *entropy*

7(h) discuss the effects on the entropy of a chemical system by the following:

- **(i)** change in temperature
- **(ii)** change in phase
- **(iii)** change in the number of particles (especially for gaseous systems)
- **(iv)** mixing of particles

[quantitative treatment is **not** required]

7(i) predict whether the entropy change for a given process or reaction is positive or negative

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7(j) state and use the equation involving *standard Gibbs free energy change of reaction*, ΔG :

$\Delta G = \Delta H - T\Delta S$

[the calculation of standard entropy change, ΔS , for a reaction using standard entropies, *S*, is **not** required]

7(k) state whether a reaction or process will be spontaneous by using the sign of ΔG

7(l) understand the limitations in the use of ΔG to predict the spontaneity of a reaction

7(m) predict the effect of temperature change on the spontaneity of a reaction, given standard enthalpy and entropy changes

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1. Peter Cann & Peter Hughes, *Cambridge international AS & A level Chemistry*, Hodder Education, Chapter 5 & 20
2. Martin S. Silberberg, *Chemistry: The Molecular Nature of Matter and Change*, 6th Edition, McGraw-Hill Higher Education, Chapter 6 & 20

LOOKING BACK

In the topic of Chemical Bonding, we saw how atoms are chemically bonded to each other. Energy changes take place when atoms combine to form different compounds. By measuring these energy changes, we can learn about the strength of the bonding that hold atoms together. For example, we saw that lattice energy is a measure of the strength of ionic bonding. Also, the concept of energy changes is fundamental to our understanding of the chemical reactions or physical processes that we observe in our everyday life. For example, the energy changes that took place during the dissolution of a solute help to explain its solubility. In this topic, we will look at other energy changes to understand why other chemical reactions or physical processes take place. We will also look at another factor, known as entropy change, which affects the spontaneity of a chemical reaction or physical process.

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1 INTRODUCTION

1.1 Enthalpy and enthalpy changes

LO 7(a): explain that most chemical reactions are accompanied by energy changes, principally in the form of heat usually associated with the breaking and forming of chemical bonds; the reaction can be exothermic (ΔH negative) or endothermic (ΔH positive).

The total chemical energy of a substance is called its **enthalpy** (or **heat content**). Chemical energy consists of kinetic energy and potential energy. The potential energy, due to electrostatic attraction between the particles, is usually the main component of the total chemical energy.

During a chemical reaction, bonds are broken and new bonds are formed. The breaking of bonds requires energy while the formation of bonds releases energy. The energy change that occurs is called the **enthalpy change**. The symbol is ΔH and the units are J mol^{-1} or kJ mol^{-1}.

1.2 Endothermic and exothermic processes

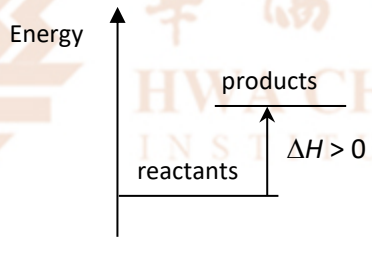
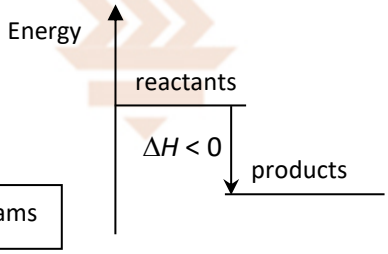
ΔH is positive, $\Delta H > 0$	**ΔH is negative, $\Delta H < 0$**
 Energy level diagrams	
The products have *higher* energy content than the reactants.	The products have *lower* energy content than the reactants.
The reaction **absorbs** heat from the surroundings. The temperature of the surroundings **decreases**.	The reaction **releases** heat to the surroundings. The temperature of the surroundings **increases**.
The reaction is said to be **endothermic**.	The reaction is said to be **exothermic**.

Table 1. Endothermic and Exothermic reactions

If the energy level of the products is lower than that of the reactants, we say the products are **energetically more stable** than the reactants.

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1.3 Energy profile diagram

LO 7(b): construct and interpret an energy profile diagram, in terms of the enthalpy change of the reaction and of the activation energy (see also Topic 6 Reaction Kinetics)

The **activation energy** of a reaction (E_a) is the **minimum energy** which the reacting particles must possess in order to overcome the energy barrier before becoming products.

The enthalpy change and activation energy of a reaction can be represented in an energy profile diagram (reaction pathway diagram) as shown in Table 2 below. An energy profile diagram is different from the energy level diagrams in Table 1.

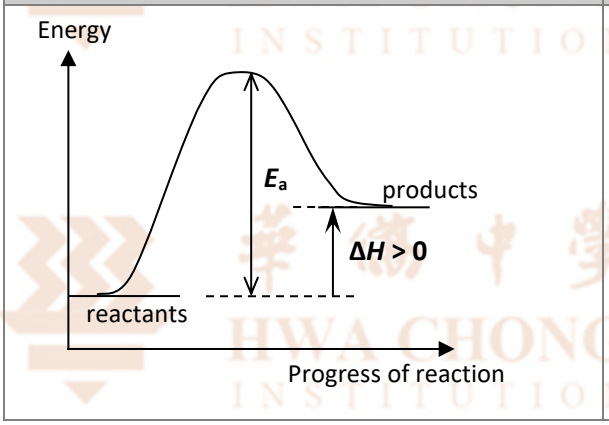
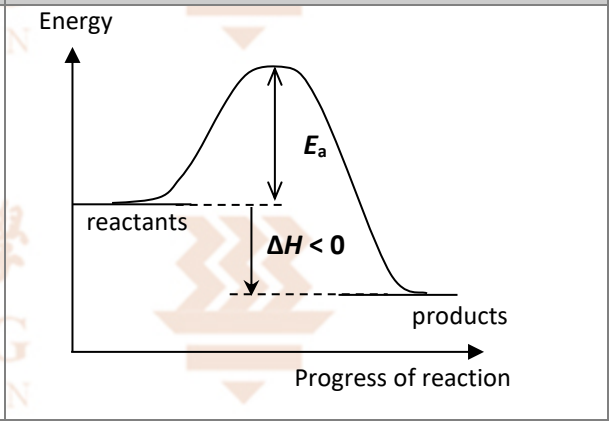
Endothermic Reaction, $\Delta H > 0$	**Exothermic Reaction, $\Delta H < 0$**
	

Table 2. Energy profile diagrams for 1-step endothermic and exothermic reactions

1.4 Thermochemical equation

A thermochemical equation is a balanced equation that includes the enthalpy change of the reaction.

E.g. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H_r = -285.9$ kJ mol^{-1}

This equation indicates that 285.9 kJ of heat is released when 1 mole of H_2 gas reacts with 0.5 mole of O_2 gas to give 1 mole of liquid H_2O.

The term 'mol^{-1}' in the ΔH_r units does not refer to 1 mole of H_2 or 1 mole of H_2O. Instead, it refers to the whole reaction as written, in this case, when 1 mole of H_2 gas reacts with 0.5 mole of O_2 gas.

It is important to include **state symbols** to all formulae given in a thermochemical equation since a change in state might be accompanied by an appreciable change in energy.

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Exercise 1.1 (Worked Example)

(a) Write down the enthalpy change of reaction for the following reactions, given that:

$H_2(g) + ½O_2(g) \rightarrow H_2O(l)$ $\Delta H_r = -285.9$ kJ mol^{-1}

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

Solution:

ΔH_r = **–(–285.9) = +285.9 kJ mol^{-1}**

Comments:

This equation is the reverse of the example given above. Since 285.9 kJ of heat is released when 1 mole of H_2 gas reacts with 0.5 mole of O_2 gas to give 1 mole of liquid H_2O, then 285.9 kJ of heat will be absorbed when 1 mole of liquid water forms 1 mole of H_2 gas and 0.5 mole of O_2 gas.

(ii) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

Solution:

ΔH_r = **2(–285.9) = –571.8 kJ mol^{-1}**

Comments:

The coefficients in this equation is twice that of the example given above. Since two the no. of moles of H_2 gas and O_2 gas are reacting, twice the amount of heat should be evolved.

(b) $H_2(g) + ½O_2(g) \rightarrow H_2O(g)$ $\Delta H_r = -241.8$ kJ mol^{-1}

Explain why the enthalpy change of the above reaction is less exothermic than –285.9 kJ mol^{-1}.

ΔH_r is less exothermic as heat is absorbed to convert liquid water to water vapour.
The difference of +44.1 kJ mol^{-1} represents the enthalpy change of vaporization of water.

Comments:

Compare the two equations. The difference between the two reactions is the state that water is in at the end of the reaction. As such, the reason for the difference in the enthalpy change of the reaction should be due to the difference in the state of water.

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1.5 Standard conditions and standard states

LO 7(c)(i)part: explain and use the term: standard conditions.

A set of **standard conditions** has been defined for thermochemistry:

Temperature	298 K (25 °C)
Pressure	1 bar (1 bar = 10^5 Pa)
Concentration of any solution	1.0 mol dm^{-3}

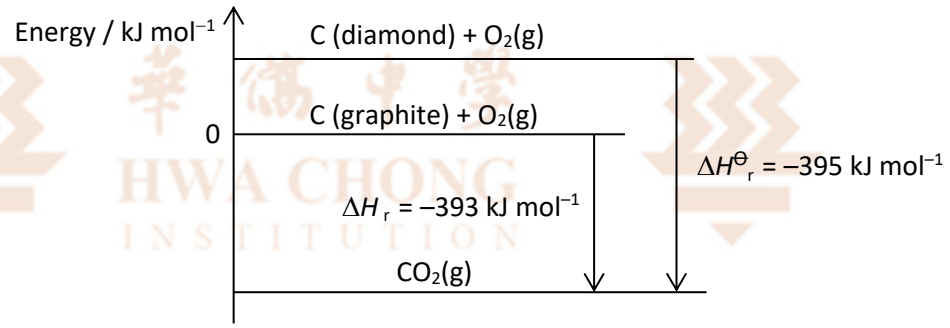
Table 3. Standard conditions for thermochemical measurements

- A substance in its normal (most stable) physical state at 298 K and 1 bar is said to be in its **standard state**. E.g. $I_2(s)$, $Br_2(l)$, C(s) (Refer to note below).
- The actual enthalpy of an element cannot be measured. Elements in their standard states under standard conditions are assigned **zero enthalpy (*H* = 0)**.
- When the enthalpy change is determined under standard conditions, it is referred to as the **standard enthalpy change** and is represented by the symbol $\Delta H^{\ominus}$.

Note:
C(s) refers to the graphite allotrope; graphite has a lower energy level and is energetically more stable than diamond.

$C(graphite) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H^{\ominus}_r = -393$ kJ mol^{-1}

$C(diamond) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H^{\ominus}_r = -395$ kJ mol^{-1}



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2 ENTHALPY CHANGES OF REACTION, FORMATION, COMBUSTION & NEUTRALISATION

LO 7(c)(i)part: explain and use the terms, enthalpy change of reaction, with particular reference to: formation; combustion.

2.1 Standard enthalpy change of reaction

The enthalpy change when **molar** quantities of reactants as specified by the chemical equation react to form products at **1 bar and 298 K (standard conditions)**.

E.g. $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$ $\Delta H^{\ominus}_r = -176$ kJ mol^{-1}

$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$ $\Delta H^{\ominus}_r = -146$ kJ mol^{-1}

2.2 Standard enthalpy change of formation

The enthalpy change when **1 mole of a substance** is formed from its **constituent elements in their standard states** at 298 K and 1 bar.

E.g. $\frac{1}{2}H_2(g) + \frac{1}{2}I_2(s) \rightarrow HI(g)$ $\Delta H^{\ominus}_f = +26.5$ kJ mol^{-1}

$2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH(l)$ $\Delta H^{\ominus}_f = -298$ kJ mol^{-1}

- From the definition, the enthalpy change of formation of **elements** in their standard state (at 298 K and 1 bar) is **0 kJ mol^{-1}**.

- $\Delta H^{\ominus}_f$ is a measure of the energetic stability of a substance relative to its constituent elements.

  If $\Delta H^{\ominus}_f$ is positive ⇒ compound is energetically <u>less stable</u> than its constituent elements
  ⇒ greater likelihood for compound to decompose into its constituent elements

  If $\Delta H^{\ominus}_f$ is negative ⇒ compound is energetically <u>more stable</u> than its constituent elements
  ⇒ less likelihood for compound to decompose into its constituent elements

- Enthalpy changes of formation are often theoretical. Some reactions may not take place in practice. E.g. C_2H_5OH cannot be formed by just mixing C, H_2 and O_2. In such cases, $\Delta H^{\ominus}_f$ can be calculated indirectly using Hess' Law (Refer to Section 4).

Exercise 2.1
Write an equation to represent the standard enthalpy change of formation of $CaSO_4(s)$.

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2.3 Standard enthalpy change of combustion

The **heat evolved** when **1 mole** of a substance is **completely burnt in excess oxygen** at 298 K and 1 bar.

E.g. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H^{\ominus}_c = -866$ kJ mol^{-1}

$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$ $\Delta H^{\ominus}_c = -601$ kJ mol^{-1}

- The enthalpy change of combustion is **<u>always exothermic</u>** i.e. heat is always evolved in combustion.

Exercise 2.2
What is the name of the enthalpy change represented by the equation: $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$?

2.4 Standard enthalpy change of neutralisation

LO 7(c)(i)part: explain and use the term, enthalpy change of neutralisation

The **heat evolved** when **1 mole of water** is formed in the neutralisation reaction between an acid and a base, at 298 K and 1 bar.

- Neutralisation is an **<u>exothermic</u>** reaction since it involves the attraction of H^+ and OH^- ions to form an O–H bond.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \qquad \Delta H^{\ominus}_{neut} = -57.0 \text{ kJ mol}^{-1}$$

- The enthalpy change of neutralisation of a **strong acid** with a **strong base** is almost the **<u>same</u>** for all strong acids and bases (–57.0 kJ mol^{-1}).

<u>Reason</u>:
Strong acids and strong bases **ionise completely** in dilute aqueous solution. Reaction between them is effectively the reaction between aqueous H^+ ions and OH^- ions.

E.g. $KOH(aq) + HNO_3(aq) \rightarrow KNO_3(aq) + H_2O(l)$ $\Delta H^{\ominus}_{neut} = -57.0$ kJ mol^{-1}

$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$ $\Delta H^{\ominus}_{neut} = -57.0$ kJ mol^{-1}

Effectively $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ $\Delta H^{\ominus} = -57.0$ kJ mol^{-1}

K^+, NO_3^-, Na^+ and Cl^- ions are essentially spectator ions in the above neutralisation reactions.

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- The enthalpy change of neutralisation involving a **weak acid** or **weak base** is slightly **<u>less exothermic</u>** than –57.0 kJ mol^{-1}.

  <u>Reason</u>:
  Weak acids (or weak bases) **do not ionise completely** in dilute aqueous solution. During neutralisation, energy is absorbed to ionise the un-ionised weak acid (or weak base). Thus, **less energy is released** and the resulting $\Delta H^{\ominus}_{neut}$ is **less exothermic**.

  E.g. $CH_3CO_2H(aq) \rightleftharpoons CH_3CO_2^-(aq) + H^+(aq)$ $\Delta H^{\ominus} = +1.8$ kJ mol^{-1}

  Then $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ $\Delta H^{\ominus} = -57.0$ kJ mol^{-1}

  Overall $NaOH(aq) + CH_3CO_2H(aq) \rightarrow CH_3CO_2^- Na^+(aq) + H_2O(l)$ $\Delta H^{\ominus}_{neut} = -55.2$ kJ mol^{-1}

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3 EXPERIMENTAL DETERMINATION OF ENTHALPY CHANGE

LO 7(d): calculate enthalpy changes from appropriate experimental results, including the use of the relationship: heat change = mc∆T

The reaction (part of the universe that is being studied) is defined as the **system**. The environment of the reaction (rest of the universe that is not part of the system) is known as the **surrounding**.

The enthalpy change at constant pressure appears as heat. The heat given out (or taken in) by a reaction is transferred to the surrounding. The surrounding is often some water or a solution containing the reactants and products.

For example, $CuSO_4(aq) + Zn(s) \rightarrow ZnSO_4(aq) + Cu(s)$ $\Delta H = -219$ kJ mol^{-1}

The system consists of the reactants and the products. The reaction between $CuSO_4$ and Zn takes place in an aqueous medium. Since the reaction is exothermic (sign of ΔH is negative), heat is released by the reaction and is transferred to the surrounding aqueous medium.

The heat that is absorbed by the aqueous medium or solution causes the temperature of the solution to rise. This amount of heat can be determined by measuring the temperature change.

$$\boxed{q = mc\Delta T}$$

q = heat change of solution (J)
m = mass of solution (g)
c = specific heat capacity of solution (J g^{-1} K^{-1})
ΔT = change in temperature of the solution (K or ^{o}C)

The **specific heat capacity**, **c**, is defined as the amount of heat required to raise the temperature of 1 g of the substance by 1 K (or 1 ^{o}C). The unit of specific heat capacity is **J g^{-1} K^{-1}**.

The **heat capacity, C,** is defined as the amount of heat required to raise the temperature of the substance by 1 K (or 1 ^{o}C). The SI unit for heat capacity is **J K^{-1}**.

If heat capacity of the solution is given instead, then the heat that is absorbed (or released) by the solution can be calculated as follows:

$$\boxed{q = C\Delta T}$$

C = heat capacity of solution (J K^{-1})

Hence by measuring the temperature change of the solution, we can determine the heat transferred to the surrounding solution and hence the heat absorbed or released by the reaction.

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The enthalpy change can be calculated as follows:

Endothermic reaction	$\Delta H = +\frac{q}{n}$	Sign of ΔH is positive. Heat is absorbed by the reaction. Temperature of the surrounding solution decreases.
Exothermic reaction	$\Delta H = -\frac{q}{n}$	Sign of ΔH is negative. Heat is released by the reaction. Temperature of the surrounding solution increases.

q = heat change (heat absorbed or released)

n = no. of moles of substance according to the definition of the enthalpy change (e.g. n_{H2O} for ΔH_{neut}, $n_{substance\ combusted}$ for ΔH_c)

Note: For a thermochemical equation whose limiting reactant's stoichiometric coefficient is not 1, q/n must be multiplied by the limiting reactant's stoichiometric coefficient to give *that* enthalpy change of reaction defined by the *thermochemical equation*. See Exercise 3.3 / 3.4.

3.1 The calorimeter

For reactions involving solutions, a simple **calorimeter** consisting of a polystyrene cup with a lid and a thermometer can be used to determine the heat change.

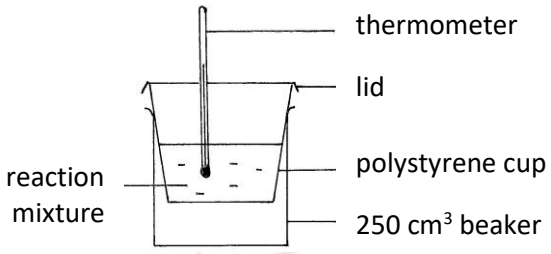


Figure 1. A simple calorimeter

Note:

- Polystyrene is an excellent insulator so heat loss from the sides is minimised. The lid also helps to minimise heat exchange with the surrounding air.
- The polystyrene cup is often supported in a 250 cm^3 beaker or using a retort stand, to prevent toppling under the weight of the thermometer. The insulation can be improved by nesting two cups.
- The temperature changes are often small, so for accurate work the thermometer should have a precision of ±0.1°C.

3.2 Assumptions in the calculations

To ensure accurate results, **all** the heat released (or absorbed) by the reaction must be used to raise (or lower) the temperature of the solution. In practice, we cannot totally eliminate heat exchanges with the surrounding air or apparatus so we make the following assumptions in our calculations.

- No heat loss to (or heat gain from) surrounding air
- Heat capacity of the calorimeter (e.g. polystyrene cup) is omitted

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In addition, it is more convenient to measure the volume of the solution. Hence to calculate the mass of the solution, we assume that the density of the solution is the same as that of water (1.00 g cm^{-3}) since the solution is very dilute.

3.3 Reaction between two aqueous solutions

Generic Procedure for reactions involving mixing of two solutions

1. **Measure** _(volume)_ cm^3 of __(solution X)__ into a polystyrene cup using a measuring cylinder / pipette / burette. Record the **initial temperature** of solution X with a **thermometer**.
2. **Measure** _(volume)_ cm^3 of __(solution Y)__ in another measuring cylinder. Record the **initial temperature** of solution Y with the thermometer.
3. **Add** solution Y quickly to solution X in the polystyrene cup and stir the mixture gently.
4. Record the **highest / lowest temperature** reached with the thermometer.

Note:

- The initial temperature to use for calculations is the weighted average (by volume) of the initial temperatures of the two solutions.

$$\text{Weighted average initial temperature} = \frac{T_{\text{solution X}} \times V_{\text{solution X}} + T_{\text{solution Y}} \times V_{\text{solution Y}}}{V_{\text{solution X}} + V_{\text{solution Y}}}$$

- The solution that kickstarts the reaction is added quickly to minimise heat loss. Hence, it should not be measured with a burette or pipette.

Exercise 3.1 (Worked Example)

40.0 cm^3 of 2.0 mol dm^{-3} HC*l*(aq) were added to 50.0 cm^3 of 2.0 mol dm^{-3} NaOH(aq) in a polystyrene cup. The following results were obtained.

Initial temperature of HC*l* (aq) / °C	22.3
Initial temperature of NaOH (aq) / °C	22.5
Highest temperature reached / °C	34.6

Calculate the enthalpy change of neutralisation.

HC*l*	+	NaOH	$\rightarrow$ NaC*l* + H_2O	ΔH_{neut} = ?
40 cm^3		50 cm^3		
2.0 mol dm^{-3}		2.0 mol dm^{-3}		
T_i = 22.3 °C		T_i = 22.5 °C		

Average initial temperature = $\frac{40\times22.3 + 50\times22.5}{40+50}$ = 22.4 °C

Comments:

This is called a weighted average, see Lecture Notes pg12 above.

Heat evolved = 90 × 4.18 × (34.6 – 22.4) = 4589 J

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Comments:
In calculating the heat evolved, two assumptions are made:

1. The density of the solution is the same as that of water (1.00 g cm^{-3}), so the mass of 90 cm^3 of solution is 90 g. Take note that this assumption is used very often in doing such calculations.
2. specific heat capacity of the solution is the same as that of water (4.18 J g^{-1} K^{-1} from Data Booklet).

Note that the value for ΔT in °C or K is the same, ΔT= 34.6 – 22.4 = 12.2 °C or 12.2 K

HC*l* is limiting (∵ same concentration of solutions, 1:1 mole ratio, but smaller volume of HC*l* used)

n(H_2O) formed = n(HC*l*) reacted = $\frac{40}{1000} \times 2.0$ = 0.08 mol

$\Delta H_{neut} = \frac{-4589}{0.08}$ = –57.4 kJ mol^{-1}

Comments:
ΔH_{neut} is the heat evolved when 1 mol of H_2O is formed in the neutralisation reaction between an acid and a base. In the experiment, 0.08 mol of H_2O is formed. Hence to calculate ΔH_{neut} here, we divide q by n(H_2O) formed. Since ΔH_{neut} is exothermic (temperature increased), the – sign must be indicated.

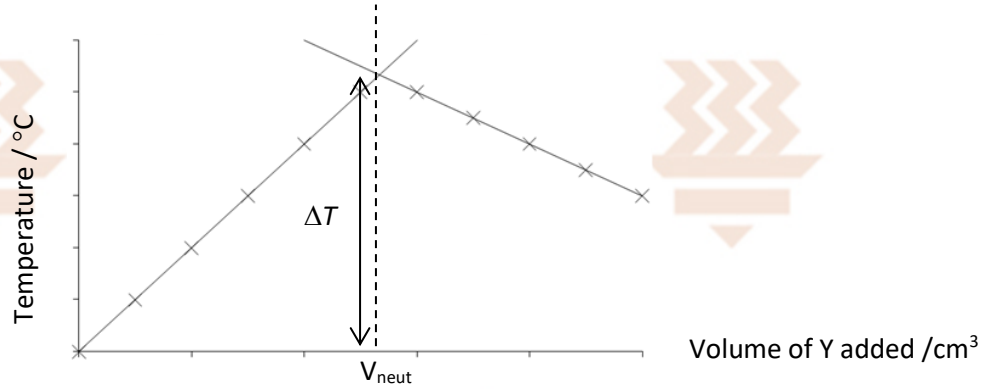
Exercise 3.2
25.0 cm^3 of 2.0 mol dm^{-3} H_2SO_4(aq) were added to 25.0 cm^3 of 2.0 mol dm^{-3} NaOH(aq) in a polystyrene cup. The initial temperatures of the solutions were 30.0 °C and 29.8 °C respectively. When the solutions were mixed, the highest temperature reached was 43.6 °C. Use the data to calculate a value for the enthalpy change of neutralisation. **[–57.3 kJ mol^{-1}]**

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Thermometric Titration

Suppose we need to determine a value for ΔH_{neut} using aqueous sodium hydroxide and hydrochloric acid but the concentration of hydrochloric acid is unknown. In this case, we are unable to determine the limiting reactant and the amount of water formed. Hence the generic procedure for reactions involving mixing of two solutions given earlier cannot be used.

Instead, we can use thermometric titration in which a series of temperatures is recorded after each (small and fixed) addition of the solution from the burette until equivalence point is reached and passed. Extrapolation on the **temperature–volume graph** allows us to determine **both** the maximum temperature and the volume at which complete neutralisation is achieved. These results can then be used to determine the unknown concentration as well as a value for ΔH_{neut}.



Generic Procedure for Thermometric Titration

1. **Pipette** (volume) cm^3 of (solution X) into a polystyrene cup.
2. **Record** the **temperature** of the solution with a **thermometer**.
3. From a burette, **add** (volume of each addition) cm^3 of (solution Y) quickly to the polystyrene cup.
4. **Stir** the mixture with the thermometer and **record** its **temperature**.
5. Repeat steps 3 and 4 until (total volume) cm^3 of (solution Y) has been added.

Note:

- No indicator is required.
- The total volume of solution added from the burette must be more than that required for complete reaction, such that there are sufficient data points to obtain a best–fit line for the downward slope of the graph.
- The actual experimental data may show gentle curves before and after the equivalence point. Before the equivalence point, each addition of solution Y releases the same amount of heat but it is spread over a larger volume of solution, thus resulting in a smaller temperature rise. After the equivalence point where the reaction is complete, further addition of solution Y that is of lower temperature cools the reaction mixture. As the temperature difference between solution Y and the reaction mixture decreases, the temperature drop becomes smaller.

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3.4 Reaction between a solid and aqueous solution

Generic Procedure for reactions involving adding a solid to a solution

1. **Weigh** accurately _(mass)_ g of __(solid X)__ in a weighing bottle using an electronic balance.
2. **Measure** _(volume)_ cm^3 of __(solution Y)__ into a polystyrene cup using a measuring cylinder / pipette / burette. Record the **initial temperature** of solution Y with a **thermometer**.
3. **Add** solid X quickly into the cup and stir the mixture gently.
4. Record the **highest / lowest temperature** reached with the thermometer.
5. **Re–weigh** the weighing bottle and the residual solid.

Note:

- The solid is added quickly to minimise heat loss.
- As the solid may not be transferred completely, the weighing bottle and the residual solid must be re–weighed to determine the exact mass of solid added.

Exercise 3.3

50.0 cm^3 of 0.10 mol dm^{-3} silver nitrate solution were placed in a polystyrene cup. A known mass of zinc powder was added and the following results were obtained.

mass of weighing bottle and Zn powder / g	4.31
mass of weighing bottle and remaining Zn / g	3.51
mass of Zn added / g	0.80

Initial temperature of solution / °C	21.1
Highest temperature reached / °C	26.3
ΔT / °C	5.2

Calculate the enthalpy change for the reaction $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$.

Heat evolved = $50 \times 4.18 \times 5.2 = 1086.8$ J

n(Zn) added = $\frac{0.80}{65.4} = 0.0122$ mol

n(Ag^+) present = $\frac{50}{1000} \times 0.10 = 0.005$ mol, Ag^+ is the limiting reactant

$Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$

$\Delta H_r = -\frac{1086.8}{0.005} \times 2 = -435$ kJ mol^{-1}

Comments:

In this reaction, the reaction between Zn and Ag^+ heats up the solution it is in. As such, the reaction between Zn and Ag^+ is treated as the 'system'. The water or solution is treated as the 'surrounding'. When calculating $mc\Delta T$, mass m refers to the 'surrounding' which in this question is the 50 cm^3 solution i.e. 50 g assuming its density is the same as that of water. The Zn is part of the 'system' and not considered in m.

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When calculating the ΔH_r, Note that the given equation shows that 2 mol of Ag^+ reacted with 1 mol of Zn. In doing the calculation, $-\frac{1086.8}{0.005}$ = –217 kJ mol^{-1}, this shows the amount of heat evolved when 1 mol of Ag^+ reacts. Hence –217 kJ mol^{-1} needs to be multiplied by 2 to give the ΔH_r with respect to the *given* equation.

ΔH_r may also be calculated based on the number of moles of Zn that reacted.

n(Zn) *reacted* = 0.005 × ½ = 0.0025 mol
$\Delta H_r = -\frac{1086.8}{0.0025}$ = –435 kJ mol^{-1}

Dividing 1086.8 J by 0.0025 mol Zn gives the ΔH_r based on 1 mol of Zn as is given in the equation.

This reaction is exothermic (temperature increased), the – sign must be indicated for ΔH_r

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3.5 Temperature correction

In many experiments, the temperature may not immediately reach a maximum (or minimum), especially when the reaction is slow and heat loss to (or gain from) the surroundings becomes significant. To account for heat loss to (or gain from) the surroundings, a series of temperatures can be recorded before and after the mixing to give a **temperature-time graph**. Extrapolation is done to the point of mixing to obtain a more accurate maximum (or minimum) temperature.



Generic Procedure to obtain Maximum/ Minimum Temperature by Extrapolation

1. **Weigh** accurately _(mass)_ g of __(solid X)__ in a weighing bottle using an electronic balance. / **Measure** _(volume)_ cm^3 of __(solution X)__ using a measuring cylinder.
2. **Measure** _(volume)_ cm^3 of __(solution Y)__ into a polystyrene cup using a measuring cylinder / pipette / burette.
3. **Record** the **temperature** of solution Y every 30 seconds for 2.5 minutes using a **thermometer**.
4. At exactly 3.0 minutes**, add** solid X / solution X quickly into the cup and stir the mixture gently.
5. Continue to **record** the **temperature** every 30 seconds from 3.5 minutes to 10.0 minutes.
6. **Re–weigh** the weighing bottle and the residual solid (if a solid is used).

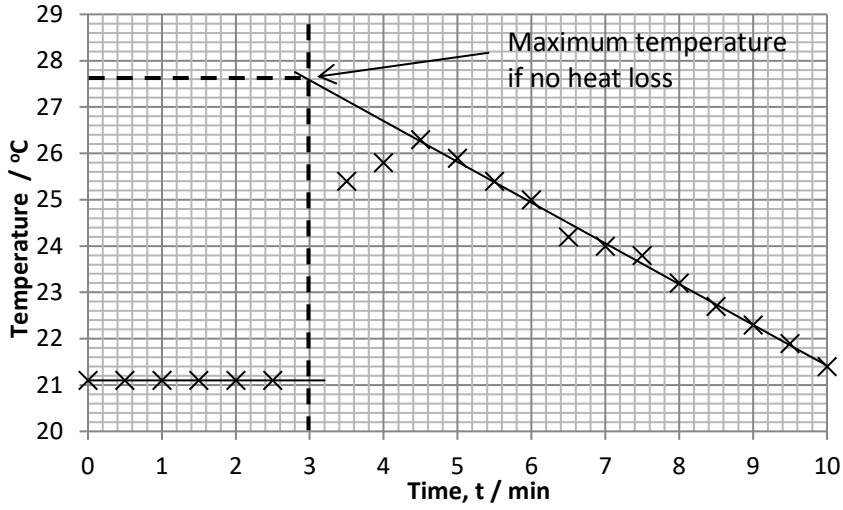
Exercise 3.4

The experiment in Exercise 3.3 was repeated using the above procedure (temperature was monitored for 10 minutes) and the following results were obtained.

Time, t / min	0	0.5	1.0	1.5	2.0	2.5	3.5	4.0	4.5	5.0
Temperature / °C	21.1	21.1	21.1	21.1	21.1	21.1	25.4	25.8	26.3	25.9
Time, t / min	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0
Temperature / °C	25.4	25.0	24.2	24.0	23.8	23.2	22.7	22.3	21.9	21.4

Use the data and graph to calculate the enthalpy change for the reaction

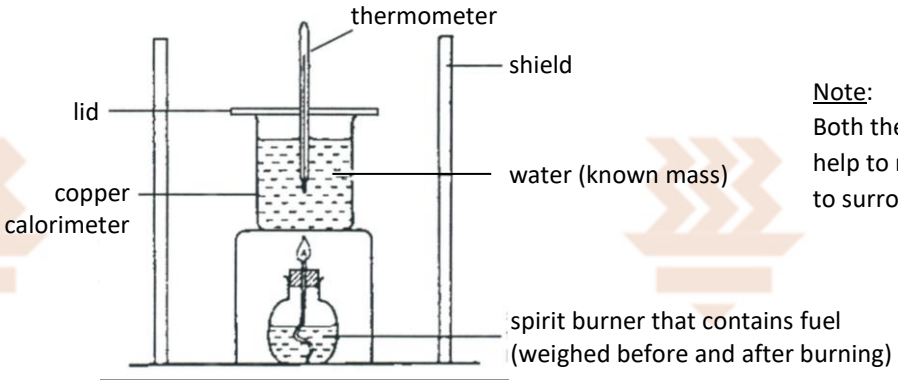
$$Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s).$$



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3.6 Experimental method to determine enthalpy change of combustion

The following experiment set-up can be used to determine the ΔH_c for a fuel such as ethanol. The heat released during combustion is used to heat a known mass of water in a copper calorimeter.



Note:
Both the shield and lid help to reduce heat loss to surroundings.

Figure 2. Experimental set-up to determine enthalpy change of combustion of a fuel



Generic Procedure for Combustion Reactions

1. **Weigh** the spirit burner containing the fuel using an electronic balance.
2. Using a measuring cylinder, place 100 cm^3 of water in a **copper calorimeter**. Record the **initial temperature** of the water with a **thermometer**.
3. Set up the apparatus as shown in the diagram.
4. **Ignite** the fuel and **heat** up the water. Stir gently with the thermometer.
5. When a temperature rise of about (temperature change) °C is reached, **extinguish** the flame and record the **maximum temperature** reached with the thermometer.
6. Allow the spirit burner to **cool** to room temperature. **Re–weigh** the spirit burner containing the remaining fuel.

Note:
Unlike the polystyrene cup, the heat absorbed by the copper calorimeter is usually included in the calculation of heat, q, because copper is a good conductor of heat. In some cases, the total heat capacity of the copper can and water may be given.

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Exercise 3.5

In an experiment to determine ΔH_c for ethanol, the following results were obtained. Calculate ΔH_c for ethanol. Compare the experimental value with the literature value of –1368 kJ mol^{-1} and account for any difference.

Mass of water in calorimeter / g	250.00
Mass of burner and ethanol before combustion / g	16.20
Mass of burner and ethanol after combustion / g	15.67
Temperature of water before combustion / °C	29.6
Temperature of water after combustion / °C	40.0

A bomb calorimeter is used to obtain highly accurate values of ΔH_c as heat loss is minimised.

Experimental Method using a Bomb Calorimeter

1. A **known mass** of the substance (whose ΔH_c is to be determined) is burnt in **excess oxygen** in a bomb calorimeter.
2. The heat released is transferred to a known mass of water in the calorimeter.
3. The rise in temperature of the water is then measured.
4. Allowance is made for the heat capacity of the bomb calorimeter and the heat evolved in burning the iron ignition wire used to ignite the substance. Thus ΔH_c can be measured accurately.

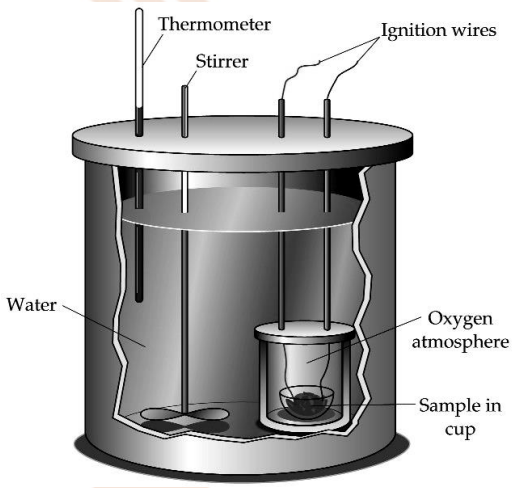


Figure 3. Bomb calorimeter

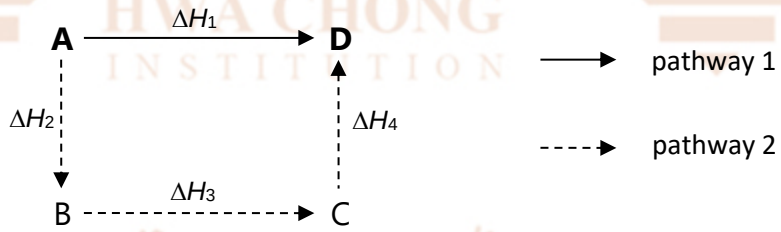
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4 HESS' LAW AND ITS APPLICATIONS

Some enthalpy changes of reaction can be determined directly by experiment (e.g. enthalpy change of combustion using a bomb calorimeter). For reactions that are diffcult to carry out directly, we can use Hess' Law to determine the enthalpy changes of these reactions from other enthalpy data.

4.1 Hess' law of constant heat summation

The enthalpy change (ΔH) of a reaction is determined only by the **initial and final states** and is **independent of the reaction pathway taken**.



By Hess' Law, enthalpy change for pathway 1 = enthalpy change for pathway 2

$$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$$

LO 7(f)(i)part: apply Hess' Law to construct simple energy cycles, and carry out calculations involving such cycles and relevant energy terms, with particular reference to: determining enthalpy changes that cannot be found by direct experiment, e.g. an enthalpy change of formation from enthalpy change of combustion

General steps to calculate ΔH of a reaction using Hess' Law:

1. Write the equation representing the enthalpy change that you are required to calculate.
2. Construct a fully labelled energy cycle incorporating the enthalpy changes provided, including state symbols.
3. Apply Hess' Law to calculate the required enthalpy change.

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4.2 Application: Calculations using standard enthalpy change of combustion

Worked Example 4.1

Given the following enthalpy changes of combustion, calculate the standard enthalpy change of formation of carbon monoxide.

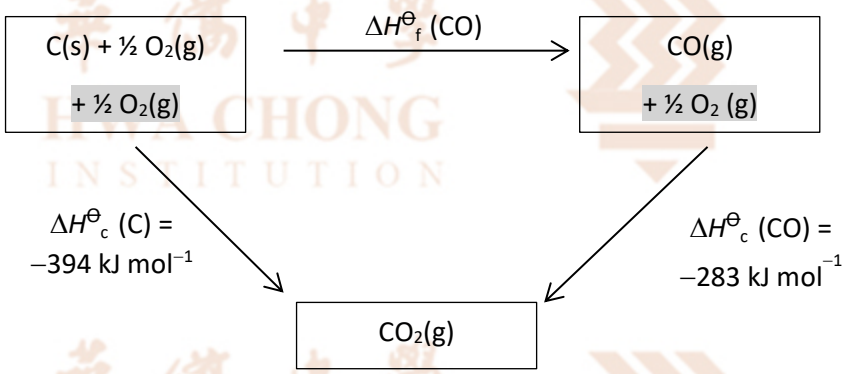
$\Delta H^{\ominus}_c$ (carbon) = –394 kJ mol^{-1}

$\Delta H^{\ominus}_c$ (carbon monoxide) = –283 kJ mol^{-1}

Method 1a: Constructing an Energy Cycle

① *Start with the equation that represents $\Delta H^{\ominus}_f$ (CO).*

② *Since $\Delta H^{\ominus}_c$ (C) and ΔH_c (CO) are given, we can draw a cycle where C(s) on the left-hand side of the equation undergoes complete combustion to form $CO_2(g)$. To do this we need to add ½ mol of $O_2(g)$. Hence ½ mol of O_2 must also be added on the right-hand side of the equation. This ½ mol of $O_2(g)$ reacts with CO(g) to form $CO_2(g)$.*



By Hess' law,

$\Delta H^{\ominus}_f$ (CO) = –394 – (–283)

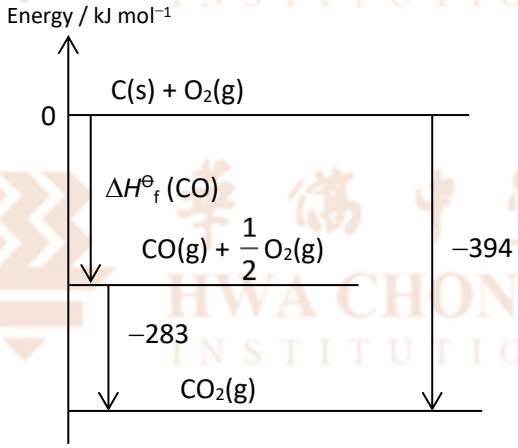
= –111 kJ mol^{-1}

Quick Check	☐ *Equations are balanced*
	☐ *State symbols are correct*
	☐ *Sign of ΔH is consistent with direction of arrow*

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Method 1b: Constructing an Energy Level Diagram

If ΔH is negative (exothermic reaction), we draw the arrow pointing down and vice versa.



By Hess' law,

$\Delta H^{\ominus}_f$ (CO) + (−283) = −394

$\Delta H^{\ominus}_f$ (CO) = −111 kJ mol^{-1}

Quick check	☐ *Equations are balanced and state symbols are correct*
	☐ *Axis is labelled*
	☐ *Zero energy level is labelled if applicable*
	☐ *Sign of ΔH is consistent with direction of arrow*

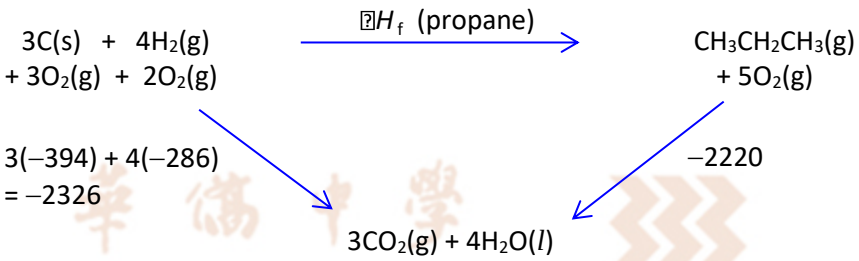
Method 2: Equation Method

C(s) + O_2(g)	→	CO_2(g)	$\Delta H = \Delta H^{\ominus}_c$ (C) = −394 kJ mol^{-1}
CO_2(g)	→	CO(g) + ½O_2 (g)	$\Delta H = -\Delta H^{\ominus}_c$ (CO) = +283 kJ mol^{-1}
C(s) + ½O_2(g)	→	CO(g)	$\therefore \Delta H^{\ominus}_f$ (CO) = −394 + 283 = −111 kJ mol^{-1}

Exercise 4.1 (Worked Example)

Calculate the standard enthalpy change of formation of propane using the combustion data provided.

Substance	$\Delta H^{\ominus}_c$ / kJ mol^{-1}
Graphite	−394
Hydrogen	−286
Propane	−2220



By Hess's Law, ΔH_f (propane) = −2326 −(−2220) = −106 kJ mol^{-1}

Comments:

In drawing an energy cycle, it might be useful to write out the chemical equations that represent the various enthalpy changes.

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Exercise 4.2

Calculate the standard enthalpy change of formation of ethanol using the combustion data provided. **[–279 kJ mol^{-1}]**

Substance	$\Delta H^{\ominus}_c$ / kJ mol^{-1}
Graphite	–394
Hydrogen	–286
Ethanol	–1367

2(–394) + 3(– –2 ∩c

General Formula: $\Delta H_r = \sum m \Delta H_c$ **(reactants)** $- \sum n \Delta H_c$ **(products)**

where m, n = stoichiometric coefficients of the reactants and products in the given reaction.

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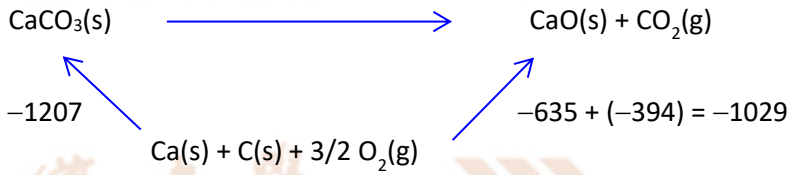
4.3 Application: Calculations using standard enthalpy change of formation

Exercise 4.3 (Worked Example)

Calculate the standard enthalpy change for the reaction below using the data given.

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

Substance	$\Delta H^{\ominus}_f$ / kJ mol^{-1}
$CaCO_3(s)$	–1207
$CaO(s)$	–635
$CO_2(g)$	–394



By Hess's Law, ΔH_r = +1207 – 1029 = +178 kJ mol^{-1}

Exercise 4.4

Calculate the standard enthalpy of formation of solid ammonium chloride, $NH_4Cl(s)$, using the given data.

$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$ $\Delta H^{\ominus}_r$ = –176.0 kJ mol^{-1}

$\Delta H^{\ominus}_f$ [$NH_3(g)$] = –46.1 kJ mol^{-1} ; $\Delta H^{\ominus}_f$ [$HCl(g)$] = –92.3 kJ mol^{-1} **[–314 kJ mol^{-1}]**

General Formula: $\Delta H_r = \sum m \Delta H_f$ **(products)** $- \sum m \Delta H_f$ **(reactants)**

where m, n = stoichiometric coefficients of the products and reactants in the given reaction.

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5 BOND ENERGY AND STANDARD ENTHALPY CHANGE OF ATOMISATION

5.1 Bond energy, B.E.

LO 7(c)(ii): explain and use the term, bond energy (ΔH positive, i.e. bond breaking) (see also Topic 2 Chemical Bonding)

Bond energy is the energy required to break **1 mole** of a **covalent** bond in the **gaseous state**.

E.g. $H_2(g) \rightarrow 2H(g)$ B.E.(H–H) = +436 kJ mol^{-1}

$HCl(g) \rightarrow H(g) + Cl(g)$ B.E. (H–Cl) = +431 kJ mol^{-1}

$\frac{1}{2}H_2O(g) \rightarrow H(g) + \frac{1}{2} O(g)$ B.E. (O–H) = +460 kJ mol^{-1}

- Bond energies are **always positive** because energy is needed to pull the two atoms apart (endothermic process) to break the covalent bond.

- Some bond energy data in the *Data Booklet* are **average values** derived from a large range of molecules containing that particular covalent bond.

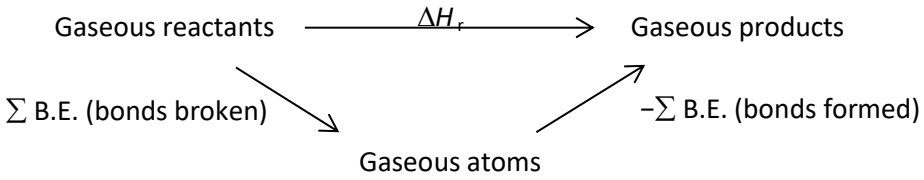
  E.g. B.E. (C–Cl) = +340 kJ mol^{-1} (from *Data Booklet*)

  However, average bond energy for the C–Cl bond in CCl_4 = +327 kJ mol^{-1}

5.2 Calculations using bond energy

LO 7(f)(iii) apply Hess' Law to construct simple energy cycles and carry out calculations involving such cycles, with particular reference to: average bond energies

- The enthalpy change of a reaction involving **gaseous molecules** can be calculated using bond energy values.



ΔH_r = $\sum$ B.E. (bonds broken) – $\sum$ B.E. (bonds formed)

- As some bond energy data in the *Data Booklet* are average values, using them in calculations can result in **discrepancies** when compared to values obtained by other means e.g. from experiments or calculated from other enthalpy changes.

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Exercise 5.1 (Worked Example)

(a) Oxyacetylene torches, which operate at temperatures as high as 3300 °C, are fuelled by the combustion of acetylene (i.e. ethyne), C_2H_2. The equation is given below:

$$2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(g)$$

Use bond energy values from the *Data Booklet* to calculate ΔH_r of the above reaction.

$$2\ H{-}C{\equiv}C{-}H + 5\ O{=}O \xrightarrow{\Delta H_r} 4\ O{=}C{=}O + 2\ H{-}O{-}H$$

bonds broken		bonds formed	
4 × C–H	4(410)	8 × C=O	8(805)
2 × C≡C	2(840)	4 × O–H	4(460)
5 × O=O	5(496)		
	5800		8280

ΔH_r = +5800 – 8280 = –2480 kJ mol^{-1}

Comments:

To help to visualize the types and number of bonds between the atoms, it is useful to draw out the full structural formula of the molecules. Take note that bond breaking is endothermic and bond forming is exothermic.

(b) Calculate another value for the ΔH_r of this reaction using the following enthalpy changes of formation.

ΔH_f [$C_2H_2(g)$] = +227 kJ mol^{-1}; ΔH_f [$CO_2(g)$] = –394 kJ mol^{-1}; ΔH_f [$H_2O(g)$] = –242 kJ mol^{-1}

ΔH_r = $\Sigma\, m\Delta H_f$ (products) – $\Sigma\, n\Delta H_f$ (reactants)
= 4(–394) + 2(–242) – 2(+227)
= –2514 kJ mol^{-1}

(c) Suggest a reason for the difference in the values of ΔH_r, obtained in parts **(a)** and **(b)**.

The bond energies given in the *Data Booklet* are the average bond energies of that particular covalent bond in different types of molecules. These values may not apply to the specific molecules in this reaction.

Exercise 5.2

Sulfur hexafluoride can be made by reacting sulfur tetrafluoride with fluorine.

$$SF_4(g) + F_2(g) \rightarrow SF_6(g) \qquad \Delta H = -434 \text{ kJ mol}^{-1}$$

By considering the bonds broken and bonds formed during the reaction, calculate a value for the average bond energy of the S–F bond. State any assumptions you have made. **[+296 kJ mol^{-1}]**

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5.3 Standard enthalpy change of atomisation

LO 7(c)(i)part: explain and use the term, enthalpy change of atomisation.

ΔH_{atom} for an element is the **energy required** when **1 mole of gaseous atoms** is formed from the **element** at 298 K and 1 bar.

E.g. $Na(s) \rightarrow Na(g)$ $\Delta H^{\ominus}_{atom} = +107$ kJ mol^{-1}

$\frac{1}{2}Br_2(l) \rightarrow Br(g)$ $\Delta H^{\ominus}_{atom} = +112$ kJ mol^{-1}

$\frac{1}{2}H_2(g) \rightarrow H(g)$ $\Delta H^{\ominus}_{atom} = +218$ kJ mol^{-1}

What are some elements with enthalpy change of atomisation = 0 kJ mol^{-1}?

ΔH_{atom} for a compound is the **energy required** to convert **1 mole of the compound** into **gaseous atoms** at 298 K and 1 bar.

E.g. $CH_4(g) \rightarrow C(g) + 4H(g)$ $\Delta H^{\ominus}_{atom} = +1662$ kJ mol^{-1}

- $\Delta H^{\ominus}_{atom}$ values are **<u>always positive</u>** since atomisation involves **<u>breaking bonds</u>**.
- For gaseous diatomic elements, enthalpy change of atomisation and bond energy are related:
  $\Delta H^{\ominus}_{atom}$ (X_2) = ½ × B.E. (X–X)

  E.g. $\frac{1}{2}\,Cl_2(g) \rightarrow Cl(g)$ $\Delta H^{\ominus}_{atom} = \frac{1}{2} \times$ B.E. (Cl–Cl) = ½(244) = +122 kJ mol^{-1}

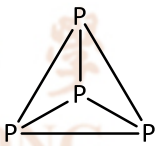
  $\frac{1}{2}\,O_2(g) \rightarrow O(g)$ $\Delta H^{\ominus}_{atom} = \frac{1}{2} \times$ B.E. (O=O) = ½(496) = +248 kJ mol^{-1}

  $\frac{1}{2}\,N_2(g) \rightarrow N(g)$ $\Delta H^{\ominus}_{atom} = \frac{1}{2} \times$ B.E. (N≡N) = ½(944) = +472 kJ mol^{-1}

LO 7(f)(iii) apply Hess' Law to construct simple energy cycles and carry out calculations involving such cycles, with particular reference to: average bond energies

Exercise 5.3

Phosphorus exists as P_4 molecule with the following structure.



Use the following data to calculate the average bond energy of P–P bond.

Standard enthalpy change of formation of $P_4(g)$ = +58.91 kJ mol^{-1}

Standard enthalpy change of atomisation of phosphorus = +314.4 kJ mol^{-1}

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6 LATTICE ENERGY AND BORN-HABER CYCLE

LO 7(c)(iii)part: explain and use the term, lattice energy (ΔH negative, i.e. gaseous ions to solid lattice)
LO 7(e): explain, in qualitative terms, the effect of ionic charge and of ionic radius on the numerical magnitude of a lattice energy
LO 7(f): apply Hess' Law to construct simple energy cycles, e.g. Born-Haber cycle, and carry out calculations involving such cycles and relevant energy terms (including ionisation energy and electron affinity), with particular reference to: the formation of a simple ionic solid

6.1 Lattice energy, L.E.

The **heat evolved** when **1 mole of solid ionic compound** is formed from its **constituent gaseous ions**.

E.g. $Na^+(g) + Br^-(g) \rightarrow NaBr(s)$ L.E. = –742 kJ mol^{-1}

$Mg^{2+}(g) + 2Cl^-(g) \rightarrow MgCl_2(s)$ L.E. = –2326 kJ mol^{-1}

- Lattice energy is **always negative** as heat is evolved in forming **electrostatic forces of attraction** between oppositely charged ions (i.e. ionic bonding).

- Lattice energy is a measure of the strength of ionic bonding and the stability of the ionic compounds. The **more exothermic** the lattice energy, the **stronger** the ionic bonding and the more stable the ionic compound.

6.2 Factors affecting lattice energy

The magnitude of lattice energy depends on:

- the **charges** on the ions
- the **sizes** of ions or inter-ionic distance

These two factors can be combined into the following expression.

$$\text{L.E.} \propto \frac{q_+ \times q_-}{r_+ + r_-}$$

q_+ and q_- are the charges on the cation and anion respectively.

$(r_+ + r_-)$ is the inter-ionic distance between the two ions in the lattice.

Compound	q_+	q_-	r_+ / nm	r_- / nm	L.E. / kJ mol^{-1}
NaCl	+1	–1	0.095	0.181	–776
$MgCl_2$	+2	–1	0.065	0.181	–2375

Table 4. Factors affecting lattice energy

- $MgCl_2$ and NaCl have the same anion. Mg^{2+} has a higher charge and smaller ionic radius than Na^+. Since $\text{L.E.} \propto \frac{q_+ \times q_-}{r_+ + r_-}$, L.E. of $MgCl_2$ is more exothermic than that of NaCl.

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6.3 Born-Haber cycle

Lattice energy can be calculated using a Born-Haber cycle. A Born-Haber cycle is usually presented in the form of an energy level diagram where the 'zero reference line' refers to the elements in the standard states.

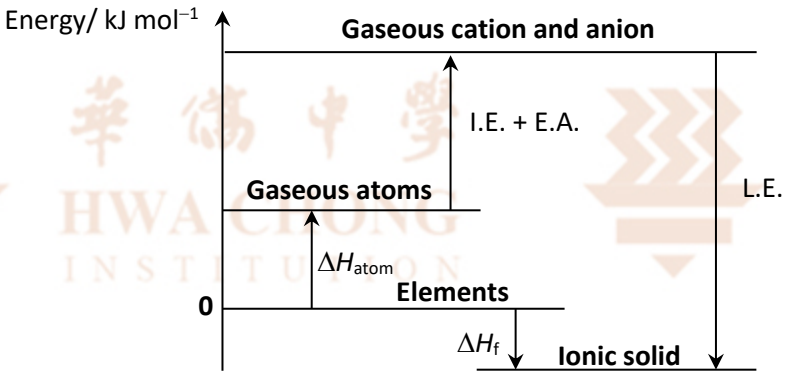


Figure 4. Outline of a Born-Haber cycle in energy level diagram format
Note: I.E. and E.A. should be represented by separate arrows. Refer to Exercise 6.1 / 6.2.

6.3.1 Ionisation Energy, I.E.

The **first** ionisation energy is the energy **required** to remove **1 mole of electrons** from **1 mole of gaseous atoms** to form **1 mole** of singly charged **gaseous cations**.

- I.E. is **always positive** since energy is required to remove an electron (endothermic process).

6.3.2 Electron Affinity, E.A.

The **first** electron affinity is the enthalpy change when **1 mole of electrons** is added to **1 mole of gaseous atoms** to form **1 mole** of singly charged **gaseous anions**.

- **1st E.A.** is usually **negative** as the effective nuclear charge of the atom leads to an attraction of the incoming electron. When the attraction is stronger, the energy given off is greater and hence E.A. is more negative.

- **2nd and subsequent E.A.** are always **positive** because energy is required to overcome the electrostatic repulsion between the incoming electron and the anion.

  E.g. $O(g) + e^- \rightarrow O^-(g)$ 1st E.A. = –141 kJ mol^{-1}

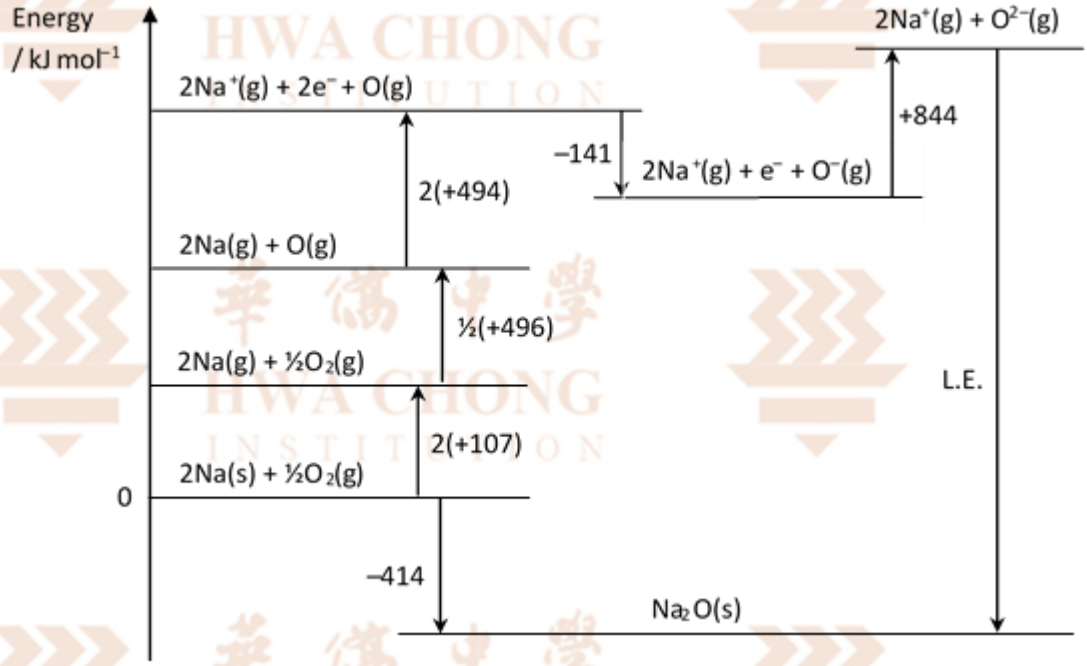
  $O^-(g) + e^- \rightarrow O^{2-}(g)$ 2nd E.A. = +844 kJ mol^{-1}

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Exercise 6.1 (Worked Example)

Construct a Born-Haber cycle for the formation of Na_2O from its elements and calculate the lattice energy of Na_2O from the following data:

	ΔH/ kJ mol^{-1}
Enthalpy change of formation of Na_2O(s)	–414
Enthalpy change of atomisation of sodium	+107
First electron affinity of oxygen	–141
Second electron affinity of oxygen	+844



By Hess's Law,

$-414 = 2(107) + ½(496) + 2(494) - 141 + 844 + \text{L.E.}$

$-414 = 2153 + \text{L.E.}$

$\therefore$ L.E.(Na_2O) = –2567 kJ mol^{-1}

Comments:

Elements are placed on the 'zero reference line' on the energy axis. As we are drawing an energy level diagram, the relative energy levels at each step need to correspond to their relative positions on the energy axis. As such, if the enthalpy change of the reaction is negative (exothermic), the arrow is drawn pointing down, and if the enthalpy change of the reaction is positive (endothermic), the arrow is drawn pointing up.

Exercise 6.2

Construct a Born-Haber cycle for the formation of $CaCl_2$ from its elements and calculate its lattice energy from the following data and relevant data from the *Data Booklet*.

ΔH_{atom} of Ca = +178 kJ mol^{-1}; ΔH_f of $CaCl_2$ = –796 kJ mol^{-1}; First E.A. of Cl = –349 kJ mol^{-1};

[–2260 kJ mol^{-1}]

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6.4 Experimental versus theoretical lattice energies

- **Experimental** lattice energy refers to the value found from experimental results **using the Born-Haber cycle**.

- Theoretical lattice energy refers to the value calculated based on a **model** which assumes that the **compound is completely ionic**.

- There is always a difference between the two values which suggests that no compound is completely ionic (Refer to Topic 2 Chemical Bonding for the continuum from a theoretical pure ionic model to purely covalent compounds.)

- A small difference shows that the ionic model is a good one for the compound.

- A large difference shows that there is **covalent character** in the ionic compound. This is most apparent when a cation with a high charge density distorts an anion with a large electron cloud.

Compound	Theoretical L.E. / kJ mol^{-1}	Experimental L.E. / kJ mol^{-1}
CsCl	–657	–659
$MgCl_2$	–2326	–2375
AgF	–953	–967
AgI	–808	–889

Table 5. Theoretical and Experimental lattice energies of some compounds

- There is good agreement between the theoretical and experimental lattice energy for CsCl but the discrepancy is greater for $MgCl_2$. Mg^{2+} has higher charge and smaller ionic radius than Cs^+. Mg^{2+} thus has higher charge density and greater polarising power than Cs^+. Hence Mg^{2+} distorts the electron cloud of Cl^- to a greater extent, resulting in greater covalent character in $MgCl_2$.

- There is also close agreement between the theoretical and experimental lattice energy for AgF but not for AgI. This is because I^- has a larger ionic radius than F^- and is hence more polarisable. Thus Ag^+ polarises the electron cloud of I^- to a larger extent, resulting in greater covalent character in AgI.

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7 STANDARD ENTHALPY CHANGES OF HYDRATION AND SOLUTION

LO 7(c)(i)part: explain and use the terms: enthalpy change of hydration; solution
LO 7(f)(ii): apply Hess' Law to construct simple energy cycles, and carry out calculations involving such cycles and relevant energy terms, with particular reference to: the formation of a simple ionic solid and of its aqueous solution

7.1 Standard enthalpy change of hydration

The heat **evolved** when **1 mole of free gaseous ions** is dissolved in an infinite volume of water at 298 K and 1 bar.

E.g. $Na^+(g) + aq \rightarrow Na^+(aq)$ $\Delta H^{\ominus}_{hyd} = -405$ kJ mol^{-1}

$Br^-(g) + aq \rightarrow Br^-(aq)$ $\Delta H^{\ominus}_{hyd} = -337$ kJ mol^{-1}

- ΔH_{hyd} is **<u>always negative</u>** (regardless of anion or cation) as heat is evolved in forming **<u>ion-dipole interactions</u>** between the ions and the polar water molecules.

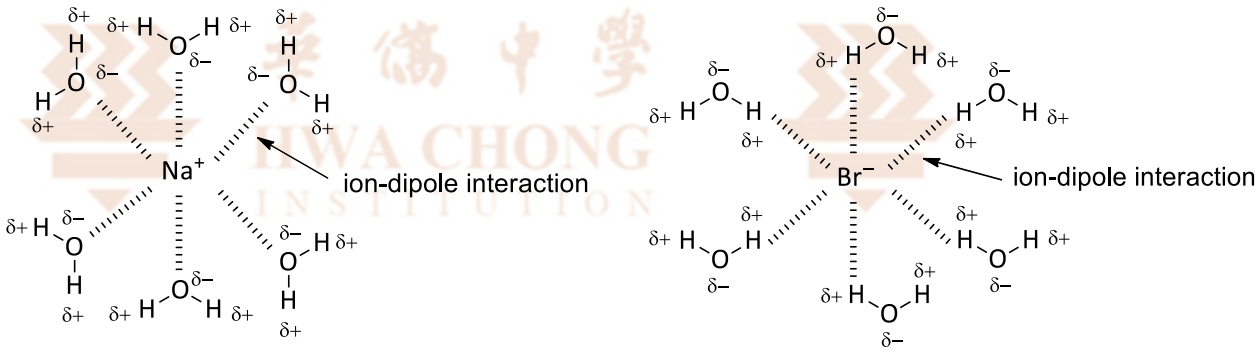


Figure 5. Hydrated Na^+ and Br^- ions

- The magnitude of ΔH_{hyd} of an ion depends on its **charge density**. (Refer to Topic 2 Chemical Bonding for the definition of charge density.)

$$\Delta H_{hyd} \propto \frac{q}{r}$$

The **<u>higher the charge density</u>** of the ion, the **<u>stronger the ion-dipole interaction</u>** and ΔH_{hyd} will be **<u>more exothermic</u>**.

E.g. $Na^+(g) + aq \rightarrow Na^+(aq)$ $\Delta H^{\ominus}_{hyd} = -405$ kJ mol^{-1} ; $Na^+ = 0.095$ nm

$Mg^{2+}(g) + aq \rightarrow Mg^{2+}(aq)$ $\Delta H^{\ominus}_{hyd} = -1920$ kJ mol^{-1} ; $Mg^{2+} = 0.065$ nm

7.2 Standard enthalpy change of solution, ΔH_{sol}

The enthalpy change when **1 mole of solute** is completely dissolved in an infinite volume of solvent at 298 K and 1 bar.

E.g. $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$ $\Delta H^{\ominus}_{sol} = +3.88$ kJ mol^{-1}

$MgCl_2(s) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$ $\Delta H^{\ominus}_{sol} = -160$ kJ mol^{-1}

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- The solute is usually an ionic compound while the solvent is usually water.
- $\Delta H^{\ominus}_{sol}$ can be either positive or negative.
  If $\Delta H^{\ominus}_{sol}$ is highly positive $\Rightarrow$ salt is likely insoluble
  If $\Delta H^{\ominus}_{sol}$ is negative $\Rightarrow$ salt is likely soluble

  Note: There are salts with positive $\Delta H^{\ominus}_{sol}$ and are soluble e.g. Na*Cl*, K*Cl*, NH_4NO_3 due to positive entropy change (Refer to Section 8).

7.3 Relationship between lattice energy, enthalpy changes of hydration and enthalpy change of solution

- The dissolution of an ionic solid MX(s) can be divided into 2 processes:

1) Breaking up the solid ionic lattice to form isolated gaseous ions.
   Process is **endothermic** (overcoming ionic bonding) and the enthalpy change is '**–LE**'.

   $MX(s) \rightarrow M^+(g) + X^-(g)$ $\Delta H = -LE$

2) Hydration of the gaseous ions.
   Process is **exothermic** (forming ion-dipole interactions between ion and water).

   $M^+(g) + X^-(g) + aq \rightarrow M^+(aq) + X^-(aq)$ $\Delta H = \Delta H_{hyd}(M^+) + \Delta H_{hyd}(X^-)$

Overall $MX(s) \rightarrow M^+(aq) + X^-(aq)$ **$\Delta H^{\ominus}_{sol}$ = – L.E. + sum of $\Delta H^{\ominus}_{hyd}$**

If | L.E. | > | $\Delta H^{\ominus}_{hyd}$ | $\Rightarrow \Delta H^{\ominus}_{sol} > 0$ (endothermic) – Refer to diagram below
If | L.E. | < | $\Delta H^{\ominus}_{hyd}$ | $\Rightarrow \Delta H^{\ominus}_{sol} < 0$ (exothermic) – try drawing the energy level diagram

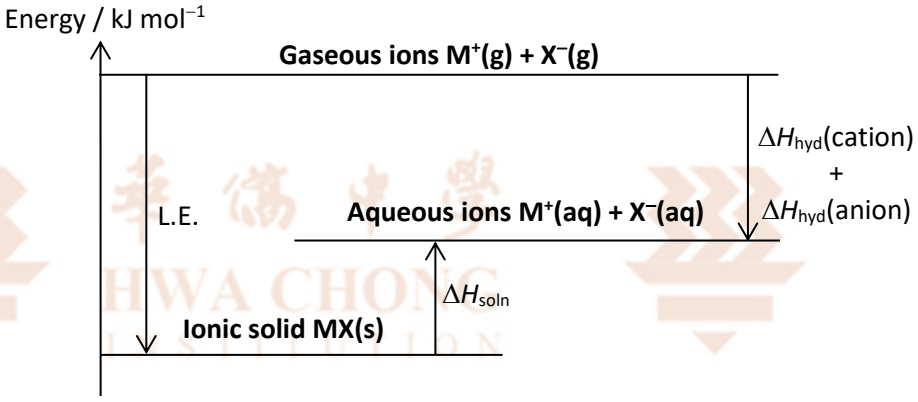


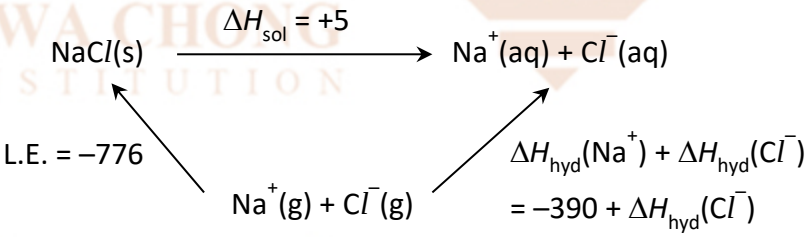
Figure 6. Energy level diagram to determine enthalpy change of solution of an ionic solid

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Exercise 7.1 (Worked Example)

(a) By means of an appropriate energy cycle, calculate the enthalpy change of hydration of the chloride ion using the data provided.

Enthalpy change of solution of NaC*l*(s)	+5 kJ mol^{-1}
Enthalpy change of hydration of Na^+(aq)	–390 kJ mol^{-1}
Lattice energy of NaC*l*(s)	–776 kJ mol^{-1}



By Hess's Law,

$-776 + 5 = -390 + \Delta H_{hyd}(Cl^-)$

$\Delta H_{hyd}(Cl^-) = -381$ kJ mol^{-1}

(b) The enthalpy change of hydration of iodide ion was found to be –296 kJ mol^{-1}. Comment on the difference between this value and the value found in **(a)**.

$|\Delta H_{hyd}| \propto \frac{q}{r}$

I^- has the same charge but a larger ionic radius than Cl^-.

So the ion-dipole attractions between I^- ion and the water molecules are weaker.

Hence, H_{hyd} of I^- is less exothermic than that of Cl^-.

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8 ENTROPY AND GIBBS FREE ENERGY CHANGE

8.1 Spontaneous processes (Background info)

From our experience, there are processes that take place on its own. For example, if we ignite a mixture of hydrogen and oxygen, they combine rapidly to form water. An iron nail rusts slowly when left to stand. All of these chemical reactions can be described as *spontaneous*. There are also physical processes which are *spontaneous*. For example, when a drop of dye is placed in a beaker of water, diffusion takes place resulting in a uniformly coloured solution.

A **spontaneous process** is one that takes place naturally in the direction stated. In other words, the change occurs without a need for continuous input of energy from outside the system.

It is useful to predict if a reaction will occur spontaneously when reactants are brought together under a certain set of conditions. When we think of spontaneous process, many of the examples we have seen, such as combustion, are exothermic processes.

However, there are endothermic reactions which are also spontaneous.

For example, $N_2O_5(s) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$ $\Delta H = +109.5$ kJ mol^{-1}

Many soluble salts (e.g. NaC*l*, KC*l*, NH_4NO_3) dissolve endothermically and spontaneously.

For example, KC*l*(s) $\rightarrow$ KC*l*(aq) $\Delta H = +25.7$ kJ mol^{-1}

Hence, the sign of ΔH by itself does not predict if a reaction is spontaneous.

If we examine the two examples above, they have one major feature in common: the chemical species (atoms, molecules, or ions) have more freedom of motion after the change. The particles have a wider range of energy of motion (kinetic energy) which means the energy has become more dispersed or distributed.

When solid N_2O_5 changes to gaseous NO_2 and O_2, the motion of the molecules in the solid state is restricted while the gaseous particles have more freedom of motion. Thus the energy of motion is more distributed after the change.

Similarly, dissolving a salt separates the ions in the crystalline solid. The ions in the aqueous state have greater freedom of motion (or are more disordered) and their energy of motion is more distributed.

Hence, a change in the freedom of motion of particles in a system, that is, the distribution of their energy of motion, is one key factor affecting the direction of a spontaneous process. This factor is known as **entropy change**.

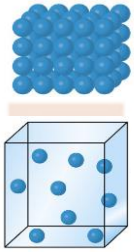
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8.2 Entropy and entropy changes

LO 7(g): explain and use the term entropy

Entropy 'S' is a measure of the randomness or disorder in a system, reflected in the number of ways that the energy of a system can be distributed through the motion of its particles. Units: **J mol^{-1} K^{-1}**.

For the same amount of a substance, entropy of solid < liquid << gas.



In a solid, the particles are relatively fixed and possess the least kinetic energy. There are few ways that the energy of particles is distributed.

In a gas, the particles are able to move freely and possess a wide range of kinetic energy. There are many ways that the energy of the particles is distributed.

Figure 7. Arrangement of particles in solid and gaseous state

Many chemical reactions or physical processes are accompanied by a **change in entropy, ΔS**.

- If a reaction or process results in more ways to disperse or distribute the energy, entropy increases ($\Delta S > 0$).
- If a reaction or process results in less ways to disperse or distribute the energy, entropy decreases ($\Delta S < 0$).

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8.3 Predicting the sign of ΔS for some processes

LO 7(h): discuss the effects on the entropy of a chemical system by the following: (i) change in temperature, (ii) change in phase, (iii) change in the number of particles (especially for gaseous systems), (iv) mixing of particles [quantitative treatment is not required]

LO 7(i): predict whether the entropy change for a given process or reaction is positive or negative

(1) Change in temperature

As temperature increases, the **average kinetic energy** of the particles and the **range of energies** increase as shown in the Maxwell-Boltzmann distribution curves below. (Refer to Topic 3 The Gaseous State for explanation on the shape of the curves.) There are **more ways to disperse the energy** among the particles. Hence, **entropy increases** (S increases, ΔS is positive).

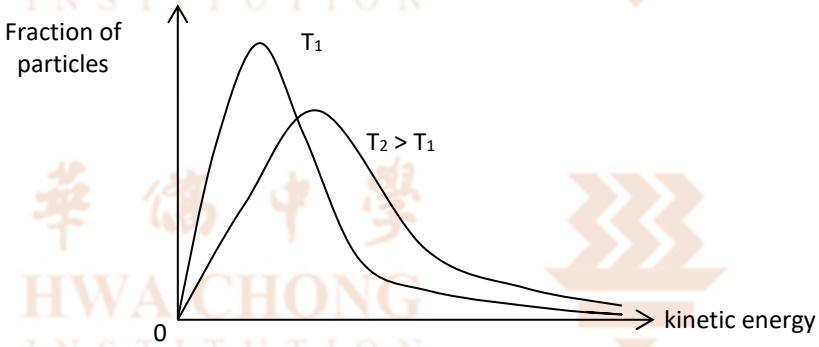


Figure 8. Maxwell–Boltzmann distribution curve

(2) Change in phase

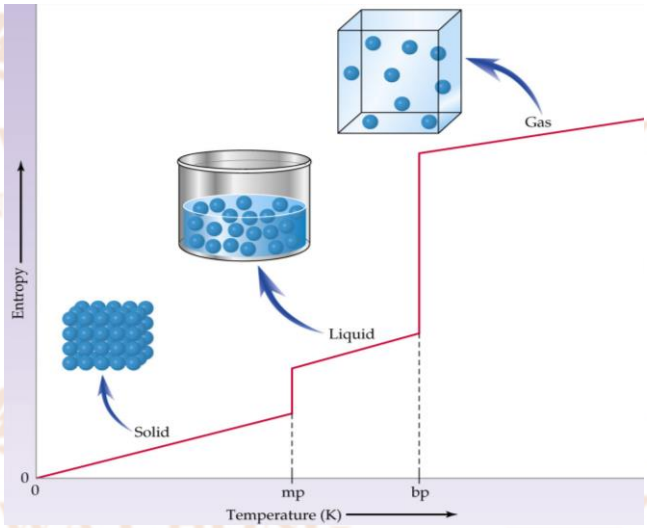


Figure 9. Change in entropy during phase change

- The particles in the solid state vibrate about their fixed positions. The energy is thus the least dispersed and the solid has the lowest entropy.

- When temperature increases, entropy increases gradually as the kinetic energy of the particles increases.

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- When the solid melts, the **particles move more freely in the liquid state and become more disordered**. Hence there is an abrupt increase in entropy ($\Delta S > 0$) as there are **more ways to distribute the particles and their energy in the liquid state**.

- Likewise, as the liquid is heated, its entropy increases as the particles gain kinetic energy. During vaporisation, the liquid converts to a gas where the **particles are able to move even more freely**. Hence there is a large increase in entropy ($\Delta S >> 0$) as there are **more ways to distribute the particles and their energy in the gaseous state**.

(3) Change in the number of particles (especially gaseous particles)

- When a chemical reaction results in an **increase in the number of gas particles**, there is a large increase in entropy. This is because the particles in gas are the **most disordered** so the number of **ways that the particles and the energy can be distributed increase greatly**.

  For example, many decomposition reactions result in an increase in the number of gas particles, hence an increase in entropy.

  $N_2O(g) \rightarrow N_2(g) + \frac{1}{2}O_2(g)$ no. of **gas** particles increase by 0.5 mol, $\Delta S > 0$
  $2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$ no. of **gas** particles increase by 3 mol, $\Delta S > 0$

- If there is **no change** in the number of gas particles, entropy may increase or decrease but ΔS will be relatively **small numerically**. For example,

  $N_2(g) + O_2(g) \rightarrow 2NO(g)$ $\Delta S \approx 0$

(4) Mixing of particles

- Consider the mixing of equimolar H_2 gas and N_2 gas at **constant pressure** as shown below. Before mixing, each gas has the same volume and pressure. After the barrier is removed, each gas expands to occupy the whole container and hence the volume of each gas doubles. The partial pressure of each gas is reduced by half but total pressure remains constant.

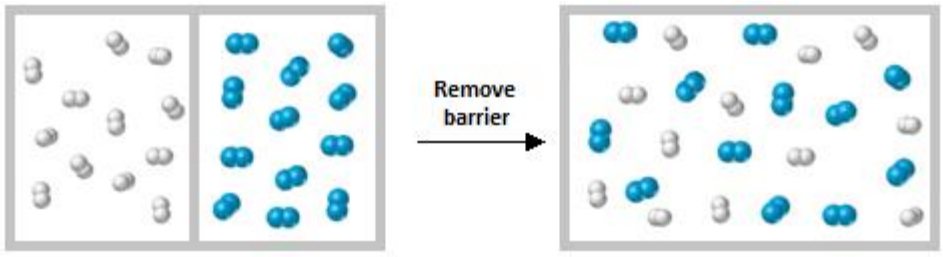


Figure 10. Mixing of 2 gases at constant pressure

As the **volume available** for each gas (H_2 and N_2) is **increased**, there are **more ways to distribute the particles and hence their energy**. Thus, **entropy increases** ($\Delta S > 0$).

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Note:
When a gas expands, the **volume available for distribution of the particles increases**. **Entropy increases** as there are **more ways that the particles and the energy can be distributed.**

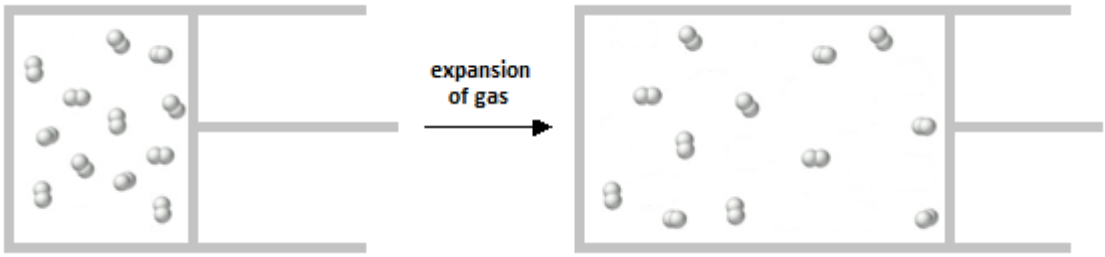


Figure 11. Expansion of gas

- When gases are mixed at **constant volume**, i.e. the **volume available to distribute each gas particle is the same**. Hence the **entropy does not change** ($\Delta S = 0$).

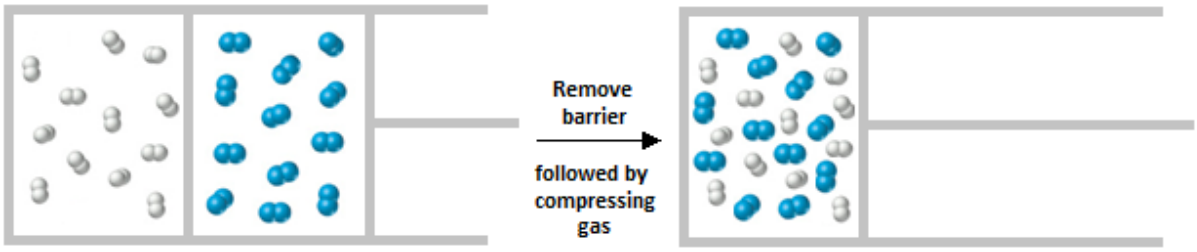


Figure 12. Mixing of 2 gases at constant volume

- When liquids with **similar polarities** (e.g. benzene and hexane) are mixed together, entropy increases. This is because total volume increases and hence there are more ways to distribute the particles and hence their energy.

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(5) Dissolution of an ionic solid

Two entropy terms operate when an ionic solid is dissolved in water:

- Entropy increases because the ions in the solid are free to move in solution.
- Entropy decreases because water molecules that were originally free to move become restricted in motion as they arrange themselves around the ions.

If the first factor is more significant, the overall entropy change **is positive**.

E.g. $NaCl(s) + aq \rightarrow Na^+(aq) + Cl^-(aq)$ $\Delta S > 0$

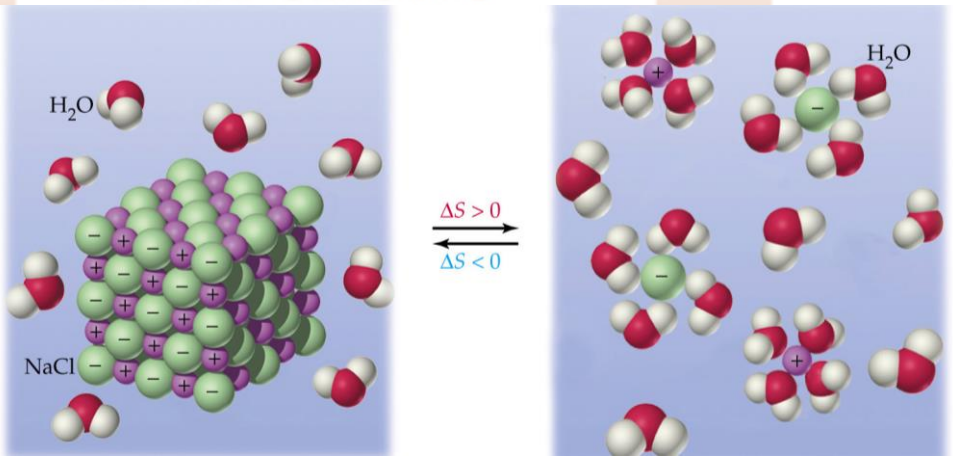


Figure 13. Entropy change during dissolution of an ionic solid

In Topic 2 Chemical Bonding, we saw that dissolution of a compound depends on the energy change. In addition to enthalpy change, the entropy change also plays a part when predicting the solubility of a compound.

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Exercise 8.1

Predict whether ΔS is positive or negative in each of the following processes.

Process	Sign of ΔS	Explanation
$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$		
$H_2O(l) \rightarrow H_2O(g)$		
$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$		
1 mol of $Cl_2(g)$ at 298K is heated to 373K		
$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$		
Ar at 2 atm $\rightarrow$ Ar at 1 atm		

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8.4 Gibbs free energy change

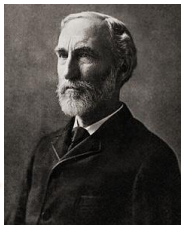
LO 7(j): state and use the equation involving standard Gibbs free energy change of reaction, ΔG : $\Delta G = \Delta H - T\Delta S$ [the calculation of standard entropy change, ΔS, for a reaction using standard entropies, S, is not required]

LO 7(k): state whether a reaction or process will be spontaneous by using the sign of ΔG

The **Gibbs free energy change of reaction** is given by:

$$\Delta G = \Delta H - T\Delta S$$

Units of ΔG and ΔH : kJ mol^{-1} or J mol^{-1}
Units of ΔS : kJ mol^{-1} K^{-1} or J mol^{-1} K^{-1}
Units of T : K



Josiah Willard Gibbs (1839 – 1903), the father of chemical thermodynamics

The **standard** Gibbs free energy change of reaction, $\Delta G^{\ominus}$, is the Gibbs free energy change needed to convert reactants into products at 1 bar and at constant temperature (usually at 298 K).

We can use the sign of ΔG to predict if a reaction is spontaneous.

$\Delta G < 0$	$\Delta G = 0$	$\Delta G > 0$
The reaction takes place **spontaneously**.	The system is at **equilibrium**. There is no net reaction in the forward or backward direction.	The reaction **cannot take place spontaneously**. It is spontaneous in the reverse direction.
The reaction is said to be *exergonic*.	E.g. ΔG = 0 during melting and boiling at the melting point and boiling point respectively	The reaction is said to be *endergonic*.

Table 6. Sign of ΔG and spontaneity of reaction

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8.4.1 Calculations using $\Delta G = \Delta H - T\Delta S$

Exercise 8.2 (Worked Example) Calculating ΔG from ΔH and ΔS

Chemical Reaction	**ΔH / kJ mol^{-1}**	**ΔS / J mol^{-1} K^{-1}**
$2Fe(s) + {}^3/_2O_2(g) \rightarrow Fe_2O_3(s)$	–825	–272

Calculate the standard Gibbs free energy change for the rusting of iron**.**

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} = -825 - 298\left(\frac{-272}{1000}\right) = -744$ kJ mol^{-1}

Comments:
The energy units of ΔH and $T\Delta S$ must be made compatible (i.e. standardise to kJ mol^{-1} or J mol^{-1}).
$^{\ominus}$ means that the temperature is at 298 K.
Since $\Delta G^{\ominus} < 0$, the rusting of iron is spontaneous at room temperature which is consistent with our observation/daily experience.

Exercise 8.3

Chemical Reaction	**ΔH / kJ mol^{-1}**	**ΔS / J mol^{-1} K^{-1}**
$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$	+130	+335

Calculate the standard Gibbs free energy change for the decomposition of **one mole** of sodium hydrogen carbonate. [+15.1 kJ mol^{-1}]

Exercise 8.4 Calculating ΔS for phase change

Given the enthalpy change of fusion of ice (conversion of solid ice to liquid water) is 6.0 kJ mol^{-1}, calculate the entropy change which accompanies the melting of ice.

Exercise 8.5

Given the enthalpy change of vaporisation of water is 44.0 kJ mol^{-1}, calculate the entropy change which accompanies the boiling of water. **[+118 J mol^{-1} K^{-1}]**
Comment on the difference in magnitude of $\Delta S_{vaporisation}$ with ΔS_{fusion} for water.

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8.4.2 Calculations of ΔG_r from ΔG_f

Like enthalpy change (ΔH), Gibbs free energy change (ΔG) is a state function. This means that the value that it takes only depends on the state of the substance, and not how it was brought to that state. The 'state' is specified by variables such as temperature and pressure. Hence ΔG of a reaction can be calculated in a similar way as ΔH in Section 4 (Hess' law). Likewise, ΔS is a state function and ΔS of a reaction can also be calculated a similar way.

Exercise 8.6

Calculate $\Delta G^{\ominus}$ for the reaction $C_2H_6(g) + \frac{7}{2} O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ using the data below.

$\Delta G^{\ominus}_f (C_2H_6(g)) = -32.9$ kJ mol^{-1}; $\Delta G^{\ominus}_f (CO_2(g)) = -394.4$ kJ mol^{-1}; $\Delta G^{\ominus}_f (H_2O(l)) = -237.2$ kJ mol^{-1};

8.4.3 Temperature dependence of ΔG

The term [$-T\Delta S$] in the equation $\Delta G = \Delta H - T\Delta S$ indicates that ΔG is temperature-dependent.

We can assume that **ΔH and ΔS remain roughly constant** regardless of temperature and use them to calculate ΔG at other temperatures. This assumption is valid as shown in the following example involving the reaction between hydrogen gas and chlorine gas at 298 K and 500 K.

	T /K	ΔH /kJ mol^{-1}	ΔS /J mol^{-1} K^{-1}	$T\Delta S$ /kJ mol^{-1}	ΔG /kJ mol^{-1}
$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$	298	–184.6	+20.0	+6.0	–190.6
$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$	500	–185.6	+17.5	+8.8	–194.4

If we were to assume that ΔH and ΔS do not change with temperature, we can use the values of ΔH and ΔS at 298 K to calculate a value for ΔG at 500 K as shown:

$$\Delta G_{500K} \approx \Delta H_{298K} - 500 \times \Delta S_{298K}$$
$$= -184.6 - 500 \times \frac{20.0}{1000} = -194.6 \text{ kJ mol}^{-1}$$

This approximate value of ΔG (–194.6 kJ mol^{-1}) is close to the actual value (–194.4 kJ mol^{-1}) obtained by using values of ΔH and ΔS at 500 K.

The assumption that ΔH and ΔS remain roughly constant is **not valid** if there is a **change in phase** of one of the reactants or products as the temperature is increased. Under these conditions, both ΔH and ΔS change significantly. For example, consider the synthesis of hydrogen iodide at 298 K and 500 K.

	T/K	ΔH/ kJ mol^{-1}	ΔS/ J mol^{-1} K^{-1}	$T\Delta S$/ kJ mol^{-1}	ΔG/ kJ mol^{-1}
$H_2(g) + I_2$**(s)** $\rightarrow 2HI(g)$	298	+53.0	+166	+49.5	+3.5
$H_2(g) + I_2$**(g)** $\rightarrow 2HI(g)$	500	–11.0	+18	+9.0	–20.0

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As a result of the phase change in I_2 (from solid to gaseous), ΔG changes from being slightly positive at 298 K to being very negative at 500 K. This means that the synthesis of HI is not spontaneous at room temperature but it becomes spontaneous if the temperature is raised above the boiling point of I_2.

Exercise 8.7 (Worked Example) Calculating the temperature at which a reaction becomes spontaneous.

The standard enthalpy change of formation, $\Delta H^{\ominus}_f$, and the standard Gibbs free energy change of formation, $\Delta G^{\ominus}_f$, of CO(g) and of CO_2(g) are as follows.

	CO(g)	CO_2(g)
$\Delta H^{\ominus}_f$ / kJ mol^{-1}	–110.5	–393.5
$\Delta G^{\ominus}_f$ / kJ mol^{-1}	–137.2	–394.4

(a) Calculate the standard entropy change of formation, $\Delta S^{\ominus}_f$, in J mol^{-1} K^{-1}, of CO(g) and of CO_2(g). [+89.6 J mol^{-1} K^{-1}; +3.02 J mol^{-1} K^{-1}]

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} \quad \Rightarrow \quad \Delta S^{\ominus} = (\Delta H^{\ominus} - \Delta G^{\ominus}) / T$

$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$

$\Delta S_f = \frac{-110.5-(-137.2)}{298} = +0.0896$ kJ mol^{-1} K^{-1}

$C(s) + O_2(g) \rightarrow CO_2(g)$

$\Delta S_f = \frac{-393.5-(-394.4)}{298} = +0.00302$ kJ mol^{-1} K^{-1}

(b) Using the $\Delta H^{\ominus}_f$ values given and your answers in **(a)**, show that the reaction: $C(s) + CO_2(g) \rightarrow 2CO(g)$ is not spontaneous at 298 K and calculate the minimum temperature at which reaction becomes spontaneous.

$C(s) + CO_2(g) \rightarrow 2CO(g)$

$\Delta H_r = \Sigma\, m\Delta H_f$ (products) $- \Sigma\, n\Delta H_f$ (reactants)

$\Delta H_r = 2(-110.5) - (-393.5) = +172.5$ kJ mol^{-1}

$\Delta S_r = \Sigma\, m\Delta S_f$ (products) $- \Sigma\, n\Delta S_f$ (reactants)

$\Delta S_r = 2(+0.0896) - (+0.00302) = +0.1762$ kJ mol^{-1} K^{-1}

At 298 K, $\Delta G_r = +172.5 - 298(+0.1762) = +120$ kJ mol^{-1} > 0

Hence, reaction is not spontaneous.

To be spontaneous, $\Delta G < 0 \Rightarrow \Delta H - T\Delta S < 0$

$T\Delta S > \Delta H$

$T > \Delta H / \Delta S$

$T > 172.5 / 0.1762$

$T > 979$ K

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Exercise 8.8

The standard enthalpy and entropy changes for the thermal decomposition of sodium hydrogencarbonate are given below:

Chemical Reaction	$\Delta H^{\ominus}$ /kJ mol^{-1}	$\Delta S^{\ominus}$ /J mol^{-1}K^{-1}
$2NaHCO(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$	+130	+335

Calculate the temperature at which the decomposition becomes spontaneous. [388 K]

8.4.4 Effect of Temperature on spontaneity of a reaction

LO 7(m): predict the effect of temperature change on the spontaneity of a reaction, given standard enthalpy and entropy changes

For a reaction to be **spontaneous**, ΔG should be **negative**. The sign of ΔG depends on the signs and magnitudes of ΔH and ΔS, as well as temperature. We observe that most exothermic reactions are spontaneous as the enthalpy contribution to ΔG is much more than the entropy contribution. Hence a highly negative ΔH is likely to make ΔG negative. However, the temperature of a reaction influences the magnitude of the term $T\Delta S$ and hence the spontaneity of many reactions depends on the temperature. We can use the equation $\Delta G = \Delta H - T\Delta S$ to predict the sign of ΔG when temperature is varied (assuming ΔH and ΔS do not change with temperature).

There are four possibilities:

If ΔH is	and ΔS is	ΔG (= $\Delta H - T\Delta S$) is	Reaction is
negative	positive	always negative	*spontaneous at **all** temperatures*
positive	negative	always positive	*not spontaneous at all temperatures*
negative	negative	negative if $\lvert\Delta H\rvert > \lvert T\Delta S\rvert$	*spontaneous at **low** temperatures (reaction is enthalpy driven)*
positive	positive	negative if $\Delta H < T\Delta S$	*spontaneous at **high** temperatures (reaction is entropy driven)*

Table 7. Effect of Temperature on spontaneity of a reaction

(1) ΔH negative and ΔS positive

$-T\Delta S$ is always negative hence **ΔG < 0 for all temperatures**. These reactions are always spontaneous, so a continuous input of energy from outside the system is not needed for such reactions.

(2) ΔH positive and ΔS negative

$-T\Delta S$ is always positive hence **ΔG > 0 for all temperatures**. Reactions of this type are **not** spontaneous and energy must be continuously supplied for the process to take place.

(3) ΔH and ΔS both negative

At **low temperatures**, $|T\Delta S| < |\Delta H|$, so **ΔG < 0**. These exothermic reactions are spontaneous **at low temperatures.**

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(4) ΔH and ΔS both positive

At **high temperatures**, $T\Delta S > \Delta H$, so $\boldsymbol{\Delta G < 0}$. These endothermic reactions, which may not be spontaneous at room temperature, become spontaneous if the temperature is sufficiently **raised**.

For example, at 25 °C, $\Delta G_{vap}(H_2O) = \Delta H_{vap}(H_2O) - T\Delta S_{vap}(H_2O) = 44.0 - 298(118/1000) = +8.84$ kJ mol^{-1} > 0. This means that boiling of water is not spontaneous at room temperature which is consistent with our observation. When temperature is raised to 100 °C, $\Delta G = 0$ which means liquid water and steam are in equilibrium. At temperature above 100 °C, $\Delta G < 0$ and hence the boiling of water is spontaneous.

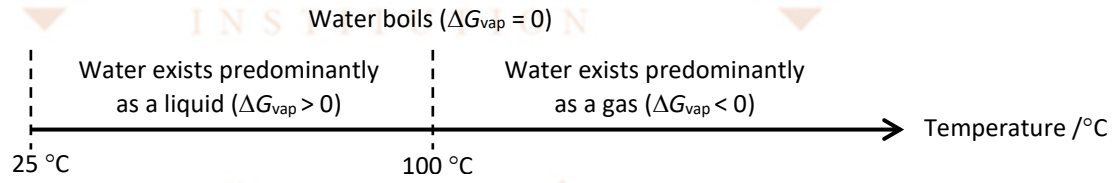


Figure 14. Effect of temperature on spontaneity of boiling of water

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Exercise 8.9

For each of the following reactions, explain whether the reaction is spontaneous at all temperatures, at low temperature, at high temperature or not spontaneous at all temperatures. Predict how ΔG will change with increasing temperature.

Reaction	Explain whether the reaction is spontaneous at all temperatures, at low temperature, at high temperature or not spontaneous at all temperatures.	Predict how ΔG will change with increasing temperature.
Example $2N_2O(g) + O_2(g) \rightarrow 4NO(g)$ $\Delta H = +197.1$ kJ mol^{-1}	***ΔS is positive*** *since there is an increase in number of moles of gas. Hence there are more ways to distribute the particles and their energies.* $\Delta G = \Delta H - T\Delta S$ ***ΔG is negative when TΔS > ΔH****, i.e. when* ***temperature is high****.* *∴The* ***reaction is spontaneous when temperature is high****.*	*When temperature increases,* ***TΔS becomes more positive****.* $\Delta G = \Delta H - T\Delta S$ *Hence* ***ΔG becomes more negative****.*
$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$ $\Delta H = -196$ kJ mol^{-1}		
$3O_2(g) \rightarrow 2O_3(g)$ $\Delta H = +286$ kJ mol^{-1}		
$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ $\Delta H = -198$ kJ mol^{-1}		

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8.5 Limitation in the use of ΔG to predict spontaneity of a reaction

LO 7(l): understand the limitations in the use of ΔG to predict the spontaneity of a reaction

8.5.1 Non-standard condition

ΔG can only be used to predict spontaneity of a reaction under standard conditions. Under non-standard conditions, ΔG must be calculated.

8.5.2 Kinetics consideration

It is important to keep in mind that just because a reaction is spontaneous does not mean that it will occur at an observable rate.

While the Gibbs free energy change can be used to determine the spontaneity of a reaction, it does not take into account the **kinetics** of the reaction, that is, the **rate** at which the reaction takes place. The reacting species may have to overcome a large energy barrier (E_a) before reaction can occur.

Some reactions are **thermodynamically** (or energetically) **favourable** (ΔG is negative) but **kinetically not favourable** (occur very slowly). Such reactions are spontaneous but slow, for example rusting. Another example is the conversion of diamond into graphite.

$$\text{C(diamond)} \rightarrow \text{C(graphite)}$$

With respect to graphite, diamond is thermodynamically less stable ($\Delta G < 0$). However, due to the high activation energy for the reaction, diamond does not turn into graphite overnight. We say that diamond is kinetically stable.

LOOKING AHEAD

We have seen in this topic that energy is the key consideration for any transformation to take place – energy (and/or matter) tends to be dispersed during a chemical or physical change. However, not all transformations take place at considerable rate (as mentioned in Section 9.4) and transformation from reactants to products may not occur to completion. In the next two topics, we will be looking at some characteristics of chemical and physical change, such as the rate of change (reaction kinetics) as well as the extent of change (chemical equilibrium). We will revisit the concept of Gibbs free energy change and learn how the value of ΔG can allow us to predict the extent of change (chemical equilibrium).

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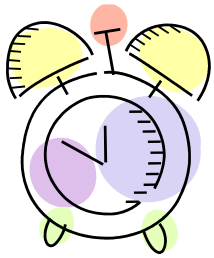
Summary of enthalpy terms

Enthalpy change	Definition	Examples	Sign
Enthalpy change of formation			
Enthalpy change of combustion			
Enthalpy change of neutralisation			
Bond energy			
Enthalpy change of atomisation			
Lattice energy			
Ionisation energy			
Electron affinity			
Enthalpy change of hydration			
Enthalpy change of solution			

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06 Reaction Kinetics

GUIDING QUESTIONS:



- What do we mean by rate of reaction? How could we measure it?
- What are the factors affecting rate? Why?
- How can we determine and express the relationship between rate and concentration mathematically? How are the other factors affecting rate featured in this equation?
- What can we infer about the mechanism of a reaction from the order of reaction? Why do many reactions not occur in a single step?
- What are the general types of catalysts? How are they similar and how do their modes of action differ?

LEARNING OUTCOMES

Students should be able to:

8(a) explain and use the terms: rate of reaction; rate equation; order of reaction; rate constant; half-life of a reaction; rate-determining step; activation energy; catalysis

8(b) construct and use rate equations of the form rate = k $[A]^m$ $[B]^n$ (limited to simple cases of single-step reactions and of multi-step processes with a rate-determining step, for which m and n are 0, 1 or 2), including:

- **(i)** deducing the order of a reaction by the initial rates method
- **(ii)** justifying, for zero- and first-order reactions, the order of reaction from concentration-time graphs
- **(iii)** verifying that a suggested reaction mechanism is consistent with the observed kinetics
- **(iv)** predicting the order that would result from a given reaction mechanism
- **(v)** calculating an initial rate using concentration data

[integrated forms of rate equations are **not** required]

8(c) **(i)** show understanding that the half-life of a first-order reaction is independent of concentration

(ii) use the half-life of a first-order reaction in calculations

8(d) calculate a rate constant using the initial rates method

8(e) devise a suitable experimental technique for studying the rate of a reaction, from given information

8(f) explain qualitatively, in terms of frequency of collisions, the effect of concentration changes on the rate of a reaction

8(g) show understanding, including reference to the Boltzmann distribution, of what is meant by the term *activation energy*

7(b) construct and interpret an energy profile diagram, in terms of the enthalpy change of the reaction and of the activation energy

8(h) explain qualitatively, in terms of both the Boltzmann distribution and of collision frequency, the effect of temperature change on a rate constant (and hence, on the rate) of a reaction

8(i) **(i)** explain that, in the presence of a catalyst, a reaction has a different mechanism, i.e. one of lower activation energy, giving a larger rate constant

(ii) interpret this catalytic effect on a rate constant in terms of the Boltzmann distribution

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8(j) outline the different modes of action of homogeneous and heterogeneous catalysis, including:

- **(i)** the Haber process
- **(ii)** the catalytic removal of oxides of nitrogen in the exhaust gases from car engines (refer to Topic 10 Alkanes under catalytic converter)
- **(iii)** the catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide
- **(iv)** catalytic role of Fe^{2+} in the $I^-/S_2O_8^{2-}$ reaction

8(k) describe enzymes as biological catalysts which may have specific activity

8(l) explain the relationship between substrate concentration and the rate of an enzyme-catalysed reaction in biochemical systems

REFERENCES

1. Cann & Hughes, *Chemistry for Advanced Level*, Chapters 8 & 21.
2. Martin S. Silberberg, *Chemistry The Molecular Nature of Matter and Change*, 6th Ed., Chapter 16
3. Petrucci & Harwiidm *General Chemistry – Principles and Modern Applications,* 6th Ed., Chapter 15

LOOKING BACK

Topic 5 Chemical Energetics looked at energy changes of reactions, in terms of enthalpy, entropy and Gibbs' free energy. While the sign of $\triangle G$ may indicate the direction of chemical change, it gives no information on how fast a reaction occurs. A thermodynamically spontaneous reaction (where $\triangle G$ is negative) may be so slow that no significant reaction could be observed. The study of the rates of chemical reactions is called kinetics. The rate of reaction depends on a number of factors, each of which can be studied separately, and can only be determined by experiment.

1 INTRODUCTION

Rates of reaction are studied for two reasons:

- To discover the best conditions to make the reaction go as quickly or as slowly as possible. Some reactions need to be fast, for example, those which occur inside your body when you take a pain reliever; while some reactions should be as slow as possible, like the rusting of iron in machinery and motor vehicles.

- To gather information about the mechanism, that is, how the reaction actually takes place. Reaction mechanisms are particularly important when studying organic reactions.

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2 THE RATE OF A REACTION

2.1 Rate of reaction

LO8(a)part: explain and use the terms: rate of reaction

*The **rate of a reaction** is defined as the **change in concentration of a reactant or a product per unit time.***

Mathematically,

$$\text{rate} = \frac{d[\text{product}]}{dt} \quad \text{or} \quad \text{rate} = -\frac{d[\text{reactant}]}{dt}$$

Since [reactant] decreases during a reaction, d[reactant]/dt is negative. The negative sign is added to give a positive value to rate.

Units of rate: **mol dm^{-3} s^{-1}** (or other units of time, e.g. mol dm^{-3} min^{-1})

Consider the reaction: $H_2 + I_2 \rightarrow 2HI$

For every mole of H_2 that is consumed, one mole of I_2 is also consumed and 2 moles of HI are formed. Hence, the change in concentrations of H_2 and I_2 are the same, but the change in concentration of HI is two times faster.

We express the rate as: $\text{rate} = -\frac{d[H_2]}{dt} = -\frac{d[I_2]}{dt} = \frac{1}{2}\frac{d[HI]}{dt}$

When there are different coefficients in the chemical equation, we commonly define the rate in terms of the substance with a coefficient of 1.

Exercise 2.1 (worked example)

For the reaction, $BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$, which of the following relationships are correct?

1 $\frac{d[Br_2]}{dt} = \frac{d[H_2O]}{dt}$

2 $\frac{d[Br_2]}{dt} = -\frac{d[BrO_3^-]}{dt} \times 3$

3 $-5\frac{d[Br^-]}{dt} = -6\frac{d[H^+]}{dt}$

A **1**, **2** and **3** are correct

B **1** and **2** only are correct

C **2** and **3** only are correct

D **1** only is correct

For every mole of $BrO_3^-(aq)$ consumed, 5 moles of $Br^-(aq)$ and 6 moles of $H^+(aq)$ are consumed, while 3 moles of $Br_2(aq)$ is produced. Hence we can see that the rate of consumption of $H^+(aq)$ is the highest, followed by rate of consumption of $Br^-(aq)$, then rate of production of $Br_2(aq)$. The rate of consumption of $BrO_3^-(aq)$ is the slowest.

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We express the rate as: rate = $-\frac{d[BrO_3^-]}{dt} = -\frac{1}{5}\frac{d[Br^-]}{dt} = -\frac{1}{6}\frac{d[H^+]}{dt} = \frac{1}{3}\frac{d[Br_2]}{dt}$ based on the coefficients of the aqueous species present. Hence only options 1 and 2 are correct.

2.2 Instantaneous, Initial and Average Rates

Since the rate of a reaction is defined as the change in concentration of a reactant or a product per unit time, we can obtain the **rate** of a reaction from the **gradient** of the tangent of a **concentration-time graph**.

Figure 1 shows the concentration-time graphs for the decomposition of dinitrogen tetraoxide into its monomers: $N_2O_4(g) \rightarrow 2NO_2(g)$.

The rate of a reaction at a specified time *t* is called the **instantaneous rate of reaction**. It can be determined from the gradient of the tangent at time *t*, as shown in Figure 1.

When *t* = 0, the rate is called the **initial rate of reaction**, which is the rate at the start of a reaction. It can be determined from the gradient of the tangent at *t* = 0.

The **average rate of reaction** is the change in concentration of a reactant or a product over a specified time interval.

A *negative* gradient indicates a *decrease* in concentration while a *positive* gradient indicates an *increase* in concentration. In Figure 1, the $[N_2O_4]$-time graph has a negative gradient since N_2O_4 is the reactant, while the $[NO_2]$-time graph has a positive gradient since NO_2 is the product.

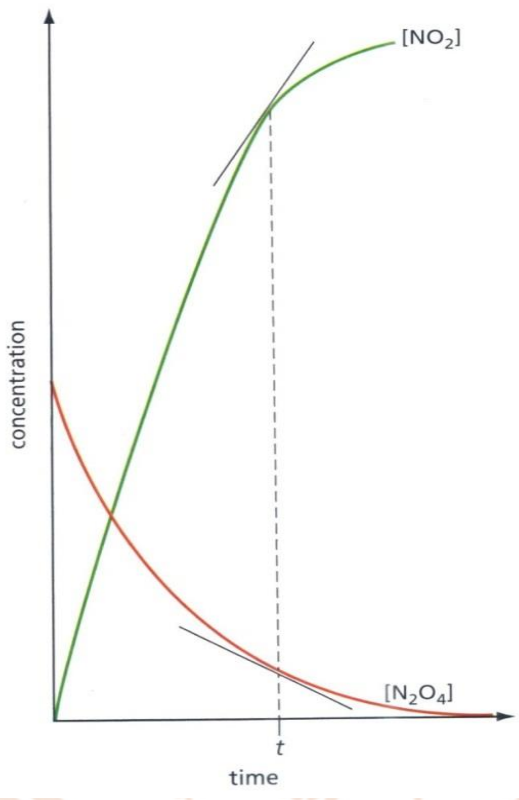


Figure 1. Concentration-time graphs for the reaction, $N_2O_4(g) \rightarrow 2NO_2(g)$

The *steeper* the gradient, the *faster* the rate of reaction. When gradient is zero, there is no change in concentration. This means rate of reaction is zero, i.e. the reaction has *stopped*.

By comparing the gradients of the tangents at time *t*, we can see that the rate of change in concentration of NO_2 is twice as fast as the rate of change in concentration of N_2O_4.

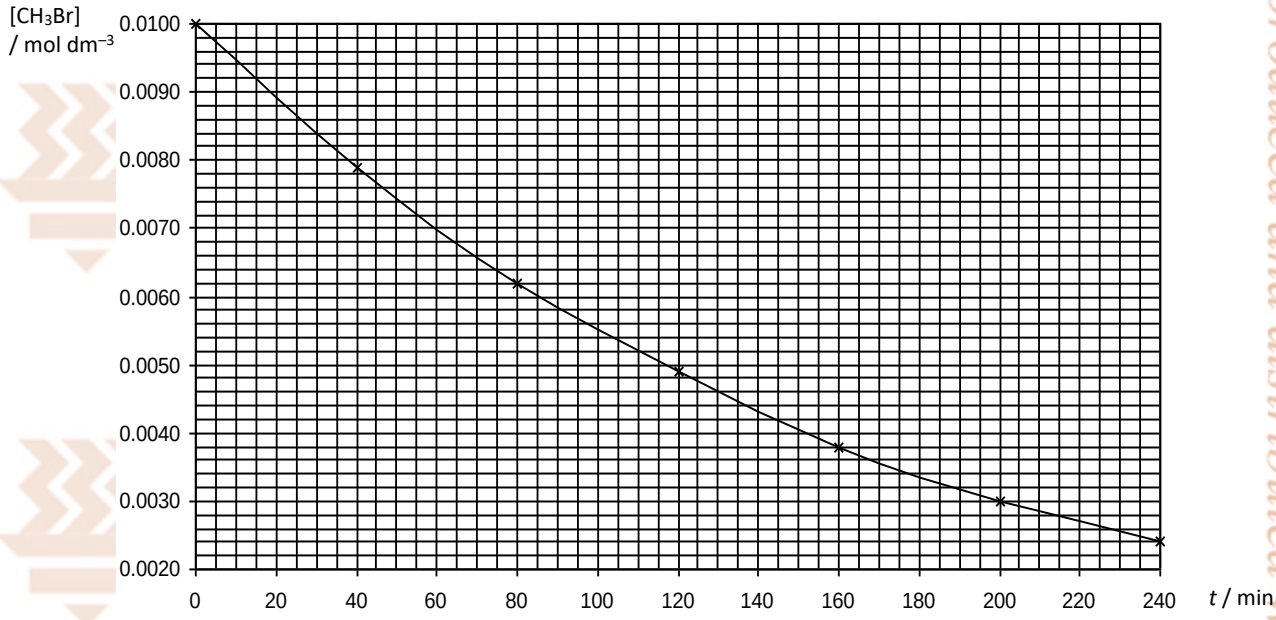
The rate of reaction at time *t* can be expressed as: rate = $-\frac{d[N_2O_4]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt}$

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Exercise 2.2 *[source of data: N2000/1/3]* **(worked example)**

The following data and graph were obtained for the reaction, $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$.

time t /min	0	40	80	120	160	200	240
$[CH_3Br]$ /mol dm^{-3}	0.0100	0.0079	0.0062	0.0049	0.0038	0.0030	0.0024



(a) Determine the initial rate of the above reaction.

Note that the units of rate follows the unit of time on the x-axis in the concentration-time graph.

The initial rate is the rate of reaction at t = 0. Draw a tangent at t = 0 min to find the gradient. Note that although the gradient is negative, the rate of a reaction is always expressed as a positive number.

$$\text{initial rate} = -\frac{0.0100 - 0.0024}{0 - 140} = \mathbf{5.43 \times 10^{-5}\ mol\ dm^{-3}\ min^{-1}}$$

A range of answers is accepted to accommodate errors. [Range: 4.80 to 6.00 $\times$ 10^{-5} mol dm^{-3} min^{-1}]

(b) Determine the instantaneous rate of the above reaction at t = 120 min.

Draw a tangent at t = 120 min to find the instantaneous rate at 120 min.

$$\text{rate at 120 min} = -\frac{0.0076 - 0.0032}{30 - 175} = \mathbf{3.03 \times 10^{-5}\ mol\ dm^{-3}\ min^{-1}}$$

[Range: 2.50 to 3.10 $\times$ 10^{-5} mol dm^{-3} min^{-1}]

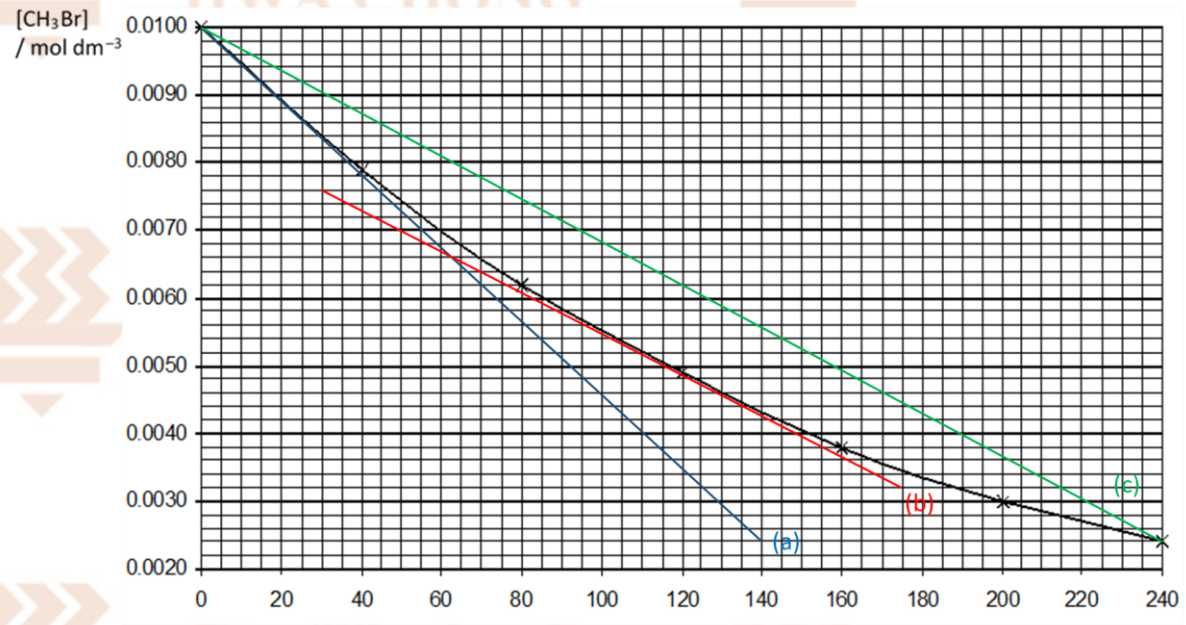
(c) Determine the average rate of the above reaction for the first 120 min.

$$\text{average rate} = \frac{\text{overall change in } [CH_3Br]}{\text{overall time taken}} = -\frac{0.0049 - 0.0100}{120} = \mathbf{4.25 \times 10^{-5}\ mol\ dm^{-3}\ min^{-1}}$$

(You draw a straight line from the first point to the last point and find the gradient of this line)
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Refer to the diagram below for the graphs you are expected to draw in each case.



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3 RATE EQUATION, ORDER OF REACTION AND RATE CONSTANT

LO8(a)part: explain and use the terms: rate equation; order of reaction; rate constant

3.1 Rate equation, order of reaction and rate constant

The stoichiometric equation cannot be used to predict how concentration of reactants affects the rate of a reaction. Instead, we obtain this data experimentally and summarise it in the form of a **rate equation**, or rate law.

Consider the reaction: $a\,\mathbf{A} + b\,\mathbf{B} \rightarrow$ products

The rate equation for this reaction is given by: rate = $k\,[\mathbf{A}]^m\,[\mathbf{B}]^n$

where m and n are the orders of reaction with respect to [**A**] and [**B**] respectively
and k is the rate constant

The **rate equation** is an experimentally determined equation that relates the rate of reaction to the concentrations of the reactants raised to appropriate powers.

The **order of reaction with respect to a reactant** is the power on its concentration term in the rate equation. The order of reaction must be determined experimentally.

The **overall (or total) order of reaction** is the sum of the individual orders.

The **rate constant**, ***k***, is the proportionality constant in the experimentally-determined rate equation. It is a constant at a given temperature.

The stoichiometric coefficients in the chemical equation are **not** necessarily related to the values of the orders of reaction in the rate equation. This is illustrated by the data in the table below.

Reaction	**Rate Equation**
$CH_3Br(aq) + OH^-(aq) \rightarrow CH_3OH(aq) + Br^-(aq)$	Rate = $k[CH_3Br][OH^-]$
$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2 + H_2O$	Rate = $k[BrO_3^-][Br^-][H^+]^2$
$CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$	Rate = $k[CHCl_3][Cl_2]^{1/2}$

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3.2 Understanding order of reaction

The order of reaction with respect to a reactant, **A**, tells us how the concentration of that reactant affects the reaction rate.

Consider the reaction: a **A** + b **B** → products

If the rate of reaction is

- **independent** of the concentration of **A**, i.e. changes in [**A**] do not change the rate of reaction, then: rate ∝ [**A**]^0 and order of reaction is **zero order** with respect to [**A**],
- **directly proportional to [A]**, i.e. when [**A**] doubles, rate doubles, then: rate ∝ [**A**]^1 and order of reaction is **first order** with respect to [**A**],
- **directly proportional to [A]^2**, i.e. when [**A**] doubles, rate quadruples (increases 4 times), then: rate ∝ [**A**]^2 and order of reaction is **second order** with respect to [**A**].

The order of reaction are usually positive integers (0, 1, 2…) although they can also be fractional or even negative.

For the reaction between nitrogen monoxide and hydrogen gas,

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

the rate equation was found experimentally to be: rate = $k[NO]^2[H_2]$

The reaction is thus second order with respect to [NO] and first order with respect to [H_2]. The overall order is third order (∵ 2 + 1 = 3). Note that the power '1' after [H_2] may be omitted in the rate equation.

Exercise 3.1 (worked example)
For the reaction between hydrogen peroxide and acidified iodide ions,

$$H_2O_2(aq) + 3I^-(aq) + 2H^+(aq) \rightarrow I_3^-(aq) + 2H_2O(l)$$

the orders of reaction with respect to [H_2O_2], [I^-] and [H^+] were found to be 1, 1 and 0 respectively.

(a) Write the rate equation for the reaction.

rate = $k[H_2O_2]^1[I^-]^1[H^+]^0$ or **rate = k[H_2O_2][I^-]**

The power '1' may be omitted in the rate equation. Any term raised to the power of zero is equal to 1, so the term [H^+]^0 could be omitted altogether.

(b) State the overall order of reaction.

overall order of reaction = 1 + 1 = **2**

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3.3 Understanding the rate constant

Besides concentration of reactants, temperature and presence of catalysts also affect the rate of a reaction. These factors are included in the rate constant, *k*.

The **Arrhenius equation** shows how the rate constant, *k*, is affected by temperature and activation energy:

$$k = Ae^{-Ea/RT}$$

where, A = pre-exponential factor
E_a = activation energy of the reaction (refer to Section 6.2)
R = molar gas constant
T = absolute temperature

From the Arrhenius equation, we can see that the rate constant, *k*

- **increases** with increase in temperature,
- **increases** with decrease in activation energy (due to presence of catalyst),
- is **unaffected** by changes in concentration (since there is no concentration term).

Consider again the rate equation, rate = $k[A]^m[B]^n$, we can see that the **larger** the rate constant, the **faster** is the rate of reaction.

The units for rate constant, *k*, depend on the **overall order** of the reaction.

For example, if the overall order is second order, the units for *k* can be deduced as follows:

$$\text{units of } k = \frac{mol\ dm^{-3} s^{-1}}{(mol\ dm^{-3})^2} = \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1} \text{ (or other units of time, e.g. mol}^{-1}\ \text{dm}^3\ \text{min}^{-1}\text{)}$$

Exercise 3.2
What are the units of the rate constant *k* for the following? Use 'second' as the units for time.

(a) Overall first order reaction: **(worked example)**

Overall first order reaction: units of $k = \frac{mol\ dm^{-3} s^{-1}}{mol\ dm^{-3}} = \mathbf{s^{-1}}$

(b) Overall third order reaction:

Overall th[illegible] dm^6 s^{-1}

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4 DETERMINING THE RATE EQUATION

To determine the rate equation, experiments are conducted to obtain data so that suitable graphs can be plotted to determine the orders of reaction with respect to each reactant. Alternatively, the initial rates method can also be used to determine the orders of reaction.

4.1 Determining order of reaction from graphs

Several graphs can be plotted to determine the order of reaction:

- concentration-time graph
- rate-concentration graph
- rate-time graph

4.1.1 Concentration-time graphs and half-life

LO8(b)part: construct and use rate equations of the form rate = k [A]^m [B]^n (limited to simple cases of single-step reactions and of multi-step processes with a rate-determining step, for which m and n are 0, 1 or 2), including: (ii) justifying, for zero- and first-order reactions, the order of reaction from concentration-time graphs
LO8(a)part: explain and use the terms: half-life of a reaction

For a particular reactant R that may affect the reaction rate, we express it as: rate = k[R]^m

How do we tell the order of reaction, m, with respect to [R] from a concentration-time graph?

Figure 2 shows three possible concentration-time graphs.

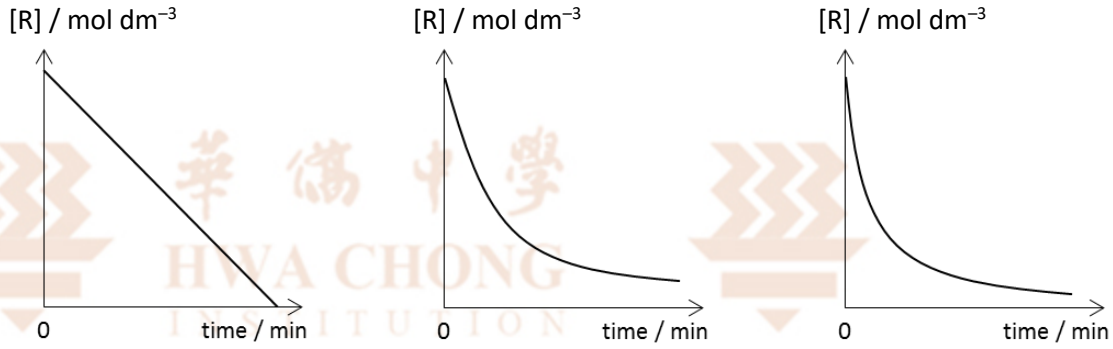


Figure 2

When studying concentration-time graphs, look at the **shape** of the graphs and when necessary the **half-life**. It is also useful to remember that the gradient represents the rate of reaction (Section 2.2).

*The **half-life**, $t_{½}$, of a reaction is the **time taken for the concentration of a reactant to decrease to half its initial value.***

- If the graph is a **straight line** with a constant gradient (Figure 2a), this means that rate is constant when [R] decreases during the course of reaction. i.e. rate is **independent** of [R]. Hence, the reaction is **zero order** with respect to [R].

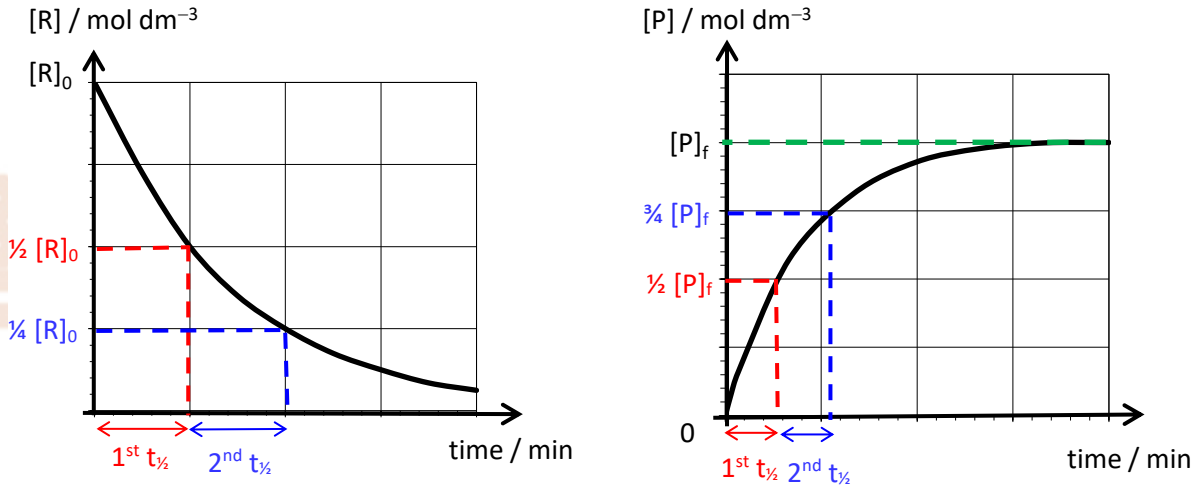
- If the graph is a **curve** with **constant half-life*** (Figure 2b), the reaction is **first order** with respect to [R]. In addition, as [R] decreases, rate decreases proportionally (see Section 4.1.2 Figure 4b).

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- If the graph is **curve** and half-lives are **not** constant (but become longer), the order of reaction with respect to [R] is **not** first order (Figure 2c). In this case, to confirm the order of reaction, we can determine the gradient (hence rate) of the concentration-time graph at various times and plot a rate-concentration graph (Section 4.1.2).

*** What does constant half-life mean?**

To show that half-life is constant, we find any **two half-lives** (usually the first and the second half-lives) and compare their values. If the two half-lives are the same, we say the reaction has a constant half-life. We can obtain half-lives from either a [reactant]-time graph (Figure 3a) or a [product]-time graph (Figure 3b).



(a) *(b)*

Figure 3

- $[R]_0$ is the initial concentration of reactant, R, at t = 0 min.
- The first half-life is the time taken for [R] to ***decrease*** from $[R]_0$ to $½[R]_0$.
- The second half-life is the time taken for [R] to ***decrease*** from $½[R]_0$ to $¼[R]_0$.
- $[P]_f$ is the final concentration of product, P, when the reaction is complete. This is obtained via stoichiometric calculations from the amount of reactants used.
- The first half-life is the time taken for [P] to ***increase*** from zero to $½[P]_f$ i.e. to produce the first 50% of the product.
- The second half-life is the time taken for [P] to ***increase*** from $½[P]_f$ to $¾[P]_f$ i.e. to produce 50% of the remaining 50% (or the next 25%).

LO8(c)(i): show understanding that the half-life of a first-order reaction is independent of concentration
LO8(c)(ii): use the half-life of a first-order reaction in calculations

For a reaction that is **first order** with respect to [R], the half-life is **independent** of [R] and is related to the rate constant, *k*, by the following equation:

$$t_{½} = \frac{\ln 2}{k}$$

where *k* is the rate constant in rate equation rate = *k*[R]

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Why is the half-life of a first order reaction constant? (Background Info):
To prove this, we need to apply some calculus.

$$\text{rate} = -\frac{d[R]}{dt} = k[R]$$

On integrating $[R]_t = [R]_0 e^{-kt}$ $[R]_0$ = [R] at time = 0; $[R]_t$ = [R] at time = t

$\ln[R]_t = \ln[R]_0 - kt$

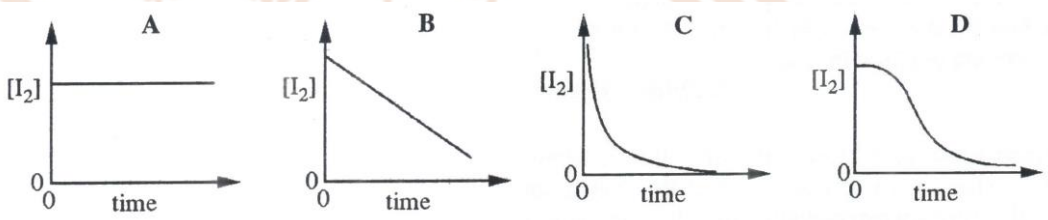
Substitute $[R]_t = ½[R]_0$ and $t = t_{½}$, $\ln ½[R]_0 = \ln[R]_0 - kt_{½}$

$$t_{½} = \frac{\ln 2}{k}$$

In addition, we can also show that [R] after *n* half-lives = $[R]_0 \times (½)^n$

Exercise 4.1

(a) The reaction of iodine with propanone in the presence of aqueous acid is zero order with respect to iodine. Which diagram represents the variation of $[I_2]$ with time? **(worked example)**



[J98/3/12]

Answer: B

The gradient of the graphs at any point tells us the rate of reaction at that point in time.

In option A, the gradient is 0. This means that there is no rate of reaction, meaning the reaction does not even occur.

In option B, the graph is a straight-line graph. This means that the rate, which is represented by the gradient of the graph, is constant throughout. Therefore rate of reaction is independent of the $[I_2]$ and it is zero order with respect to iodine.

In option C, the gradient is decreasing over time, so the rate of reaction decreases when $[I_2]$ decreases. Hence it cannot be zero order with respect to iodine.

The last graph shows a graph with a rate that is slow at the beginning, increases over time, then decreasing again nearing the end of the reaction. It is definitely not zero order with respect to iodine.

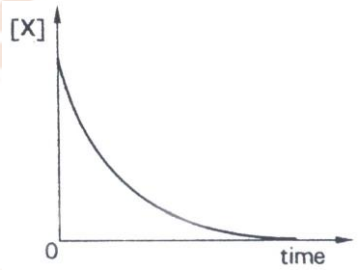
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(b) The following reaction was believed to be of first order.

$$\mathbf{X} \rightarrow \text{products}$$

In an experiment, [**X**], the concentration of **X**, varied with time as shown in the graph.



What can the graph be used for?

1 to determine the rate of reaction at any given instant
2 to check whether the reaction is of first order throughout
3 to determine the half-life of the reaction

[N92/4/34] modified

Exercise 4.2

(a) The rate of removal of the pain-killing drug paracetamol from the body is a first order reaction with a rate constant, k = 0.26 hr^{-1}. How long will it take to remove 75% of the paracetamol that a patient consumes? **(worked example)** *[PrelimIJC14/I/15]*

half-life = $\frac{\ln 2}{k} = \frac{\ln 2}{0.26}$ hr

Since [R] after n half-lives = $[R]_0 \times (½)^n$

$1 - 0.75 = 0.25 = 1 \times (\frac{1}{2})^n \Rightarrow n = 2$

Time taken = $2 \times \frac{\ln 2}{0.26}$ = **5.3 hr**

You can also view the video explanation via this link.

(b) Lead is the final product formed by a series of changes in which the rate-determining stage is the radioactive decay of uranium-238. This radioactive decay is a first-order reaction with a half-life of 4.5 × 10^9 years. What would be the age of a rock sample, originally lead-free, in which the molar proportion of uranium to lead is now 1:3? *[PromoNYJC12/I/18]*

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4.1.2 Rate-concentration graphs

Besides concentration-time graphs, another way to find the order is to use rate-concentration graphs. To obtain a rate-concentration graph, we find the gradient of the concentration-time graph at various points to obtain the rates. These rates can then be plotted against their corresponding concentrations.

For a particular reactant R that may affect the reaction rate, we express it as: rate = $k[R]^m$

How do we tell the order of reaction, m, with respect to [R] from a rate-concentration graph?

Figure 4 shows three possible rate-concentration graphs.

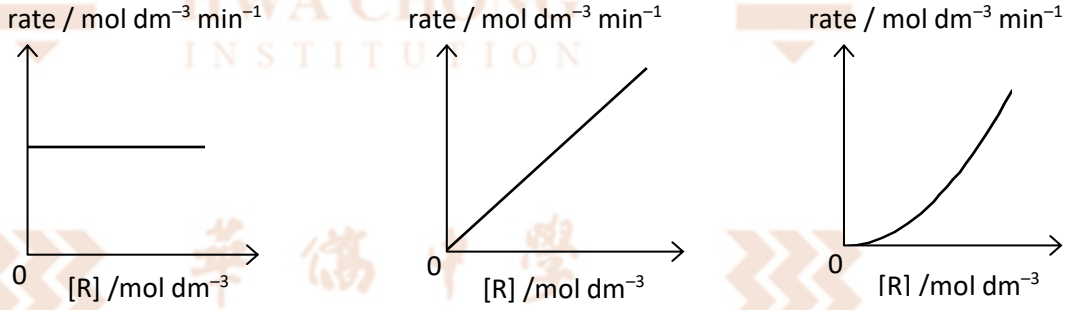


Figure 4

When studying rate-concentration graphs, look at the **shape** of the graphs. It is also useful to deduce the mathematical equation of the graph.

- If the graph is a **horizontal line** (Figure 4a), rate is constant when [R] changes or rate is **independent** of [R], i.e. rate = $k[R]^0$. The reaction is **zero order** with respect to [R].

- If the graph is a **straight line passing through the origin** (Figure 4b), rate is **directly proportional** to [R], i.e. rate = $k[R]^1$. The reaction is **first order** with respect to [R].

- If the graph is a **parabola** (Figure 4c), the order of reaction with respect to [R] is not 1. In order to confirm the order of reaction, we should plot a graph that is a straight line.

  For example, if the order of reaction is 2, the rate equation is rate = $k[R]^2$. We can plot rate on the y-axis and $[R]^2$ on the x-axis as shown in Figure 5a. Alternatively, we can also obtain the log form of the rate equation: lg rate = lg k + 2lg[R]. When lg rate is plotted against lg [R], the gradient is the order of reaction (Figure 5b).

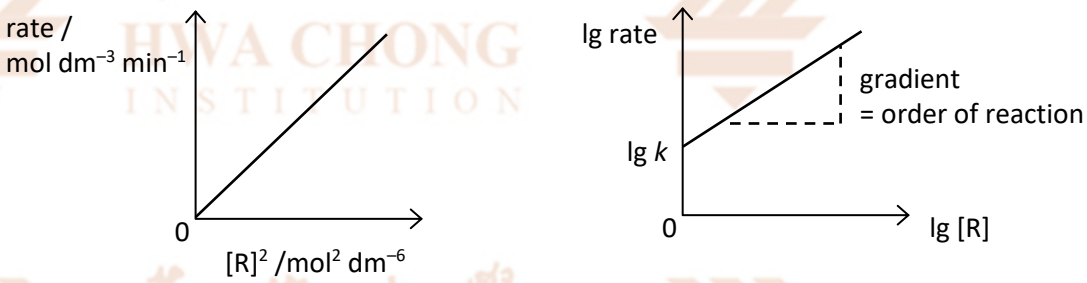


Figure 5

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Exercise 4.3 (worked example)

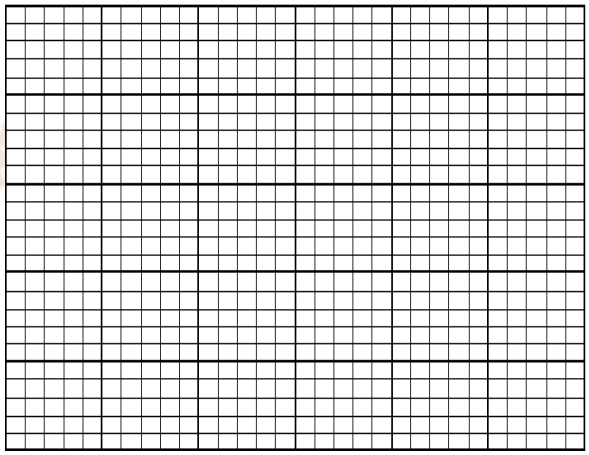
In tetrachloromethane at 45 °C, dinitrogen pentaoxide, N_2O_5, decompose as follows:

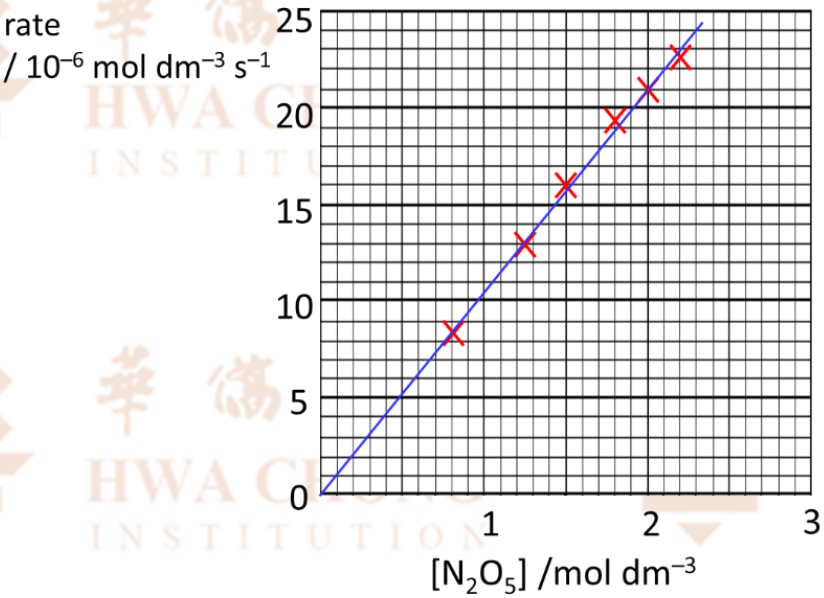
$$N_2O_5 \rightarrow 2NO_2 + \tfrac{1}{2}O_2$$

The rate of the reaction was measured for different concentrations of N_2O_5. The results are shown in the table below.

$[N_2O_5]$ / mol dm^{-3}	2.21	2.00	1.79	1.51	1.23	0.82
rate / mol dm^{-3} s^{-1}	22.7 x 10^{-6}	21.0 x 10^{-6}	19.3 x 10^{-6}	15.7 x 10^{-6}	13.0 x 10^{-6}	8.3 x 10^{-6}

(a) Plot a graph of rate against $[N_2O_5]$.





(b) Use your graph to find the order of the reaction with respect to $[N_2O_5]$.

Since the graph is a straight line passing through the origin, rate is directly proportional to $[N_2O_5]$. Hence, the reaction is first order with respect to $[N_2O_5]$.

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(c) Write the rate equation for the reaction.

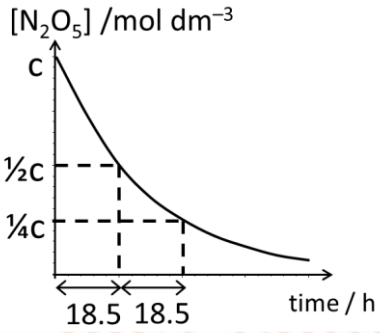
rate = $k[N_2O_5]$

(d) Calculate the rate constant, giving its units.

This is a graph of rate vs $[N_2O_5]$.

Hence, k = gradient of graph = $24 \times 10^{-6} / 2.3$ **= 1.04 × 10^{-5} s^{-1}**

(e) Sketch the graph of $[N_2O_5]$ against time. Mark clearly the value of the half-life on your graph.



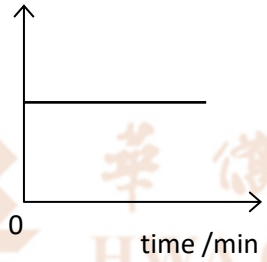
4.1.3 Rate-time graphs

Rate-time graphs are less useful because they do not offer much more information than the concentration-time graphs on which they are based. To obtain a rate-time graph, we find the gradient of the concentration-time graph at various points to obtain the rates. These rates can then be plotted against time.

Figure 6 shows the rate-time graphs for reactions which are zero, first and second order with respect to [R] respectively.

zero order

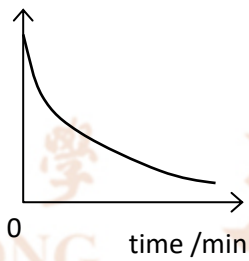
rate / mol dm^{-3} min^{-1}



- rate remains constant, except when the reaction is complete

first order

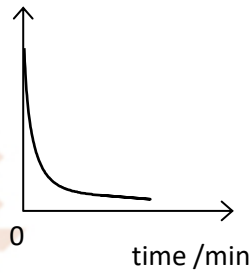
rate / mol dm^{-3} min^{-1}



- rate decreases exponentially with time

second order

rate / mol dm^{-3} min^{-1}



- rate decreases exponentially with time
- decrease is faster compared to a first order reaction

Figure 6

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4.2 Determining order of reaction using initial rates method

LO8(b)part: construct and use rate equations of the form rate = k $[A]^m$ $[B]^n$ (limited to simple cases of single-step reactions and of multi-step processes with a rate-determining step, for which m and n are 0, 1 or 2), including: (i) deducing the order of a reaction by the initial rates method (v) calculating an initial rate using concentration data
LO8(d): calculate a rate constant using the initial rates method

The initial rates method is studying how the initial rate changes when the initial concentration of a reactant is changed, and hence determine the order of reaction with respect to that reactant. Typically, the initial concentration of all other reactants are kept constant.

Initial rate is found from the gradient of tangent at *time* = 0 of a concentration-time graph (Section 2.2). Initial rate can also be approximated to average rate using a 'clock' method (Section 5.2).

Exercise 4.4 (worked example)

In investigations of the reaction, 2**A**(aq) + 2**B**(aq) + **C**(aq) → products, the following results are obtained.

Experiment	Initial concentration / mol dm^{-3}			Initial rate of reaction / mol dm^{-3} s^{-1}
	[**A**]	[**B**]	[**C**]	
1	0.010	1.00	0.50	2.0×10^{-3}
2	0.030	1.00	0.50	6.0×10^{-3}
3	0.030	2.00	0.50	2.4×10^{-2}
4	0.030	2.00	0.25	2.4×10^{-2}
5	0.040	2.50	0.40	?

(a) Determine the order of reaction with respect to **A**, **B** and **C**.

Let the rate equation be: rate = k $[\mathbf{A}]^x$ $[\mathbf{B}]^y$ $[\mathbf{C}]^z$

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k\,(0.03)^x(1.0)^y(0.5)^z}{k\,(0.01)^x(1.0)^y(0.5)^z}$$

$$\frac{6 \times 10^{-3}}{2 \times 10^{-3}} = \frac{(0.03)^x}{(0.01)^x}$$

$$3 = 3^x$$

$\Rightarrow$ order of reaction w.r.t. [**A**] = x = 1

$$\frac{\text{rate}_3}{\text{rate}_2} = \frac{k\,(0.03)^x(2.0)^y(0.5)^z}{k\,(0.03)^x(1.0)^y(0.5)^z}$$

$$\frac{2.4 \times 10^{-2}}{6 \times 10^{-3}} = \frac{2^y}{1^y}$$

$$4 = 2^y$$

$\Rightarrow$ order of reaction w.r.t. [**B**] = y = 2

$$\frac{\text{rate}_3}{\text{rate}_4} = \frac{k\,(0.03)^x(2.0)^y(0.5)^z}{k\,(0.03)^x(2.0)^y(0.25)^z}$$

$$\frac{2.4 \times 10^{-2}}{2.4 \times 10^{-2}} = \frac{(0.5)^z}{(0.25)^z} = 2^z$$

$\Rightarrow$ order of reaction w.r.t. [**C**] = z = 0

Alternative method (by inspection):

Comparing experiments 1 and 2, [**B**] and [**C**] are constant, when [**A**] is increased 3 times, initial rate increased 3 times. $\therefore$ rate $\propto$ [**A**], the reaction is first order with respect to [**A**].

In experiments 2 and 3, [**A**] and [**C**] are unchanged. When [**B**] is increased 2 times, initial rate increased 4 times. $\therefore$ rate $\propto$ $[\mathbf{B}]^2$, order of reaction with respect to [**B**] = 2.

Compare experiments 3 and 4, only [**C**] is changed but the initial rate does not change.

$\therefore$ reaction is zero order with respect to [**C**].

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(b) Write the rate equation for the reaction.

rate = k [**A**] [**B**]^2

(c) Calculate the rate constant for the reaction, indicating units.

From experiment 1, $k = \frac{\text{rate}}{[A][B]^2} = \frac{2.0\times10^{-3}}{0.010\times1.00^2}$ = **0.200 mol^{-2} dm^6 s^{-1}**

(Note: you can choose to use any experiment, the answer will still be the same.)

(d) Calculate the initial rate for Experiment 5.

initial rate for Experiment 5 = k [**A**] [**B**]^2 = $0.2 \times 0.04 \times (2.5)^2$ = **0.0500 mol dm^{-3} s^{-1}**

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Exercise 4.5

(a) **(worked example)** Trichloromethane reacts with aqueous sodium hydroxide according to the equation shown below.

$$2CHCl_3 + 7OH^- \rightarrow CO + HCO_2^- + 6Cl^- + 4H_2O$$

Some data were recorded in order to study the kinetics of the reaction:

Expt	Initial [$CHCl_3$] / mol dm^{-3}	Initial [OH^-] / mol dm^{-3}	Initial rate / mol dm^{-3}s^{-1}
1	0.100	0.120	1.0×10^{-4}
2	0.050	0.240	1.0×10^{-4}
3	0.050	0.480	2.0×10^{-4}

If k is the rate constant, what is the rate equation?

A rate = $k[OH^-]$ **B** rate = $k[CHCl_3]\,[OH^-]$

C rate = $k[CHCl_3]^2\,[OH^-]$ **D** rate = $k[CHCl_3]\,[OH^-]^2$

Comparing experiments 2 and 3, [**$CHCl_3$**] and [**OH^-**] are constant, when [**OH^-**] is increased 2 times, initial rate increased 2 times. ∴ rate ∝ [**OH^-**], the reaction is first order with respect to [**OH^-**].

Let the rate equation be: rate = k [**$CHCl_3$**]^x [**OH^-**]

$$\frac{rate_2}{rate_1} = \frac{k\,(0.050)^x(0.240)}{k\,(0.100)^x(0.120)}$$

$$\frac{1.0\times10^{-4}}{1.0\times10^{-4}} = \frac{(0.050)^x}{(0.100)^x} \times 2 \Rightarrow x = 1$$

⇒ order of reaction w.r.t. [**$CHCl_3$**] = x = 1

rate = $k[OH^-]$

(b) Hydrogen peroxide reacts with acidified iodide ions, liberating iodine. In investigations of this reaction, the following results were obtained.

Initial concentrations of reactants / mol dm^{-3}			**Initial rate of formation of iodine / mol dm^{-3} s^{-1}**
[H_2O_2]	**[I^-]**	**[H^+]**	
0.010	0.010	0.10	2.0×10^{-6}
0.030	0.010	0.10	6.0×10^{-6}
0.030	0.020	0.10	1.2×10^{-5}
0.030	0.020	0.20	1.2×10^{-5}

Which statements follow from these results?

1 The rate equation for the reaction can be written: rate = $k[H_2O_2][I^-]$.
2 The reaction is zero order with respect to the acid.
3 The rate constant is 2×10^{-1} mol^{-2} dm^6 s^{-1}.

A **1**, **2** and **3** are correct
B **1** and **2** only are correct
C **2** and **3** only are correct
D **1** only is correct

[N96/IV/34]

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(c) The table shows experimental results obtained for the following reaction:

$$2XO(g) + O_2(g) \rightarrow 2XO_2(g)$$

Partial pressure of XO (in arbitrary units)	Partial pressure of O_2 (in arbitrary units)	Relative rate
100	100	1.00
100	25	0.25
50	100	0.50
50	?	0.125

What is the missing value of the partial pressure of O_2 in the table?

A 25 **B** 40 **C** 50 **D** 75

[N90/1/13]

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Summary

The rate equation is an experimentally determined equation that relates the rate of reaction to the concentrations of the reactants raised to appropriate powers.

$$\text{rate} = k\,[\mathbf{A}]^m\,[\mathbf{B}]^n$$

effects of temperature and catalyst are included in k

The order of reaction can be determined from concentration-time graphs or rate-concentration graphs. Alternatively, we can determine initial rates and apply the initial rates method.

Complete the table below by sketching the graphs for a particular reactant that may affect the reaction rate where rate = k[reactant]^m (m = 0, 1 or 2).

zero order **rate = k[reactant]^0 = k**	**first order** **rate = k[reactant]^1**	**second order** **rate = k[reactant]^2**
rate 0 [reactant]	rate 0 [reactant]	rate 0 [reactant]
[reactant] 0 time	[reactant] 0 time	[reactant] 0 time
[product] 0 time	[product] 0 time	[product] 0 time

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5 EXPERIMENTAL TECHNIQUES FOR STUDYING RATE OF REACTION

LO8(e): devise a suitable experimental technique for studying the rate of a reaction, from given information

In Section 4, we looked at two ways to determine order of reaction: using graphs e.g. concentration-time graph and using the initial rates method. In this section, we will look at how experiments can be carried out to obtain the data to plot the graphs or to obtain initial rates.

There are two approaches we can use:

- sampling method – involves taking samples from a reaction mixture at regular time intervals to analyse a reactant or product so that we know how fast it is consumed or produced; the data collected is used to plot 'concentration'-time graphs.
- 'clock' method – involves recording the time taken for the reaction to occur to a small extent; the time taken gives us an approximation of initial rates.

5.1 Sampling method

Depending on the reaction we are studying, the concentration of a 'chosen' reactant or product may be determined by titration or by measuring a physical property which changes as the reaction proceeds (e.g. the volume of gas produced, colour intensity of the reaction mixture etc.). Measuring a physical property can be more convenient because it does not 'disturb' the reaction. Both the titres and the physical properties can be related to changes in concentration of a reactant or product.

5.1.1 Sampling and titration

The acid-catalysed iodination of propanone can be studied by sampling followed by titration.

$$CH_3COCH_3(aq) + I_2(aq) \xrightarrow{H^+} CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

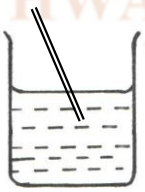
The experiment consists of the following steps:

Step 1 Preparation of reaction mixture

Reactants and acid catalyst of known volumes and concentrations are mixed thoroughly

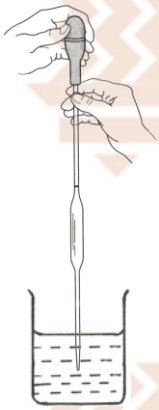


stop-watch started at the instant of mixing



The reaction mixture should be placed in a thermostatically controlled water bath as rate is affected by temperature.

Step 2 Withdrawal of sample



A **small fixed sample** e.g. 10.0 cm^3 is withdrawn from the reaction mixture using a pipette before the time of e.g. 5 min.

Step 3 Quenching of reaction in sample

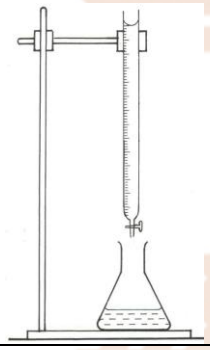
At exactly 5 min (in this e.g.), excess $NaHCO_3(aq)$ is added into the withdrawn sample (to remove the acid catalyst). This slows down the reaction significantly such that it may be regarded as virtually stopped.

excess $NaHCO_3(aq)$



withdrawn sample placed in conical flask

Step 4 Analysis of sample by titration



Titrate iodine remaining in the quenched sample with aqueous sodium thiosulfate, $Na_2S_2O_3(aq)$, of known concentration, using starch as indicator.

Repeat steps 2 to 4 at 10 min, 15 min, etc., to collect sufficient number of data points to plot a 'concentration'-time graph.

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There are several points to note for a sampling and titration method:

- The concentration of the reactants and products in the samples that are withdrawn (at various times) are the same as the concentrations in the reaction mixture.

- To determine the concentration of a reactant or product at a specific time, **the reaction in the sample should not continue to take place while it is being analysed**. Hence, quenching of the sample must be done before the titration by adding a large volume of cold water to slow down the reaction (by rapid dilution and cooling) or by neutralising an acidic reactant with a base or vice-versa which will stop the reaction completely.

- Since the **titre is proportional to the concentration** of the reactant (or product), a titre-time graph would be equivalent to a concentration-time graph. The order of reaction can then be determined from the graph (see Section 4.1.1).

- All other factors that might affect the rate should be kept constant:
  - **Temperature** can be kept **constant** by placing the reaction mixture in a thermostatically controlled water bath.

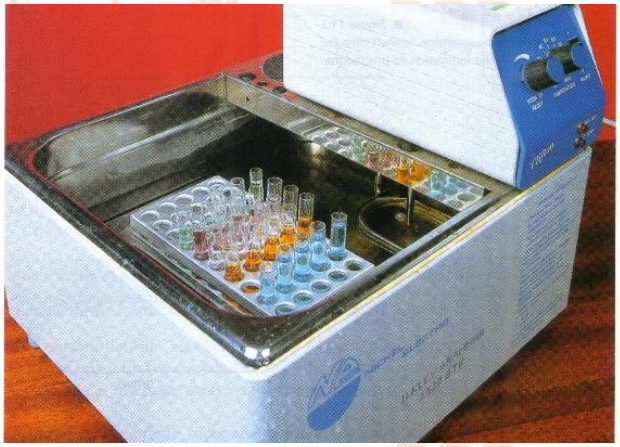


Figure 7. A thermostatically controlled water bath

  - The other reactants which are not being 'monitored' are used in **large excess** (around 10 times more concentrated). During the course of the reaction, their concentrations vary so little that they 'appear' constant. We assume they **do not affect the rate**, i.e. we say the reaction is **pseudo zero order** with respect to these reactants. Their actual order may not be zero and has to be determined by further experiments.

For example, in the acid-catalysed iodination of propanone, we follow the changes in $[I_2]$ so propanone and H^+ have to be in large excess. The graph of $[I_2]$ vs time reflects the order w.r.t. $[I_2]$ *only* if [propanone] and $[H^+]$ do not vary much during the course of reaction.

Reactant	Initial concentration /mol dm^{-3}	Concentration at the end of the reaction /mol dm^{-3}
I_2	0.002	0
propanone	0.4	0.4 – 0.002 = 0.398
H^+	0.4	0.4 + 0.002 = 0.402

H^+ is not used up during the reaction because it is a catalyst; its concentration increases because it is also being produced by the reaction.

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Generic procedure for sampling followed by titration

1. To prepare the reaction mixture, **measure** _(volume)_ cm^3 of __(reactant X)__ into a 250 cm^3 beaker (or conical flask) using a _(volume)_ cm^3 measuring cylinder.
2. **Measure** _(volume)_ cm^3 of __(last reactant)_ using a **measuring cylinder**. **Add** __(last reactant)__ to the mixture and **start the stop-watch at the same time**. Swirl to ensure mixing.
3. Before _(your chosen time, say 5 min from the start of the reaction)__, pipette 10.0 cm^3 of the reaction mixture into a conical flask.
4. **At (your chosen time), quench** the withdrawn sample by adding to it _(volume)_ cm^3 of __(suitable quenching reagent)__. Record the exact time of quenching (but don't stop the stop-watch!).
5. Carry out the **titration** of the quenched sample. (Details of titration steps needed. Refer to the Planning section in Topic 4 Reactions & Stoichiometry)
6. Before ___(each of your subsequent chosen times)___, repeat steps 3 and 4. Carry out the **titration** of each quenched sample. (At least 5 samples are collected to obtain data points to plot the graph.)

Note:

- Only one accurate titration is possible for each withdrawn sample.
- The reactant under study should be isolated, i.e. the other reactants should be in large excess (around 10 times more concentrated), so that the order of reaction with respect to that reactant alone can be determined.
- A burette cannot be used to add the last reactant (Step 2) as it has to be added *rapidly*.

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Exercise 5.1 [N91/3/3 modified] **(worked example)**
A dilute solution of hydrogen peroxide can be used to bleach hair. It decomposes slowly in aqueous solution according to the following equation:

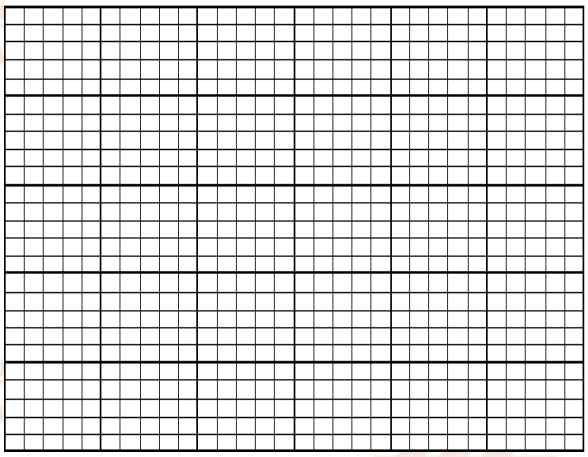
$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

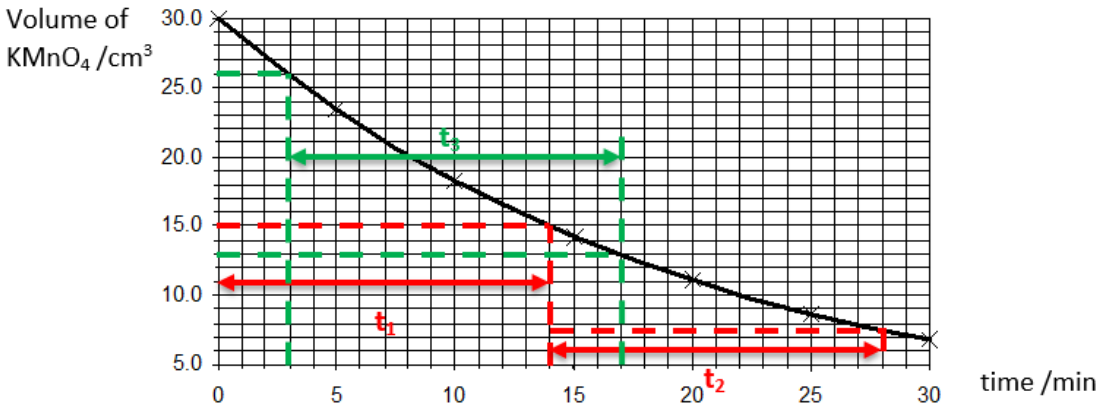
A solution with an original concentration of 3.0 mol dm^{-3} was placed in a bottle contaminated with transition metal ions, which act as catalysts for the decomposition. The reaction was followed by withdrawing 10.0 cm^3 portions at various times and titrating with acidified 0.1 mol dm^{-3} $KMnO_4$(aq). (5 mol of H_2O_2 react with 2 mol of $KMnO_4$)

The following results were obtained:

Time /min	0	5	10	15	20	25	30
Volume of $KMnO_4$ /cm^3	30.00	23.40	18.30	14.20	11.10	8.70	6.80

(a) Plot a graph of volume of $KMnO_4$ against time and use it to find the order of reaction with respect to hydrogen peroxide.





$t_1 = t_2 = 14$ min, ∴ **half-life is constant at 14 min**
∴ reaction is **first order** with respect to $[H_2O_2]$

At time t, volume of $KMnO_4$ $\propto$ $[H_2O_2]_{mixture}$
Hence, graph of volume of $KMnO_4$ vs time is equivalent to graph of $[H_2O_2]_{mixture}$ vs time.
We can use the graph of volume of $KMnO_4$ vs time to deduce the order w.r.t. $[H_2O_2]$.

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(b) Write the rate equation for the reaction and calculate the rate constant, indicating its units.

rate = k [H_2O_2]

$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{14}$ = **0.0495 min^{-1}**

(c) Calculate the concentration of the H_2O_2 at the time the first portion was withdrawn. Hence estimate how long the solution had been in the contaminated bottle.

Amount of H_2O_2 in 1st portion = 5/2 × amount of MnO_4^- used in 1st titration
= 5/2 × 30/1000 × 0.1
= 7.50×10^{-3} mol

[H_2O_2] at the time the first portion was withdrawn = $\frac{7.5\times10^{-3}}{10} \times 1000$ = **0.750 mol dm^{-3}**

3.0 mol dm^{-3} → 1.5 mol dm^{-3} → 0.750 mol dm^{-3}
Two half-lives have passed.
∴ the solution had been in the bottle for 2 × 14 = 28 min

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5.1.2 Sampling and measuring a physical property

- **Measuring volume of gas produced**

This method is useful for reactions which produce gaseous products. For example, the reaction, $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$, may be studied by measuring the volume of O_2 gas produced using a graduated gas syringe or via the water displacement method.



Generic procedure for sampling via gas collection

The generic procedure is similar to the ones stated in the Planning section in Topic 3 The Gaseous State. In that section, two different set-ups were shown. We shall use set-up A as an example:

1. Using an electronic balance, weigh accurately about (mass) g of (solid reactant) in a weighing bottle.
2. Using a measuring cylinder, transfer (volume) cm^3 of (aqueous reactant) into a 250 cm^3 conical flask.
3. Carefully lower the weighing bottle containing (solid reactant) into the conical flask, ensuring the reactants do not mix. Insert the stopper to ensure a closed set-up.
4. **Set up** the apparatus as shown in the diagram (draw an appropriate diagram – refer to Planning section in Topic 3 The Gaseous State).
5. Record the **initial reading** (x cm^3) on the gas syringe.
6. **Shake** the conical flask to mix the reactants and **start the stopwatch at the same time**.
7. Continue to gently swirl the flask and **record the reading** on the gas syringe every ___(your chosen time interval)___ minute until the reaction is complete.

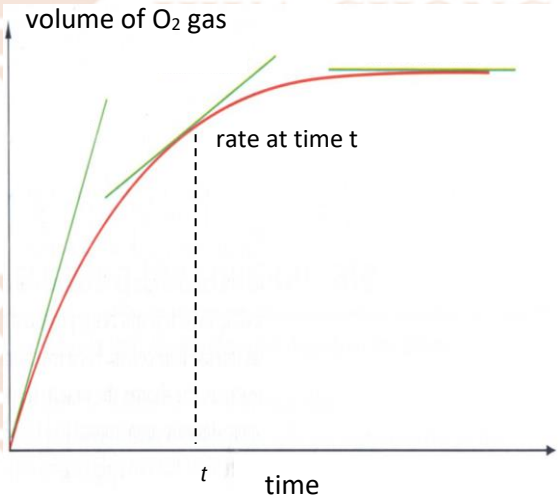


Figure 8. A typical graph of volume against time for a reaction that gives off a gas

The experimental results can be used to plot a graph of volume of O_2 gas produced against time.

The volume of O_2 produced is proportional to the *concentration* of O_2 at time *t*. The rate of change in volume of O_2 (gradient of tangent at time t) is directly proportional to the rate of reaction at time t.

Hence, Figure 8 is equivalent to a product concentration-time graph.

To determine the order of reaction with respect to $[H_2O_2]$, look at the shape of the graph and check if the half-life is constant (see Section 4.1.1).

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- **Measuring a change in absorbance using a colorimeter**

This method is suitable for a reaction in which one of the substances (reactant or product) is coloured or has a different colour from the others.

$$\underset{\text{brown}}{CH_3COCH_3(aq) + I_2(aq)} \xrightarrow{H^+} CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

For example, the reaction between iodine and propanone can be studied using this method.

A colorimeter measures the amount of light which is absorbed as it passes through a coloured solution – recorded as the absorbance of the solution. The more concentrated the coloured species is in the solution, the more light it will absorb and the greater the absorbance. The absorbance can be measured at regular time intervals using the colorimeter, and the rate of reaction is directly proportional to the rate of change in absorbance.

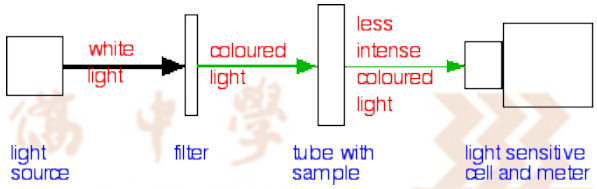


Figure 9. A simplified diagram of a colorimeter

- **Measuring a change in electrical conductivity**

This method is applicable for a reaction in aqueous solution in which there is a change in the **concentration of ions** (hence electrical conductivity).

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

For example, the reaction between bromate(V) and bromide ions results in a decrease in concentration of ions. The electrical conductivity of the aqueous solution can be measured at regular time intervals using a conductivity meter, and the rate of reaction is directly proportional to the rate of change in conductivity.

- **Measuring a change in gas pressure**

This method is suitable for reactions which involve a change in the **number of moles of gases** (hence total pressure).

For example, the reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ shows a reduction in number of moles of gases, hence total pressure decreases as the reaction proceeds. The total pressure of the reacting system is measured at regular time intervals by connecting the reaction flask to a **manometer**. The gaseous system is kept in a fixed-volume reactor maintained at constant temperature. Rate of reaction is directly proportional to the rate of change in pressure.

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Exercise 5.2 (worked example)

Hydrogen peroxide reacts with potassium manganate(VII) as follows:

$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$$

Suggest how two physical properties can be measured to study the rate of this reaction.

Measure intensity of purple colour of MnO_4^- using a colorimeter. The intensity of the purple colour is an indication of the concentration of MnO_4^-.
Measure volume of O_2 gas using a graduated gas syringe.

Exercise 5.3

Suggest methods of measuring the rates of the following reactions:

(a) zinc powder with aqueous copper sulfate (hint: write out the chemical equation first)

(b) oxidation of KI(aq) by $K_2S_2O_8$(aq), $S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$

(c) esterification: $CH_3CO_2H + C_2H_5OH \rightarrow CH_3CO_2C_2H_5 + H_2O$

(d) $(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + H^+ + Br^-$

(e) $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

5.2 'Clock' method and initial rate

A sampling method can be very tedious if the analysis is by titration. An alternative is to use a 'clock' method.

A 'clock' method involves measuring the time taken for the reaction to occur to a **small extent**. The reaction is set up to produce a *prominent change* e.g. colour change, when a small fixed volume (e.g. 5 cm^3) of gas or small amount of precipitate is formed. The **time taken for the prescribed change** to occur may be used as an **approximation of the initial rate of the reaction**.

By comparing the initial rates of two reaction mixtures, in which a different initial concentration of one reactant is used, we can deduce the order of reaction with respect to that reactant. Alternatively, the graph of initial rate vs initial concentration can be plotted and the reaction order deduced from the shape of the graph (see Section 4.1.2).

5.2.1 Reaction of $S_2O_8^{2-}$ and I^- (Iodine Clock)

The reaction between $S_2O_8^{2-}$ and I^- can be followed using a 'clock' method. The two reactants are mixed with a known small amount of sodium thiosulfate, $Na_2S_2O_3$, and a little starch indicator.

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq) \qquad \text{Reaction (1)}$$
$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq) \qquad \text{Reaction (2)}$$

Reaction (1) is the reaction whose kinetics is to be investigated. Initially, the I_2 produced in reaction (1) reacts with the $S_2O_3^{2-}$ to produce colourless products in reaction (2). Hence, the characteristic blue-

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black colour of the I_2-starch complex is not observed. When all the $S_2O_3^{2-}$ has been used up, the I_2, which is still being produced by reaction (1), reacts with the starch to give a blue-black colour.

The time taken, *t*, for this colour to appear may be used as an approximate measure of the initial rate of reaction (1). This is only an approximate value as it **assumes that the concentration-time graph is a straight line** from the origin to the point when the blue-black colour appears (Figure 10). The approximation is valid provided the reaction occurs to a **small extent**, i.e. the change in $[I_2]$, y, is small.

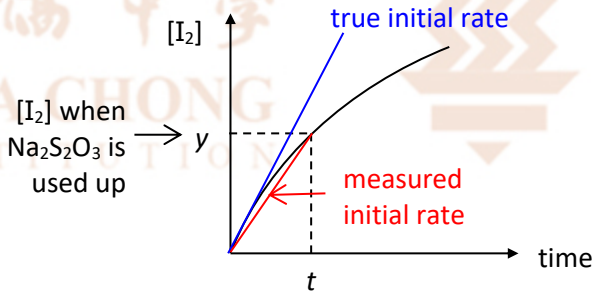


Figure 10

When y is small, initial rate = $\frac{d[I_2]}{dt} \approx \frac{y}{t}$ (i.e. the average rate)

If a *fixed amount of $Na_2S_2O_3$* is used in each reaction mixture, then *y* is constant, i.e. the blue colour appears for each reaction mixture after the *same amount of I_2 is produced*. We can then say **initial rate** $\propto \frac{1}{t}$.

The shorter the time, *t*, the faster the initial rate. We can simply compare the time taken for two experiments to compare their initial rates. For example, if the time taken is halved, the initial rate is doubled.

To find the order of reaction with respect to $[I^-]$, we prepare two reaction mixtures: Experiment 1 with $[I^-]$ = 0.2 mol dm^{-3}, and Experiment 2 with $[I^-]$ = 0.1 mol dm^{-3}. The rate of Experiment 1 is approximately equal to $\frac{y}{t_1}$, and the rate of Experiment 2 is approximately equal to $\frac{y}{t_2}$ (Figure 11).

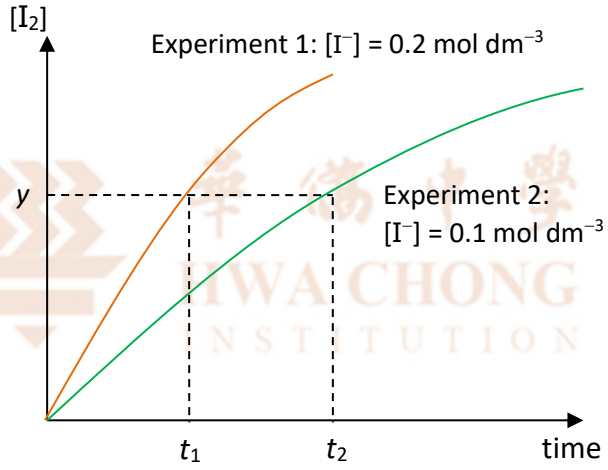


Figure 11

The ratio of times taken gives the ratio of the rates: $\frac{rate_1}{rate_2} = \frac{y/t_1}{y/t_2} = \frac{t_2}{t_1}$

Since $\frac{[I^-]_1}{[I^-]_2} = \frac{0.2}{0.1} = 2$, we can compare this ratio to that of the initial rates to deduce the order of reaction with respect to $[I^-]$.

To find the order of reaction with respect to $[S_2O_8^{2-}]$, we can prepare reaction mixtures with different initial concentrations of $S_2O_8^{2-}$ and analyse the results as above for I^-.

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5.2.2 Reaction of $S_2O_3^{2-}$ and H^+ (Sulfur Clock)

The reaction between hydrochloric acid and thiosulfate ions can also be studied using a 'clock' method.

$$Na_2S_2O_3(aq) + 2HCl(aq) \rightarrow \underset{\text{pale yellow ppt}}{S(s)} + SO_2(g) + 2NaCl(aq) + H_2O(l)$$

The fine precipitate of sulfur produced gradually makes the solution opaque. The time taken for the cross under the beaker to *just* become obscured may be used as an approximate measure of the initial rate.

Unlike the iodine clock in Section 5.2.1, we do not have to add another chemical to the reaction mixture to 'act' as the clock. By using the same cross, we ensure that the amount of sulfur produced each time in the different reaction mixtures (with different reactant concentration) are fixed.

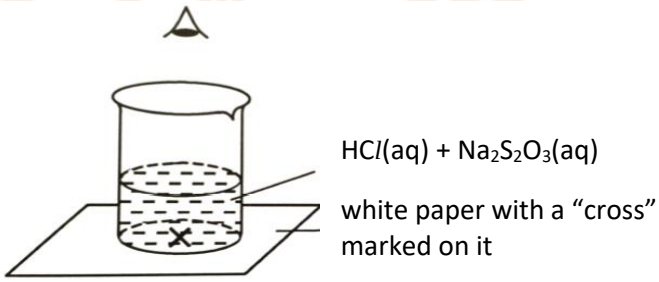


Figure 12. Experimental setup for the reaction between $Na_2S_2O_3(aq)$ and $HCl(aq)$

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To determine the order of reaction with respect to a reactant **A**, we measure the initial rates for a number of experiments in which the concentration of **A** is varied while keeping the concentrations of other reactants constant. Initial rates are often obtained by timing the formation of a ***small, fixed*** amount of product.

Generic procedure for 'clock' method to obtain initial rates

1. To prepare the reaction mixture, **measure** (volume) cm^3 of (reactant X) into a 250 cm^3 beaker (or conical flask) using a measuring cylinder.
   Repeat for all other reactants except for the last reactant which kick–starts the reaction.
2. **Measure** (volume) cm^3 of (last reactant) using a **measuring cylinder**. **Add** (last reactant) to the mixture and **start the stop–watch at the same time**. Swirl to ensure mixing.
3. **Stop the stop–watch** when (state distinct visual change) is observed. Record the time taken, *t*.
4. **Repeat** steps 1 to 3 with **different volumes** of (reactant studied) and deionised water, keeping the **total volume constant**. (Use a table to show the list of different volumes to use in each experiment.)

Note:

- The distinct visual change can be when sufficient precipitate is formed to just obscure a mark; or when a particular colour first appears.
- The total volume of the mixture is kept constant so that $[A]_{initial}$ is directly proportional to the volume of reactant **A**. E.g., when volume of **A** is doubled, $[A]_{initial}$ is doubled; when volume of **A** is unchanged, $[A]_{initial}$ is kept the same.
- $\frac{1}{t}$ obtained in this way is a measure of the initial rate of reaction, hence comparing the values of $\frac{1}{t}$ and volume of **A** can give us the order w.r.t. **A** e.g. when volume of A is doubled and $\frac{1}{t}$ is also doubled, it shows that the reaction is first order w.r.t **A**. Alternatively, plotting the values of $\frac{1}{t}$ vs volume of **A** will effectively give us the rate-concentration graph, the shape of which will allow us to determine the order w.r.t. **A** (see Section 4.5).
- Measuring cylinders are usually used to measure the volumes of liquids (common capacities: 10 cm^3, 25 cm^3, 50 cm^3, 100 cm^3). A burette may be used if a chemical is to be added in a small quantity which has to be *exactly* the same quantity for all experiments. However, a burette cannot be used to add the last reactant (Step 2) which has to be added *rapidly*.

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Summary

Experimental methods to determine *m* in
rate = k [**A**]^m [**B**]^n
for reaction a**A** + b**B** → products

Sampling Method

- Measure [**A**] or [product] at regular time intervals in one reaction mixture
- Initial [**B**] is used in large excess
  ⇒ pseudo-zero order w.r.t. [**B**]
  ⇒ rate = k'[**A**]^m where k' = k[**B**]^n ≈ constant

'Clock' Method

- Measure the time for a small and fixed prescribed (visual) change in at least 2 reaction mixtures where
  - initial [**A**] is different
  - initial [**B**] is the same

How to measure [**A**] or [product] in a reaction mixture over time?

- Remove samples to titrate (**Section 5.1.1**)
- Measure vol. of gas produced (**Section 5.1.2**)
- Measure absorbance of mixture (**Section 5.1.3**)

etc.

How to vary [**A**] in different reaction mixtures?

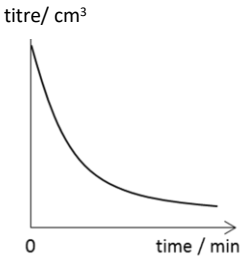
Vary vol. of **A** and keep total volume constant
E.g.

Expt	V_A / cm^3	V_B / cm^3	V_{water} / cm^3	t/s
1	10	20	0	t_1
2	5	20	5	t_2

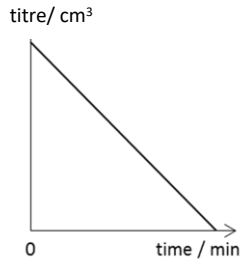
How to determine *m* from results?

- Plot 'concentration'-time graph (**Section 4.1.1**)

  E.g. since V_{titre} α [**A**], plot titre vs time graph



If half-life is constant, order w.r.t. [**A**] = 1



Straight line graph
⇒ rate is constant
⇒ rate is indept. of [**A**]
⇒ zero order w.r.t. [**A**]

To determine the order w.r.t. [**B**], repeat the same experiment with a different initial [**B**]. Determine the initial rates from the 2 graphs and use the initial rates method to determine the value of *n*.

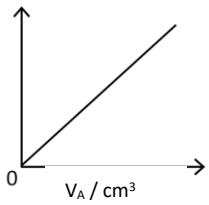
How to determine *m* from results?

- Initial rates method (**Section 4.2**)

  E.g. $\frac{rate_1}{rate_2} = \left(\frac{[A]_1}{[A]_2}\right)^m \Rightarrow \frac{t_2}{t_1} = \left(\frac{10}{5}\right)^m$
  Solve for m

- Plot 'rate-concentration' graph (**Section 4.1.2**) if there are 5 or more sets of results

  E.g. since V_A α [**A**] and initial rate α $\frac{1}{t}$, plot $\frac{1}{t}$ vs V_A graph



Straight line through the origin
⇒ rate is directly proportional to [**A**]
⇒ rate = k[**A**]
⇒ first order w.r.t. [**A**]

To determine the order w.r.t. [**B**], perform Experiment 3 where vol. of **B** is varied but vol. of **A** and total volume are the same as those in Experiment 1.
E.g. V_A = 10 cm^3, V_B = 10 cm^3, V_{water} = 10 cm^3

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6 COLLISION THEORY, ACTIVATION ENERGY AND MAXWELL-BOLTZMANN DISTRIBUTION

6.1 Collision Theory

The Collision Theory states that to react, the reactant particles must **collide** with **sufficient energy** and with the **correct orientation**.

These collisions are the **effective** collisions which will result in product formation.

6.2 Activation energy and Maxwell-Boltzmann distribution

LO8(a)part: explain and use the term: activation energy
LO8(g): show understanding, including reference to the Boltzmann distribution, of what is meant by the term activation energy

*The **activation energy** of a reaction (E_a) is the **energy barrier** the reactants must overcome in order to become the products.*

In any sample, the particles present will possess a range of energies. In order to estimate the fraction of collisions that have sufficient energy to overcome the activation energy barrier, we need to know their energy distribution. For gases, the distribution of energies can be represented by the Maxwell-Boltzmann energy distribution curve (refer to Topic 3 The Gaseous State for explanation on the shape of the curve).

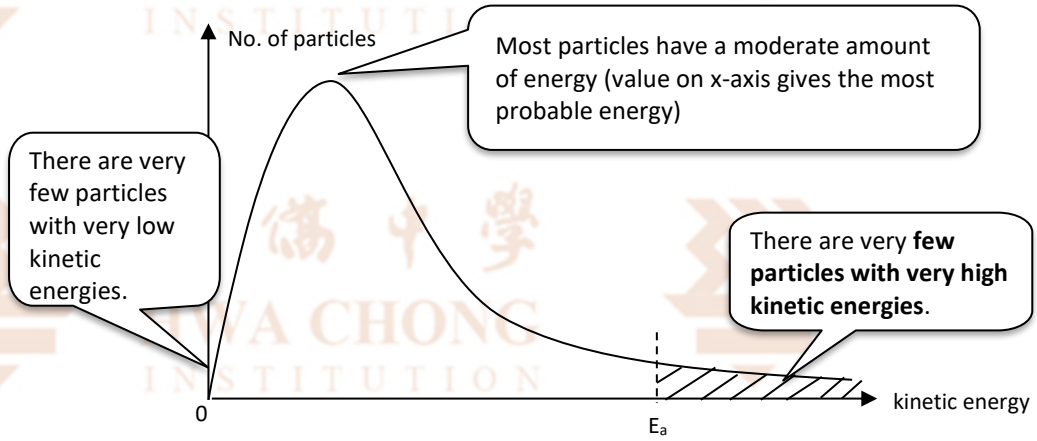


Figure 13. The Maxwell-Boltzmann energy distribution curve

The total area under the graph represents the total number of molecules present.

The **shaded area** represents the fraction of molecules that have **kinetic energies greater than or equal to E_a**, the activation energy for a particular reaction. This fraction is usually small.

In general,

- Reactions with **low E_a** are **fast** because a large proportion of molecules have sufficient energy to overcome the energy barrier. Examples of such **kinetically favourable** reactions include:
  - reactions between two free radicals
  - reactions between ions of opposite charge
  - acid-base (neutralisation) reactions

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- Reactions with **high E_a** are **slow** because only a small proportion of molecules have sufficient energy to overcome the energy barrier. Examples of such **kinetically unfavourable** reactions include:
  - reactions between two neutral molecules or involve breaking strong covalent bonds
  - reactions between ions of similar charge
  - reactions where a bond breaks to form free radicals (which are usually highly unstable)

6.3 Molecular orientation

Consider the reaction, $NO_2Cl + Cl \rightarrow NO_2 + Cl_2$, where a collision between a NO_2Cl molecule and a Cl atom forms a NO_2 molecule and a Cl_2 molecule.

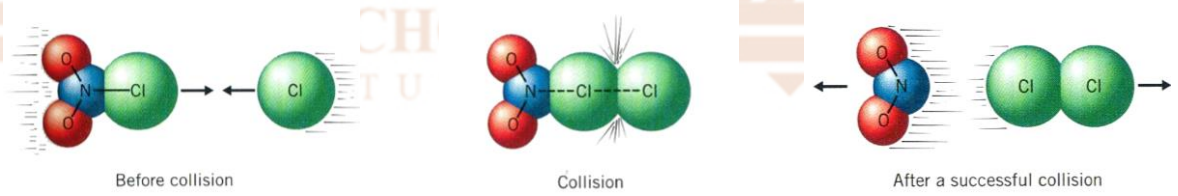


Figure 14. A correctly oriented collision

In a poorly oriented collision, the two colliding particles "bounce off" without any reaction.

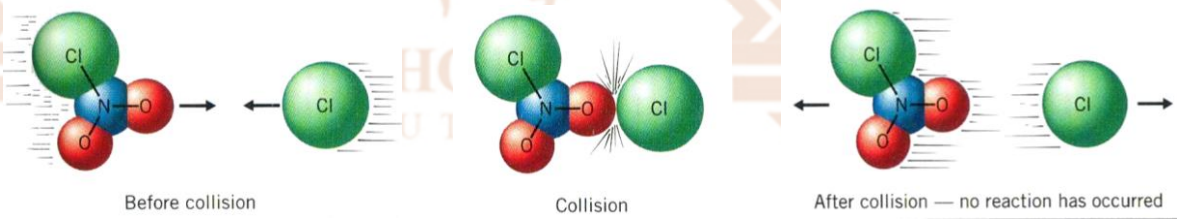


Figure 15. A poorly oriented collision

6.4 Activation energy and energy profile diagram

LO7(b): Construct and interpret an energy profile diagram, in terms of the enthalpy change of the reaction and of the activation energy

An energy profile diagram (or reaction pathway diagram) shows the change in the energy of the reactants as they become the products. The activation energy, E_a, as well as the enthalpy change, ΔH, of a reaction are also reflected in such a diagram.

Figure 16 shows the energy profile diagram for an exothermic single-step reaction.

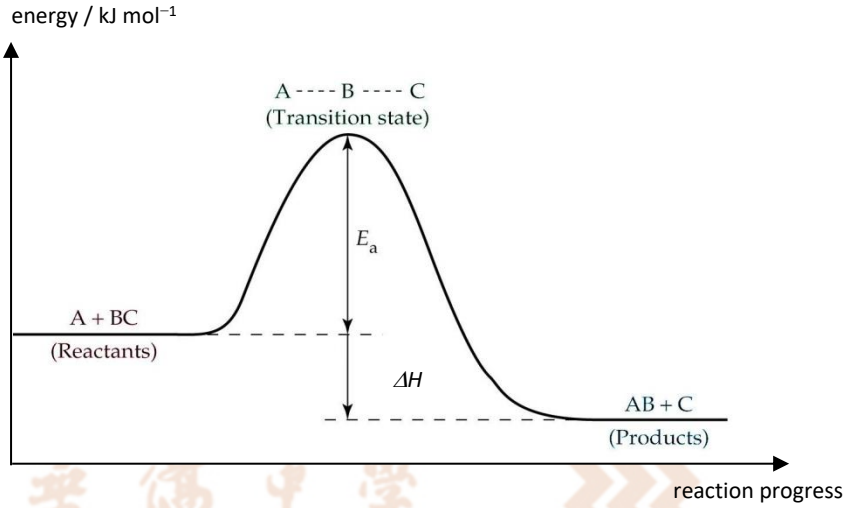


*Figure 16. Energy profile diagram for a single-step, exothermic reaction, **A + BC → AB + C***

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- Single-step reactions have a single **transition state** (or activated complex). Transition states are hypothetical species that cannot be isolated. They correspond to the energy maxima i.e. the peaks in the energy profile diagram.

- The **activation energy**, **E_a**, is measured from the energy level of the reactants to the energy level of the transition state.

- **Enthalpy change, ΔH**, is the difference between the energy levels of the products and reactants.

The magnitude of the activation energy barrier does not depend on the magnitude of ΔH. '*How fast*' a reaction occurs depends on its E_a, not ΔH. An exothermic ΔH tells us the products are *energetically* more stable than the reactants. However, if the E_a is high, the rate of reaction is negligible at room temperature. For example, the combustion of methane is highly exothermic (–890 kJ mol^{-1}) but a mixture of methane and oxygen do not react at room temperature until a spark is introduced.

Figure 17 shows the energy profile diagram for an exothermic two-step reaction. A two-step reaction has two transition states and an **intermediate**. An intermediate is a definite species which is formed during the reaction but are not part of the final products (as they are consumed in a later step). Intermediates are relatively reactive with energy higher than the reactants and products, but may be stable enough to be detected or isolated. Unlike a transition state (which occurs at an energy maximum), an intermediate occurs at an energy minimum, i.e. the valleys in the energy profile diagram.

The first step in Figure 17a has a larger E_a so it is the slower step while the second step in Figure 17b is the slower step as it has a larger E_a.

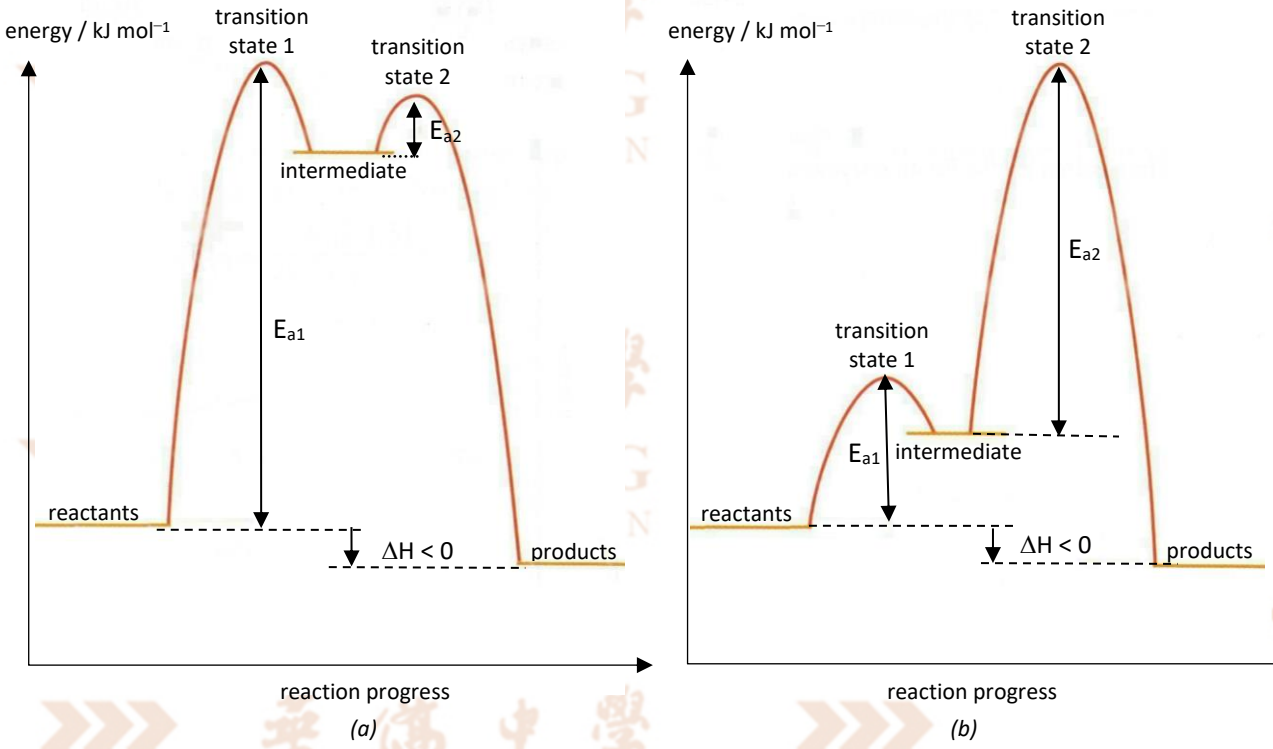


Figure 17. Energy profile diagrams for a two-step reaction. In (a), step 1 is slower than step 2. In (b), step 2 is slower than step 1.

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7 REACTION MECHANISM

7.1 Reaction mechanism and rate-determining step

LO8(a)part: explain and use the term: rate-determining step

Many chemical reactions are too complex to occur in one simple step. Instead, the reaction may involve a series of steps.

A **reaction mechanism** is a *sequence of elementary steps* that *adds up to the overall reaction*. It shows us how the reaction actually takes place at the *particulate level* – how the atoms in the reactants rearrange to form the products and the order in which bonds are broken and formed. Reaction mechanisms are postulated from kinetics studies which include experiments to obtain the rate equation (see Sections 4 and 5) and experiments to test the mechanism (see examples on 87).

Elementary steps cannot be broken down into simpler steps. The number of particles (atoms, molecules or ions) reacting in an elementary step is the **molecularity** of that step. *Unimolecular* reactions involve only 1 particle; *bimolecular* reactions involve the collision of 2 particles; *termolecular* reactions involve the collision of 3 particles. Molecularity does *not* apply to an overall reaction.

Elementary steps must be physically reasonable. It seldom involves the collision of 3 particles (low probability) or collision between ions of the same charge (high E_a).

In the example below, the mechanism consists of two *elementary steps*:

- Step 1 is *unimolecular*; one **A** reacts in this step.
- Step 2 is *bimolecular*; one **B** reacts with one **E** (which is an intermediate).

step 1:	**A** $\rightarrow$ **E** + **D**	(slow)
step 2:	**E** + **B** $\rightarrow$ **C**	(fast)
overall equation:	**A** + **B** $\rightarrow$ **C** + **D**	

The **rate-determining step (r.d.s.)** is the **slowest** (elementary) **step** in a mechanism. In a single-step mechanism, the only step must be the rate-determining step. In a multi-step mechanism, the step with the *highest activation energy* is the r.d.s. (see Figure 17).

The rate of the r.d.s. is essentially the *overall rate* of the reaction. Any step before the r.d.s. should also affect the overall rate. Any step that takes place after the r.d.s. has no effect on the overall rate.

In the example above, step 1 is the slower step of the two, hence it is the rate determining step. The rate of step 1 (r.d.s.) gives the overall rate of the reaction. This means that if experiments are done to measure the reaction's rate, we are measuring the rate of step 1.

The rate of step 1 is affected by changes in [**A**]. Since one **A** reacts in that step, when [**A**] is doubled, number of **A** reacting per unit time doubles so rate is also doubled, implying the order of reaction w.r.t. [**A**] is one. Hence, we can relate the order of reaction (obtained from experiments) to the molecularity of the r.d.s. (and any steps before it since they also affect the overall rate). This will be elaborated further using the examples in Section 7.2.

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7.2 Reaction mechanism and rate equation

7.2.1 Verifying that a reaction mechanism is consistent with rate equation

LO8(b)part: construct and use rate equations of the form rate = k [A]^m [B]^n (limited to simple cases of single-step reactions and of multi-step processes with a rate-determining step, for which m and n are 0, 1 or 2), including: (iii) verifying that a suggested reaction mechanism is consistent with the observed kinetics

Given a rate equation, we can verify if a suggested reaction mechanism is consistent with it.

Consider the reaction, **X** + 2**Y** → **XY**$_2$, with the experimentally determined rate equation: rate = k[**Y**]^2.

Are the following mechanisms consistent with the rate equation?

Mechanism 1: **X** + **Y** → **XY** (slow)
XY + **Y** → **XY**$_2$ (fast)

Mechanism 2: 2**Y** → **Y**$_2$ (slow)
Y$_2$ + **X** → **XY**$_2$ (fast)

Deductions from the rate equation:

- [**Y**] appears in the rate equation ⇒ [**Y**] affects the rate so **Y** must react either in the r.d.s or in the steps before it.
- The order of reaction w.r.t. [**Y**] is 2, hence a total of two **Y** will react in these steps.
- [**X**] does not appear in the rate equation ⇒ [**X**] does not affect the rate so it should only react after the r.d.s.

Mechanism 1 is inconsistent with the rate equation. The slow step in Mechanism 1 involves one **X** reacting with one **Y**. This is inconsistent with the 2nd and 3rd bullet points.

Mechanism 2 is consistent with the rate equation. The slow step in Mechanism 2 involves two **Y** reacting. **X** is not involved in the slow step.

It is also important to ensure the elementary steps add up to the overall stoichiometric equation as shown:

2**Y** → ~~**Y**$_2$~~ (slow)
~~**Y**$_2$~~ + **X** → **XY**$_2$ (fast)
2**Y** + **X** → **XY**$_2$ (overall)

Exercise 7.1 (worked example)

For the reaction, **X** + 2**Y** → **XY**$_2$, the experimental rate equation is found to be: rate = k[**Y**]^2.
Suggest if the following mechanism is consistent with the rate equation. Explain your answer fully.

2**Y** ⇌ **Y**$_2$ (fast)
Y$_2$ + **X** → **XY**$_2$ (slow)

[**Y**] appears in the rate equation hence [**Y**] affects the rate. **Y** must react either in the r.d.s or in the steps before it. The order of reaction w.r.t. [**Y**] is 2, hence a total of two **Y** will react in these steps.
[**X**] does not appear in the rate equation hence [**X**] does not affect the rate. **X** should only react after the r.d.s.
The mechanism is inconsistent with the rate equation. The slow step is the second step so the overall rate is also affected by the first step. Hence, rate is affected by both [**X**] and [**Y**].
Note: Y_2 is an intermediate. The concentrations of intermediates do not appear in the rate equation (since they do not appear in the overall stoichiometric equation). See Section 7.2.2 Mechanism 5 for the correct rate equation for the given mechanism. In Mechanism 5, you may treat **X** as O_2 and **Y** as NO.

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Exercise 7.2 *[N1999/3/33modified]* **(worked example)**
Which suggested mechanism is consistent with the experimentally determined rate equation?

	rate equation	suggested mechanism		
1	rate = k_1 $[NO]^2[H_2]$	$2NO(g) + H_2(g)$ $N_2O(g) + H_2(g)$	$\rightarrow N_2O(g) + H_2O(g)$ $\rightarrow N_2(g) + H_2O(g)$	(slow) (fast)
2	rate = k_2 $[H_2][I_2]$	$H_2(g)$ $2H(g) + I_2(g)$	$\rightarrow 2H(g)$ $\rightarrow 2HI(g)$	(slow) (fast)
3	rate = k_3 $[HBr][O_2]$	$2HBr(g) + O_2(g)$ $HBrO(g) + HBr(g)$	$\rightarrow 2HBrO(g)$ $\rightarrow H_2O(g) + Br_2(g)$	(slow) (fast)

Option 1 is correct.
Since NO and H_2 are in the slow step, they appear in the rate equation.
rate = $k[NO]^2[H_2]$ since 2 molecules of NO and 1 molecule of H_2 reacts in the slow step.

Option 2 is correct. There is only 1 molecule of H_2 reacting in the slow step.
rate = $k[H_2]$

Option 3 is not correct.
There are 2 molecules of HBr and 1 molecule of O_2 reacting in the slow step.
rate = $k[HBr]^2[O_2]$

You can also view the video explanation via this link.

7.2.2 Predicting order of reaction from a reaction mechanism

LO8(b)part: construct and use rate equations of the form rate = k $[A]^m$ $[B]^n$ (limited to simple cases of single-step reactions and of multi-step processes with a rate-determining step, for which m and n are 0, 1 or 2), including: (iv) predicting the order that would result from a given reaction mechanism

Given a reaction mechanism, we can construct the rate equation by deducing the order of reaction w.r.t. a reactant from the rate determining step and the steps before it.

Mechanism 3: $CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$

Recall that in a single-step mechanism, the only step must be the rate-determining step.
The coefficient of CH_3CH_2Br and OH^- in this r.d.s. are both 1. Hence, the order of reaction w.r.t. $[CH_3CH_2Br]$ and $[OH^-]$ are both 1. Thus, the rate equation is: rate = $k[CH_3CH_2Br][OH^-]$.

Mechanism 4:	Step 1	$NO_2 + F_2 \rightarrow NO_2F + F$	(slow)
	Step 2	$NO_2 + F \rightarrow NO_2F$	(fast)

The r.d.s. is the first step. The coefficient of NO_2 and F_2 in the r.d.s. are both 1. Hence, the order of reaction w.r.t. $[NO_2]$ and $[F_2]$ are both 1. Thus, the rate equation is: rate = $k[NO_2][F_2]$ and the overall stoichiometric equation is: $2NO_2 + F_2 \rightarrow 2NO_2F$ (sum of the elementary steps).

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Mechanism 5: Step 1 $NO + O_2 \rightleftharpoons NO_3$ (reversible, fast)
Step 2 $NO_3 + NO \rightarrow 2NO_2$ (slow)
The overall stoichiometric equation is: $2NO + O_2 \rightarrow 2NO_2$

Unlike Mechanism 4, the r.d.s. is <u>not</u> the first step. The rate equation cannot be rate = $k_2[NO_3][NO]$ since NO_3 is an **intermediate** which does not appear in the stoichiometric equation, and therefore its **concentration does not appear in the rate equation**. To obtain the overall rate equation, we need to look at the rate equation of the r.d.s. i.e. step 2:

Rate equation for step 2 is rate = $k_2[NO_3][NO]$ ----- (i) where k_2 is the rate constant for step 2

Since NO_3 is an intermediate, we need to substitute $[NO_3]$ with the reactants concentrations, by using steps <u>before</u> this r.d.s. i.e. step 1:

Since step 1 is an equilibrium, we can write: $K_c = \dfrac{[NO_3]}{[NO][O_2]}$

(K_c will be discussed in Topic 7 Chemical Equilibria)

Rearranging, $[NO_3] = K_c[NO][O_2]$ ----- (ii)

Substitute (ii) into (i), rate = $k_2K_c[NO][O_2][NO] = k_2K_c[NO]^2[O_2]$

Hence the overall rate equation is: rate = $k[NO]^2[O_2]$ where $k = k_2K_c$

In summary,

- The elementary steps must <u>add up</u> to the overall stoichiometric equation.
- Reactants whose concentrations appear in the rate equation react <u>before or at</u> the r.d.s. (in order to affect the reaction rate).
- Reactants whose concentrations do not appear in the rate equation react <u>after</u> the r.d.s.
- The concentrations of <u>intermediates do not appear</u> in the rate equation (since they do not appear in the overall stoichiometric equation).
  Note: A <u>homogeneous catalyst</u> (see Section 9.1) does not appear in the overall stoichiometric equation, but its concentration appears in the rate equation.
- If the r.d.s. is the first step, the <u>order</u> w.r.t. a reactant is <u>equal</u> to its <u>coefficient</u> in the r.d.s.
- If the r.d.s. is not the first step, the <u>order</u> w.r.t. a reactant is <u>derived</u> from its coefficient in the r.d.s. and the steps before the r.d.s.

Exercise 7.3 (worked example)

The reaction between nitric oxide, NO, and oxygen is one of the reactions involved in atmospheric pollution from car exhausts.
Kinetics studies have shown that the reaction is third order overall, and it has been suggested that the mechanism involves the following two steps.

$$2NO \xrightarrow{\text{fast}} N_2O_2$$

$$N_2O_2 + O_2 \xrightarrow{\text{slow}} 2NO_2$$

What is the rate equation for the overall reaction?

A rate = $k\,[NO]^2\,[N_2O_2]$ **B** rate = $k\,[N_2O_2]\,[O_2]$
C rate = $k\,[NO]^2\,[O_2]$ **D** rate = $k\,[N_2O_2]^2\,[O_2]$

[N05/3/1]

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N_2O_2 is an intermediate as it is produced in the first step and consumed in the second step. Intermediates do not appear in the rate equation, so **A**, **B**, and **D** cannot be correct.

The rate equation based on the slow step is rate = $k[N_2O_2][O_2]$. N_2O_2 (the intermediate) is produced from 2 NO molecules. We can replace $[N_2O_2]$ with $[NO]^2$. Hence the correct rate equation is **C**.
You can view the video explanation via this link.

Experiments techniques to verify mechanisms (Background Info)
Two techniques used to verify postulated mechanisms are described below.

- Isotopic labeling – for example, when esters labeled with ^{18}O are reacted with water (a hydrolysis reaction), the ^{18}O appears in the alcohol and not in the carboxylic acid group. This shows that the C–O bond (1), and not the C–O bond (2), is the one that is broken.

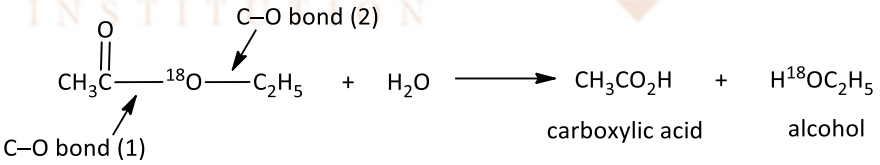


Figure 18. Hydrolysis of ethyl ethanoate to give ethanoic acid and ethanol

- Kinetic isotope effect – for example, the C–D bond is slightly harder to break than the C–H bond. This means that if this bond is broken during the rate-determining step, a compound containing C–D bonds reacts more slowly than a compound with C–H bonds; if the reaction rate is the same rate for both compounds, the breakage of this bond does not occur in the slow step.
  C_6H_6 and C_6D_6 reacts with NO_2^+ at the same rate. This shows that the rate-determining step is the initial attack by NO_2^+, and not the elimination of the proton, H^+.

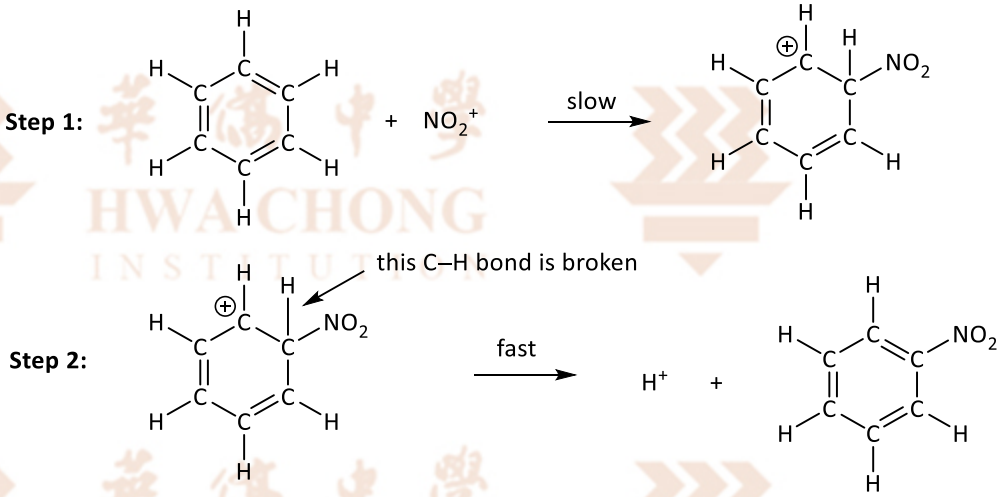


Figure 19. Mechanism for the nitration of benzene

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8 FACTORS AFFECTING RATES OF REACTION

According to the collision theory, a reaction occurs only if the particles collide with sufficient energy and correct orientation. At the molecular level, the rate of reaction depends on two factors:

- the **collision frequency**

  The simplest way to increase the collision frequency is by increasing the concentration of the reactants, and for gaseous reactions, the pressure (Section 8.1).

- the **proportion of the particles that have sufficient energy to overcome the activation energy**

  A typical fraction might be one in ten thousand million (1 in 10^{10}) which is very small. We can increase this fraction by:
  - increasing the energy of the collisions (Section 8.2),
  - finding another route with a lower activation energy (Section 8.3).

8.1 Effect of concentration or pressure on rate

LO8(f): explain qualitatively, in terms of frequency of collisions, the effect of concentration changes on the rate of a reaction

At a **higher** concentration (or pressure), there are more reactant particles per unit volume. The reactant particles are **closer** together and collide more frequently. **Frequency of effective collisions increases**. Hence, rate of reaction **increases**.



(a) *low reactant concentration* ***(b)*** *high reactant concentration*

Figure 20. Effect of concentration on frequency of collisions

Recall that it is possible the order of reaction with respect to a reactant is zero, i.e. the concentration of this reactant does not appear in the rate equation. In this case, changing its concentration would have no effect on the rate.

For example, the rate equation for the acid-catalysed iodination of propanone

$$CH_3COCH_3(aq) + I_2(aq) \xrightarrow{H^+} CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

is rate = $k[CH_3COCH_3][H^+]$. Increasing the concentration of iodine will not increase the reaction rate.

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8.2 Effect of temperature on rate and rate constant

LO8(h): explain qualitatively, in terms of both the Boltzmann distribution and of collision frequency, the effect of temperature change on a rate constant (and hence, on the rate) of a reaction

What is the effect of temperature change on rate?

When temperature is increased, the reactant particles have **greater average kinetic energy**. They move more quickly and so **collide more frequently**. More importantly, the **proportion** of particles that have kinetic energies greater than or equal to the activation energy **increases** (see Figure 21). **Frequency of effective collisions** hence rate of reaction **increases**.

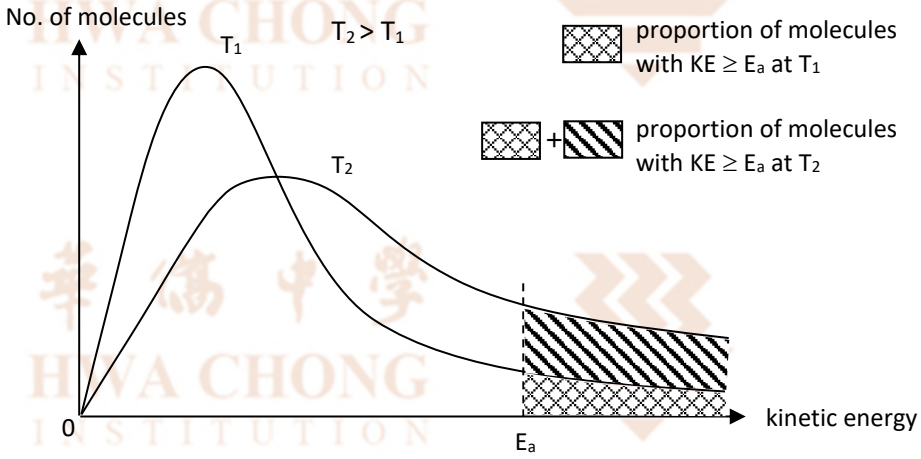


Figure 21. Maxwell-Boltzmann distribution showing the effect of temperature change on the proportion of particles with kinetic energies greater than or equal to the activation energy

What is the effect of temperature change on the rate constant?

From the rate equation, rate = k $[A]^m[B]^n$
If [A] and [B] are kept constant, **rate** $\propto$ ***k***
When temperature increases, rate increases so k must have increased.

In other words, since an increase in temperature, while keeping concentrations the same, increases the rate of a reaction, the rate constant must have increased.

Alternatively, the Arrhenius equation, $k = Ae^{-Ea/RT}$ (Section 3.3) can also be used to show that when temperature increases, rate constant k increases exponentially.

Exercise 8.1 *[J2003/I/12]* **(worked example)**
It is often said that the rate of a typical reaction is roughly doubled by raising the temperature by 10 °C.
What explains this observation?

A Raising the temperature by 10 °C doubles the average energy of each molecule.

B Raising the temperature by 10 °C doubles the velocity of each molecule.

C Raising the temperature by 10 °C doubles the number of molecular collisions in a given time.

D Raising the temperature by 10 °C doubles the number of molecules having more than a certain minimum energy.

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From the Boltzmann Distribution, it is clear that the main reason for an increase in rate of reaction is due to the increase in proportion of particles having kinetic energy greater than or equal to the activation energy. **D** is correct.

8.3 Effect of catalyst on rate and rate constant

LO8(i): (i) explain that, in the presence of a catalyst, a reaction has a different mechanism, i.e. one of lower activation energy, giving a larger rate constant (ii) interpret this catalytic effect on a rate constant in terms of the Boltzmann distribution

*A **catalyst** is a substance that **speeds up a chemical reaction by providing an alternative reaction pathway of lower activation energy** (see Figure 22), while **remaining chemically unchanged at the end of the reaction**.*

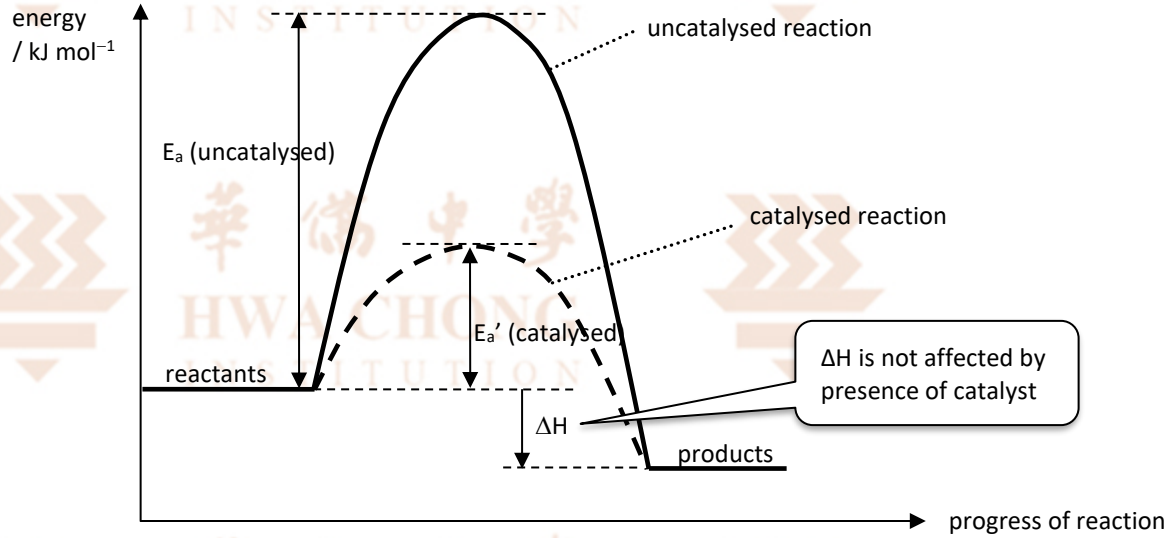


Figure 22. Energy profile diagram for a reaction, with and without a catalyst

What is the effect of a catalyst on rate?

Since a catalyst provides an **alternative reaction pathway of lower activation energy** (see Figure 22), the **proportion** of particles that have kinetic energies greater than or equal to the lower E_a **increases** (see Figure 23). **Frequency of effective collisions** hence rate of reaction **increases**.

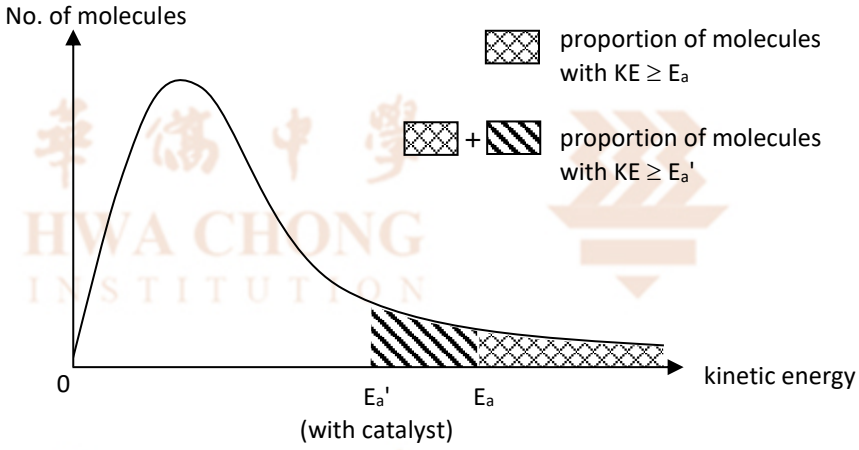


Figure 23. Maxwell-Boltzmann distribution showing the effect of catalyst on the proportion of particles with kinetic energies greater than or equal to the activation energy

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What is the effect of a catalyst on the rate constant?

From the rate equation, rate = k $[A]^m[B]^n$
If [A] and [B] are kept constant, **rate** $\propto$ ***k***
In the presence of a catalyst, rate increases so k must have increased.

In other words, since a catalyst increases the rate of a reaction, while keeping concentrations the same, the rate constant must have increased.

Alternatively, in the presence of a catalyst, the reaction proceeds via a different mechanism that is of lower E_a (see Figure 22), giving a larger rate constant k (see Arrhenius equation: $k = Ae^{-Ea/RT}$).

Other factors that affect rate:

Effect of surface area (of solids) on rate

For a chemical reaction involving a solid, only the particles on its surface are available for reaction. If the solid reactant is in a more finely divided state, the **surface area of the boundary between the reactants** (e.g. between the solid and a solution) is larger. Hence, collision frequency increases, reaction rate increases.

For example, powdered calcium carbonate reacts faster with acid than lumps of the solid do.

Effect of light on rate

Reactions that are affected by light are called **photochemical reactions**. They tend to be slow in the dark but take place rapidly in the presence of light. When the reactant molecules absorb light energy, the average kinetic energy of the particles increases, hence increasing the fraction of reacting particles with enough energy to overcome the activation energy barrier.
Examples of photochemical reactions include:

- breakdown of silver bromide to silver and bromine (used in black-and-white photography):

$$AgBr \rightarrow Ag + \tfrac{1}{2} Br_2$$

- reaction of hydrogen with chlorine which is slow in the dark but explosive in sunlight:

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

- chlorination of alkanes:

$$CH_4 + Cl_2 \xrightarrow{\text{UV light}} CH_3Cl + HCl$$

Did you know?

Photochromic sunglasses darken on exposure to ultraviolet (UV) radiation. Photochromic or photochromatic lenses have millions of particles of substances such as silver chloride embedded in them. When exposed to UV rays, as in direct sunlight, the particles undergo a chemical reaction that causes them to change shape. The new structure absorbs portions of the visible light, causing the lenses to darken. The number of particles that change shape varies with the intensity of the UV rays. When you go indoors and out of the UV light, a different chemical reaction takes place. The absence of UV radiation causes the particles to "snap back" to their original shape, resulting in the loss of their light absorbing properties. In both directions, the entire process happens very rapidly.

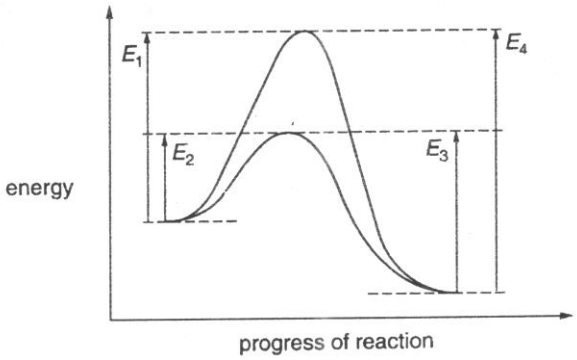


[Source: http://science.howstuffworks.com/innovation/science-questions/question412.htm]

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Exercise 8.2

The energy diagram represents the reaction occurring with and without a catalyst.



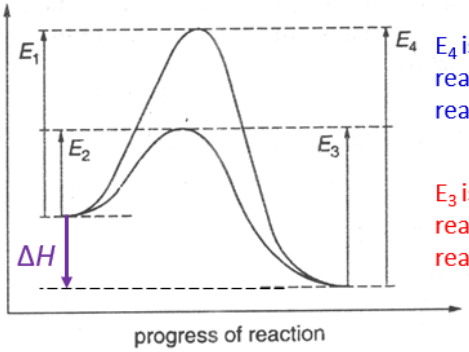
Which of the following statements are correct?

1 E_2 is the activation energy for the catalysed reaction.
2 The enthalpy change of reaction is ($E_2 - E_3$).
3 The enthalpy change of reaction is reduced by using a catalyst.

A **1**, **2** and **3** are correct
B **1** and **2** only are correct
C **2** and **3** only are correct
D **1** only is correct

E_1 is the E_a of the forward reaction of the unanalyzed reaction

E_2 is the E_a of the forward reaction of the catalysed reaction



E_4 is the E_a of the backward reaction of the uncatalysed reaction

E_3 is the E_a of the backward reaction of the catalysed reaction

$\Delta H = E_2 - E_3$
$= E_1 - E_4$

Hence options 1 and 2 are correct. Option 3 is incorrect because ΔH is constant even when the catalyst is added.

You can view the video explanation via this link.

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9 CATALYSIS

LO8(a)part: explain and use the term: catalysis

Catalysis refers to the process of increasing the rate of a reaction with a catalyst. This is preferred over increasing temperature which may increase cost and decompose the reactants or products.

Catalysts may be homogeneous or heterogeneous. A **homogeneous catalyst** acts in the **same phase as the reactants** and is uniformly mixed with them. A **heterogeneous catalyst** acts in a **different phase from the reactants**. There is also an important of class of catalysts called **enzymes**.

What does same phase and different phase mean? (Background Info):
If you look at a mixture and can see a *boundary* between two of the components, those substances are in different phases. If you cannot see a *boundary* between the components, they are in the same phase. For example, a mixture of water and oil (both liquids) consists of two phases; you could see the boundary between them. A mixture of various chemicals in a single solution consists of one phase.

A homogeneous catalyst must be involved in the rate-determining step in order for it to affect the rate of reaction. As such, the concentration of the homogeneous catalyst usually appears in the rate equation for the catalysed pathway, even though it does not appear in the overall balanced stoichiometric equation. For example, the iodination of propanone catalysed by H^+ ions:

$$CH_3COCH_3(aq) + I_2(aq) \xrightarrow{H^+} CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

has the rate equation, rate = $k[CH_3COCH_3][H^+]$.

Heterogeneous catalysis often involves a solid catalyst interacting with gaseous or liquid reactants. Since solids do not have a 'concentration', the effect of heterogeneous catalysts is included in the value of the rate constant, *k*.

9.1 Homogeneous catalysis

Homogeneous catalysis usually involves the formation of an *intermediate* between the catalyst and one of the reactants. The catalyst is then regenerated in a later step of the reaction. The catalysed reaction may involve *two or more steps*, each of which must has a *lower activation energy* than the uncatalysed reaction.

9.1.1 Mode of action of homogeneous catalysis: Catalytic role of Fe^{2+} in the $I^-/S_2O_8^{2-}$ reaction

LO8(j)part: outline the different modes of action of homogeneous and heterogeneous catalysis, including: (iv) catalytic role of Fe^{2+} in the $I^-/S_2O_8^{2-}$ reaction

Iodide ions react with peroxodisulfate ions in the redox reaction:

$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

The uncatalysed reaction is **slow** as the **repulsion** between the **two negative ions** results in a **high activation energy**. The reaction is catalysed by some transition metal cations e.g. Fe^{2+}, and involves the following steps:

Step 1:	$2Fe^{2+}(aq)$	+	$S_2O_8^{2-}(aq)$	$\rightarrow$	$2Fe^{3+}(aq)$	+	$2SO_4^{2-}(aq)$
Step 2:	$2Fe^{3+}(aq)$	+	$2I^-(aq)$	$\rightarrow$	$2Fe^{2+}(aq)$	+	$I_2(aq)$
Overall equation:	$2I^-(aq)$	+	$S_2O_8^{2-}(aq)$	$\xrightarrow{Fe^{2+}(aq)}$	$I_2(aq)$	+	$2SO_4^{2-}(aq)$

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The catalyst Fe^{2+} and the intermediate Fe^{3+}, being positively charged, easily attract the negative $S_2O_8^{2-}$ and I^- respectively. Thus, in the catalysed pathway, each step has a lower activation energy than the uncatalysed reaction (see Figure 24).

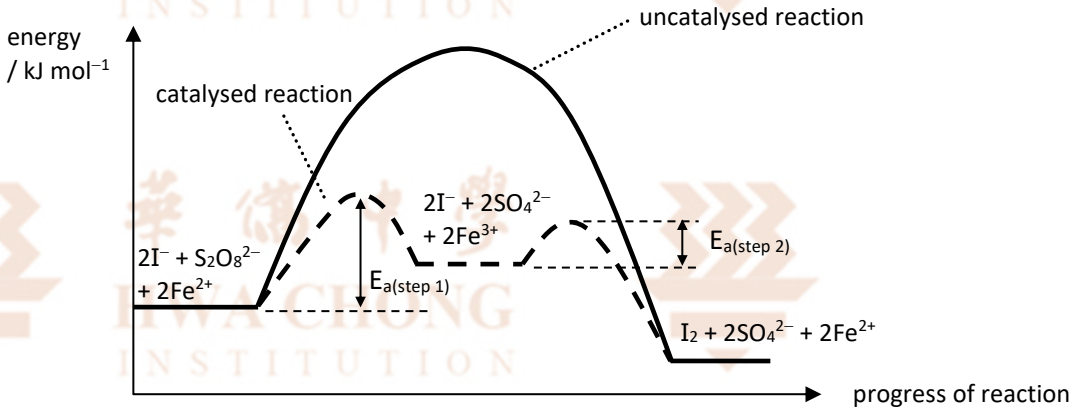


Figure 24. Energy profile diagram for the reaction, $2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$, with and without a catalyst

Exercise 9.1 (worked example)
Write equations to show how Fe^{3+} catalyses the redox reaction between iodide ions and peroxodisulfate ions and explain why Fe^{3+} can be described as a *homogeneous catalyst*.

$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

Step 1: $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$
Step 2: $2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$

Fe^{3+} is acting as a homogeneous catalyst as it is in the same phase as I^- and $S_2O_8^{2-}$. In addition, it is regenerated (or not used up) at the end of reaction.

9.1.2 Mode of action of homogeneous catalysis: Catalytic role of NO_x in the oxidation of atmospheric SO_2

LO8(j)part: outline the different modes of action of homogeneous and heterogeneous catalysis, including: (iii) the catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide

Nitrogen dioxide may catalyse the oxidation of SO_2 to SO_3 in the atmosphere in the following steps:

Step 1:	$SO_2(g)$	+	$NO_2(g)$	→	$SO_3(g)$	+	$NO(g)$
Step 2:	$NO(g)$	+	$\frac{1}{2}O_2(g)$	→	$NO_2(g)$		
Overall equation:	$SO_2(g)$	+	$\frac{1}{2}O_2(g)$	→	$SO_3(g)$		

In the presence of moisture in air or rainwater, SO_3 produces H_2SO_4 resulting in acid rain.

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

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Exercise 9.2 *[J97/I/2 modified]* **(worked example)**
Nitrogen dioxide in the atmosphere contribute to the formation of acid rain by catalysing the oxidation of SO_2 to SO_3. Write equations to show how this occurs, and state the type of catalysis.

$NO_2(g) + SO_2(g) \rightarrow NO(g) + SO_3(g)$
$NO(g) + ½O_2(g) \rightarrow NO_2(g)$

NO_2 is acting as a homogeneous catalyst.

9.2 Heterogeneous catalysis

In heterogeneous catalysis, the catalytic action occurs at the '**active sites' on the surface** of the catalyst. A **larger surface area** exposes more active sites and **increases the rate of reaction**. The catalyst is usually made into pellets, wire gauze or finely-powdered form spread on ceramic, silica or asbestos support.

Many heterogeneous catalysts are transitions metals or their compounds:

Reaction	Catalyst
Manufacture of ammonia (Haber Process) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	finely divided Fe(s) or $Fe_2O_3(s)$
One of the reactions involved in the manufacture of sulfuric acid (Contact Process): $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	$V_2O_5(s)$
Hydrogenation of alkenes $CH_2{=}CH_2(g) + H_2(g) \rightarrow CH_3CH_3(g)$	Ni(s) or Pt(s)
Removal of oxides of nitrogen, CO and unburnt hydrocarbons in the exhaust gases from car engines	Pt(s), Pd(s), Rh(s) in the catalytic converter

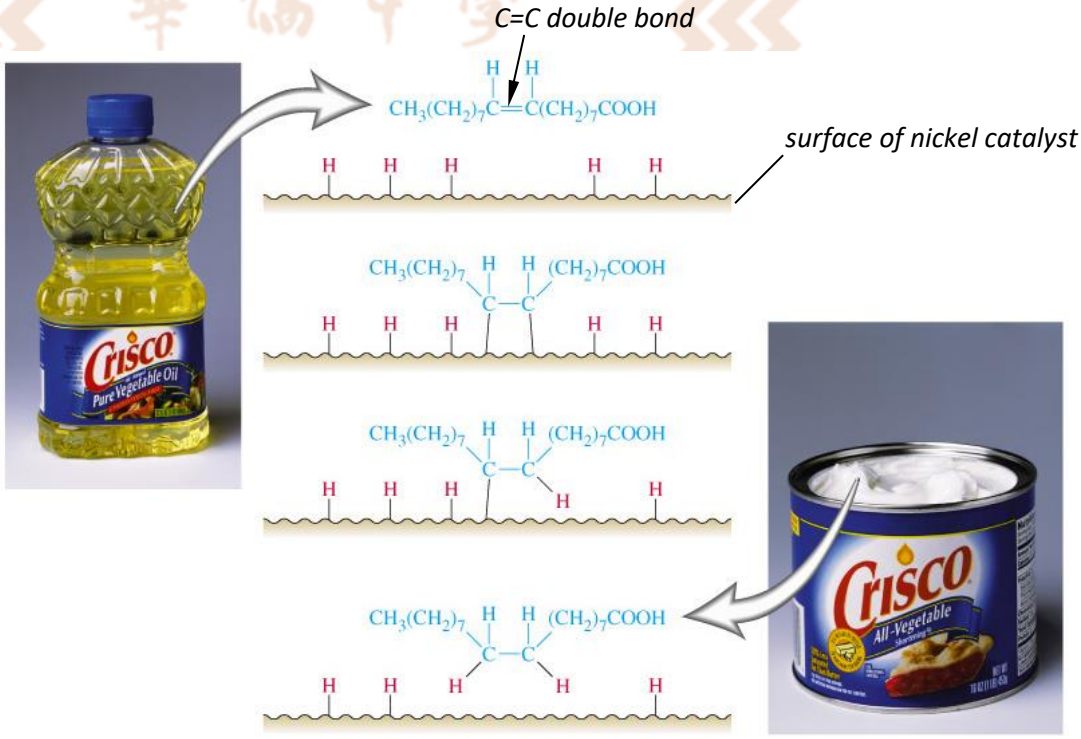


Figure 25. Catalytic hydrogenation of alkenes is used in the conversion of inedible vegetable oils to edible margarine

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9.2.1 Mode of action of heterogeneous catalyst: Haber process

LO8(j)part: outline the different modes of action of homogeneous and heterogeneous catalysis, including: (i) the Haber process

The mode of action of heterogeneous catalyst is explained below with reference to the reaction in the Haber process: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, catalysed by finely divided iron.

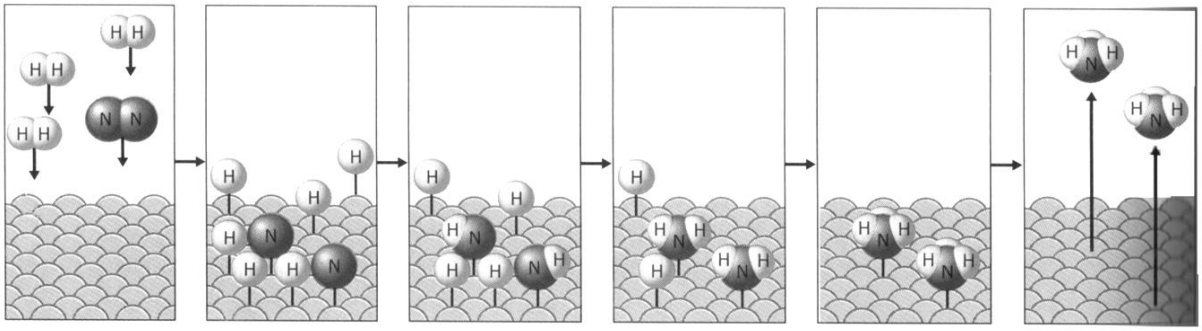


Figure 26. Mode of action of heterogeneous catalysis in the Haber Process

The three stages involved are:

- ***Adsorption*** (Figure 26a): The gaseous reactant molecules (N_2 and H_2) are **adsorbed** onto the **active sites** by formation of weak attraction forces. This process brings reactant molecules **closer together** (increasing their surface concentration), **weakens the covalent bonds** in the reactant molecules, thus **lowering the activation energy**, and **orientates** reactant molecules **correctly** for reaction to occur.

- ***Reaction*** (Figure 26b-e): Reaction occurs where bonds are broken and new bonds are formed.

- ***Desorption*** (Figure 26f): Product molecule (NH_3) **desorbs** from the catalyst surface so that **active sites are exposed for further reaction**.

The rate of reaction is controlled by how fast the gaseous reactants are adsorbed and how fast the products are desorbed. When the active sites are fully occupied (i.e. when the catalyst is **saturated**), there is no increase in reaction rate even if the concentration of reactants or pressure of the system is increased. Since rate is no longer affected by [reactant], *order of reaction with respect to [reactant] becomes zero when the catalyst is saturated*.

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9.2.2 Application of heterogeneous catalysis: Catalytic removal of harmful gases in the exhaust gases from car engines

LO8(j)part: outline the different modes of action of homogeneous and heterogeneous catalysis, including: (ii) the catalytic removal of oxides of nitrogen in the exhaust gases from car engines

The combustion of petrol in car engines not only gives carbon dioxide and water but also three harmful products:

- oxides of nitrogen (from the reaction between N_2 and O_2 from the air, under the high temperatures in the car engine)
- carbon and carbon monoxide (from incomplete combustion)
- unburnt hydrocarbon

Catalytic converters are used to remove these harmful gases by oxidising or reducing them.

- reduction of NO to N_2: $CO + NO \rightarrow CO_2 + \frac{1}{2}N_2$
- oxidation of CO to CO_2: $CO + \frac{1}{2}O_2 \rightarrow CO_2$
- oxidation of hydrocarbons to CO_2 and H_2O: hydrocarbon + $O_2 \rightarrow CO_2 + H_2O$

The exhaust gases are passed through the converter, which contains metals such as platinum and rhodium coated on a honeycomb support (see Figure 27). The harmful gases are *adsorbed* onto the surface of the metals, go through a *reaction* and the harmless gases then *desorb* from the surface.

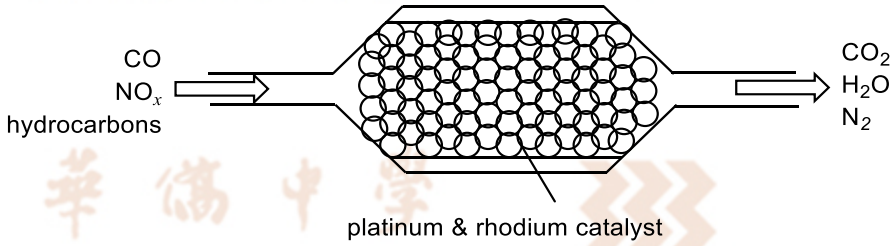


Figure 27. A catalytic converter

Catalytic converters only work with unleaded petrol because lead 'poisons' the catalyst in the converter (i.e. destroy their catalytic action).

Exercise 9.3 *[J95/IV/39 modified]*
A catalytic converter converts harmful gases from the exhaust system of a car into carbon dioxide, nitrogen and water vapour.
Which processes take place in the catalytic converter?

1 Carbon monoxide and hydrocarbons react together.
2 Carbon monoxide and nitrogen oxide react together.
3 Platinum and rhodium catalyse redox reactions.

A **1**, **2** and **3** are correct
B **1** and **2** only are correct
C **2** and **3** only are correct
D **1** only is correct

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9.3 Autocatalysis

In autocatalysis, the reaction is catalysed by one of its **products**. For example, Mn^{2+} ions catalyse the reaction between manganate(VII) ions and ethanedioate ions:

$$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2\mathbf{Mn^{2+}}(aq) + 10CO_2(g) + 8H_2O(l)$$
autocatalyst

Figure 28 shows the characteristic concentration-time graph for an autocatalytic reaction. Compare this graph to the concentration-time graphs in Section 4.1.1.

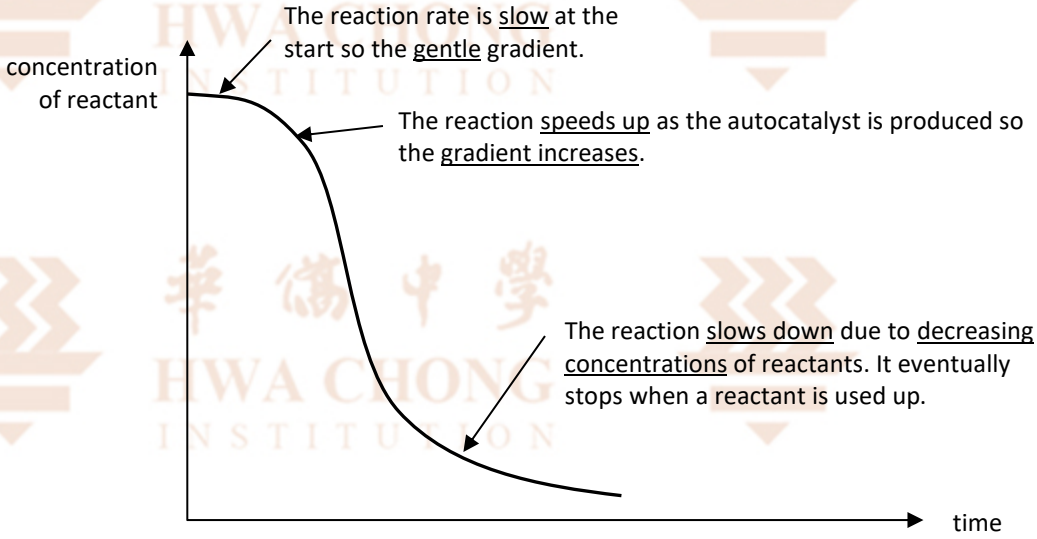
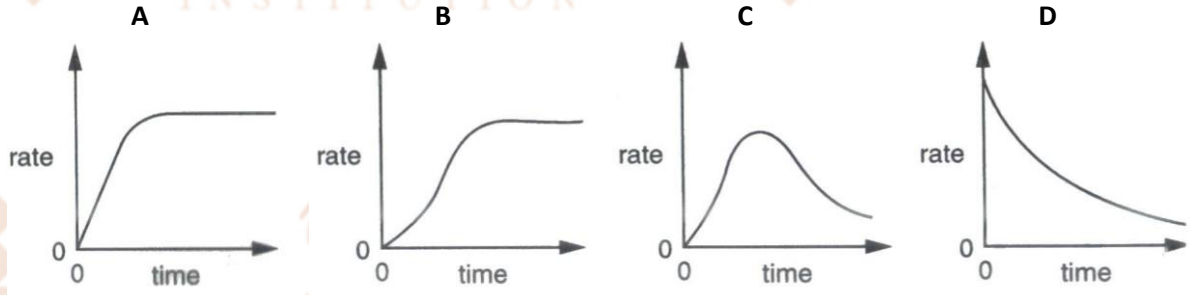


Figure 28. Typical concentration-time graph for a reaction in which autocatalysis occurs

Exercise 9.4 *[J02/I/11, N89/3/10]* **(worked example)**
Which curve is obtained if the rate of reaction is plotted against time for an autocatalytic reaction (i.e. a reaction in which one of the products catalyses the reaction)?



As the reaction starts, the rate is slow because very little catalyst is present. As the autocatalyst is produced, the rate increases and reaches a maximum before falling due to the falling concentration of reactants (which would slow down the rate).

You can view the video explanation via this link.

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9.4 Biological catalysts – Enzymes

9.4.1 Catalytic action of enzymes

LO8(k): describe enzymes as biological catalysts which may have specific activity

Enzymes are biological catalysts that speed up chemical reactions in living cells. They are **proteins**, which are polymers made up of hundreds of units of **amino acids**. Enzymes are mainly globular proteins which are soluble in water. Hence they are **homogeneous** catalysts, though the mechanism of **action** resembles **heterogeneous** catalysis.

The mechanism, described as a 'lock-and-key' hypothesis, is illustrated in Figure 29. It may be simplified as the following two steps:

$$\text{enzyme} + \text{substrate} \rightleftharpoons \text{enzyme-substrate complex} \quad \text{(fast)}$$
$$\text{enzyme-substrate complex} \rightarrow \text{enzyme} + \text{products} \quad \text{(slow, rate-determining)}$$

The **substrate** first **binds** to the **active site** of the enzyme to form the **enzyme-substrate complex**. Within the complex, the substrate molecule then undergoes **reaction** (bond reorganisation and/or reaction with other molecules). Finally, the products are **released** from the enzyme and diffuse away. The active site is empty again and ready to take in another substrate.

Substrate: the reactant that binds to the enzyme's active site
Active site: specific point on the enzyme where reaction takes place

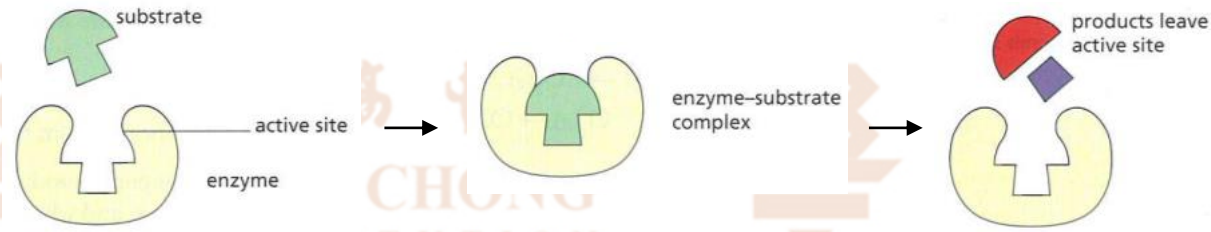


Figure 29. 'Lock-and-Key' mechanism of enzymes

Most enzymes are **highly specific**, catalysing only one reaction, or one group of similar reactions. Only a reactant molecule of the correct size and shape can attach to the enzyme's active site.

Enzymes are **highly efficient**. Enzyme-catalysed reactions have *very low activation energies*. Virtually every collision of the substrate with the active site leads to reaction. Hence, despite the low body temperature and concentrations, reactions in living cells take place rapidly.

Enzymes extracted from organisms are used in many industrial processes such as the manufacture of antibiotics and laundry detergents. Genetically engineered enzymes have also been used to make useful compounds such as 1,3-propanediol for making polymers, esters used in cosmetics and drugs for treatment of diabetes and cancer.

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Some examples of enzyme-catalysed reactions are as follows:

- Hydrogen peroxide, produced in many metabolic reactions, is harmful to cells. It is rapidly decomposed to water and oxygen in the presence of the enzyme, *catalase*:

$$H_2O_2(aq) \xrightarrow{\text{catalase}} H_2O(l) + \tfrac{1}{2}O_2(g)$$

Activation energies for the decomposition of hydrogen peroxide (for your information)

	uncatalysed	catalyst: platinum	catalyst: catalase
E_a / kJ mol^{-1}	76	50	8

- Yeast contains a mixture of enzymes called *zymase*, which converts sucrose into ethanol and carbon dioxide:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{\text{zymase}} \underset{\text{ethanol}}{4CH_3CH_2OH(aq)} + 4CO_2(g)$$

9.4.2 Relationship between [substrate] and rate of an enzyme-catalysed reaction

LO8(l): explain the relationship between substrate concentration and the rate of an enzyme-catalysed reaction in biochemical systems

Figure 30 shows the characteristic relationship between rate of an enzyme-catalysed reaction and [substrate]. Compare this graph to the rate-concentration graphs in Section 4.1.2.

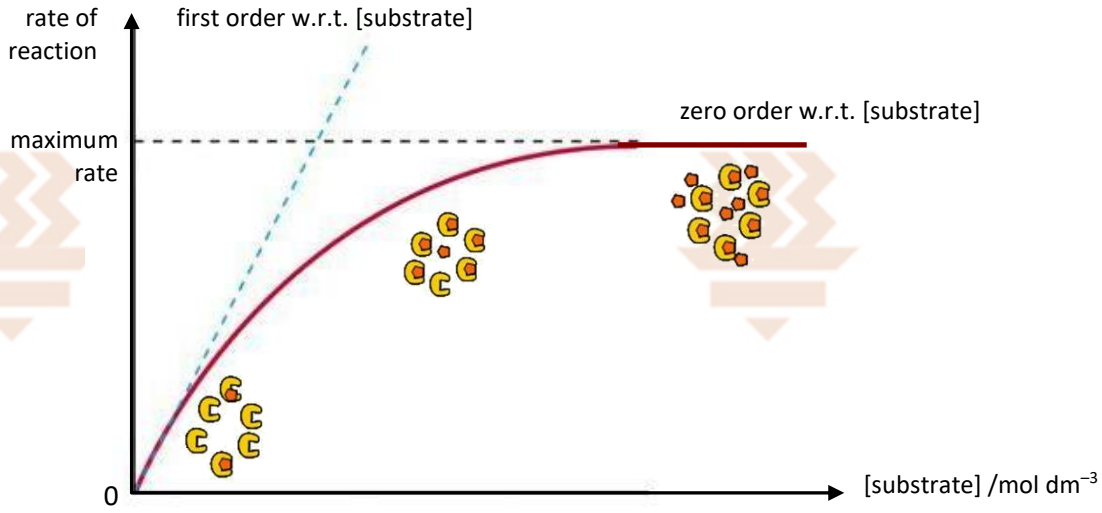


Figure 30. Graph of rate of an enzyme-catalysed reaction against substrate concentration

At **low [substrate]**, the enzyme concentration is greater than substrate concentration. The rate of reaction increases proportionally with increasing substrate concentration as shown by the straight line graph. The reaction is **first order** with respect to the [substrate].

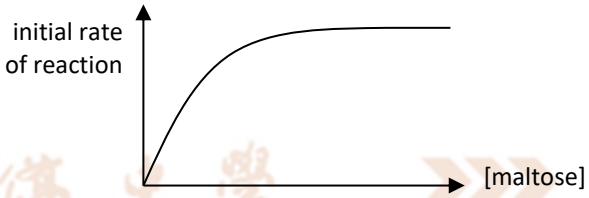
At **high [substrate]**, all the active sites are filled (i.e. saturated) with substrate molecules. Further increase in [substrate] does not affect the rate as shown by the horizontal line. The reaction is now **zero order** with respect to the [substrate].

To further increase the maximum rate of reaction, the concentration of the enzyme has to be increased.

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Exercise 9.5 *[N2001/III/34]* **(worked example)**

The graph shows the results of an investigation of the initial rate of hydrolysis of maltose by the enzyme amylase. In the experiments, the initial concentration of maltose was varied but that of amylase was kept constant.



Which conclusions can be deduced from these results?

1 When [maltose] is low, the rate is first order with respect to [maltose].
2 When [maltose] is high, the rate is independent of [maltose].
3 When [maltose] is high, the rate is independent of [amylase].

A **1**, **2** and **3** are correct
B **1** and **2** only are correct
C **2** and **3** only are correct
D **1** only is correct

Option 3 is not true because at high [maltose], initial rate is independent of [maltose] since changing [maltose] will not change the rate as the enzyme's active sites are saturated.

It is possible to increase the maximum rate of reaction by increasing the concentration of the enzyme itself, i.e. increasing [amylase]as this will increase the number of active sites.

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9.4.3 Effects of temperature and pH on enzyme activity

Each enzyme has an optimum set of temperature and pH at which it functions best. Changes in these conditions will cause the enzymes to **denature**. The denatured enzyme loses their globular structure, i.e. the active site changes shape and can no longer bind to the substrate (see Figure 31).

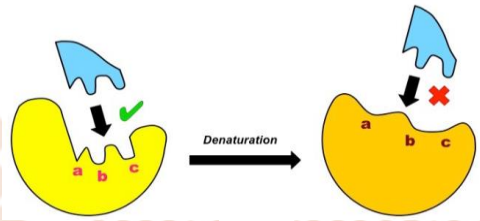


Figure 31. Denaturation of enzymes

Denaturation: Process where the (globular) structure of proteins is changed and it loses its three-dimensional shape.

Figure 32 shows the effect of temperature and pH changes on the rate of enzyme activity.

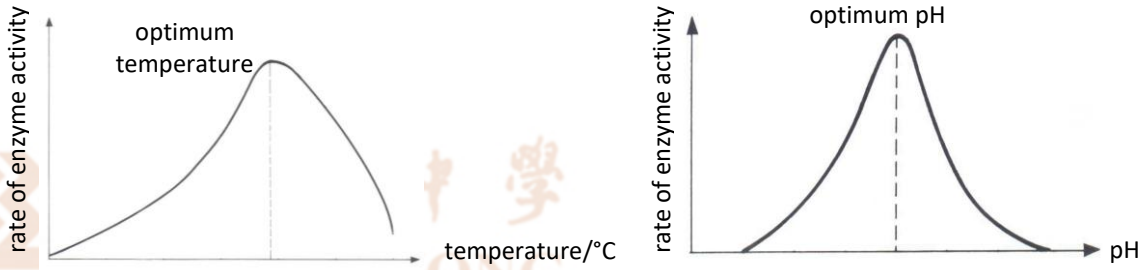


Figure 32. Enzyme activity is affected by (a) temperature and (b) pH

LOOKING AHEAD

Transformation of matter involves the study of the spontaneity (thermodynamics), rate (kinetics) and extent of chemical reactions (concept of equilibrium). Concepts learnt in Topic 5 Chemical Energetics and Topic 6 Reaction Kinetics will be used again in Topic 7 Chemical Equilibria to explain concepts related to the extent to which a reaction proceeds.

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07 Chemical Equilibria

GUIDING QUESTIONS

- What are the characteristics of a system that has reached dynamic equilibrium? How can we describe such a system at equilibrium?
- Why would systems tend towards a state of equilibrium?
- What happens when a system at equilibrium is disturbed?
- What are the factors to consider for optimal yield in a reversible reaction?

LEARNING OUTCOMES

Students should be able to:

9(a) explain, in terms of rates of the forward and reverse reactions, what is meant by a *reversible* reaction and *dynamic equilibrium*

9(b) state Le Chatelier's Principle and apply it to deduce qualitatively (from appropriate information) the effects of changes in concentration, pressure or temperature, on a system at equilibrium

9(c) deduce whether changes in concentration, pressure or temperature or the presence of a catalyst affect the value of the equilibrium constant for a reaction

9(d) deduce expressions for equilibrium constants in terms of concentrations, K_c, and partial pressures, K_p [treatment of the relationship between K_p and K_c is **not** required]

9(e) calculate the values of equilibrium constants in terms of concentrations or partial pressures from appropriate data

9(f) calculate the quantities present at equilibrium, given appropriate data (such calculations will not require the solving of quadratic equations)

9(g) show understanding that the position of equilibrium is dependent on the standard Gibbs free energy change of reaction, $\ominus G^{\ominus}$
[Quantitative treatment is **not** required]

9(h) describe and explain the conditions used in the Haber process, as an example of the importance of an understanding of chemical equilibrium in the chemical industry

REFERENCES

1. Peter Cann and Peter Hughes (2015), *Chemistry*, Hodder Education, Chapter 9
2. Martin S. Silberberg (2009), *Chemistry: The Molecular Nature of Matter and Change*, 5th Edition, McGraw Hill, Chapter 17

LOOKING BACK

Theoretically all reactions may be considered as reversible and occur to different extents. The position of equilibrium where a reaction lies, is related to the thermodynamics of the reaction, which we learnt under Topic 5 Chemical Energetics & Thermodynamics. Here we shall find out how the standard Gibbs free energy change, $\ominus G^{\ominus}$, and the equilibrium position are related. Also relevant are concepts from Topic 6 Reaction Kinetics, as we consider the rates of forward and backward reactions, and how their concentration-time graphs look like in a reversible reaction.

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1 INTRODUCTION

Many chemical reactions appear to go to **completion**, converting reactants to products until the limiting reactant is used up. An example is the combustion of methane:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

A reaction is considered as having gone to completion if any reactants in the final mixture are present at such low concentrations that they cannot be detected when the mixture is analysed. In practical terms, this means that if the reaction is more than 99% complete, it can be regarded as having gone to completion. Reactions that go to completion may be represented using the concentration-time graph below:

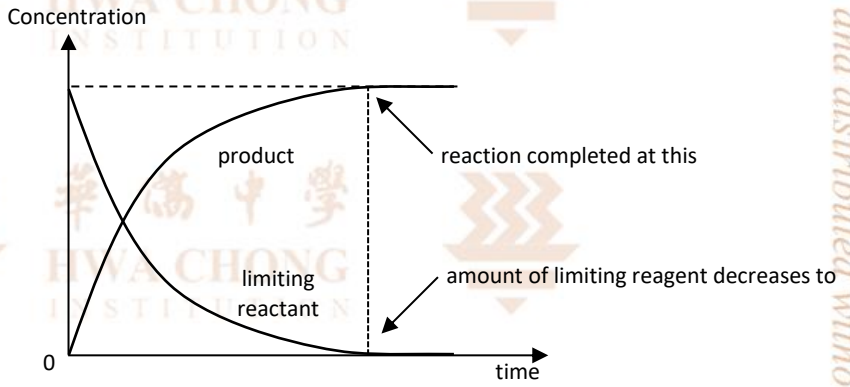


Figure 1. Concentration-time graph for reactions that go to completion

However, there are other reactions which may not go to completion. At the end of these reactions, a detectable amount of reactant remains, mixed with the product. Such reactions are called **reversible reactions**.

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2 Reversible Reactions

LO9(a)part: explain, in terms of rates of the forward and reverse reactions, what is meant by a reversible reaction

A **reversible reaction** is one which can occur in both directions.

A double-headed arrow '⇌' is used to denote a reversible reaction.

Examples of reversible reactions include:

Haber Process: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Contact Process: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

Esterification: $CH_3CO_2H(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3CO_2CH_2CH_3(l) + H_2O(l)$

Reversible reactions may be represented using the concentration-time graph below:

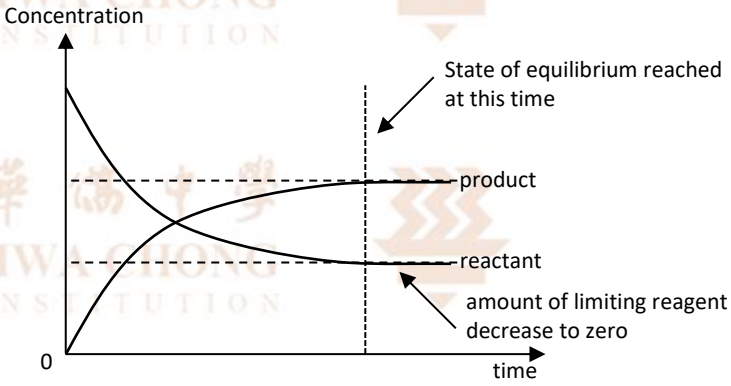


Figure 2. Concentration-time graph for a reversible reaction

2.1 Dynamic Equilibrium

LO9(a)part: explain, in terms of rates of the forward and reverse reactions, what is meant by dynamic equilibrium

A reversible reaction will reach a state of equilibrium where no overall change of reactant and product concentrations is observed. It seems as though the reaction has stopped, but it is actually not the case. The *forward reaction continues to occur* since reactants are still present! The reason why concentrations are not changing is because the *reverse reaction* is also going at *exactly the same rate*, turning the 'new' products back into reactants.

A **dynamic equilibrium** refers to a reversible reaction in which the forward and reverse reactions are both taking place at the same rate resulting in no overall changes in concentrations.

The word 'dynamic' means that the reactions are still taking place although there is no observable change, i.e. **the equilibrium is not static**. An analogy of dynamic equilibrium is that of a child running up an escalator which is moving in the opposite direction. When the child and the escalator are moving at the same rate, the position of the child appears unchanged (although he is still running). An analogy of static equilbrium would be that of two children on a see-saw. At 'equilibrium', the see-saw remains horizontal (i.e. not moving up or down) and the positions of the children are fixed.

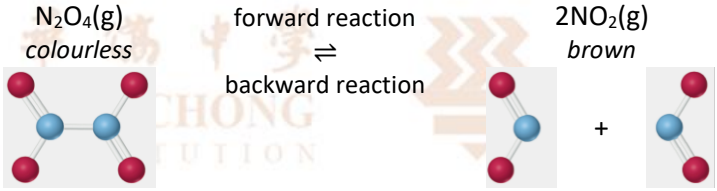
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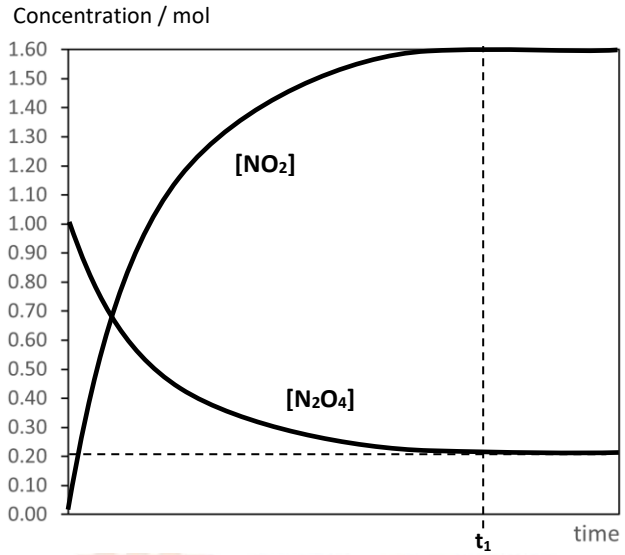
(a) *Analogy of dynamic equilibrium* ***(b)*** *Analogy of static equilibrium*

Figure 3

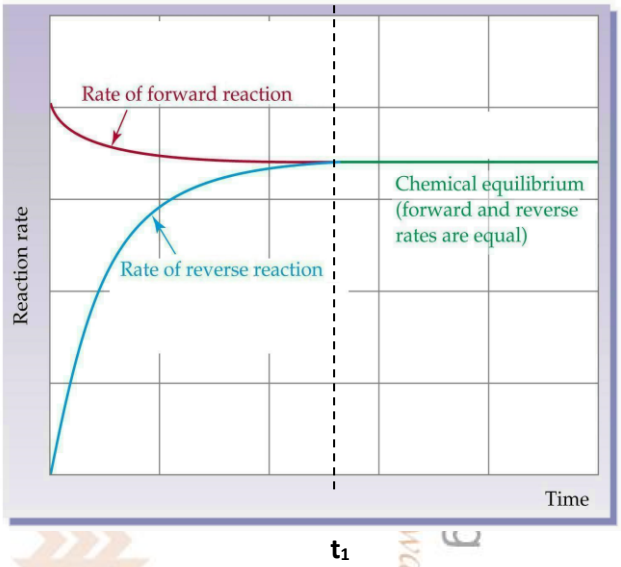
Consider the decomposition of N_2O_4 into its monomers:



1.00 mol of colorless $N_2O_4(g)$ is added into a 1 dm^3 flask. The flask is sealed and maintained at a particular temperature e.g. 200 °C. Figure 4 shows the concentration-time graph and the rate-time graph for the decomposition reaction.



a) *Concentration-time graph*



b) *Rate-time graph*

Figure 4. Decomposition of N_2O_4 into its monomers

- At time = 0 (start of reaction), only N_2O_4 is present. Then the forward reaction starts to occur: N_2O_4 decomposes to form brown NO_2 gas.
- As $[N_2O_4]$ decreases, rate of forward reaction ($rate_f$) decreases. On the other hand, $[NO_2]$ increases so rate of reverse reaction ($rate_b$) increases.
  Observation: The contents of the flask slowly turn pale brown and darken.

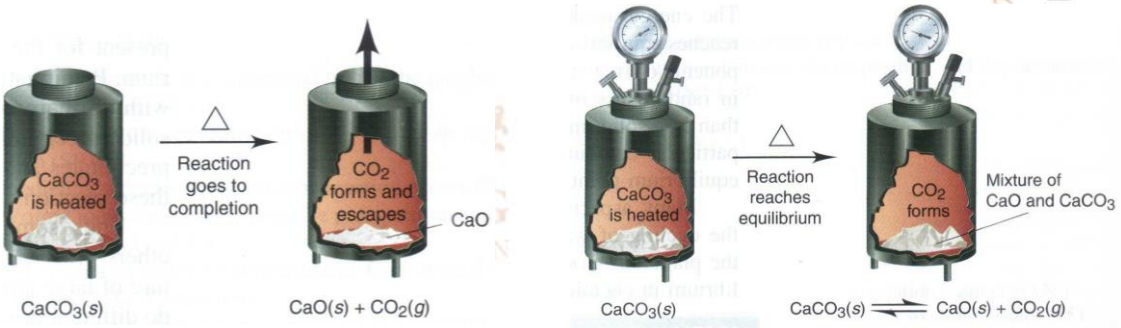
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- At time = t_1, the system reaches **dynamic equilibrium**. $[N_2O_4]$ and $[NO_2]$ remain constant i.e. there is **no net change in concentrations** (note $[N_2O_4]$ does not decrease to zero) and **$rate_f$ = $rate_b$ (but not zero)**.
  Observation: Intensity of the brown colour stops changing.

In this example, the flask has to be sealed as **equilibrium can only be achieved in a closed system**, one in which no substances are lost to or gained from the surroundings. An open system allows substances to escape or to enter and equilibrium cannot be established.

Consider the thermal decomposition of $CaCO_3$: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

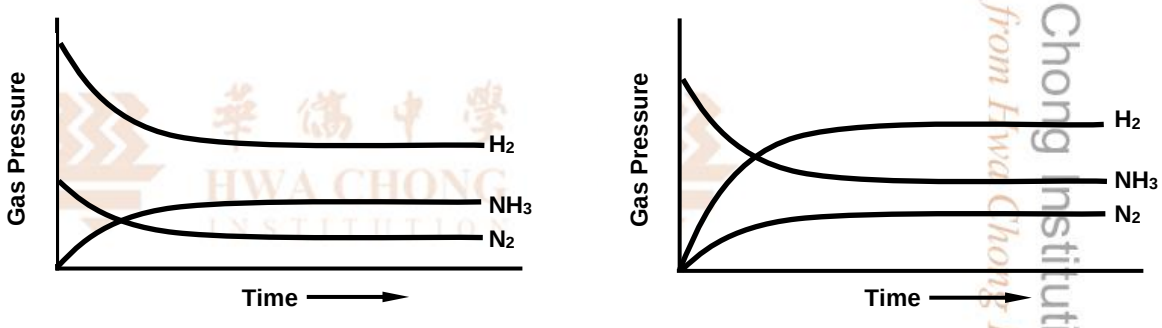
In an open system, CO_2 once formed escapes and is not present to react with CaO. Eventually, all the $CaCO_3$ is decomposed, i.e. forward reaction goes to completion. In the closed system, CO_2 is able to react with CaO to form $CaCO_3$. Eventually, the system reaches equilibrium. Further heating will not change the amount of $CaCO_3$, CaO and CO_2.



***(a)** Heating $CaCO_3$ in an open container* ***(b)** Heating $CaCO_3$ in a closed container*

Figure 5

Equilibrium can be achieved "from either direction". This means that we can establish equilibrium starting with either the reactants or products (or actually any amounts of reactants and products). This is illustrated in Figure 6 using the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$.



***(a)** Approaching equilibrium from the reactants side* ***(b)** Approaching equilibrium from the product side*

Figure 6

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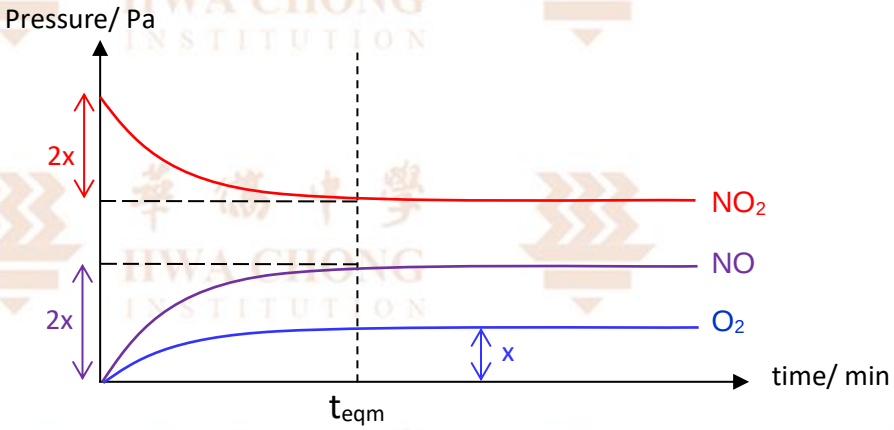
Exercise 2.1 (Worked Example)

Some NO_2 was placed in a closed vessel. Sketch a graph showing how the pressure of each substance varies over time until equilibrium is reached.

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

Let x (in Pa) be the increase in P_{O_2}.

The change in the partial pressures of the reactants and the products must follow the stoichiometry of the chemical equation. Hence as P_{O_2} changes by x Pa, it must mean that P_{NO_2} & P_{NO} change by 2x Pa. This is reflected in the relative height of the changes shown in the graph. Note also that the pressures of all the 3 compounds reaches the new equilibrium values at the same time. This time, t_{eqm}, signifies that a new equilibrium position has been achieved.



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3 EQUILIBRIUM CONSTANT

3.1 Expression for Equilibrium Constant

*LO9(d): deduce expressions for equilibrium constants in terms of concentrations, K_c, and partial pressures, K_p [treatment of the relationship between K_p and K_c is **not** required]*

The **Equilibrium Law** states that for any system at equilibrium, the product of the concentrations of each product (raised to the power equal to its coefficient in the equation) divided by the product of the concentrations of each reactant (raised to the power equal to its coefficient in the equation) has a **constant value** called the **equilibrium constant**, *K*, at a **constant temperature**.

Equilibrium constant can be expressed in terms of:

- concentration (in mol dm^{-3}), denoted by K_c
- partial pressure (usually in Pa or atm), denoted by K_p

Consider the reversible reaction: $a\,A + b\,B \rightleftharpoons c\,C + d\,D$

$$K_c = \frac{[C]_{eqm}^{c}[D]_{eqm}^{d}}{[A]_{eqm}^{a}[B]_{eqm}^{b}} \text{ which is simplified to } K_c = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

If the above is a **gaseous** system,

we can write $K_p = \dfrac{(p_C)^c(p_D)^d}{(p_A)^a(p_B)^b}$ (since [gas] $\langle$ P_{gas})

where partial pressure of A = $p_A = \dfrac{n_A}{\text{total no. of moles of gases}} \times p_{total}$

The units of K_c or K_p depend on their expressions. Using the above expressions, units of K_c are $(\text{mol dm}^{-3})^{(c+d)-(a+b)}$ and units of K_p are $(\text{Pa})^{(c+d)-(a+b)}$ or $(\text{atm})^{(c+d)-(a+b)}$.

Relationship between K_c and K_p (Background Info)

If the mixture behaves as an ideal gas, $[A] = \dfrac{n_A}{V} = \dfrac{p_A}{RT}$ (by rearranging pV = nRT)
Since R and T are constant, [A] $\langle$ P_A

Substitute into K_c, $K_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b} = \dfrac{(\frac{p_c}{RT})^c(\frac{p_d}{RT})^d}{(\frac{p_a}{RT})^a(\frac{p_b}{RT})^b} = \dfrac{(p_c)^c(p_d)^d}{(p_a)^a(p_b)^b}(RT)^{(a+b)-(c+d)}$

$K_c = K_p(RT)^{(a+b)-(c+d)}$

When the number of moles of gases is the same on each side of the stoichiometric equation, $K_c = K_p$!

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Exercise 3.1

For each of the following reactions, write the equilibrium constant expressions, K_c and K_p, and state the units. Assume that gas pressure is measured in Pa.

	Equilibrium	K_c & units	K_p & units
(a)	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$ $mol^{-2}\ dm^6$	$K_p = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$ Pa^{-2}
(b)	$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$		
(c)	$\frac{1}{2}N_2O_4(g) \rightleftharpoons NO_2(g)$		

3.2 Equilibrium constant for reactions involving pure liquids and solids

Consider the following equilibria involving pure liquids and solids:

(a) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(b) $CH_3CO_2H(l) + C_2H_5OH(l) \rightleftharpoons CH_3CO_2C_2H_5(l) + H_2O(l)$

(c) $CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

Reaction (a) is an example of **heterogeneous** equilibrium as the components are in **different phases**. Reactions (b) and (c) are examples of **homogeneous** equilibria as the components are in the **same phase**.

Applying the Equilibrium Law, the equilibrium constant expression for reaction (a) may be written as:

$$K = \frac{[CaO][CO_2]}{[CaCO_3]}$$ (note: $[CaCO_3]$ and $[CaO]$ are constant)

Rearranging, $K \times \frac{[CaCO_3]}{[CaO]} = [CO_2]$ (group the constant terms together)

$K_c = [CO_2]$ mol dm^{-3}

or $K_p = p_{CO_2}$ Pa

Hence, when writing equilibrium constant expressions for **heterogeneous equilibria**, we **omit the concentration of pure solids or liquids** as they are considered a constant.

Why are the concentrations of pure solids or liquids considered constant? (Background Info)

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concentration of pure solid = $\frac{n}{V} = \frac{m}{M_r V} = \frac{\text{density}}{M_r}$ = constant (since density and M_r are constant)

This also applies to the concentration of a pure liquid. For example,

$$[H_2O(l)] = \frac{1\ \text{g cm}^{-3}}{18\ \text{g mol}^{-1}} \times 1000\ \text{cm}^3 = 55.5\ \text{mol dm}^{-3}$$

The **concentration** of liquids which are acting as a **solvent remains almost constant** since a solvent is present in large excess so the changes, if any, will be negligible.

Hence, for reaction (c), $K_c = \frac{[H_2CO_3]}{[CO_2]}$ (no units)

Connecting Equilibrium and Kinetics: Equilibrium Constant and Rate Constant (Background Info)

For a reversible reaction:

$$A + B \underset{\text{rate}_b}{\overset{\text{rate}_f}{\rightleftharpoons}} C$$

The equilibrium constant *K* can be derived from Kinetics.

If the reaction proceeds in a single step, rate of forward reaction, $\text{rate}_f = k_f [A][B]$

and rate of backward reaction, $\text{rate}_b = k_b[C]$

At dynamic equilibrium,

$$\text{rate}_f = \text{rate}_b$$

$$k_f [A][B] = k_b[C]$$

$$\frac{k_f}{k_b} = \frac{[C]}{[A][B]}$$

$$\therefore K = \frac{k_f}{k_b}$$

This expression is true only if the chemical reaction proceeds in a single step. Many reactions do not proceed in one step but through complicated multi-step mechanisms.

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4 Position of Equilibrium and Equilibrium Constant

The **position of equilibrium** refers to the composition of an equilibrium mixture, i.e. the **relative proportion of products to reactants** in an equilibrium mixture. Position of equilibrium may lie on the **right** (i.e. towards the products) or lie on the **left** (i.e. towards the reactants).

The **magnitude** of K_c or K_p is a measure of the **position** of equilibrium or the **extent** to which reactants are converted into products (i.e. **how *far*** the *forward* reaction occurs).

- A **small *K*** means the position of equilibrium lies on the **left**. The **extent** of conversion of reactants into products is **small**, so the proportion of products to reactants is low.
- A **large *K*** means the position of equilibrium lies on the **right**. The **extent** of conversion of reactants into products is **large**, so the proportion of products to reactants is high.

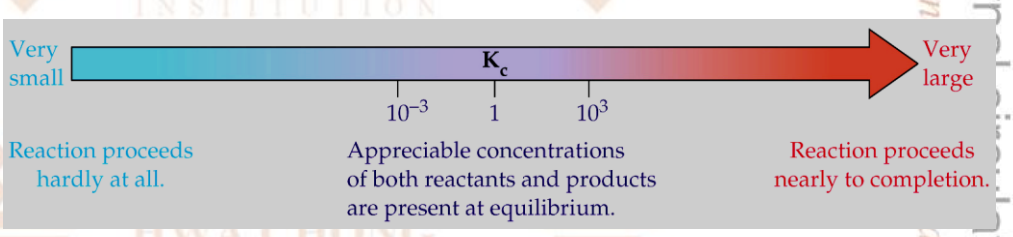


Figure 7. Magnitude of K is a measure of the position of equilibrium

The magnitude of K_c or K_p gives **no information about the rate** of reaction (how *fast* the reaction occurs). Some slow reactions may eventually yield a large amount of product e.g. rusting of iron. Others reach equilibrium quickly but reacts only to a small extent e.g. dissociation of weak acids. Knowing the extent of a reaction allows us to adjust the conditions to get a high yield.

The equilibrium constant, *K*, is not the same as the position of equilibrium. The position of equilibrium can shift, but *K* is a constant which changes only with temperature.

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5 Position of Equilibrium and Le Chatelier's Principle

LO9(b): state Le Chatelier's Principle and apply it to deduce qualitatively (from appropriate information) the effects of changes in concentration, pressure or temperature, on a system at equilibrium
LO9(c): deduce whether changes in concentration, pressure or temperature or the presence of a catalyst affect the value of the equilibrium constant for a reaction

Changes in conditions such as concentration, pressure or temperature, can disturb the position of equilibrium of a system. The system reacts in a way to re-attain equilibrium. The changes in the position of equilibrium can be predicted (qualitatively) from **Le Chatelier's Principle.**

> ***Le Chatelier's Principle*** *states that if the* ***conditions*** *of a system at equilibrium are* ***changed****, the position of equilibrium* ***shifts*** *so* ***as to reduce that change****.*

5.1 Effect of Changes in Concentration

Consider the equilibrium: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

What is the effect of adding some N_2 to the equilibrium mixture?

- When some N_2 is added to the equilibrium mixture, **concentration of N_2 increases**.
- By Le Chatelier's principle, position of equilibrium **shifts to the right** to consume some of the N_2 **so as to decrease concentration of N_2.**
- Concentration of H_2 will also decrease while that of NH_3 will increase.

Figure 8 shows how the concentrations of N_2, H_2 and NH_3 changes with time, when N_2 is added at t_1.

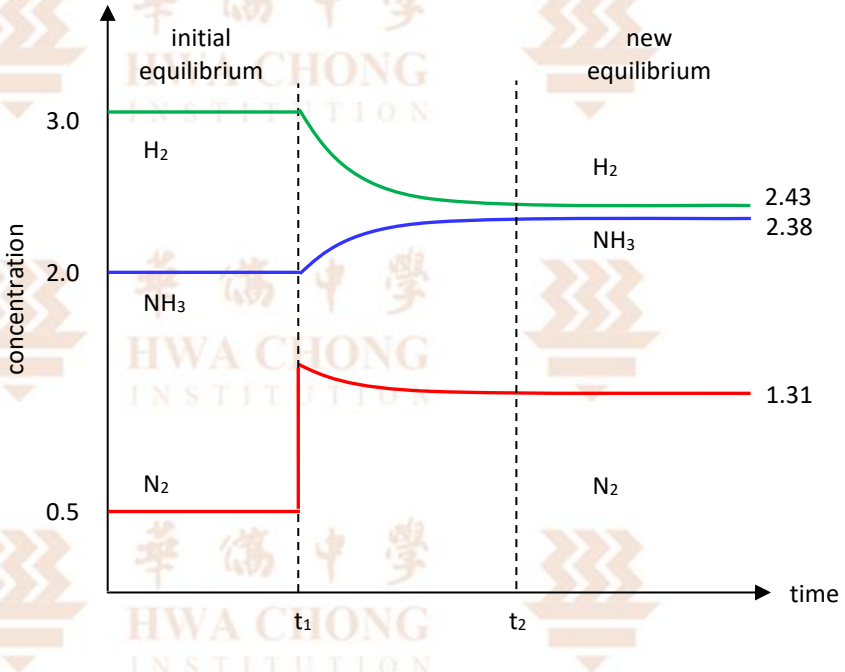


Figure 8. Changes in concentration after some N_2 is added at t_1

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Key points to note:

- At t_1, $[N_2]$ increases sharply due to the addition of N_2.
- As predicted, $[NH_3]$ at the new equilibrium position is higher than its original concentration.
- $[N_2]$ still ends up higher than before the addition at t_1. The position of equilibrium can only shift to **reduce** (not completely remove) the change.
- $[H_2]$ ends up lower than before because some reacted with the added N_2.
- Most importantly, although the position of equilibrium shifted to the right, **the value of equilibrium constant, K_c, remains the same**.

  Before t_1 (initial equilibrium), $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{2^2}{(0.5)(3)^3} = 0.30\ mol^{-2}\ dm^6$

  After t_2 (new equilibrium), $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{2.38^2}{(1.31)(2.43)^3} = 0.30\ mol^{-2}\ dm^6$

  Changing $[N_2]$ affects the position of equilibrium but does not change the value of K_c.

As the above is a gaseous system, the partial pressure of N_2 is also increased when some N_2 is added since $[N_2] \langle P_{N2}$. Hence, we can say that changing the partial pressure of a gaseous component, *by adding some of that component* e.g. N_2, will have the same effect as changing its concentration.

Consider another equilibrium: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

Adding more $CaCO_3$ or CaO will not affect the position of equilibrium because the **position of equilibrium** is **unaffected by pure solids or liquids** since their concentrations are considered constant (see Section 3.2).

Exercise 5.1 (Worked Example)

Consider the reaction in equilibrium below:

$Fe^{3+}(aq)$	+	$SCN^-(aq)$	$\rightleftharpoons$	$[FeSCN]^{2+}(aq)$
pale yellow		colourless		blood-red

State and explain the observations when NaSCN(s) is added to the above equilibrium mixture.

The NaSCN(s) added dissolves in the aqueous solution, $[SCN^-]$ increases.

By Le Chatelier's principle, position of equilibrium shifts to the right to decrease $[SCN^-]$.

Thus the red colour darkens / deepens.

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Exercise 5.2

Haemoglobin (Hb) is a protein found in red blood cells. They are large proteins that contain *heme* groups in them. Each haemoglobin molecule contains four *heme* groups, and each *heme* group contains an iron at its active sites which allow for reversible binding to O_2 molecule. Each Hb can bind up to four oxygen molecules and the binding occurs in successive steps.

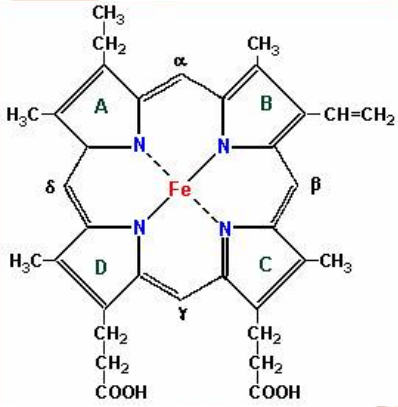
The entire system of oxygen transport and delivery in the body depends on the pickup and release of O_2 by haemoglobin according to the series of equilibria:

$Hb + O_2 \rightleftharpoons Hb(O_2)$

$Hb(O_2) + O_2 \rightleftharpoons Hb(O_2)_2$

$Hb(O_2)_2 + O_2 \rightleftharpoons Hb(O_2)_3$

$Hb(O_2)_3 + O_2 \rightleftharpoons Hb(O_2)_4$



Heme group

(a) With reference to the above series of equilibria, comment on the position of equilibrium

(i) in oxgen-starved muscles where P_{O_2} is low

(ii) in the lungs where P_{O_2} is high

(b) How do people at high altitude (low P_{O_2}) adapt?

5.2 Effect of Changes in Total Pressure

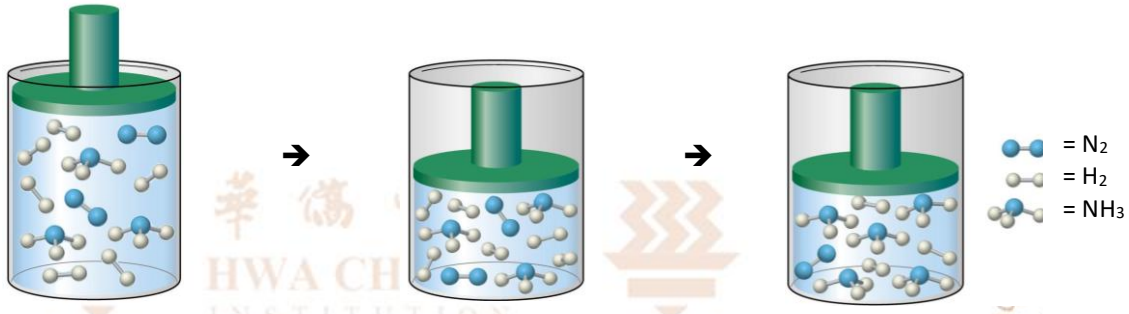
For a system with **gaseous** components, changing the volume of the container changes the total pressure. The change in total pressure can cause the position of equilibrium to shift. The effect on systems containing only liquids and solids is negligible as liquids and solids are nearly incompressible.

Consider the same equilibrium: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

What is the effect of decreasing the volume of the container?

- If the volume of the container is decreased, the **pressure** will **increase** (Figure 9b).
- The system will try to **reduce** the pressure by reducing the total number of gas molecules.
- Hence, the position of equilibrium will shift **right** towards the side with **fewer moles of gas**.

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initial equilibrium

N_2 molecule: 2 units
H_2 molecule: 6 units
NH_3 molecule: 3 units

(a)

at the instant when volume is decreased

N_2 molecule: 2 units
H_2 molecule: 6 units
NH_3 molecule: 3 units

(b)

new equilibrium

N_2 molecule: 1 unit (□ by 1
H_2 molecule: 3 units (□ by 3 units)
NH_3 molecule: 5 units (□ by 2 units)

(c)

Figure 9. Changes in the no. of molecules when volume of container decreases

Figure 9 shows that when $[NH_3]$ increases by 2 units, $[N_2]$ and $[H_2]$ decrease by 1 unit and 3 units respectively. Overall, there is a decrease of 2 units of gas molecules. At the new equilibrium (Figure 9c), the pressure is lower than the pressure immediately after volume decreases (Figure 9b).

Figure 10 shows how the concentration of N_2, H_2 and NH_3 changes with time, when volume of the container is decreased at t_1.

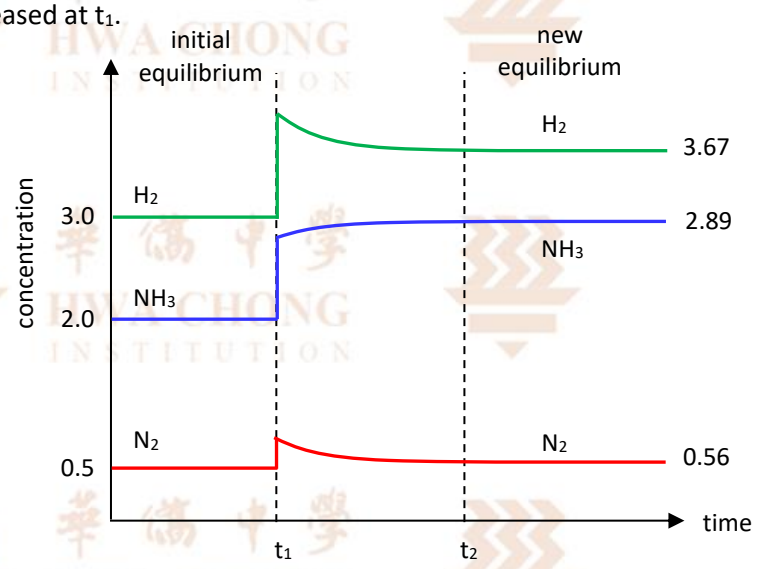


Figure 10. Changes in concentration after pressure is increased by reducing volume of container at t_1

Key points to note:

- At t_1, $[N_2]$, $[H_2]$ and $[NH_3]$ all increase sharply due to the reduction in volume of container.
- As predicted, since the position of equilibrium shifts right, $[NH_3]$ is higher than its concentration at t_1 when the volume of container is decreased, but $[N_2]$ and $[H_2]$ are lower.
- Similar to changing concentration, although the position of equilibrium shifted to the right, **the value of equilibrium constant, K_c, remains the same**.

In some reactions, the total number of moles of gases on each side of the stoichiometric equation are the same i.e. number of moles of gases do **not** change during reaction. For example,

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

In this case, changes in pressure have **no effect** on the position of equilibrium.

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Exercise 5.3

Consider the following system at equilibrium:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$
colourless brown

How would increasing the total pressure affect the position of the equilibrium? What would you observe?

When the total pressure increases, by Le Chatelier's principle, the position of equilibrium shifts to the **left** so as to **decrease** the pressure by favouring the reaction that results in **fewer moles of gases**. Thus less NO_2 will be present and **intensity of brown colour decreases**.

5.3 Effect of Changes in Temperature

The effect of temperature on the position of equilibrium depends on the enthalpy change of the reaction.

Consider the equilibrium: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\otimes H_r = -92$ kJ mol^{-1}

What is the effect of decreasing the temperature of the equilibrium mixture?

- When temperature is decreased, the system will try to **produce additional heat** by favouring the **exothermic** reaction.
- Since the forward reaction is exothermic in this equilibrium, by Le Chatelier's Principle, the position of equilibrium **shifts to the right**.
- Hence, $[NH_3]$ increases while $[N_2]$ and $[H_2]$ decreases.

If a forward reaction is endothermic, the position of equilibrium would shift to the left instead.

Figure 11 shows how the concentrations of N_2, H_2 and NH_3 changes with time when temperature is decreased at t_1.

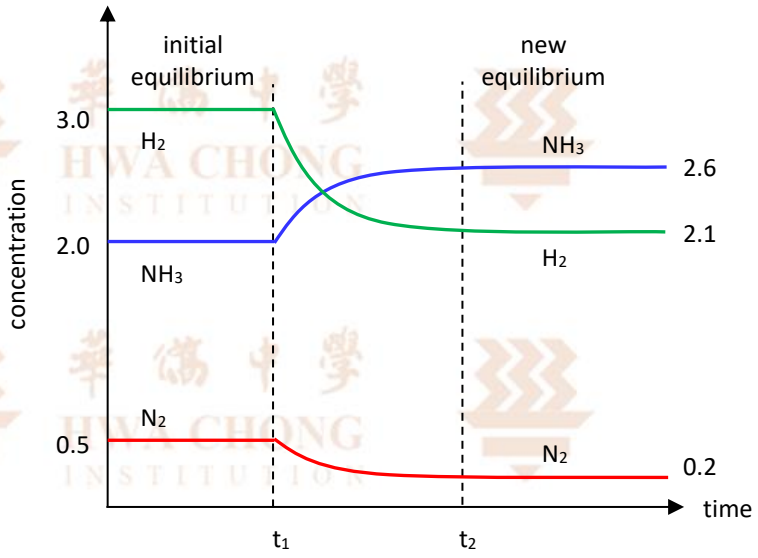


Figure 11. Changes in concentration after temperature is decreased at t_1

Key points to note:

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- Unlike changes in concentration or pressure, at t_1, $[N_2]$, $[H_2]$ and $[NH_3]$ did not change sharply.
- As predicted, at the new equilibrium position, $[NH_3]$ increases while $[N_2]$ and $[H_2]$ decreases.
- Unlike changes in concentration or pressure, changes in temperature affects **both** the position of equilibrium and the value of the equilibrium constant.

  Before t_1 (initial equilibrium), $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{2^2}{(0.5)(3)^3} = 0.3\ \text{mol}^{-2}\ \text{dm}^6$

  After t_2 (new equilibrium), $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{2.6^2}{(0.2)(2.1)^3} = 3.8\ \text{mol}^{-2}\ \text{dm}^6$

  When the forward reaction is **exothermic**, a **decrease in temperature increases the value of K_c or K_p.**

Why does *K* increase when temperature decrease for exothermic reactions? (Background Info)

In Section 3.2 Background Info, we derived the relationship: $K = \frac{k_f}{k_b}$.

The Arrhenius equation (Topic 6 Reaction Kinetics) shows that when temperature is decreased, rate constant, k, will decrease. Hence when temperature is decreased, **both the rate constants** of the forward and backward reactions, k_f and k_b, **will decrease**. So **both** the forward and backward reactions become **slower**.

However, since the forward reaction is exothermic, the backward reaction has a larger activation energy. Hence, k_b will **decrease more** than k_f when temperature decreases so ***K* increases** since $K = \frac{k_f}{k_b}$.

Because the rate of the backward reaction decreases more than that of the forward reaction, the system would favour the forward reaction to produce additional heat (as predicted by Le Chatelier's Principle).

Alternatively, the *van't Hoff* equation can be used to show how the equilibrium constant, K, increases when temperature is decreased for exothermic reactions:

$$ln\ K = -\frac{\cancel{H^\ominus}}{R}\left(\frac{1}{T}\right) + \frac{\cancel{S^\ominus}}{R}$$

Section 9 (Background Info) will show the derivation of the *van't Hoff* equation from thermodynamics.

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Exercise 5.4

Watch the video *"Effect of Temperature on Cobalt Complex"* on Google site and answer the following questions. The equation for the reaction in the video is given below.

$$\underset{\textit{pink}}{[Co(H_2O)_6]^{2+}(aq)} + 4Cl^-(aq) \rightleftharpoons \underset{\textit{blue}}{[CoCl_4]^{2-}(aq)} + 6H_2O(l)$$

(a) What was the colour of the solution of cobalt(II) ions at room temperature?

(b) What did you observe when the solution was heated?

(c) What did you observe when the solution was cooled in an ice bath?

(d) Using your answers in **(b)** and **(c)**, deduce whether the reaction (as shown in the equation) is exothermic or endothermic. Explain your answer.

5.4 Effect of Presence of a Catalyst

In Topic 6 Reaction Kinetics we learnt that a catalyst is a substance that speeds up a chemical reaction by providing an alternative reaction pathway of lower activation energy, while remaining chemically unchanged at the end of the reaction.

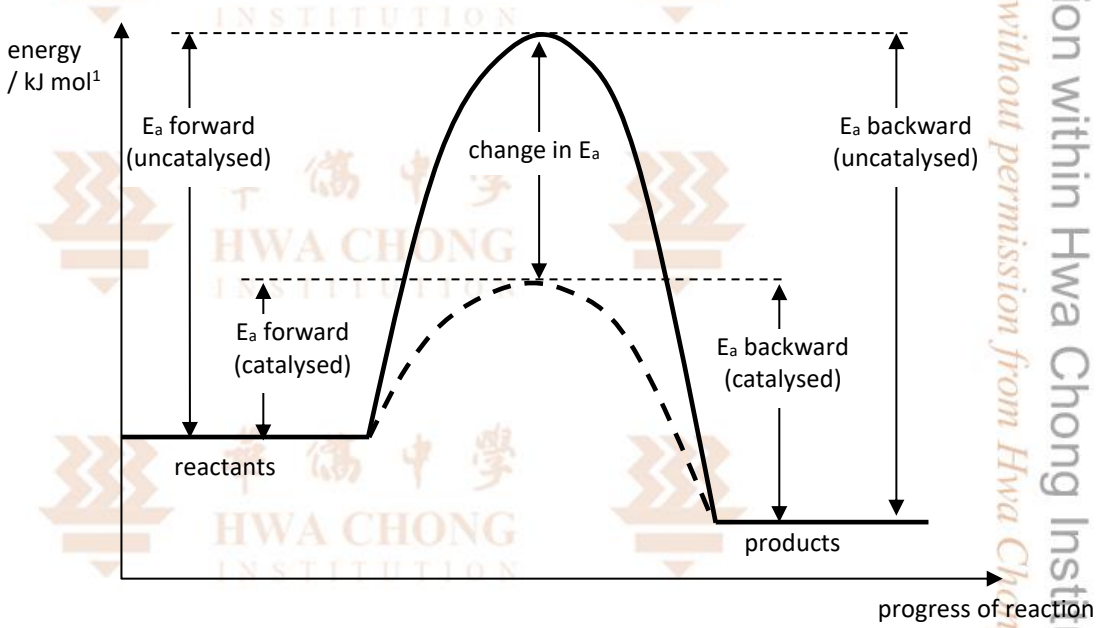


Figure 12. Effect of adding a catalyst on activation energies

- A catalyst lowers the activation energy of both forward and backward reactions by the same amount. Hence, **both forward and backward reaction rates increase by the same extent**.
- The **time** taken to reach equilibrium is **shortened**.
- However, the **position of equilibrium** (i.e. extent of conversion of products into reactants or yield) is **not affected**.
- The value of equilibrium constant, K_c or K_p, is also **unaffected** by the presence of a catalyst.

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6 The Reaction Quotient

Consider the reversible reaction: $a\,A + b\,B \rightleftharpoons c\,C + d\,D$

At any **instant**, $Q_c = \dfrac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$ where [ ] denotes the **instantaneous** concentration in mol dm^{-3}

Units of Q_c is $(\text{mol dm}^{-3})^{(c+d)-(a+b)}$

Q_c and K_c have the same expressions and units. However, at a given temperature, Q_c can take on any value while K_c has a constant value. **When $Q_c = K_c$, the system is at equilibrium**.

We can compare the values of Q_c and K_c to determine the direction in which a reaction will proceed towards equilibrium.

- If **$Q_c < K_c$,** reaction will **proceed in the forward direction** to consume more reactants and form more products until Q_c equals to K_c (i.e. until system reaches equilibrium).
- If **$Q_c > K_c$,** reaction will **proceed in the backward direction** to form more reactants and consume more products until Q_c equals to K_c (i.e. until system reaches equilibrium).

Using the above, the changes in the position of equilibrium due to changes in concentration or pressure can be predicted (quantitatively).

Exercise 6.1 (Worked Example)

Consider the reaction: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

There are 0.249 mol of N_2, 3.21×10^{-2} mol of H_2 and 6.42×10^{-4} mol of NH_3 in a 3.50 dm^3 reaction vessel at 375 °C. The numerical value of the equilibrium constant, K_c, is 1.20 at this temperature. Decide whether the system is at equilibrium. If it is not, predict in which direction the reaction will proceed to achieve equilibrium.

We first convert the quantities of each compound from moles to mol dm^{-3} as the Qc expression contains concentration terms.

$[N_2] = 0.249 / 3.50 = 7.114 \times 10^{-2}$ mol dm^{-3}

$[H_2] = (3.21 \times 10^{-2}) / 3.50 = 9.171 \times 10^{-3}$ mol dm^{-3}

$[NH_3] = (6.42 \times 10^{-4}) / 3.50 = 1.834 \times 10^{-4}$ mol dm^{-3}

$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(1.834\times10^{-4})^2}{(7.114\times10^{-2})(9.171\times10^{-3})^3} = 0.613 \text{ mol}^{-2}\text{ dm}^6$$

$Q_c \neq K_c$ so the system is not at equilibrium.

Since $Q_c < K_c$, reaction will proceed in the forward direction to increase $[NH_3]$, and decrease $[N_2]$ and $[H_2]$, until $Q_c = K_c$.

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Exercise 6.2

Predict and explain what would be observed when water is added to a pink solution containing the following equilibrium.

$$Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6H_2O(l)$$

pink blue

Effect of adding an inert gas to an equilibrium (Application Example)

Consider the equilibrium: $2NO_2(g) \rightleftharpoons N_2O_4(g)$

When an inert gas (e.g. argon) is added to this equilibrium mixture at constant total pressure, it is incorrect to conclude, using Le Chatelier's Principle, that the position of equilibrium is not affected since pressure is constant. In actual fact, the position of equilibrium shifts left.

We can explain this by comparing the values of Q_p and K_p.

The reaction quotient is written as: $Q_p = \frac{p_{N_2O_4}}{(p_{NO_2})^2}$ ----- (i)

Since $p_{N_2O_4} = \frac{N_2O_4}{total} \times P_{total}$ and $p_{NO_2} = \frac{NO_2}{total} \times P_{total}$,

upon substitution into (i) and simplification, $Q_p = \frac{\eta_{N_2O_4}}{(\ NO_2)^2} \times \frac{\eta_{total}}{P_{total}}$ ----- (ii)

When argon is added at constant pressure, the total moles of gases, η_{total}, increases. Since the other terms in equation (ii) are not changed, Q_p increases. This makes $\mathbf{Q_p > K_p}$. Hence, the position of equilibrium **shifts left**.

On the other hand, if argon is added to the mixture at constant volume, it is incorrect, again, to conclude that since total pressure increases, position of equilibrium will shift to the right. In actual fact, the position of equilibrium remains unchanged. This can also be explained using equation (ii).

Assuming the gases behave ideally (and obeys the ideal gas equation pV = nRT), when volume and temperature are constant, pressure, p_{total} is directly proportional to the total moles of gases, η_{total}. Adding argon at constant volume cause both η_{total} and p_{total} to increase, but their ratio remains the same. Hence Q_p (in equation (ii)) is unchanged and still equals to K_p, i.e. $\mathbf{Q_p = K_p}$ so there is **no effect** on the position of equilibrium.

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7 CALCULATIONS IN CHEMICAL EQUILIBRIUM

LO9(e): Calculate the values of equilibrium constants in terms of concentrations or partial pressures from appropriate data
LO9(f): Calculate the quantities present at equilibrium, given appropriate data (such calculations will not require the solving of quadratic equations)

Exercise 7.1 (Worked Example)

For the reaction, $CH_3CO_2H(l) + C_2H_5OH(l) \rightleftharpoons CH_3CO_2C_2H_5(l) + H_2O(l)$,
a 10.0 cm^3 mixture contained the following initial amounts in mol: ethanoic acid, 0.0525; ethanol, 0.0515; ester, 0.0314; water, 0.0167.

The equilibrium amount of ethanoic acid was found to be 0.0255 mol. Calculate the equilibrium amounts (in mol) of ethanol, ester and water. Hence, calculate K_c for the reaction.

We construct an ICE (initial, change, equilibrium) table to help simplify the thought process in working out the quantities of each compound in the chemical equation. Fill in the initial amounts of each compound as given in the question. We can work out that the change in amount of ethanoic acid is as follows:

$n_{ethanoic\ acid}$ reacted at equilibrium = 0.0525 – 0.0255 = 0.0270 mol

This then means that the changes in quantity for the other compounds in the equation is the same, since the stoichiometric ratio is 1 : 1 for all of them. The reactants therefore change by – 0.0270 while the products change by + 0.0270. The equilibrium quantities are then easily calculated by adding or subtracting the change from the initial values respectively.

	CH_3CO_2H	+	C_2H_5OH	⇌	$CH_3CO_2C_2H_5$	+	H_2O
initial amt / mol	0.0525		0.0515		0.0314		0.0167
change / mol	– 0.0270		– 0.0270		+ 0.0270		+ 0.0270
equilibrium amt / mol	0.0255		0.0245		0.0584		0.0437

$$K_c = \frac{[ester][water]}{[ethanoic\ acid][ethanol]} = \frac{(0.0584/V)(0.0437/V)}{(0.0255/V)(0.0245/V)} = 4.085 \text{ (no units)}$$

*Do remember to show that concentration = $\frac{no.of\ moles}{volume}$

Exercise 7.2

In the reaction shown below, 4.0 mol of H_2 and 2.0 mol of I_2 are allowed to react in a 2.0 dm^3 vessel at 440 °C. The equilibrium concentration of HI is 1.9 mol dm^{-3}.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Calculate the value of the equilibrium constant, K_c, for the reaction at 440 °C.

	$H_2(g)$	+	$I_2(g)$	⇌	$2HI(g)$
initial conc. / mol dm^{-3}					
change / mol dm^{-3}					
equilibrium conc. / mol dm^{-3}					

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Exercise 7.3 (Worked Example)

A gaseous mixture of 0.500 mol of H_2 and 0.500 mol of I_2 was placed in a reaction flask (with constant volume) at 430 °C.

Given that the equilibrium constant, K_c, for the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, is 54.3 at 430 °C, calculate the equilibrium number of moles of H_2, I_2 and HI.

Let x be the no. of moles of H_2 reacted.

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
initial amount / mol	0.500		0.500		0
change / mol	$-x$		$-x$		$+2x$
equilibrium amount / mol	$0.500 - x$		$0.500 - x$		$2x$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{0.5-x}{V}\right)^2} = \frac{(2x)^2}{(0.5-x)^2} = 54.3$$

where V = volume of reaction flask

$$\Rightarrow \quad \frac{2x}{0.5-x} = \sqrt{54.3} = 7.369$$

$$2x = 3.684 - 7.369x$$

$$x = \frac{3.684}{9.369} = 0.393 \text{ mol}$$

At equilibrium,

$n_{H_2} = 0.500 - 0.393 = 0.107 \text{ mol} = n_{I_2}$

$n_{HI} = 2 \times 0.393 = 0.786 \text{ mol}$

Exercise 7.4

K_c for the dissociation reaction **R**(aq) ⇌ **S**(aq) is 0.50 at 75 °C. A solution of **R**, with initial concentration of 15.0 mol dm^{-3}, is allowed to reach equilibrium at the same temperature. Calculate the equilibrium concentration of **R** and **S**.

Exercise 7.5 (Worked Example)

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Consider the reaction: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(a) PCl_5 is 30.0% dissociated at a certain temperature and a pressure of 1.01×10^5 Pa. Determine the value of K_p for the dissociation at this temperature.

(b) Calculate the pressure needed to achieve the degree of dissociation of $PCl_5(g)$ as 0.485, at the same temperature.

Note: In **(b)**, degree of dissociation of $PCl_5 = \dfrac{n_{PCl_5}\text{ dissociated}}{\text{initial } n_{PCl_5}} = 0.485$

(a) Consider basis of working: 1 mol of PCl_5 present initially

At equilibrium, n_{PCl_5} dissociated = 0.3 mol

Note that the change is described in % rather than an absolute value. In such cases, it is simply easier to set the starting amount as 1 mole. Any starting amount may be used (e.g. 10 mol) but 1 mole is a small value and easy to deal with, hence it was used in the worked solution that follows.

	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$	
initial amount / mol	1		0		0	
change / mol	– 0.3		+ 0.3		+ 0.3	
equilibrium amount / mol	1 – 0.3 = 0.7		0.3		0.3	Total = 1.3
equilibrium mole fraction	$\frac{0.7}{1.3}$		$\frac{0.3}{1.3}$		$\frac{0.3}{1.3}$	
equilibrium partial pressure / Pa	$\frac{0.7}{1.3} \times P_T$		$\frac{0.3}{1.3} \times P_T$		$\frac{0.3}{1.3} \times P_T$	

$P_T = 1.01 \times 10^5$ Pa (after dissociation)

$$K_p = \frac{p_{PCl_3}\,p_{Cl_2}}{p_{PCl_5}} = \frac{\left(\frac{0.3}{1.3} \times P_T\right)\left(\frac{0.3}{1.3} \times P_T\right)}{\left(\frac{0.7}{1.3} \times P_T\right)} = 9.989 \times 10^3 \text{ Pa}$$

(b) Let initial n_{PCl_5} be 1 mol, n_{PCl_5} dissociated = 0.485 mol

	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$	
initial amount / mol	1		0		0	
equilibrium amount / mol	1 – 0.485 = 0.515		0.485		0.485	Total = 1.485

Let pressure needed be P_T in Pa. At the same temperature, K_P remains constant.

$$K_p = \frac{\left(\frac{0.485}{1.485} \times P_T\right)\left(\frac{0.485}{1.485} \times P_T\right)}{\left(\frac{0.515}{1.485} \times P_T\right)} = \frac{(0.485)^2 P_T}{(1.485)(0.515)} = 9.989 \times 10^3 \text{ Pa } (K_P \text{ from a})$$

$\therefore$ total pressure needed, $P_T = 3.248 \times 10^4$ Pa

Note: In **(b)**, degree of dissociation of $PCl_5 = \dfrac{n_{PCl_5}\text{ dissociated}}{\text{initial } n_{PCl_5}} = 0.485$

Exercise 7.6 *[HCI Prelim 2006]*

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Carbon monoxide and hydrogen react according to the following equation.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

A 62.8 mol sample of carbon monoxide was added to 146 mol of hydrogen. When equilibrium was reached at a given temperature, the mixture contained 26.2 mol of methanol and the total pressure was 9.50 MPa.

(i) Write an expression for the equilibrium constant, K_p, for this reaction.

(ii) Calculate K_p at this temperature, giving its units.

(iii) Some hydrogen gas was added to the equilibrium system, and the partial pressure of methanol increased to 2.0 MPa at the new equilibrium. What is the new equilibrium partial pressure of hydrogen?

Exercise 7.7

A sample of pure NO_2 gas when heated to 1000 °C decomposes according to the following equation:

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

The equilibrium constant K_p is 158 atm. Analysis shows that the partial pressure of oxygen is 0.25 atm at equilibrium. Calculate the partial pressure of NO and of NO_2 in the equilibrium mixture.

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Determining K_c for an equilibrium reaction

Scenario:
To plan an experiment to determine a value of the equilibrium constant K_c of a given reaction, and to verify that a change in concentration has no effect on the value of K_c.

Approach:
Depending on the nature of the participating reactants and products, the techniques used in the experiment will vary greatly.
In general, bear the following in mind:

- Most reversible reactions take time to reach equilibrium, and therefore your plan must allow time for the equilibrium to be established (ranging from a few minutes to several days depending on the reaction).
- All K_c values are dependent on temperature, and so the temperature must be maintained (usually in a water bath), and be recorded.
- Your experiment must collect the data on all initial amounts of reactants and products, and the equilibrium amount of one of them. The rest of the equilibrium amounts can then be worked out using the Initial-Change-Equilibrium (ICE) table.
- To verify that a change in concentration has no effect on K_c, you need to set up several (usually five) different reaction mixtures with different starting concentrations of the reactants / products.

Examples:

1. Esterification of ethanoic acid by ethanol

   $CH_3CO_2H(l) + C_2H_5OH(l) \rightleftharpoons CH_3CO_2C_2H_5(l) + H_2O(l)$

   Hydrochloric acid is added to the mixture as a catalyst (it enables the equilibrium to be reached in a much shorter time without affecting the K_c value).
   The equilibrium mixture can be titrated with standard NaOH; this gives the total amount of acids (HC*l* and CH_3CO_2H) present at equilibrium. Subtracting the amount of HC*l* from this total amount will give the equilibrium amount of CH_3CO_2H, from which the K_c can be determined using the ICE table.
2. Formation of the iron(III)-thiocyanate complex

   $[Fe(H_2O)_6]^{3+}(aq) + SCN^-(aq) \rightleftharpoons [Fe(SCN)(H_2O)_5]^{2+}(aq) + H_2O(l)$

The $[Fe(SCN)(H_2O)_5]^{2+}$complex ion typically has a deep red colour. A colorimeter could be used to determine the equilibrium concentration of the complex ion. Usually, a calibration curve of absorbance against concentration is first determined using solutions of known concentrations of the complex. Then the equilibrium concentrations of various mixtures can be determined using the calibration curve. Once again, the K_c can be determined from the ICE table.

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8 HABER PROCESS

LO9(h): Describe and explain the conditions used in the Haber process, as an example of the importance of an understanding of chemical equilibrium in the chemical industry

The principles of Chemical Equilibria and Reaction Kinetics play an important part in the design and working conditions of an industrial process. The conditions are chosen so that reactants are converted into products as *quickly* as possible (a ***kinetics*** problem) and as *completely* as possible (an ***equilibrium*** problem).

The Haber process is used to manufacture ammonia from nitrogen and hydrogen.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \ominus H_r = -92 \text{ kJ mol}^{-1}$$

The reaction is slow and does not go to completion. Figure 13 shows that a high yield of NH_3 is produced by low temperature and high pressure.

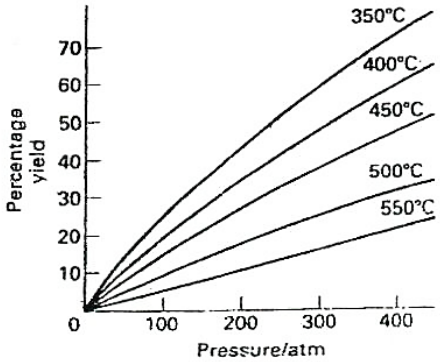


Figure 13. Effect of temperature and pressure on percentage yield of NH_3 in the Haber process.

However, the optimal conditions used in the Haber process are:

- Temperature: **450 °C**
- Pressure: **250 atm**
- Catalyst: **finely divided iron catalyst**

- A low temperature would favour the forward exothermic reaction and increase the yield of NH_3 but the reaction would be too slow to be economical. In practice, the operating temperature is kept at a moderate temperature of about **450 °C**.
- A **catalyst** is used to increase the rate of reaction thus increasing efficiency without affecting yield.
- A high pressure favours the forward reaction as it reduces the number of moles of gases but the cost and maintenance of the equipment would be too high. In practice, the operating pressure is relatively high at **250 atm**.
- The yield of NH_3 is further increased by removing it as it forms as this continuously shifts the position of equilibrium to the right.

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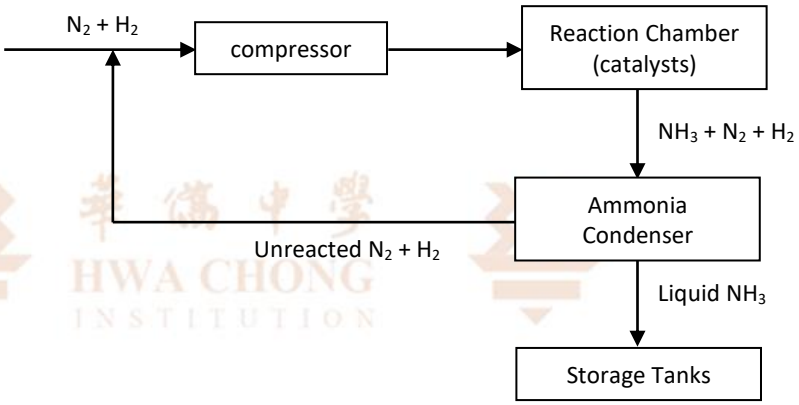


Figure 14. Simplified schematic diagram of the Haber process

Exercise 8.1 *[J2003/P2/Q3]*

In the Haber Process, ammonia is synthesised from its elements.

(a) Write an equation for the Haber Process and state whether it is endothermic or exothermic.

(b) What are three usual operating conditions of the Haber Process?

(c) Explain the considerations which lead to the temperature you have stated in **(b)** being used.

(d) Under certain conditions the equilibrium pressures of the three gases are

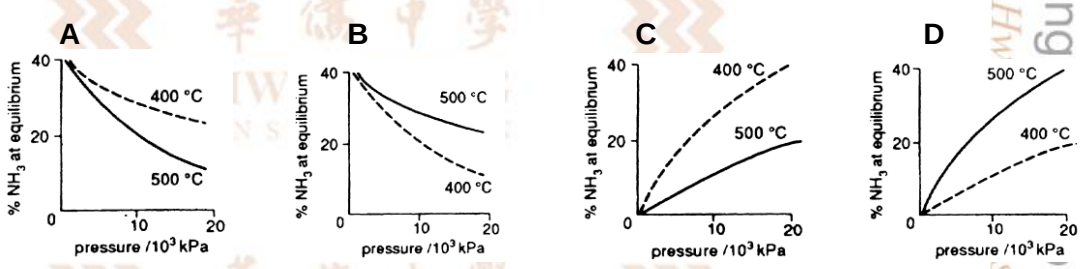
nitrogen	44.8 atm
hydrogen	105.6 atm
ammonia	37.2 atm

(i) Write an expression for the equilibrium constant, K_p, for the Haber Process.

(ii) Calculate K_p from these data, giving the units.

Exercise 8.2

Which of the following graphs correctly represents the percentage of ammonia obtainable in the Haber process at different temperatures?



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FRITZ HABER (Background Info)



'A scientist belongs to his country in times of war and to all mankind in times of peace.' – Fritz Haber (1868–1934), German Chemist

The main areas of Fritz Haber's research were electrochemistry and catalysis. Much of his work shaped the world we live in today. His work on the synthesis of ammonia (which won him the Nobel Prize in Chemistry in 1918) and the development of mustard gas (used in chemical warfare) sparked much debate, demonstrating the dilemmas and impact of the scientific applications on society and the environment.

Haber's motivation for developing a method for producing ammonia was to increase the supply of fertilisers due to the limited supply of natural fertilisers. Many predicted that there could be massive starvation in Europe unless this was done. While ammonia is a precursor for the production of nitrates for fertilisers, Haber's work also boosted the nitrate supply for the manufacturing of explosives in Germany in the early 1900s, which indirectly prolonged World War I. In addition, massive use of fertilisers caused the 'bloom' of phytoplankton resulting in the depletion of oxygen and death of aquatic animals (known as eutrophication).

Mustard gas was a horrible instrument of war that caused much suffering. Ironically, many compounds related to mustard gas could be used as anti-cancer agents.

Haber was eventually driven out of Germany before World War II despite his loyalty to his country, due to his Jewish ancestry.

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9 Equilibrium Constant and Gibbs Free Energy (connecting Equilibrium and Thermodynamics)

*LO9(g): Show understanding that the position of equilibrium is dependent on the standard Gibbs free energy change of reaction, ⊗$G^{⦵}$ [Quantitative treatment is **not** required]*

Recall in Topic 5 Chemical Energetics & Thermodynamics, that standard Gibbs free energy change of reaction ($\Delta G^{⦵}$) is the change in Gibbs free energy needed to convert reactants into products at 1 bar and constant temperature (usually at 298 K). Its sign can be used to predict where the position of equilibrium (POE) lies for a reversible reaction.

A negative value for $\Delta G^{⦵}$ represents a driving force in the forward direction, and POE lies to the right. A positive value represents a driving force in the reverse direction, and POE lies to the left.

Relation between $\Delta G^{⦵}$ and K (Useful Tool)

For a reversible reaction taking place under non-standard conditions, the Gibbs free energy change, ΔG, is related to the *standard Gibbs free energy change*, $\Delta G^{⦵}$, according to this equation:

$$\Delta G = \Delta G^{⦵} + RT \ln Q$$

where R is the gas constant
T is temperature in Kelvin
Q is the reaction quotient

For a reaction at equilibrium, $Q = K$ and $\Delta G = 0$, and the previous equation may be written as:

$$0 = \Delta G^{⦵} + \mathrm{RT} \ln K$$

Rearranging the equation gives us:

$$\boldsymbol{\Delta G^{⦵} = -RT \ln K}$$

This equation provides a useful link between these two essential ideas, standard Gibbs free energy change and equilibrium constant, both are measures of the extent of a reversible reaction.

The table below summarises how the sign for $\Delta G^{⦵}$ can provide information on POE.

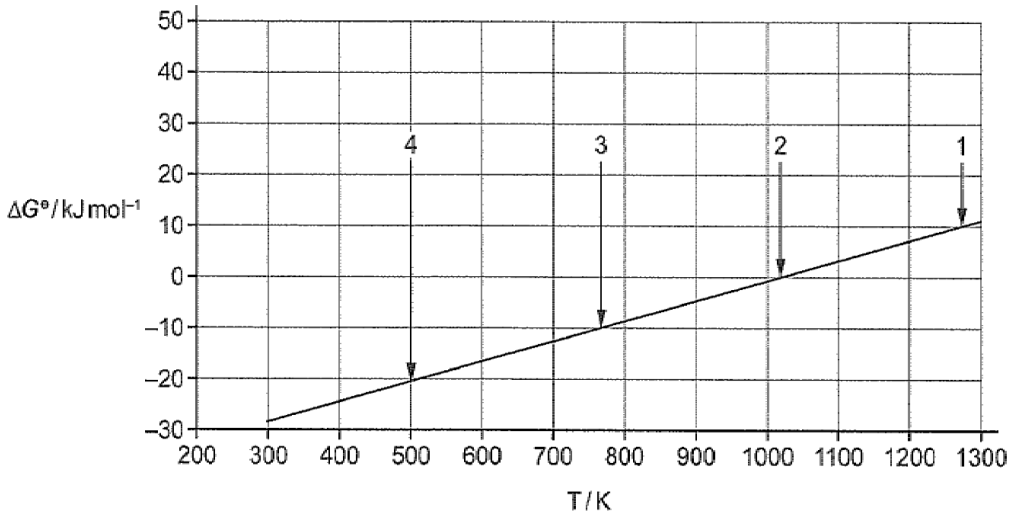
$\Delta G^{⦵}$	Position of equilibrium	Dominant species at equilibrium	K
−	lies to the right	product	> 1
+	lies to the left	reactant	< 1

The more negative the $\Delta G^{⦵}$, the greater the proportion of products present and the larger the value of K.

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Exercise 9.1 *[N2017 P1 Q14]*
The graph shows how $\Delta G^{\ominus}$ changes with temperature for the reaction shown.

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$



Equimolar amounts of H_2O and CO were introduced into a sealed container and allowed to reach equilibrium.

At which points will the concentration of H_2 be **greater** than the concentration of H_2O at equilibrium?

A 1 and 2 **B** 1 only **C** 2, 3 and 4 **D** 3 and 4 only

Temperature dependence of Equilibrium Constant (Background Info):

We now have an equation that relates standard free energy change for a reaction to the equilibrium constant:

$$G^{\ominus} = -RT\ ln\ K$$

In thermodynamics, we can derive an equation for how free energy change for a reaction depends on temperature:

$$G^{\ominus} = H^o - TS^o$$

We can therefore combine these two equations to obtain an equation for how the equilibrium constant depends on temperature.

$$-RTln\ K = H^o - TS^o$$

Dividing both sides by *RT* gives:

$$-lnK = \frac{H^o}{RT} - \frac{TS^o}{RT}$$

Rearranging, we get:

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$$lnK = -\frac{H^{\ominus}}{R}\left(\frac{1}{T}\right) + \frac{S^{\ominus}}{R}$$ --- *van't Hoff* equation

If we plot ln *K* on the y-axis and $\frac{1}{T}$ (T in Kelvins) on the x-axis, we obtain a straight line from which the gradient ($-\frac{H^{\ominus}}{R}$), and the y-intercept ($\frac{S^{\ominus}}{R}$) can be used to find $\ominus H^{\ominus}$ and $\ominus S^{\ominus}$ respectively.

LOOKING FORWARD

In this topic, we looked at general concepts related to the chemical equilibria of reversible reactions. These concepts will be revisited in Topic 13 Solubility Equilibria and Topic 14 Acid-Base Equilibria, where we shall apply them to understand precipitation reactions and acid-base reactions at a deeper level.

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08 Introduction to Organic Chemistry

GUIDING QUESTIONS

- What are the main classes of organic compounds?
- What are some terms commonly used in the description of organic reactions and reactivities?
- What are the main types of organic reactions?
- How do electrons flow in polar organic reactions?

LEARNING OUTCOMES

Students should be able to:

11.1 (a) interpret, and use the nomenclature, general formulae and displayed formulae of the following classes of compound:

- **(i)** hydrocarbons (alkanes, alkenes and arenes)
- **(ii)** halogen derivatives (halogenoalkanes and halogenoarenes)
- **(iii)** hydroxyl compounds (alcohols and phenols)
- **(iv)** carbonyl compounds (aldehydes and ketones)
- **(v)** carboxylic acids and derivatives (acyl chlorides and esters)
- **(vi)** nitrogen compounds (amines, amides, amino acids and nitriles)

*students are expected to be able to interpret and use the following types of representations in the description of organic molecules: empirical formula, molecular formula, structural formula, full structural or displayed formula, skeletal formula and stereochemical formula.

11.1 (b) interpret, and use the following terminology associated with organic reactions:

- **(i)** functional group
- **(ii)** degree of substitution: primary, secondary, tertiary, quaternary
- **(iii)** homolytic and heterolytic fission
- **(iv)** carbocation
- **(v)** free radical, initiation, propagation, termination (Refer also to Topic 10 Alkanes)
- **(vi)** electrophile (Lewis acid), nucleophile (Lewis base)
- **(vii)** addition, substitution, elimination, condensation, hydrolysis
- **(viii)** oxidation and reduction

[in equations for organic redox reactions, the symbols [O] and [H] are acceptable]

11.1 (c) interpret, and use the following terminology associated with organic reactivities:

- **(i)** delocalisation
- **(ii)** electronic effect (electron-donating and electron-withdrawing effect)
- **(iii)** steric effect (steric hindrance)

11.1 (d) describe sp^3 hybridization, as in ethane molecule, sp^2 hybridization, as in ethene and benzene molecules, and sp hybridization, as in ethyne molecule (Refer to Topic 2 Chemical Bonding and Topic 12 Arenes)

11.1 (e) explain the shapes of, and bond angles in, the ethane, ethene, benzene and ethyne molecules in relation to σ and π carbon-carbon bonds (Refer to Topic 2 Chemical Bonding and Topic 12 Arenes)

11.1 (f) predict the shapes of, and bond angles in, molecules analogous to those specified in **11.1 (e)**

11.1 (g) apply **11.1 (b)** and **11.1 (c)** to the understanding of mechanisms in terms of organic structure and bonding

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11.1 (h) recognise that the mechanisms of polar reactions involve the flow of electrons from electron-rich to electron-poor sites

*students are expected to be able to interpret and use the curly arrow notation to represent the movement of electrons in organic reaction mechanisms.

REFERENCES

1. Peter Cann and Peter Hughes, *Chemistry for Advanced Level*, 5th Ed., Hodder Education, Chapter 12
2. John McMurry, *Organic Chemistry*, 8th Ed., Brooks/Cole, Chapter 2

LOOKING BACK

The study of organic chemistry in the A-Level syllabus is based on the chemistry of different functional groups. Besides the first two general topics on Introduction and Isomerism, each topic in organic chemistry will cover one functional group: its nature, physical properties, chemical reactivity, reactions and mechanisms.

The properties and reactivities of the functional groups can be explained using concepts in Topic 1 Atomic Structure and Topic 2 Chemical Bonding: atomic orbitals, hybridization, electronegativity, covalent bonding, and intermolecular forces. Their reactions and mechanisms can be understood based on concepts in Topic 4 Reactions & Stoichiometry (stoichiometry, redox, acid-base reactions), Topic 5 Energetics & Thermodynamics (bond energies, enthalpy changes) and Topic 6 Reaction Kinetics (rate equations, orders of reaction, transition states, intermediates).

Besides drawing on knowledge from previous topics, the organic topics themselves are also closely linked because each functional group can be converted to other functional groups via reactions. It is helpful to draw up a concept map at the end of all the organic topics to get a visual overview of all possible reactions and functional group conversions.

1 INTRODUCTION

The study of organic chemistry is centred on the structures, properties and reactions of **organic compounds**. Organic compounds are compounds that contain **carbon**, and usually hydrogen and/or halogens. Other elements such as oxygen, nitrogen, phosphorus and sulfur can also be present. (Note that carbon dioxide, carbonates, cyanides are not considered organic compounds.)

Carbon can form many compounds because:

- a carbon atom can form covalent bonds to as many as 4 other atoms
- it can form stable and strong covalent bonds with other carbon atoms and/or atoms of many different elements
- it can form different types of bonds, e.g. single, double and triple bonds
- it can form long chains or rings of carbon atoms

Due to the unique properties above, carbon atoms can bond with one another and with atoms of different elements in a multitude of ways, to form large numbers of organic compounds. Fuels, plastics, painkillers, antibiotics and vitamins are organic compounds that have become vital to our present way of life.

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2 CLASSES OF ORGANIC COMPOUNDS

Organic compounds can be classified based on the:

- types of carbon chain (Section 2.1)
- functional groups present (Section 2.2)

2.1 Types of carbon chain

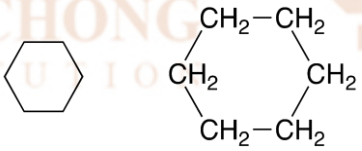
Organic compounds can be grouped based on whether they are saturated, contain rings or aromatic systems, e.g.:

Aliphatic compounds

- compounds with open chains of carbon atoms, e.g. propane
- may be unbranched or branched
- may contain single, double or triple bonds or combinations of these

Alicyclic compounds

- compounds with closed rings of carbon atoms, e.g. cyclohexane:



Aromatic compounds

- compounds containing at least one aromatic system such as a benzene ring: 

Organic compounds (aliphatic or alicyclic) containing only single bonds are **saturated**. Compounds with at least one double or triple bond or aromatic ring are **unsaturated**.

2.2 Functional groups

LO11.1(b)part: interpret, and use the following terminology associated with organic reactions: (i) functional group

Organic compounds can be grouped into different classes based on functional groups they contain. **Functional groups** refer to particular atoms or a group of atoms within an organic molecule, that define the physical properties and chemistry of that compound.

The following page shows the classes of organic compounds in the A Level syllabus, with their corresponding functional groups.

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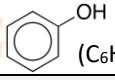
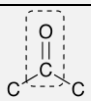
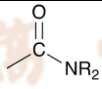
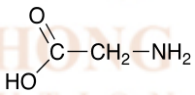
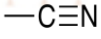
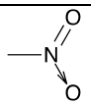
Class of organic compound	Characteristic group of atoms present	Name of Functional Group
Hydrocarbons	N.A. (only C–C and C–H bonds present)	alkane
	C=C	alkene
	e.g. benzene:  (C_6H_6)	arene
Halogen derivatives	C–X where X: halogen	chloroalkane, bromoalkane etc.
	e.g. benzene ring attached to X  (C_6H_5X)	chloroarene, bromoarene etc.
Hydroxy compounds	C–OH	primary/secondary/tertiary alcohol
	e.g. benzene ring attached to OH  (C_6H_5OH)	phenol
Carbonyl compounds	–CHO or 	aldehyde
	–C=O or 	ketone
Carboxylic acids	–CO_2H or 	carboxylic acid
Carboxylic acid derivatives	–COX or 	acyl chloride, acyl bromide etc.
	–CO_2R or  where R: alkyl group	ester
Nitrogen compounds	C–NR_2 where R: alkyl group or H	primary/secondary/tertiary amine
	–$CONR_2$ or  where R: alkyl group or H	amide
	amino acid e.g. 	carboxylic acid, amine
	–CN or 	nitrile
	–NO_2 or 	nitro

Table 1. Classes of organic compounds and names of functional groups

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2.2.1 Homologous series

A homologous series is a family of compounds containing the same functional group, and each successive member increases by one –CH_2– unit.

Compounds of the same homologous series:

1. can be represented by a general molecular formula
2. show a regular trend in physical properties
3. can usually be prepared by similar methods
4. have similar chemical properties

An example of a homologous series is that of alkanes, with general molecular formula C_nH_{2n+2}. The table below shows the trend in the boiling point of the first six members of the series.

Formula	Name	Boiling point / °C
CH_4	methane	–162
CH_3CH_3	ethane	–89
$CH_3CH_2CH_3$	propane	–42
$CH_3CH_2CH_2CH_3$	butane	0
$CH_3CH_2CH_2CH_2CH_3$	pentane	36
$CH_3CH_2CH_2CH_2CH_2CH_3$	hexane	69

Table 2. Homologous series of alkanes

2.2.2 Degree of Substitution

LO11.1 (b)part: interpret, and use the following terminology associated with organic reactions: (ii) degree of substitution: primary, secondary, tertiary, quaternary

Some organic compounds are classified based on how many **substituents** (usually **alkyl** or **aryl**) are joined to the carbon atom bearing the functional group.

A **substituent** refers to an atom or group of atoms that takes the place of a hydrogen atom on the hydrocarbon chain.

- An **alkyl group** is a type of substituent derived from alkanes by removing a hydrogen atom:

No. of carbons atoms in the alkyl group	**name**	**structure**
1	methyl	$–CH_3$
2	ethyl	$–CH_2CH_3$
3	propyl	$–CH_2CH_2CH_3$
4	butyl	$–CH_2CH_2CH_2CH_3$

Table 3. Examples of alkyl groups

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- An **aryl group** is a type of substituent derived from an aromatic ring (such as a benzene ring) by removing a hydrogen atom. An example of an aryl group is the phenyl group, represented by  .

A useful way of classifying alcohols is to place them in one of the three categories: **primary (1°), secondary (2°) and tertiary (3°)**. Figure 1 shows primary, secondary, and tertiary alcohols have one, two and three alkyl or aryl groups (represented by R) attached respectively, to the carbon bearing the OH group. The same classification can be applied to halogenoalkanes, radicals and carbocations.

For amines, however, it is the number of alkyl or aryl groups attached to the *nitrogen* atom, that determines whether an amine is primary, secondary or tertiary. Note that there can be a **quaternary (4°)** ammonium cation when the nitrogen atom uses its lone pair to form a fourth bond to an alkyl (or aryl) group.

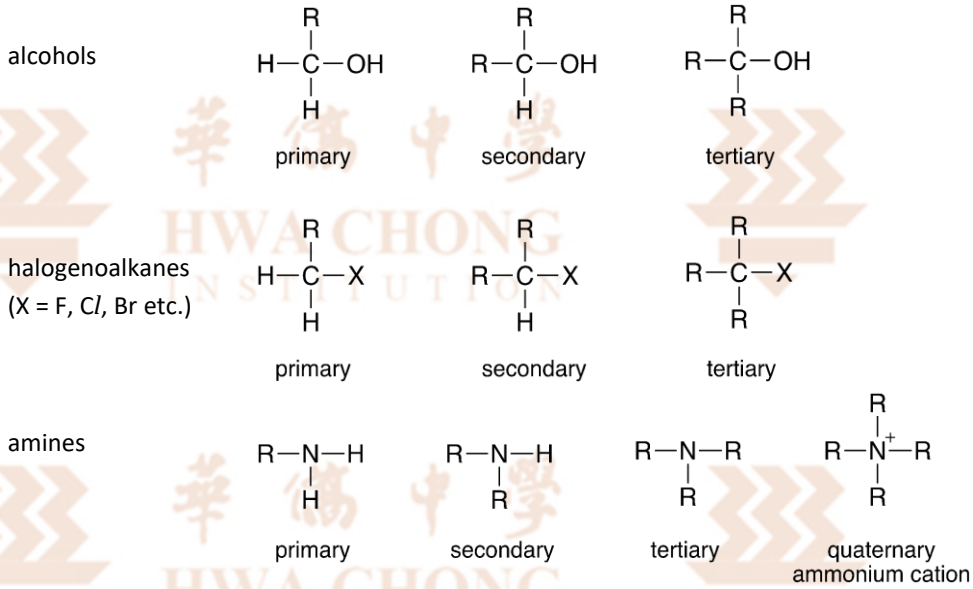
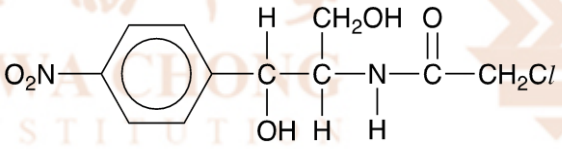


Figure 1. Different degrees of substitution for alcohols, halogenoalkanes and amines

Exercise 2.1

The structure below shows a molecule of an antibiotic drug. Circle and name the functional groups present.



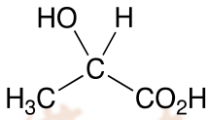
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3 TYPES OF FORMULAE FOR ORGANIC COMPOUNDS

LO11.1(a)part: interpret, and use the general formulae and displayed formulae of classes of compounds

**students are expected to be able to interpret and use the following types of representations in the description of organic molecules*

There are six types of formulae that can be used to represent organic compounds. We shall illustrate them by using lactic acid:



Empirical Formula

- simplest ratio of the number of atoms of the elements present in one molecule, e.g. lactic acid: CH_2O

Molecular Formula

- actual number of atoms of the elements present in one molecule, e.g. lactic acid: $C_3H_6O_3$

Structural Formula

- shows how the atoms of a molecule are joined together in an **unambiguous** way, with minimal detail, e.g. lactic acid: $CH_3CH(OH)CO_2H$

Displayed (or full structural) Formula

- detailed structure of molecule showing the relative placing of atoms and **all** the bonds between them, e.g. lactic acid:

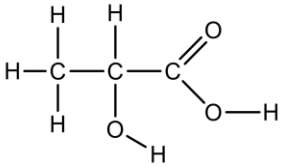


Figure 2. Displayed formula of lactic acid

- rings of atoms are often represented by their skeletal formulae (explained next):

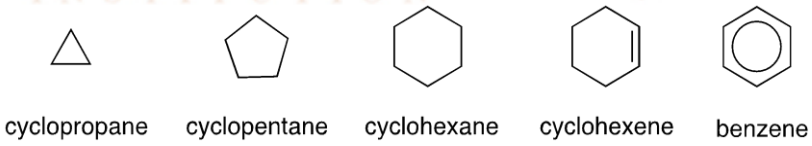


Figure 3. Skeletal formulae of carbon rings

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Skeletal Formula

- simplified representation derived from the displayed formula by removing hydrogen atoms (and their bonds) and carbon atoms from alkyl chains, leaving just the carbon–carbon bonds in the carbon skeleton and the functional groups, e.g. lactic acid:

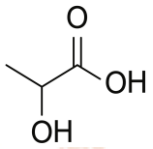


Figure 4. Skeletal formula of lactic acid

- each C–C bond in the carbon skeleton is a line (each end of the line is a carbon atom)
- double and triple lines indicate double and triple bonds respectively
- partial skeletal representations are also used where they are unambiguous, e.g. lactic acid:

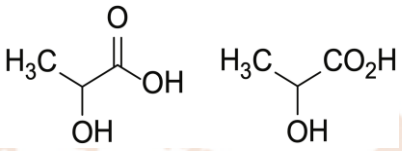


Figure 5. Partial skeletal formulae of lactic acid

Stereochemical Formula

- show the 3-D spatial arrangement of bonds, atoms and groups around an atom, usually a stereochemical centre (Topic 9 Isomerism), e.g. lactic acid:

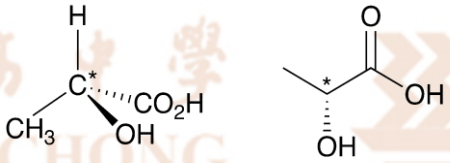


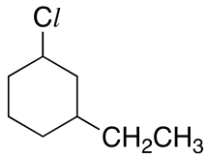
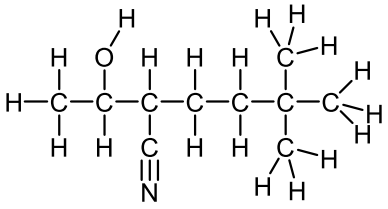
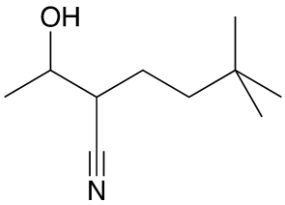
Figure 6. Different stereochemical formulae of lactic acid

- solid wedges (◀) indicate bonds **pointing out** of the plane of the paper towards you
- dashed wedges or hashed lines (⁞⁞⁞⁞⁞⁞⁞⁞) indicate bonds **pointing into** the plane of the paper away from you
- lines (———) indicate bonds in the plane of the paper

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Exercise 3.1

Complete the following table by writing the different types of formulae for compounds **A** and **B**.

Type of formula	Compound A (Worked Example)	Compound B
Empirical formula	$C_{10}H_{19}ON$	
Molecular formula	$C_{10}H_{19}ON$	
Structural formula	$CH_3CH(OH)CH(CN)(CH_2)_2C(CH_3)_3$	
Displayed formula		
Skeletal formula	 (given)	

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4 NOMENCLATURE

LO11.1(a)part: interpret, and use the nomenclature of classes of compounds

Many organic molecules have 'common names' derived from living organisms or sources from which they were originally extracted from; e.g. formic acid isolated from ants (‘ants’ in Latin: *formica*), acetic acid (‘vinegar’ in Latin: *acetum*), menthol (‘peppermint’ in Latin: *Mentha piperita*) etc. However, this naming becomes unsatisfactory for organic compounds entirely synthesised in the lab (no plant/animal source) and when the number of compounds becomes too large to remember specific names for each of them.

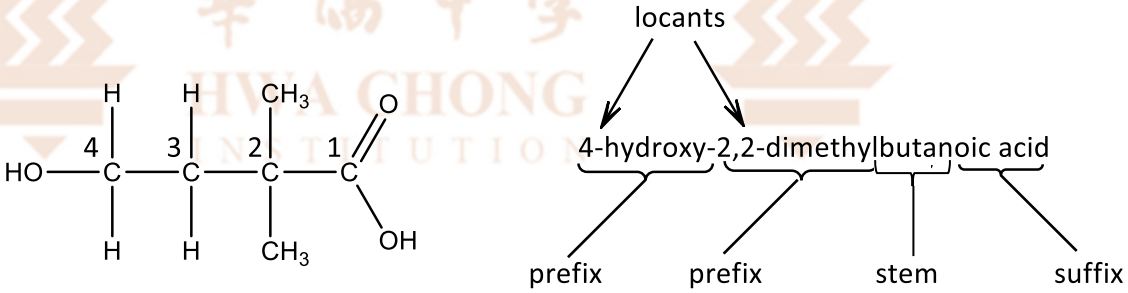
4.1 IUPAC Nomenclature

Chemists have devised a logical and systematic form of nomenclature, which has been adopted by the International Union of Pure and Applied Chemistry (IUPAC). Following a set of internationally recognised rules, chemists can now translate names of organic compounds they have not previously encountered, into its structural formula, and vice versa.

A systematic name for an organic compound is often based on the ‘parent’ hydrocarbon. Each name consists of the following components (not all will be present, depending on the complexity of the molecule):

1. Stem
2. Suffix
3. Prefix
4. Locant
5. Stereochemical identifier

For example:



Stem

The stem specifies the number of carbon atoms in the longest carbon chain in the molecule and indicates the type of carbon-carbon bonds (single, double, triple):

(a) number of carbon atoms in the longest carbon chain

Stem	meth-	eth-	prop-	but-	pent-	hex-	hept-	oct-	non-	dec-
No. of carbon atoms in the longest carbon chain	1	2	3	4	5	6	7	8	9	10

If the carbon atoms are joined in a ring, ‘cyclo’ is added in front of the stem.

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(b) type of carbon-carbon bond(s) present in the longest carbon chain:

stem	longest carbon chain contains:
-an	all C–C single bonds
-en	one C=C double bond
-dien	two C=C double bonds
-trien	three C=C double bonds
-yn	one C≡C triple bond

Suffix

The suffix specifies the highest priority functional group in the molecule, identified according to the following hierarchy:

Group		**Name as suffix**
Carboxylic acid, $–CO_2H$	(highest priority)	-oic acid
Ester, $–CO_2R$		-oate
Acyl halide, –COX		-oyl halide
Amide, $–CONR_2$		-amide
Nitrile, –CN		-nitrile
Aldehyde, –CHO		-al
Ketone, –COR		-one
Alcohol, –OH		-ol
Amine, $–NR_2$		-amine
Alkene, C=C		-ene
Arene e.g. 	(lowest priority)	-benzene

Prefix

Prefix(es) specify the other groups present in the molecule. The use of 'di', 'tri', 'tetra', 'penta' etc. indicates multiple substitution of the same group. Different prefixes in a name are placed in alphabetical order.

Group	**Name as prefix**
Nitrile, –CN	cyano
Aldehyde, –CHO	formyl
Ketone, –COR	oxo
Alcohol, –OH	hydroxy
Amine, $–NR_2$	amino
Nitro, $–NO_2$	nitro
Chloro, –*Cl*; Bromo, –Br	chloro; bromo
Arene e.g. 	phenyl
Alkyl groups	methyl, ethyl, propyl, butyl etc.

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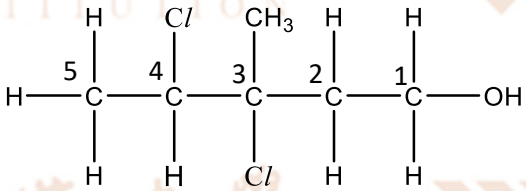
Locant

Locants are numbers attached to the front of each prefix and the suffix, to specify the position of each group in the molecule. The rule is to number the carbon atoms in the longest carbon chain from one end to the other, making sure that the suffix is given the smallest number as its locant. The locant can be omitted if the position of the group is obvious without it.

Stereochemical identifier

For compounds that exhibit stereoisomerism (Topic 9 Isomerism), the name of the stereoisomer is placed in front, for instance: *cis*-but-2-ene, *trans*-but-2-ene.

For example:



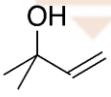
3,4-dichloro-3-methylpentan-1-ol

1. The longest carbon chain has five C atoms and has all C-C single bonds (**stem**: pentan-)
2. The **suffix** (highest priority functional group) is identified as the alcohol functional group –OH (suffix: -ol)
3. Number the C atoms along the longest carbon chain such that
   (i) the smallest number is given to the suffix (C bonded to –OH group numbered as C_1)
   (ii) the smallest set of numbers is given to the groups identified as prefixes
4. Identify the **prefixes** (substituents) and assign their **individual locant** (position in the molecule)
   - One $–CH_3$ substituent on C_3 position (3-methyl)
   - Two –*Cl* substituents on C_3 and C_4 positions (3,4-dichloro)

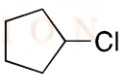
   Placing the prefixes in alphabetical order: 3.4- dichloro-3-methyl. (This alphabetical order does not take into consideration 'di', 'tri', 'tetra' etc, This means that the "dichloro" substituents are placed before "methyl" in the name despite the presence of "d" in "dichloro" as we still follow the first letter of the original name of the substituent i.e. "c" in chloro.)

   Note: Use commas (,) to separate numbers and use hyphens (-) to separate numbers and words.
5. The systematic IUPAC name of the molecule is obtained by putting together the prefixes, stem and suffix: 3,4-dichloro-3-methylpentan-1-ol

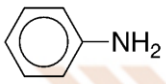
Further examples of compounds and their systematic IUPAC names:



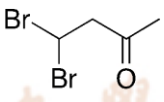
2-methylbut-3-en-2-ol



chlorocyclopentane



phenylamine



4,4-dibromobutanone

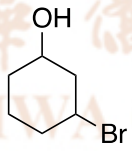
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In subsequent organic chemistry topics, we shall look in greater detail at the IUPAC nomenclature of compounds containing specific functional groups.

Exercise 4.1

1. Draw the structures of the following compounds:

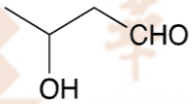
   (a) (Worked Example) 3-bromocyclohexanol



   (b) ethylbenzene

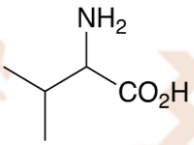
2. What are the systematic IUPAC names of the following compounds?

   (a) (Worked Example)



   3-hydroxybutanal

   (b)



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5 KEY IDEAS IN ORGANIC REACTIONS

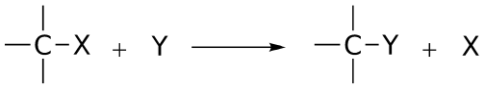
5.1 Types of organic reactions

LO11.1(b)part: interpret, and use the following terminology associated with organic reactions: (vii) addition, substitution, elimination, condensation, hydrolysis (viii) oxidation and reduction

In addition to acid-base reactions (transfer of H^+ ions) learnt in Topic 4 Reactions and Stoichiometry, there are seven types of reactions applicable to organic reactions.

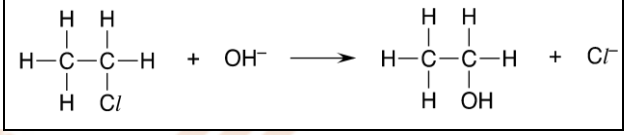
Study carefully the changes that occur in each type of reaction so that you can recognise them in novel reactions.

Substitution

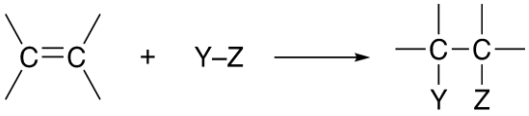


When one atom or group of atoms replaces another atom or group in a molecule.

e.g.

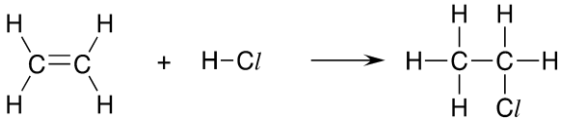


Addition

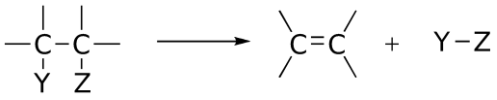


When an organic molecule, usually containing a double bond (e.g. C=C), reacts with another molecule to give only one product. The π bond of the double bond breaks to form two new σ bonds. Opposite of elimination.

e.g.

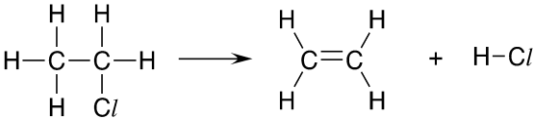


Elimination



When a double bond (e.g. C=C) is formed with the removal of a molecule (from adjacent carbon atoms) e.g. H_2O from a molecule of an alcohol, or HX from a molecule of a halogenoalkane. Opposite of addition.

e.g.

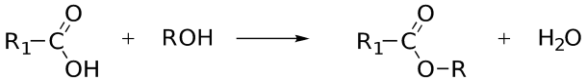


Condensation

When two molecules come together to form a bigger molecule, with the elimination of a small molecule such as water or HC*l* etc.

***Not** the same as elimination which requires formation of a new double bond.

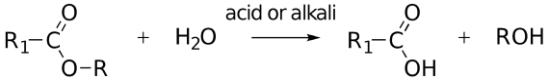
e.g.



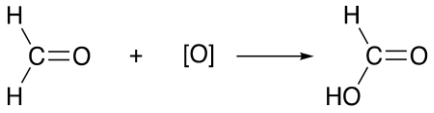
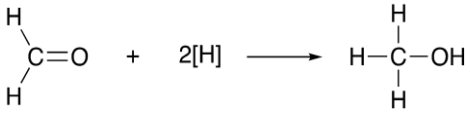
Hydrolysis

When a molecule is split into two by the action of water, often catalysed by dilute acids or dilute alkalis.

e.g.



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Oxidation	**Reduction**
When **O <u>atoms</u> are added** to the molecule OR **H <u>atoms</u> are removed** from the molecule. The **oxidation number** of an atom in the functional group must **increase**. e.g. when methanal, HCHO is oxidised to methanoic acid, HCO_2H: ● oxidation no. of C in methanal = 0 ● oxidation no. of C in methanoic acid = +2	When **O <u>atoms</u> are removed** from the molecule or **H <u>atoms</u> are added** to the molecule. The **oxidation number** of an atom in the functional group must **decrease**. e.g. when methanal, HCHO is reduced to methanol, CH_3OH: ● oxidation no. of C in methanal = 0 ● oxidation no. of C in methanol = –2
Writing balanced redox equations in organic chemistry The symbol [O] is used to denote the oxygen atoms added, and [H] is used to denote the H atoms added. For oxidation reactions, add H_2O to balance the H and then [O] to balance the remaining O. For reduction reactions, add H_2O to balance the O and then [H] to balance the remaining H.	
e.g. oxidation of methanal to methanoic acid:	e.g. reduction of methanal to methanol:
	

Exercise 5.1

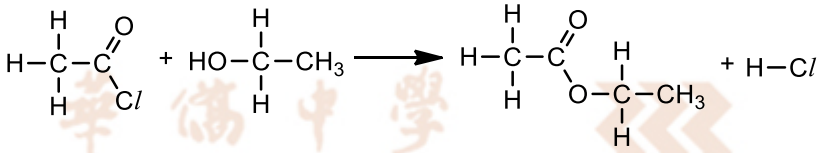
(a) The following are examples of organic reactions. State what type of reaction is taking place.

(i) **(Worked Example)**



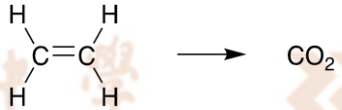
(not balanced)

Ans: Oxidation

(ii) 

(iii) 

(b) Potassium manganate(VII) can be used to oxidise ethene to carbon dioxide. Write a balanced equation for this oxidation of ethene.



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5.2 Mechanisms of organic reactions

**students are expected to be able to interpret and use the curly arrow notation to represent the movement of electrons in organic reaction mechanisms*

The mechanism of a reaction is a detailed description of which bonds break, which bonds form, and the sequence in which they occur in the reaction. Since bonds consist of shared electrons, a mechanism shows how electron(s) move to break bonds and form new bonds when reactants are converted to products.

In organic chemistry we use the **curly arrow notation** to show the movement of electrons:
The **tail** of the arrow represents the source of the electron(s) e.g. an unpaired electron, lone pair or a bond while the **head** of the arrow represents where the electron(s) go to e.g. an atom or a new bond.

To represent the movement of **a single electron**, we use a partial head or 'fish-hook' arrow:

To represent the movement of **a pair of electrons**, we use a full head arrow:

5.2.1 Bond Breaking represented by curly arrow notation

LO11.1 (b)part: interpret, and use the following terminology associated with organic reactions: (iii) homolytic and heterolytic fission (iv) carbocation (v)part: free radical

Homolytic fission

- Breaking of a covalent bond where the bonding pair of electrons are given **equally** to **each** atom. Since this involves movement of single electrons, we use the fish-hook arrow:



Figure 7. Homolytic fission of a covalent bond

- Results in the **formation of free radicals**, i.e. species containing unpaired electron(s) and are highly reactive. They readily form bonds with other atoms or molecules.

Example: In the homolytic fission of a C–H bond in methane, the C atom and H atom each take one electron from the bonding pair of electrons to form two radicals.

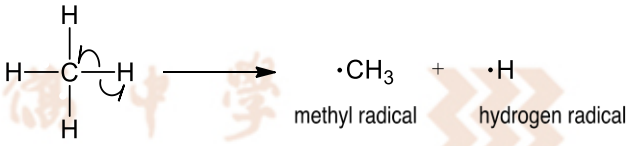


Figure 8(a). Example of a homolytic fission of C–H bond in methane

Figure 8(b) shows the actual electron distribution and movement:

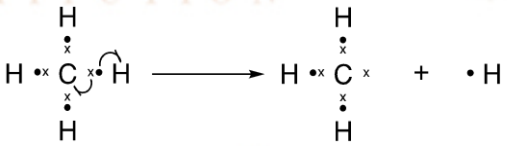


Figure 8(b). Actual electron distribution and movement of electrons in the homolytic fission of C–H bond in methane

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Heterolytic fission

- Breaking of a covalent bond where **both** bonding electrons are given to **one** of the atoms, usually the more electronegative atom. Since this involves movement of a pair of electrons, we use the full head arrow:

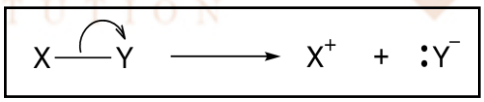


Figure 9. Heterolytic fission of a covalent bond

- Results in the **formation of ions**.

In heterolytic fission of a C–X bond, either the carbocation or carbanion can be formed, depending on the electronegativity of X relative to that of C.

- Heterolytic fission forming **carbocations**

  - **Carbocations** are species containing a positively-charged carbon atom, which has only six electrons in its outer shell.

  - In the C–C*l* bond below, chlorine is *more electronegative* than carbon, so it takes both the bonding electrons to form the chloride ion. The carbon atom loses its electron (originally used to form the C–C*l* bond) and a **carbocation** is formed.

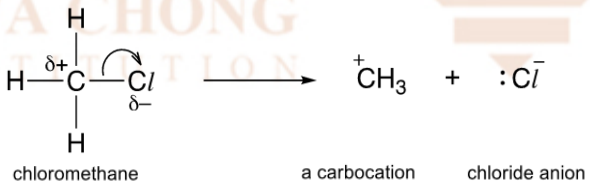


Figure 10(a). Example of a heterolytic fission to form a carbocation

  - Figure 10(b) shows the actual electron distribution and movement:

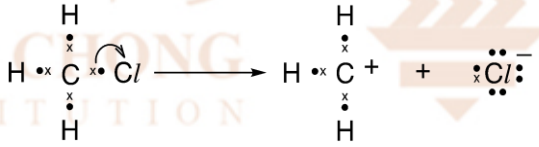


Figure 10(b). Actual electron distribution and movement of electrons in the heterolytic fission of C–Cl bond

- Heterolytic fission forming **carbanions**

  - **Carbanions** are species containing a negatively-charged carbon atom, which has a full octet of electrons in its outer shell.

  - In the C–Li bond below, carbon is *more electronegative* than Li, so it takes both the bonding electrons to form the **carbanion**. The lithium atom loses its electron (originally used to form the C–Li bond) and a lithium cation is formed.

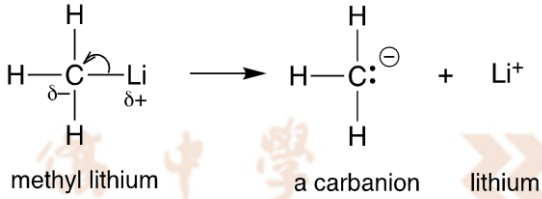


Figure 11. Example of a heterolytic fission to form a carbanion

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5.2.2 Bond Formation represented by curly arrow notation

- **via movement of single electron**

The **'fish-hook' arrow** shows the movement of an unpaired electron from radical Z• to X in molecule XY, forming the new bond.



Figure 12. Bond formation via single electron movement

At the same time, X–Y bond undergoes *homolytic fission*, forming the radical Y•.

- **via movement of electron pairs**

The **full head arrow** shows the movement of the lone pair of electrons from Z^- ion to X in molecule XY, forming the new bond.



Figure 13. Bond formation via electron pair movement

At the same time, X–Y bond undergoes *heterolytic fission*, forming the anion Y^-.

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5.2.3 Polar Reactions and their Mechanisms

LO11.1 (b)part: interpret, and use the following terminology associated with organic reactions: (vi) electrophile (Lewis acid), nucleophile (Lewis base)
LO11.1(g): apply 11.1 (b) and 11.1 (c) to the understanding of mechanisms in terms of organic structure and bonding
LO11.1(h): recognise that the mechanisms of polar reactions involve the flow of electrons from electron-rich to electron-poor sites

In polar reactions, **heterolytic** fission and bond formation occur. **Electron pairs move from electron-rich to electron-poor sites**. Electron-rich sites are termed "**nucleophilic**" and electron-poor sites are termed "**electrophilic**".

The diagram below shows a mechanism of a polar reaction:

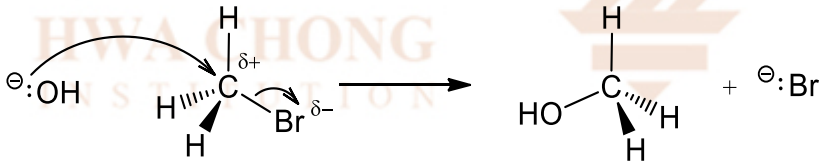


Figure 14. Example of a mechanism of a polar reaction

- OH^- ion has a lone pair of electrons and is electron-rich. It donates its lone pair to the electron-poor (electron-deficient) carbon in CH_3Br. Hence in this mechanism, OH^- acts as the **nucleophile**.

- CH_3Br contains the partial positively-charged carbon atom which is electron-deficient. Hence CH_3Br is acting as the **electrophile**, and its **electrophilic site** is at the δ+ carbon atom.

Electrophile
An electrophile is a species that **accepts an electron pair to form a covalent bond** in a reaction. It is **electron-deficient** due to having:
- a positively-charged centre (e.g. H^+, NO_2^+, and carbocations like CH_3^+), or
- an induced or permanent partial positive charge "δ+" (e.g. polarised Br_2, HBr)

Electrophiles are also known as *Lewis acids*.

Nucleophile
A nucleophile is a species that **donates an electron pair to form a covalent bond** in a reaction. It is electron-rich and possesses electrons that can be shared, such as:
- lone pairs of electrons (H_2O, NH_3, OH^-, CN^-, carbanions)
- π bond (e.g. ethene, benzene)

Nucleophiles are also known as *Lewis bases*.

Did you know?
The terms *nucleophile* and *electrophile* were introduced by British chemist, Christopher Kelk Ingold, in 1933. Derived from the word *philos* – which means "love" in Greek – *electrophile* means "electron-loving" and *nucleophile* means "nucleus-loving"!

- Placement of each curly arrow in a mechanism is *very important*: the tail of the first arrow is placed *precisely* at the **source of the electron pair** i.e. the lone pair on OH^- (not at the negative charge, or O or H!), while the head of the arrow is placed *exactly* **at the atom where the new covalent bond forms** i.e. at the carbon atom in CH_3Br.

- The second curly arrow represents a heterolytic fission. Its tail starts *precisely* from the C–Br bond which is to be broken (i.e. **the source of electron pair**) and ends with its head pointing *exactly* at the Br atom, **the atom which receives both electrons**, to form Br^- ion.

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The result of the movement of electron pairs is that a **new C–O bond is formed, and the C–Br bond is broken** in this reaction. When faced with a novel polar reaction, try to identify the exact bonds broken and formed, as well as the nucleophile and electrophile, to deduce a possible mechanism.

5.2.4 Non-Polar Reactions and their Mechanisms

In non-polar reactions, **homolytic** fission and bond formations with radicals occur via movement of single electrons. Unlike polar reactions, they do not involve ions.

Figure 15 below shows two radicals combining to form a new bond. Fish-hook arrows describe the movement of each unpaired electron from its source (the radical) to the location in between the two atoms i.e. where the new bond forms.

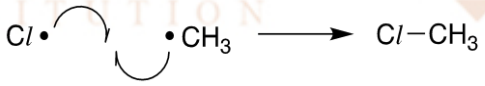


Figure 15. Representing bond formation with radicals using curly arrows

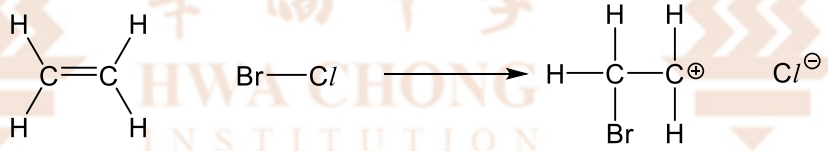
Most organic reactions in the A Level syllabus are polar reactions, with mechanisms involving electrophiles and nucleophiles. Only one mechanism is a non-polar reaction i.e. free radical substitution in Topic 10 Alkanes.

Exercise 5.2

1. (Worked Example)

In the reaction below,

(a) identify the bonds broken and new bond formed
(b) identify the electrophile and nucleophile, label any relevant partial charges
(c) draw curly arrows to show the movement of electrons



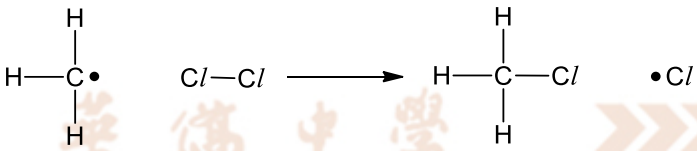
(a) Br–C*l* bond is broken; C–C π bond is broken; new C–Br bond is formed

(b) electrophile is BrC*l*, nucleophile is $H_2C{=}CH_2$, label δ+ on Br and δ– on C*l* in BrC*l*.

(c)



2. Draw a possible mechanism for the reaction below, using curly arrows notation:



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5.3 Factors Affecting Organic Reactivities

LO11.1 (c): interpret, and use the following terminology associated with organic reactivities: (i) delocalisation (ii) electronic effect (electron-donating and electron-withdrawing effect) (iii) steric effect (steric hindrance)

5.3.1 Electronic Effects

Electronic effects influence the distribution of electrons in a particular chemical species and hence its reactivity. They can be electron-withdrawing or electron-donating, depending on the functional groups involved.

- **Inductive effect**

The inductive effect arises from the polarisation of electron density in a bond due to the **electronegativity** of nearby atoms.

Consider chloroethane, propan-1-ol and ethylamine below. C*l*, O and N are more electronegative than C, hence they draw electron density away from carbon, resulting in a partial positive charge (δ+) on the carbon next to them. This is the inductive effect.

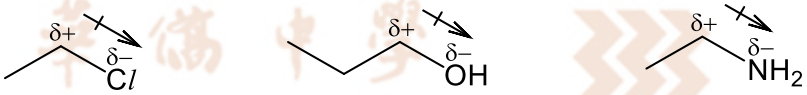


Figure 16. Inductive effect in chloroethane, propan-1-ol and ethylamine molecules

Inductive effect occurs via **σ bonds** and decreases along the σ bond as we go further away from the electronegative atoms. Hence in the above molecules, the carbon atoms further away from the one labelled with δ+ also have a slight partial positive charge but which is much weaker due to greater distance from the electronegative atoms.

Since -C*l*, -OH and -NH_2 groups draw electron density away from carbon adjacent to them, they are *inductively* **electron-withdrawing** groups.

Alkyl groups, on the other hand, are *inductively* **electron-donating** groups. The reason is due to hyperconjugation which will not be covered here. We shall see examples of how inductive electron-withdrawing and electron-donating effects affect reactivities of organic compounds in subsequent topics.

- **Delocalisation**

Delocalisation of electrons occurs when ***p* orbitals on 3 or more adjacent atoms overlap**, forming a **π electron cloud** in which the electrons from all the overlapping *p* orbitals can be found. These electrons are said to be 'delocalised'. This delocalisation of electrons in compounds generally results in stabilisation, which is also known as the resonance stabilisation effect.

Consider the buta-1,3-diene molecule which has alternating single and double bonds:



(a) (b)

Figure 17(a). Buta-1,3-diene structure (b). Overlap of p orbitals of the carbon atoms in butadiene indicated by dotted lines

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The p orbitals of the four adjacent carbon atoms in buta-1,3-diene overlap and form a π electron cloud. The π electrons in the two C=C double bonds of butadiene are delocalised throughout the π electron cloud, and not just localised at their respective double bonds. As a result, the carbon-carbon bond labelled α (in Figure 17a) has partial double bond character, and we expect it to be somewhat shorter and stronger than a C–C single bond.

Organic molecules with delocalised electrons include benzene, carboxylic acids and amides. We will discuss in subsequent topics how the delocalisation of electrons affects their reactivities.

In summary:

Inductive effect	**Delocalisation**
• Due to difference in electronegativity between atoms in covalent bonds • Occurs via σ bonds • Gets weaker with distance	• Due to 3 or more *p* orbitals overlapping • Occurs via a π electron cloud • Independent of distance

5.3.2 Steric Effect

Steric effect is another factor associated with the reactivities of organic molecules. Unlike electronic effects that involve the distribution of electrons in σ bonds and π electron clouds, steric effect results from the **repulsion between electron clouds** of groups or substituents, depending on their size and number.

In Topic 6 Reaction Kinetics, the collision theory states that reactions occur only when reactant molecules collide with each other with correct orientation and sufficient energy to overcome the activation energy barrier. Molecules with bulky substituents crowded around their reactive sites would hinder the approach of the other reactant for an effective collision. When steric effect hinders the rate of reaction, we call it **steric hindrance**.

Consider the example below. Each halogenoalkane contains an electrophilic carbon atom, which can be attacked by a nucleophile.

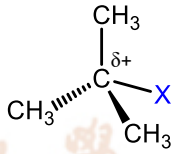
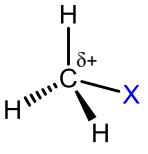
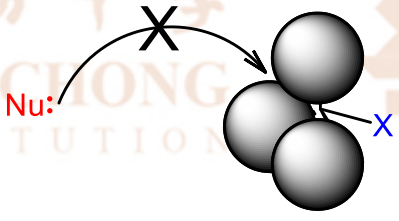
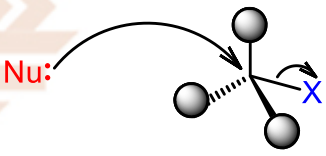
	(a)	(b)
Halogenoalkane		
Approach of nucleophile (Nu:) towards the electrophilic carbon atom		

Figure 18. Example of steric hindrance due to bulky substituents

Consider the size of the electron cloud of three CH_3 groups to that of three H atoms. In (a), the electrophilic carbon atom is 'shielded' from the incoming nucleophile's approach, due to repulsion from bulky CH_3 groups. This reaction will be slower due to steric hindrance, compared to (b) where H atoms

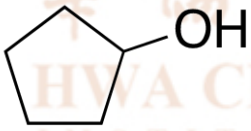
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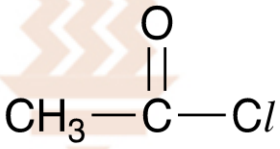
are small and provide less steric hindrance. The **larger** the groups and the **greater the number** of groups crowding around the site of reaction, the greater the steric hindrance.

Exercise 5.3

(a) In the molecules below,

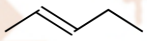
- identify the group(s) that are *inductively* electron-withdrawing
- label the partial charge on the carbon atom just adjacent to the group(s)

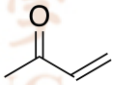
(i) 

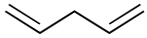
(ii) 

(b) **(Worked Example)**

State whether any delocalisation of electrons occur for the molecules below. Explain your answers.

(i) 

(ii) 

(iii) 

(i) No delocalisation of electrons since p orbitals of *only two* adjacent atoms overlap.

(ii) There is delocalisation of electrons here because p orbitals of four adjacent atoms overlap. The four p electrons in the C=O and C=C are delocalised over O-C-C-C.

(iii) No delocalisation of electrons since the two C=C double bonds are separated by an sp^3 carbon, so the two adjacent p orbitals on one double bond cannot overlap with the p orbitals of the other double bond.

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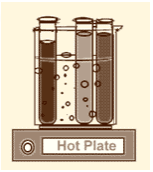
6 PRACTICAL ASPECTS OF ORGANIC CHEMISTRY

6.1 Distinguishing Tests

A **distinguishing test** is a simple chemical test that aims to confirm the presence of a particular compound, or differentiate between organic compounds, through identification of key functional groups. Such tests require an **observable chemical change** (e.g. colour change, appearance of precipitate, evolution of a gas, etc.) and are usually quick tests carried out in test tubes (unlike in synthesis) **without use of complicated set-up or equipment** (i.e. no reflux or distillation set-ups).



Planning an experiment involving distinguishing tests



You may be asked to:

- present the sequence of tests. (You may use a flowchart or table.)
- write the procedure with essential details of quantities and conditions for each test.
  - In general, all tests are carried out in clean test-tubes using about 1 cm^3 (or 1 cm depth) of the unknown solution or 1 spatula of the unknown solid unless otherwise required.
  - Reagents are added dropwise until no further change occurs.
  - Heating, if required, is carried out using a water bath/oil bath/sand bath or a heating mantle.
- state the expected observations for both positive and negative tests.
- explain the chemistry underlying each test: type of reaction, identity of species responsible for precipitate/gas/colour change observed, name or structure of functional group/structure of organic product etc.

6.2 Synthesis

An organic **synthesis** generally involves carrying out a reaction to form the desired organic product with reasonable yield and purity. Various strategies are used in syntheses to obtain high yield and good purity of products. This usually involves careful sequencing of steps, controlled reaction conditions, complex set-up and/or equipment, and often, the investment of time. The product must also be isolated (i.e. separated from the reaction mixture) and purified.

The main stages in an organic synthesis are:

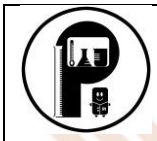
- Carrying out the reaction by heating the reaction mixture under reflux.
- Separation and purification of product by filtration, extraction with separating funnel, distillation or recrystallisation.
- Checking purity of product by determining its melting or boiling point.
- Determining structure of the product via spectroscopy methods e.g. IR, UV, MS, NMR etc. (H3 Chem)

6.2.1 Carrying out the reaction

Compared to inorganic reactions between ionic compounds in solutions, organic reactions are generally slow (as such reactions typically have high activation energy due to breaking covalent bonds) so the organic reaction mixture needs to be heated for some time. You will be learning many reactions that involve heating reagents under reflux in the A-level organic chemistry syllabus.

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Heating under **reflux** means to heat the mixture in a flask so that the solvent boils continually. A condenser is placed vertically in the neck of the flask to condense the solvent vapour. This method allows the temperature of the reaction mixture to be kept at the boiling point of the solvent, while minimizing the loss of solvent, reactants or products due to evaporation.



Generic procedure for heating under reflux

1. **Measure** (mass/volume) of (reactant/reactants) using a (apparatus e.g. measuring cylinder for liquids/micropipette for small volumes <5cm^3/electronic mass balance and weighing bottle for solids). **Transfer** to a 100 cm^3 /250 cm^3 **round–bottom flask**).
2. **Set up** the apparatus as shown in the diagram.
3. Gently **heat** the mixture under reflux for (duration in minutes/hours).

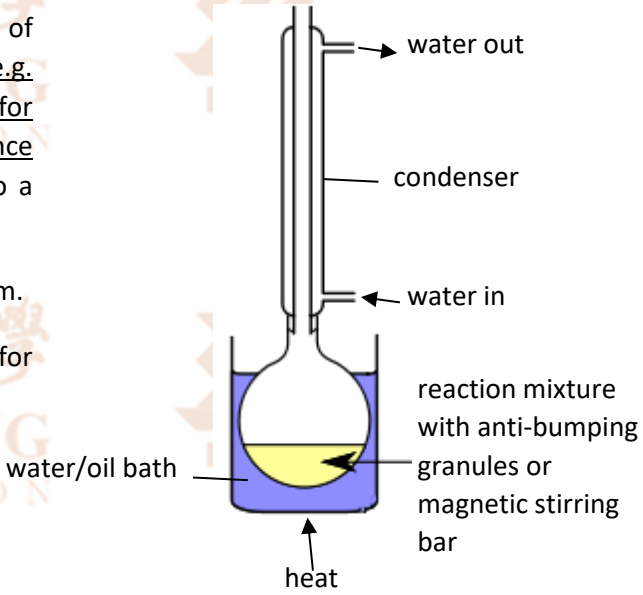


Figure 19. A reflux set-up

Notes:

- ✓ As most organic compounds are volatile and flammable, heating is done using a **water/oil/sand bath** or **heating mantle** (instead of a Bunsen flame)**.**
- ✓ For very exothermic reactions (e.g. when diluting a concentrated acid), cooling may be necessary when adding the reagents to each other, e.g. by immersing the reaction flask in an ice water bath.
- ✓ A **dropping funnel** is used if the reactant needs to be added slowly (see diagram below).

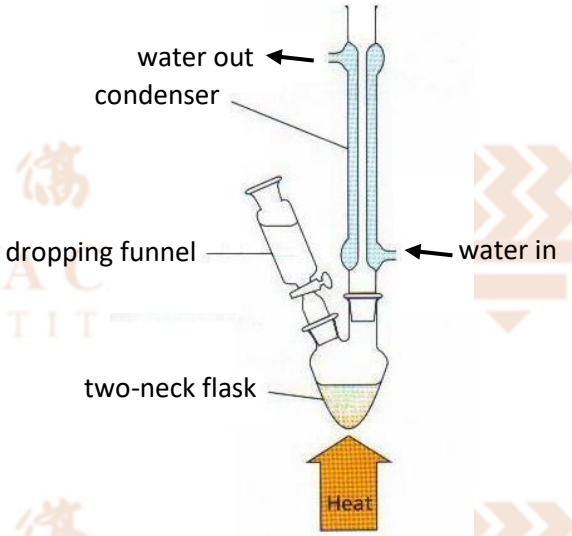


Figure 20. Two-neck flask with dropping funnel and condenser

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6.2.2 Separation and Purification Techniques

One or more of the following techniques may be used to isolate and purify the crude product.

- Filtration

Used to separate a solid product from a solid-liquid mixture. The flask may be connected to a vacuum pump for more rapid filtration.

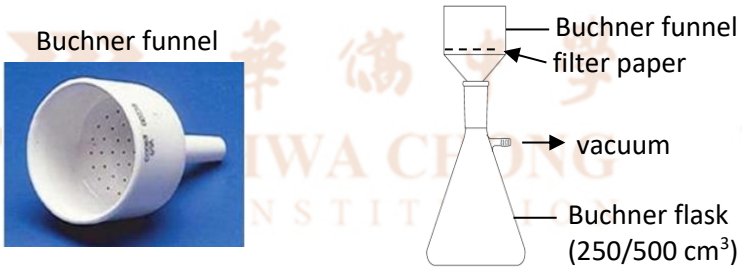


Figure 21. Vacuum filtration set-up

- Extraction

Extraction involves two *immiscible* (do not mix) solvents. The first solvent contains the reaction mixture and crude product. A second solvent is chosen such that the solubility of the product in the second solvent is greater than that in the first. The two liquids are shaken together in a separating funnel and left to stand. The product will be extracted into the second solvent and obtained by evaporating the solvent.

Generic procedure for extraction

1. **Place** (crude organic product / reaction mixture) into a **separating funnel**.
2. Using a measuring cylinder, **add** (volume) of (usually an acid or base/suitable solvent) .
3. **Stopper and shake** well. **Leave to stand** to allow the two immiscible layers to separate.
4. **Collect** the (usually organic) layer which is at the (top / bottom) in a conical flask. **Discard** the (usually aqueous) layer.
5. **Add** (drying agent) to the (usually organic) layer.
6. **Filter** and collect the (usually organic) layer (filtrate).
7. **Evaporate** the solvent to obtain the organic product.

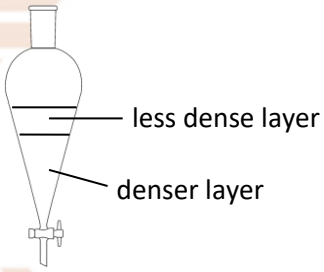


Figure 22. Separating funnel (common capacities: 50 – 500 cm³)

Notes:

✓ As a precaution, when shaking the separating funnel, pressure should be released regularly especially if a gas is produced e.g. when $NaHCO_3$ (aq) is used to remove acid impurities, CO_2 gas is formed.

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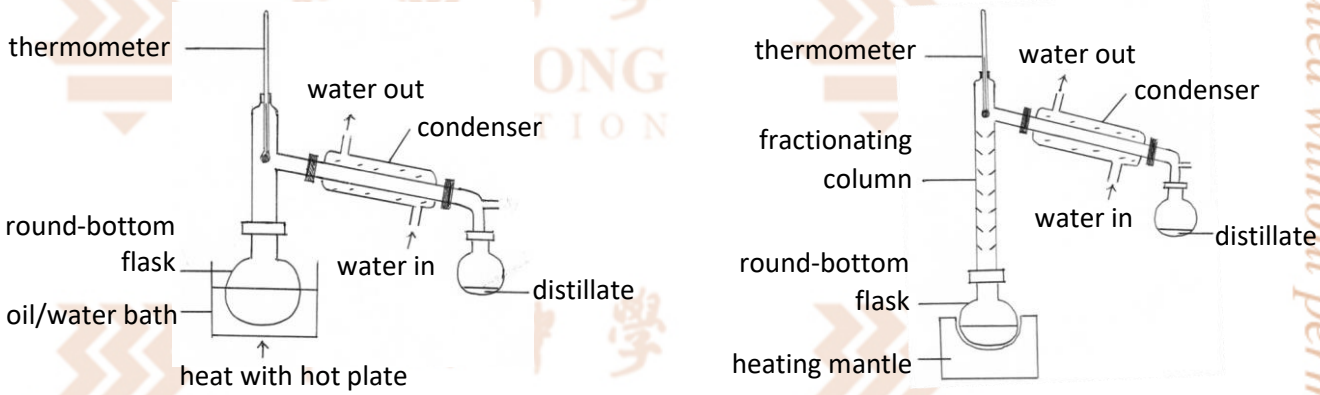
✓ Do not assume the aqueous layer is always the denser layer. (If you do not know the densities of the compounds, check for the aqueous layer by adding water and noting which layer the water enters.)

✓ Common **drying agents**: anhydrous calcium chloride ($CaCl_2$), anhydrous sodium sulfate (Na_2SO_4) or anhydrous magnesium sulfate ($MgSO_4$).

- Distillation (for liquids)

Simple distillation is usually used to separate a volatile liquid from non-volatile impurities or to separate two liquids that differ in boiling point by at least 10 °C. See Figure 23(a) for the experimental setup. The **pure** desired compound is collected at its **boiling point**, condensed and collected as the distillate. An example of a reaction involving distillation is in the oxidation of primary alcohols to aldehydes, taught in Topic 17 Carbonyl compounds.

To separate liquids with boiling points that are close to each other (< 10 °C apart), fractional distillation is used instead – see Figure 23(b).



(a) simple distillation *(b) fractional distillation*

Figure 23. Experimental setup for distillation

- Recrystallisation (for solid products)

Recrystallisation is used to purify a crude product by dissolving it in a suitable solvent at or near boiling point, and then cooling to allow the pure product to crystallise.

Generic procedure for recrystallisation

1. **Dissolve** the crude solid product in a **minimal** volume of **hot** solvent in a conical flask to obtain a saturated solution.
2. **Filter** the hot solution to remove any solid impurities.
3. **Cool** the (saturated) solution in an ice-bath to allow the product to crystallise out.
4. **Filter** the solution to obtain the pure solid crystals as residue. **Wash** the crystals with a small volume of **cold** solvent.
5. Collect the crystals and allow the crystals to **dry**.

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Notes:

✓ A suitable solvent would be one that dissolves the product when hot but not when cold.

✓ The solid may be dried in air or in a desiccator, shown below. If the solid is thermally stable, it can be dried in an oven or under an infra-red lamp.



Figure 24. A desiccator

Exercise 6.1 (Worked Example)

Refer to the reflux set up in Figure 19 and answer the following questions.

i. What is the purpose of adding anti-bumping granules?

The anti-bumping granules will help the solution to boil evenly, thus preventing the solution from boiling suddenly and violently (what is known as 'bumping'), which might be dangerous.

ii. What is one advantage of using a magnetic stirrer instead of anti-bumping granules?

Using a magnetic stirring bar will prevent bumping just like anti-bumping granules. The magnetic stirring bar can be easily removed using another piece of magnet, whereas the anti-bumping granules can only be removed by filtration.

iii. Why should the condenser not be stoppered?

Stoppering the condenser will cause pressure to build up and might cause glassware to break.

Refer to the generic procedure for recrystallisation in Section 6.2.2 and answer the following questions.

i. What is the purpose of using "**hot**" solvent in step 1?

Hot solvent is used as compounds are generally more soluble at higher temperatures. As the solution cools, the solubility of the compound in the solution decreases and the compound recrystallises from the solution. Using hot solvent maximises the amount of compound to recrystallise out at the lower temperatures (usually in ice-bath), thus increasing the yield.

ii. Why do we use only a "**minimal**" volume of the solvent in step 1? What happens when we use too much solvent?

After recrystallization, some of the desired compound would still remain in solution even at the lower temperatures. Hence when too much solvent is used, more compound would remain dissolved and not be obtained as crystals.

iii. Why is "**cold**" solvent used to wash the crystals in step 4?

Cold solvent is used so as to minimize the amount of crystals that redissolve back into the solvent. This is to maximise the yield of the desired compound.

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6.2.3 Checking purity of product

A simple way to check the purity of the product is by measuring its melting point (for solid) or boiling point (for liquid) and comparing the value with reference tables or databases.

Most pure organic solids melt at a **sharp temperature**. Pure liquids are clear (not cloudy) and should distil over a **narrow temperature range** (±2 °C) at the boiling point. Solid/liquid samples which melt/distil over a wide range of temperatures indicate presence of impurities and moisture.

Other techniques to check purity of product include thin-layer chromatography (TLC) and infra-red (IR) spectroscopy.

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09 Isomerism

GUIDING QUESTIONS

- What is isomerism? What are the different types of isomerism?
- What are the structural criteria for exhibition of the different types of isomerism?
- How do the physical and chemical properties of different types of isomers differ?

LEARNING OUTCOMES

Students should be able to:

11.2(a) describe constitutional (structural) isomerism

11.2(b) describe *cis-trans* isomerism in alkenes, and explain its origin in terms of restricted rotation due to the presence of π bonds [use of *E*, *Z* nomenclature is **not** required]

11.2(c) explain what is meant by a chiral centre

11.2(d) deduce whether a given molecule is chiral based on the presence or absence of chiral centres and/or a plane of symmetry

11.2(e) recognize that an optically active sample rotates plane-polarised light and contains chiral molecules

11.2(f) recognise that enantiomers have identical physical properties except in the direction in which they rotate plane-polarised light [usage of the term diastereomers is **not** required]

11.2(g) recognise that enantiomers have identical chemical properties except in their interactions with another chiral molecule

11.2(h) recognise that different stereoisomers exhibit different biological properties, for example in drug action

11.2(i) deduce the possible isomers for an organic molecule of known molecular formula

11.2(j) identify chiral centres and/or *cis-trans* isomerism in a molecule of given structural formula

REFERENCES

1. Albert Lehninger, *Principles of Biochemistry*, 5th Edition, W.H. Freeman
2. Peter Cann, *Chemistry for Advanced Level*, Hodder Education
3. https://www.chemguide.co.uk/basicorg/isomerism
4. IUPAC Compendium of Chemical Terminology, The Gold Book, http://goldbook.iupac.org/index.html

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1 INTRODUCTION

Isomers are molecules with the **same molecular formula**, but **different arrangement of the atoms**.

Imagine that you have a model of a molecule. To create an isomer of this molecule, you have to take the model apart, i.e. break the bonds and reconnect the atoms in a different way. If you make a 'seemingly different' molecule just by rotating the original model as a whole or rotating about the single bonds, it is **not** an isomer – it is still the same molecule!

For example, Figure 1 shows the **same** butane molecule, rotated about the centre C–C single bond:

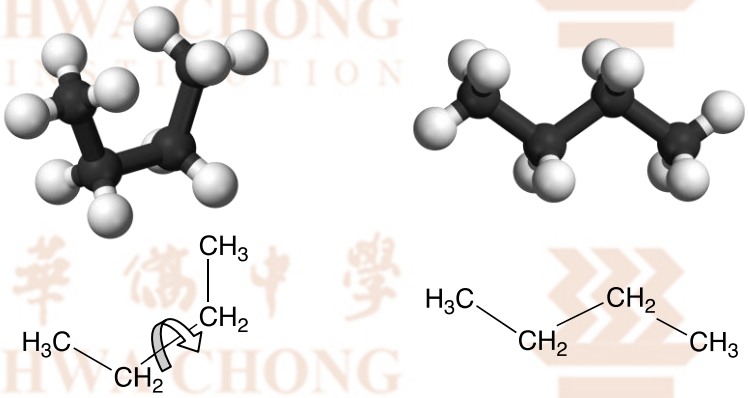


Figure 1. The same butane molecule, rotated about its centre C–C bond

There are many ways a molecule of butane can possibly twist itself, because there is completely **free rotation around all the C–C single bonds**. If you rotate the centre C–C bond through various angles, you obtain different *conformations* of butane, **not** isomers. At room temperature, a particular molecule will be constantly changing from one conformation to another due to free rotation of its single bonds e.g. pentane:



Figure 2. Different conformations of the pentane molecule

When drawing isomers, take care not to draw repeats of the same isomer. For example, the following structures all describe the **same** pentane molecule. They are **not isomers**.

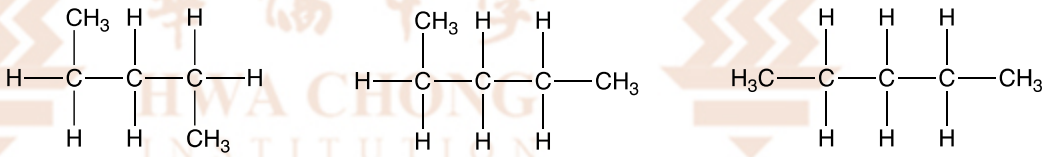


Figure 3. Structural formulae of the same pentane molecule

Isomers have different IUPAC names, which tells us that they are different molecules.

In this topic, we will focus on the following types of isomerism: constitutional isomerism, *cis-trans* isomerism and enantiomerism.

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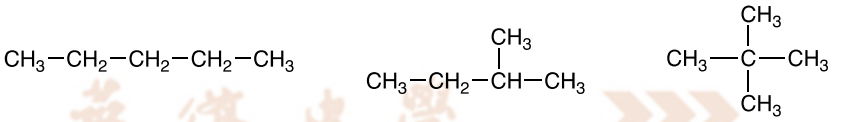
2 CONSTITUTIONAL (STRUCTURAL) ISOMERISM

LO11.2(a): describe constitutional (structural) isomerism

Constitutional isomers are molecules with the **same molecular formula** but **different structural formula**. The physical and chemical properties of constitutional isomers can be very different due to different carbon chains and functional groups. Constitutional isomerism can be categorised into three categories – chain isomerism, positional isomerism and functional group isomerism. Do note that there is no need to memorise these three terms – they are merely guides to help identify constitutional isomerism in compounds.

2.1 Constitutional isomers with different carbon chains (chain isomers)

These isomers arise because of the possibility of **branching in carbon chains**. For example, pentane, 2-methylbutane and 2,2-dimethylpropane are isomers with the molecular formula C_5H_{12}:



pentane 2-methylbutane 2,2-dimethylpropane

Figure 4. Constitutional isomers with different carbon chains due to branching

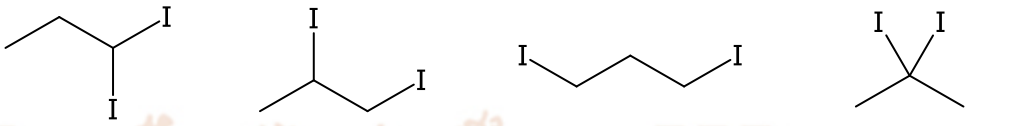
2.2 Constitutional isomers with different positions of same functional group (positional isomers)

These isomers arise because of the possibility of placing the **functional group at different carbon atoms** in the carbon chain. For example, pent-1-ene and pent-2-ene are isomers with molecular formula C_5H_{10}, where the position of the alkene (C=C) functional group differs.



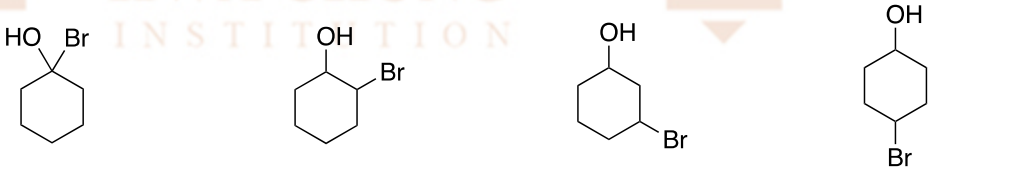
pent-1-ene pent-2-ene

With more functional groups, the number of possibilities increases:



1,1-diiodopropane 1,2-diiodopropane 1,3-diiodopropane 2,2-diiodopropane

This type of isomerism also occurs in ring systems:

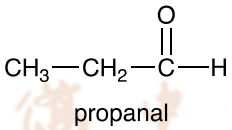


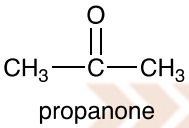
1-bromocyclohexanol 2-bromocyclohexanol 3-bromocyclohexanol 4-bromocyclohexanol

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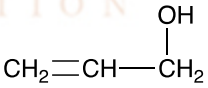
2.3 Constitutional isomers with different functional groups (functional group isomers)

These isomers arise when **different functional groups** consist of the **same type of atoms and bonds**. For example, aldehydes and ketones can be constitutional isomers because they both consist of one oxygen atom and a C=O bond. Hence propanal and propanone are isomers with molecular formula C_3H_6O:


propanal

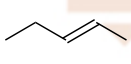

propanone

The following molecule, which has an alkene and an alcohol functional group, is also a constitutional isomer of propanal and propanone:


prop-2-en-1-ol

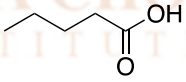
Further examples are shown below:

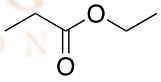
molecular formula: **C_5H_{10}**


2-pentene (alkene)

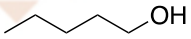

cyclopentane (cycloalkane)

molecular formula: **$C_5H_{10}O_2$**


pentanoic acid (carboxylic acid)


ethyl propanoate (ester)

molecular formula: **$C_5H_{12}O$**


pentan-1-ol (alcohol)

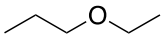

1-ethoxypropane (ether)

Figure 5. Further examples of functional group isomers. Note: ether consists of a C–O–C group

2.4 Deducing possible constitutional isomers

LO11.2(i): deduce the possible isomers for an organic molecule of known molecular formula

Here is a **systematic way** to draw all constitutional isomers with a given molecular formula:

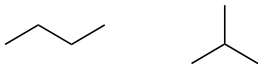
1. From the molecular formula, **identify likely functional group(s)** and check if any double/triple bond or ring present – see Section 2.4.1.
2. Using the number of carbon atoms, draw **all possible carbon chains**: start with straight chain first, then gradually increase the branching to draw all possible branched chains.
3. For each carbon chain from step 2, draw structures with the functional group(s) **placed at all possible different positions on the carbon chain**.
4. Repeat step 3 with **other** likely functional group(s), until all possibilities are exhausted.

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2.4.1 Degrees of unsaturation (Useful Info)

We can find out how many **double bonds, triple bonds or ring(s)** are present in a compound by comparing its **molecular formula** with the **general formula of alkanes** with same number of C atoms.

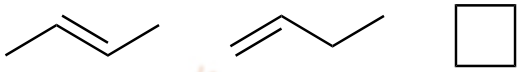
Recall aliphatic alkanes have the general formula, $\mathbf{C_nH_{2n+2}}$. They are saturated and have zero degrees of unsaturation e.g. butane or methylpropane is C_4H_{10}:



If a compound with *n* carbon atoms has **fewer H atoms** than $2n + 2$, it must contain double/triple bonds and/or ring(s).

How to tell how many double/triple bonds or rings?

- **Every decrease of two H atoms** from the alkane general formula contributes to **1° unsaturation**.
- A **1° unsaturation** indicates **either one double bond or one ring** present, hence e.g. C_4H_8 can be butene or cyclobutane.

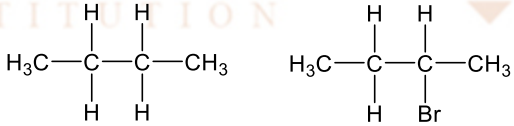


- A 2° unsaturation indicates the compound has either:
  - 2 double bonds, or
  - 2 ring structures, or
  - 1 double bond plus 1 ring structure, or
  - 1 triple bond.

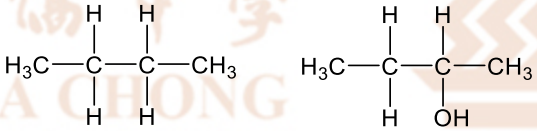
The more degrees of unsaturation, the more possible combinations of double, triple bonds or rings. Double bonds include C=C, C=O, C=N and triple bonds include C≡C, C≡N so this also provides clues on the likely functional groups present.

What if the molecule contains atoms other than C and H?

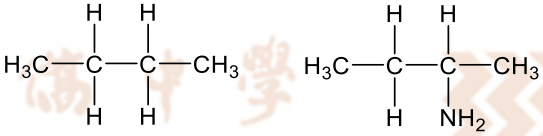
- Halogen atoms do not affect the degree of unsaturation, e.g. C_4H_9Br has 0° unsaturation, just like C_4H_{10}.



- O and S atoms do not affect the degree of unsaturation, e.g. $C_4H_{10}O$ has 0° unsaturation, just like C_4H_{10}.



- For every N atom present, there will be one additional H atom compared to the general saturated formula e.g. $C_4H_{11}N$ has one more H atom than C_4H_{10} though both have 0° unsaturation.



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Try this example!

A compound has molecular formula C_5H_7OF. How many double/triple bonds or ring(s) could it possibly have?

n = 5, 2(5) + 2 = **12** so there should be twelve H atoms for 0° unsaturation.
The compound has one F atom, so no. of 'H' atoms is **8** (count halogens as H atoms).
O atoms have no impact.
=> 12 – 8 = **4** so there are four H atoms fewer ∴ 2° unsaturation (each decrease of two H atoms is 1° unsaturation)
Hence the compound can have either 2 double bonds/2 rings/1 double bond plus 1 ring/1 triple bond.

Exercise 2.1

(a) **(Worked Example)** How many constitutional isomers are there in $C_4H_{10}O$? Draw their skeletal formulae.
[Hint: These isomers are either alcohols (-OH) or ethers (C–O–C).]

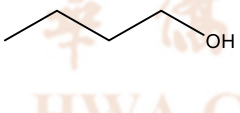
One strategy: You can first try to draw all the possible alcohol constitutional isomers. Start with isomers with 4 carbons in the longest carbon chain, followed by the isomers with 3 carbons in the longest carbon chain.

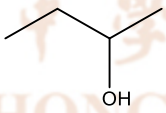
Next, draw all the ether constitutional isomers. Start by drawing the ether  *group first, then add in the rest of the 4 carbons (straight chains followed by branched chains).*

Hence there are 7 constitutional isomers for $C_4H_{10}O$.

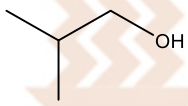
<u>Alcohols</u>

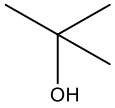
4-carbon chain



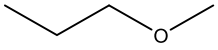


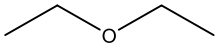
3-carbon chain

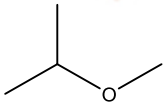




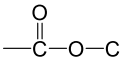
<u>Ethers</u>







(b) Propanoic acid, $CH_3CH_2CO_2H$, and hydroxypropanone, CH_3COCH_2OH, are isomers with molecular formula $C_3H_6O_2$.

(i) Draw the structures of another two isomers which are esters (contain  group).

(ii) Draw the structures of another two isomers with both alcohol (OH) group and carbonyl (C=O) group.

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Exercise 2.2

(a) Draw the skeletal formulae of all constitutional isomers with molecular formula $C_3H_6Br_2$.

(b) In general, how do constitutional isomers differ in their physical properties and chemical reactivities? Circle the correct options below.

(i) Constitutional isomers with **different carbon chains but same functional groups** would have similar/different physical properties and similar/different chemical reactivities.

(ii) Constitutional isomers with **same functional groups in different positions of same carbon chain** would have similar/different physical properties and similar/different chemical reactivities.

(iii) Constitutional isomers with **different functional groups but same carbon chain** would have similar/different physical properties and similar/different chemical reactivities.

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3 STEREOISOMERISM

Stereoisomers are molecules with the **same molecular formula and structural formula** but **different arrangement in space**. They contain the same atoms bonded to each other, the bonding and functional groups are identical and differ only in the way the atoms are arranged in 3-D space.

3.1 *Cis–trans* isomerism

*LO11.2(b): describe cis-trans isomerism in alkenes, and explain its origin in terms of restricted rotation due to the presence of π bonds [use of E, Z nomenclature is **not** required]*
LO11.2(j)part: identify cis-trans isomerism in a molecule of given structural formula

For a molecule to exhibit *cis–trans* isomerism, it must have:

1) a covalent **bond with restricted rotation** , e.g. presence of π bond or ring structure, **AND**
2) **non-identical groups attached to each end** of this bond with restricted rotation

3.1.1 Alkenes

Unlike the case of the C–C single bond which rotates freely at room temperatures, it is not possible to rotate one end of a double bond (e.g. C=C) with respect to the other end, without breaking the π bond:

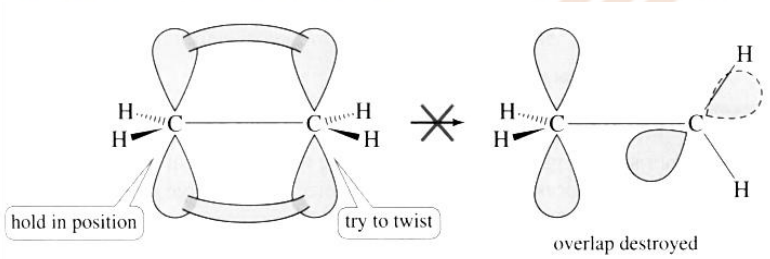
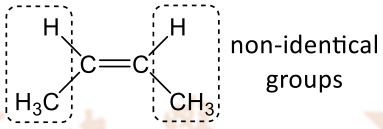


Figure 6. Rotating a C=C bond in an ethene molecule

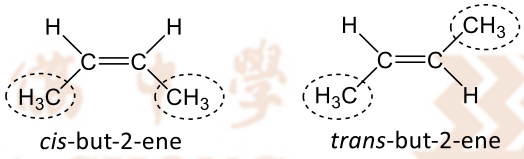
Breaking of the π bond requires much more energy than available at normal temperatures. Hence in alkenes, there is **restricted rotation about the C=C bond due to presence of the π bond**.

Alkenes with **two non-identical groups attached to each carbon of the C=C double bond** will exhibit *cis-trans* isomerism, e.g. but-2-ene:



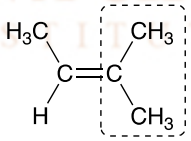
Since the C=C bond cannot rotate freely, these two forms are not readily interconvertible by rotation, hence they are distinct isomers – they have the same structural formula but different arrangements in space i.e. stereoisomers.

The ***cis*** isomer has **identical groups** on the **same side** of the double bond while the ***trans*** isomer has **identical groups** on the **opposite sides** of the double bond, e.g. but-2-ene:

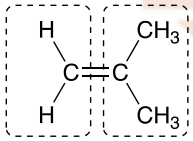


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The following alkenes, methylbut-2-ene and methylpropene, do **not** exhibit *cis-trans* isomerism because one end, or both ends, of the double bond have identical groups attached.

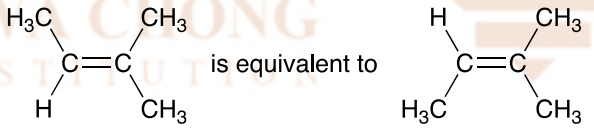


one end has identical groups
- no cis-trans isomerism

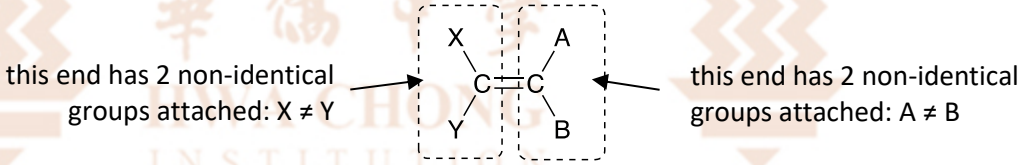


both ends have identical groups
- no cis-trans isomerism

Note that the two structures below are identical compounds (not distinct). They are **not** *cis-trans* isomers!



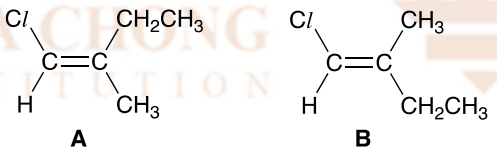
In summary, to deduce whether an alkene can exhibit *cis-trans* isomerism, look at each end of the C=C bond. If each end has two non-identical groups attached like below, the alkene can exhibit *cis-trans* isomerism.



If there are ***n*** such C=C double bonds in a molecule, the <u>*maximum*</u> number of *cis-trans* isomers will be 2^n.

How do we name the *cis-trans* isomers if X, Y, A and B are all different groups?

The "*cis-trans*" nomenclature of isomers applies only when we have **same groups** on the same/opposite sides. If we have four different groups in an alkene e.g.:



We will be able to tell **A** and **B** are *cis-trans* isomers but won't be able to assign "*cis*" or "*trans*" as there are no identical groups on same/opposite sides. The *E/Z* convention is used for such isomers and is not in the A Level H2 syllabus.

- **Cycloalkenes**

  Cycloalkenes with small rings such as cyclohexene and cyclopentene <u>**cannot exhibit *cis-trans* isomerism**</u> as they exist <u>**only**</u> in the ***cis*** isomer form at room temperatures, even though each carbon atom of the C=C bond may be attached to non-identical groups.

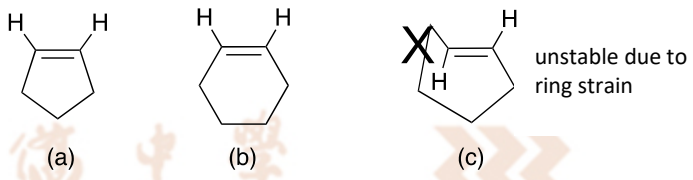
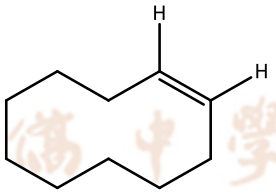


Figure 7. (a) cis-cyclopentene; (b) cis-cyclohexene; (c) unstable trans isomer of cyclohexene (H atoms drawn to illustrate the cis and trans forms)

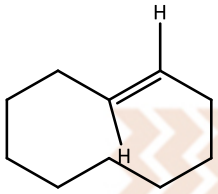
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The ***trans*** isomer forms of cycloalkenes with smaller rings are not stable due to large ring strain. If you make a model of this *trans* isomer, it would be quite impossible to close the ring while maintaining the *trans* form and the trigonal planar geometry at the C=C double bond.

Larger rings, e.g. 8 or more atoms, are able to accommodate the *trans* form, so both their *cis* and *trans* isomers are stable at room temperatures e.g. cyclodecene:



cis-cyclodecene

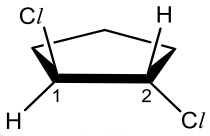


trans-cyclodecene

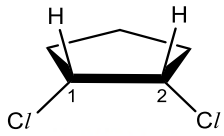
3.1.2 Ring structures (other examples of *cis-trans* isomers)

Cis-trans isomerism also occurs in ring structures. It is not possible for single bonds that form a ring to rotate freely, without first breaking the ring. Hence there is **restricted rotation about single bonds that form part of a ring**.

Ring structures with **non-identical groups attached to two or more atoms in the ring** will exhibit *cis-trans* isomerism e.g. 1,2-dichlorocyclopentane:



trans-1,2-dichlorocyclopentane



cis-1,2-dichlorocyclopentane

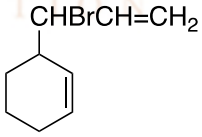
There is restricted rotation about the C1–C2 single bond **and** C1 and C2 atoms are each attached to two non-identical groups.

The ***cis*** isomer has identical groups on the same side of the plane of the ring, whereas the ***trans*** isomer has identical groups on the opposite sides.

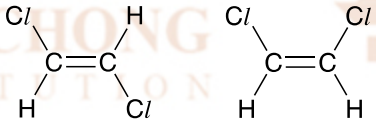
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Exercise 3.1 (Worked Example)

Which of the following alkenes exhibit *cis-trans* isomerism? Draw the *cis-trans* isomers if any, and label them *cis* or *trans*.

(a) ClCH=CHCl **(b)** 

(a) There is presence of a covalent bond with restricted rotation, and 2 non-identical groups attached to each end of the carbon-carbon double bond. Hence ClCH=CHCl can exhibit *cis-trans* isomerism.



trans *cis*

(b) Cyclohexene cannot exhibit *cis-trans* isomerism whereas there are 2 identical groups attached to one end of the carbon-carbon double bond in the alkyl side chain, thus this compound does not exist as *cis-trans* isomers.

Exercise 3.2

Which molecules have isomers that exhibit *cis-trans* isomerism? *(N2005/I/21)*

C_3H_6BrI	C_3H_5I	$C_3H_4I_2$	C_3H_4BrI
I	**II**	**III**	**IV**

A **I**, **II** and **III** only
B **II**, **III** and **IV** only
C **II** and **IV** only
D **III** and **IV** only

Exercise 3.3

Linoleic acid is an essential fatty acid in human diet, with the following structural formula:

$$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7CO_2H$$

In linoleic acid, both double bonds are in the *cis* configuration. Representing the formula by the abbreviated structure A–CH=CH–CH_2–CH=CH–B, draw the structure of:

(a) linoleic acid; and
(b) all its *cis–trans* isomers.

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3.1.3 *Cis–trans* isomers in nature (Application)

- **Retinal**

Our sight is dependent on a compound known as retinal. When light enters the eye, retinal molecules bound to opsin proteins in the eye are converted from the 11–*cis* isomer to the all–*trans* isomer within a few picoseconds. Once formed, the *trans*-retinal diffuses away from the opsin protein and takes several minutes to be isomerized back to the *cis*-isomer.

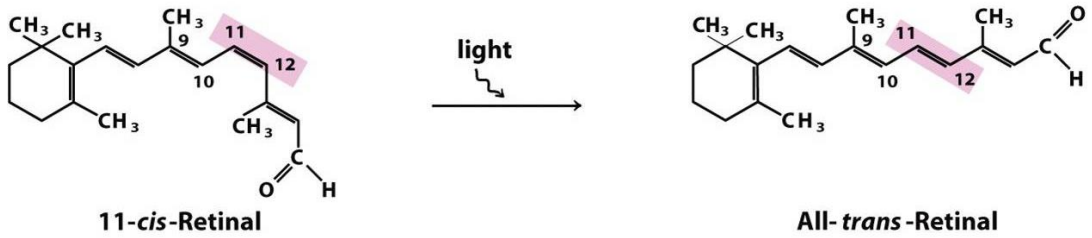


Figure 8. Conversion of 11-cis-retinal to trans-retinal upon absorption of light
Source: Lehninger, Principles of Biochemistry, 5th Edition

Retinal is usually produced by the biological system through consumption of beta-carotene present in foods such as carrots, sweet potatoes and apricots.

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3.2 Enantiomerism

LO11.2(d): deduce whether a given molecule is chiral based on the presence or absence of chiral centres and/or a plane of symmetry

For a molecule to exhibit enantiomerism (i.e. to be **chiral**, pronounced '*kai-ral*'), **its mirror image must be non-superimposable onto itself**. These two non-superimposable mirror images are called **enantiomers**.

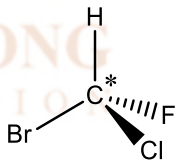
Molecules which exhibit enantiomerism:

1) often contain one or more **chiral centres**
2) do **not** possess any **internal plane** (or centre) **of symmetry**

3.2.1 Molecules with one chiral centre

LO11.2(c): explain what is meant by a chiral centre
LO11.2(j)part: identify chiral centres in a molecule of given structural formula

Consider molecule I below. The central carbon atom has four different groups attached to it in a tetrahedral geometry. This carbon atom is referred to as a chiral centre. Any **atom with a tetrahedral geometry around it that is bonded to four different groups** is known as a **chiral centre**. A chiral centre is denoted with an asterisk(*) on the structure.



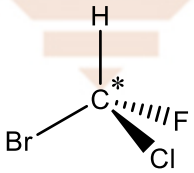
molecule I

(▬) wedged bonds show the bond pointing out of the paper towards you

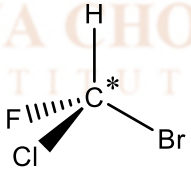
(┈┈) hashed bonds show the bond pointing into the paper away from you

these bonds show the arrangement of atoms/groups in 3D space in stereochemical formulae, particularly important in this topic

Now consider molecule II, the **mirror image** of molecule I.

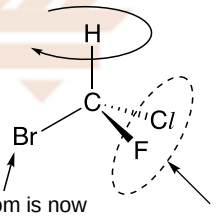


molecule I



molecule II

mirror plane



this Br atom is now aligned with the one in Molecule I

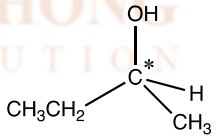
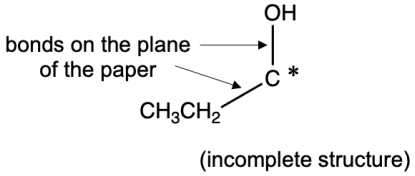
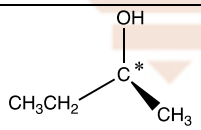
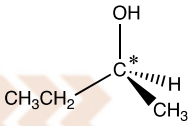
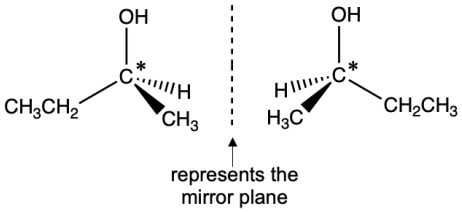
imagine turning Molecule II about the C–H bond to align the C–Br bond to the same position as in Molecule I, you will find that the C*l* and F atoms are still not superimposable onto Molecule I.

Molecule II also has a chiral centre attached to the same four groups that are present in molecule I. They have the same structural formula. However, the two molecules differ in the spatial arrangement of these groups around the chiral centre. Because of this different arrangement in space, these **two molecules that are non-superimposable mirror images of each other** are called **enantiomers**.

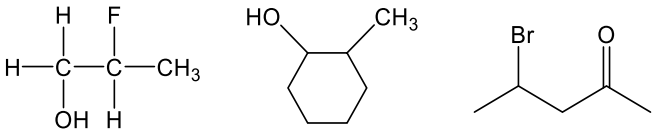
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Exercise 3.4 (Worked Example)

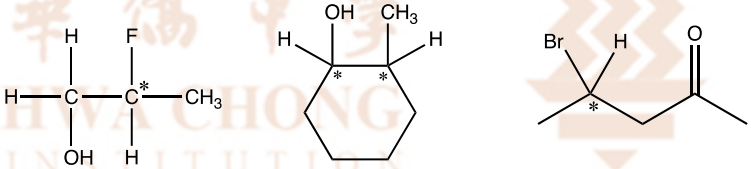
(a) Draw the enantiomers of butan-2-ol. Indicate the chiral centres (*).

Step 1.	Identify the chiral carbon. 	Recall that any atom with a tetrahedral geometry around it that is bonded to four different groups is known as a chiral centre.
Step 2.	Keep any 2 bonds on the plane of the paper, assign them as 'stick lines'. For example, keep the bonds to $–CH_2CH_3$ and –OH on the plane of the paper.	 (incomplete structure)
Step 3.	Draw in the third group with a solid wedge or a dashed wedge.	 (incomplete structure)
Step 4.	Draw in the last group with the wedge not used in step 3, in this example it is the dashed wedge.	
Step 5.	To draw the other enantiomer, simply draw a mirror image of the enantiomer you ended with in Step 4. Groups on the plane remain on the plane, and groups pointing towards the mirror plane will continue to point towards it. Similarly, groups pointing away from the mirror plane will continue to point away. There are other acceptable presentations, please check with your tutors.	 Note: $CH_3–$ or $–CH_3$ or $H_3C–$ are accepted. For longer carbon chains, do not invert the H and C e.g. writing "$H_3CH_2C–$" is not acceptable!

(b) Identify the chiral centres, if any, in the molecules below:



Recall that a chiral centre is any atom with a tetrahedral geometry and is bonded to 4 different groups.

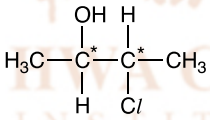


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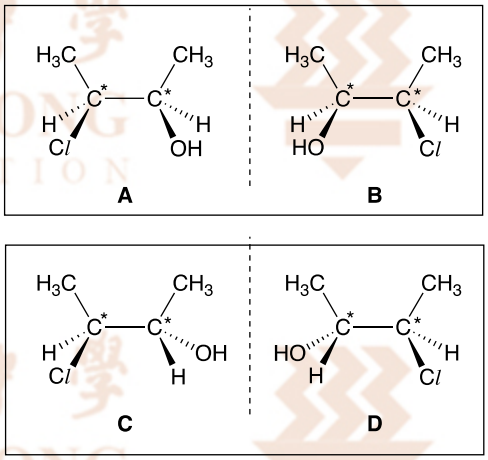
3.2.2 Molecules with more than one chiral centre

Molecules with more than one chiral centre can also exhibit enantiomerism (i.e. be chiral), **if they do not possess any internal plane of symmetry**.

Consider molecule III below. It contains two chiral centres. Each chiral centre can have two ways of arranging its four different groups in 3D space, giving two enantiomers. Hence there can be a total of 4 stereoisomers for molecule III, i.e. 2 pairs of enantiomers:



molecule **III**

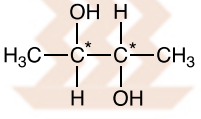


A and **B** are enantiomers because they are non-superimposable mirror images of each other. **C** and **D** are also enantiomers.

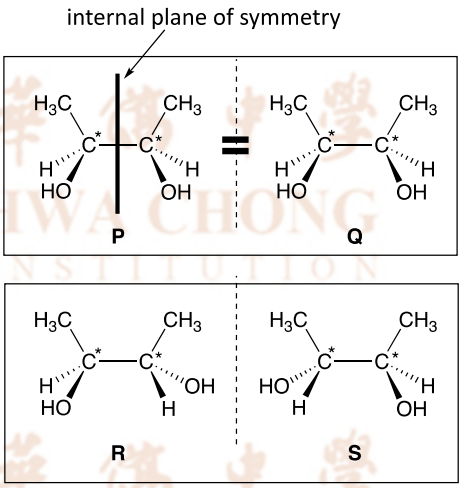
Note that for **A** and **C**, however, the arrangement around one chiral centre (the carbon on the left-hand side) is exactly the same, so **A** and **C** are not enantiomers, just stereoisomers. Similarly, **B** and **D** are not enantiomers. Stereoisomers with at least one chiral centre of the same arrangement are called "diastereomers" (usage of this term is not required for H2 Chemistry). **The arrangement around *all* chiral centres must be different in order for two stereoisomers to be considered enantiomers**.

- **Meso compounds**

Consider molecule IV. It also contains two chiral centres. However, each chiral centre is bonded to the same four groups: OH, H, CH_3 and $CH(OH)CH_3$. Again we may draw 4 possible stereoisomers:



molecule **IV**



Note that **P** and **Q** are equivalent structures, **not** enantiomers!
P has an internal plane of symmetry, so its mirror image is **superimposable onto itself**.
Hence, **P** is **achiral** (i.e. not chiral) even though it has chiral centres, due to its internal plane of symmetry.

A **stereoisomer with two or more chiral centres but no optical activity due to an internal plane of symmetry** is called a **meso compound**.

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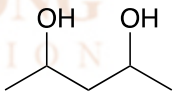
Hence molecule IV has only three stereoisomers: enantiomers **R** and **S**, and meso compound labelled **P** or **Q**.

If there are ***m*** chiral centres in a molecule, the *maximum* number of stereoisomers will be 2^m.

The *actual* number of stereoisomers is determined by considering any **internal plane of symmetry** in the possible structures.

Exercise 3.5

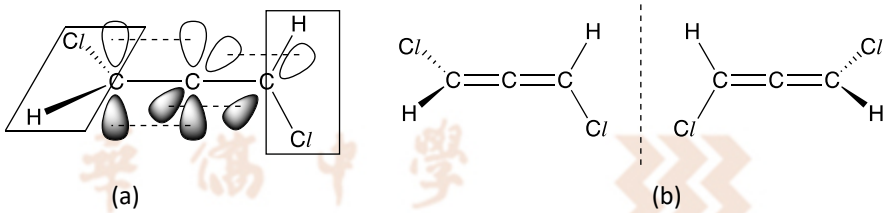
Identify the chiral centres in the pentane-2,4-diol molecule below. Draw the stereoisomers for pentane-2,4-diol.



3.2.3 Molecules without chiral centres (other examples of chirality)

Enantiomerism can occur in molecules without chiral centres. Consider 1,3-dichloropropa-1,2-diene. It has the allene functional group: C=C=C.

Due to the orientation of the overlapping *p* orbitals forming the two π bonds – see Figure 9(a), the H and C*l* atoms at one end do not lie in the same plane as the other end (they lie in perpendicular planes). There is no internal plane of symmetry in the molecule. Its mirror image is non-superimposable onto itself, hence it has two enantiomers, and is chiral.



(a) (b)

Figure 9. (a) orbital overlap of the two π bonds in allene functional group (b) enantiomers of 1,3-dichloropropa-1,2-diene

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3.2.4 Properties of Enantiomers

Enantiomers have mostly identical physical and chemical properties, since they have the same structural formula. However, when placed in a chiral environment or interacting with chiral molecules, the enantiomers will behave differently from each other.

- **Physical properties**

LO11.2(e): recognise that an optically active sample rotates plane-polarised light and contains chiral molecules
*LO11.2(f): recognise that enantiomers have identical physical properties except in the direction in which they rotate plane-polarised light [usage of the term diastereomers is **not** required]*

Enantiomers have **identical** physical properties **except in the direction in which they rotate plane-polarised light**.

Each enantiomer rotates plane-polarised light by the **same angle but in opposite directions**. A 50:50 mixture of the two enantiomers therefore does not rotate plane-polarised light, as the clockwise rotation caused by one enantiomer is *exactly* cancelled by the anticlockwise rotation of the other enantiomer. This mixture containing **equal proportions of each enantiomer** is called a **racemic mixture**. **The direction of rotation cannot be predicted from the structure of the enantiomer** and is determined by direct measurement using a polarimeter.

When a sample is able to rotate plane-polarised light, this sample is said to be **optically active** and contain chiral molecules. Mixtures containing only achiral molecules, or a racemic mixture will have no effect on plane-polarised light, and are therefore **optically inactive**.

The optical activity of a sample can be measured using a polarimeter.

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- **Plane-polarised light (Background Info)**

Light is an electromagnetic wave. It is made up of an electric field and a magnetic field oscillating perpendicular to each other and to its direction of propagation. The oscillation of each light wave is assigned along the plane of the electric field.

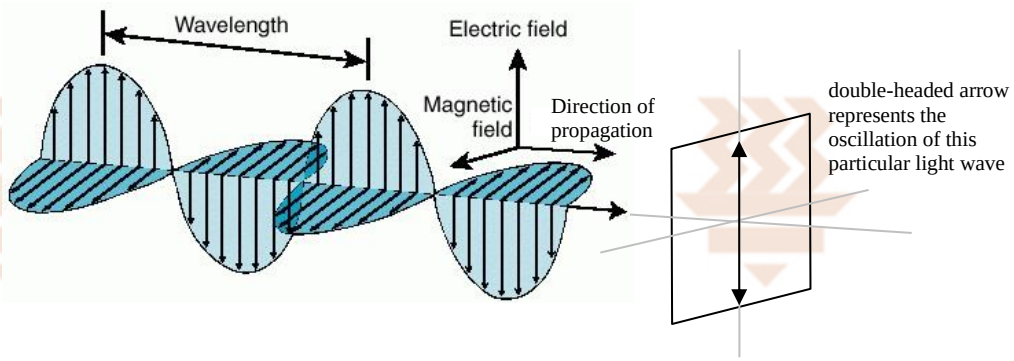


Figure 10. Direction of propagation and oscillation of a light wave

Unpolarised light emitted from common light sources consists of light waves oscillating in all directions. By passing it through a polariser, only light waves oscillating in one particular plane are allowed to pass through, resulting in plane-polarised light.

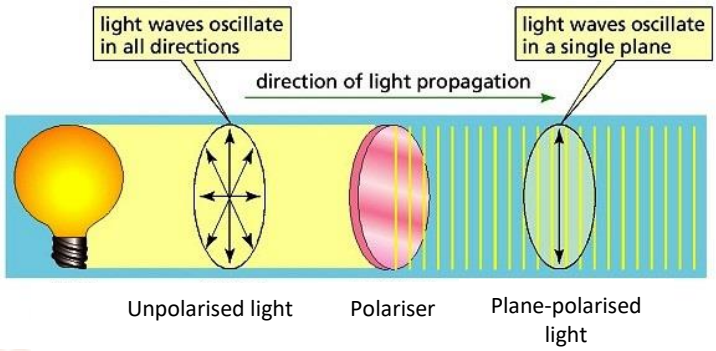


Figure 11. Obtaining plane-polarised light using a polariser

- **Measuring Optical Activity using a Polarimeter (Background Info)**

In a polarimeter, plane-polarised light is allowed to pass through a sample solution. If the sample contains chiral molecules of a pure enantiomer, the plane-polarised light would rotate by a certain angle (depending on concentration) either clockwise or anticlockwise. The rotated plane-polarised light is analysed by another polarizer and the angle of rotation measured.

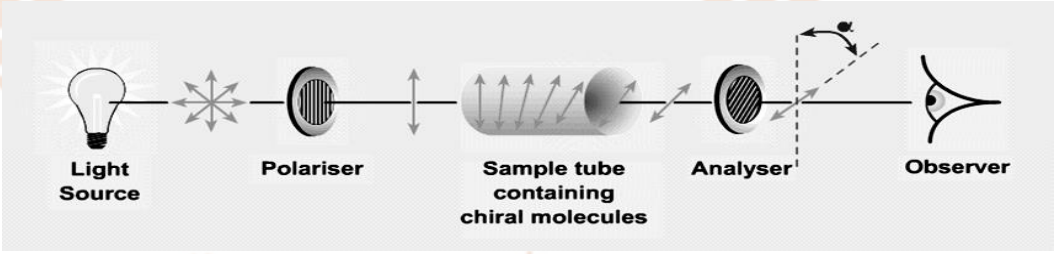


Figure 12. How a polarimeter works to measure the angle of rotation of plane-polarised light

The enantiomer that rotates plane-polarised light in a *clockwise* direction is said to be *dextrorotatory* (Latin *dextro*: "right"), and we add a (+) prefix to its name. The enantiomer that rotates plane-polarised light in an *anticlockwise* direction is said to be *laevorotatory* (Latin *laevo*: "left"), and we add a (–) prefix

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to its name. **The direction of rotation cannot be predicted from its structure** and is determined by direct measurement using a polarimeter.

To distinguish between enantiomers based on structure alone, chemists use a set of systematic rules to assign each chiral centre to either an *R* or *S* configuration. This *R/S* convention is not in the A-level H2 syllabus.

Sunglasses (Application of polarized light)

Try this!

When buying sunglasses, some are claimed to have polarising effects. How do you know the claim is true? Here is a simple way to check:

- If they are on the same rack with others, take two pairs and hold them such that you are looking through both. Then slowly rotate one pair of glasses through 90°. You should see the lenses turn darker and darker.

- **Chemical properties**

LO11.2(g): recognise that enantiomers have identical chemical properties except in their interactions with another chiral molecule
LO11.2(h): recognise that different stereoisomers exhibit different biological properties, for example in drug action

Enantiomers have **identical** chemical properties **except in their interactions with another chiral molecule**.

Since the human body is a chiral environment, it responds differently depending on which enantiomer is interacting with it. Hence enantiomers have **different biological properties** and this has particular relevance in **drug action**.

Examples:

- (–)-carvone gives a spearmint taste, while (+)-carvone gives an earthy taste of citrus and pepper.
- Pure (+)-lactic acid is produced in our muscles when we exercise anaerobically while a racemic mixture of (+)-lactic acid and (–)-lactic acid is often produced when milk is fermented.
- (–)-epinephrine is a natural hormone also known as adrenaline with a stimulating effect while (+)-epinephrine cannot fit into the enzyme active site and is mildly toxic.

Figure 13 shows how the two enantiomers of epinephrine interact differently with the same enzyme active site, due to the fixed spatial arrangement within the active site.

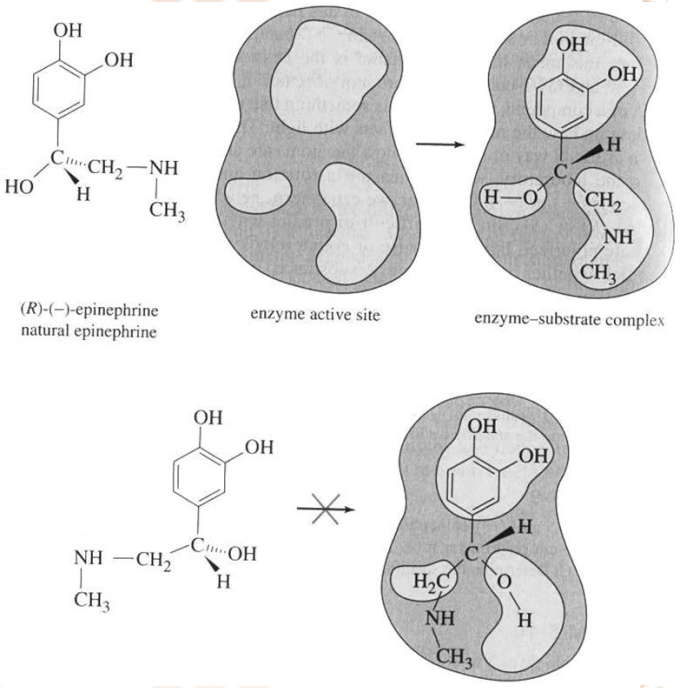


Figure 13. Different interactions of (–)-epinephrine and (+)-epinephrine with the same enzyme active site

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The story of thalidomide

In the late 50s, thalidomide was a drug prescribed to pregnant women for morning sickness. It seemed to be a very successful, non-toxic sedative with no known side effects. Thousands of pregnant women took the drug to relieve their symptoms. Soon there was a huge increase in birth defects, especially in Europe and Canada. It was discovered that thalidomide was responsible for this, causing children to be born with missing or extra limbs.



Figure 14. Photo by Leonard McCombe/Time Life Pictures/Getty Images)

Research showed that while (+)-thalidomide was an effective and safe sedative, (–)-thalidomide was the culprit in damaging the fetus. Originally it was thought that the problem had been due to contamination by the (–)isomer during production, but subsequent research showed that racemization of the pure (+)isomer occurs rapidly as soon as it enters the bloodstream. Within 10 min, racemization is over 50% complete. Hence even if the (+)isomer is administered, the terrible effects of the (–)isomer cannot be avoided.

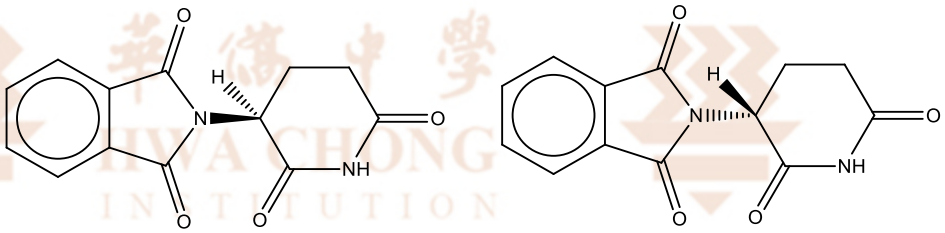


Figure 15. The two enantiomers of thalidomide

An important lesson

Following the thalidomide incident, there was increased fear in the safety of pharmaceutical drugs. It brought on a change in drug testing and increased awareness of potential side effects of drugs. It led to much stricter testing before drug licensing.

The biological impact of enantiomers also highlights the importance of enantiomeric purity in the medicinal industry. This has to be achieved either through synthesis of only one particular enantiomer or the separation of mixtures of enantiomers.

As enantiomers have mostly identical chemical and physical properties, it is very difficult to separate them from a mixture. The only way is to involve other chiral compounds, since enantiomers interact differently with chiral molecules. One method, kinetic resolution, makes use of the different reaction rates of the enantiomers with a chiral reagent.

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- **Kinetic Resolution (Method of separation of enantiomers)**

In kinetic resolution, a mixture of enantiomers is reacted with a chiral reagent. The chiral reagent is chosen such that it reacts quickly with one enantiomer but reacts very slowly with the other enantiomer.

For example, to separate an enantiomer of mandelic acid from its racemic mixture, we add a limited amount of a pure sample of (–)-menthol (chiral reagent). Only one enantiomer of mandelic acid reacts with the (–)-menthol to produce an ester. The other enantiomer of mandelic acid, due to difference in rate of reaction, does not form an ester with the (–)-menthol.

The ester product now has different physical and chemical properties with the unreacted mandelic acid and can be easily separated through conventional separation techniques. The desired enantiomer is then recovered by hydrolysing the ester.

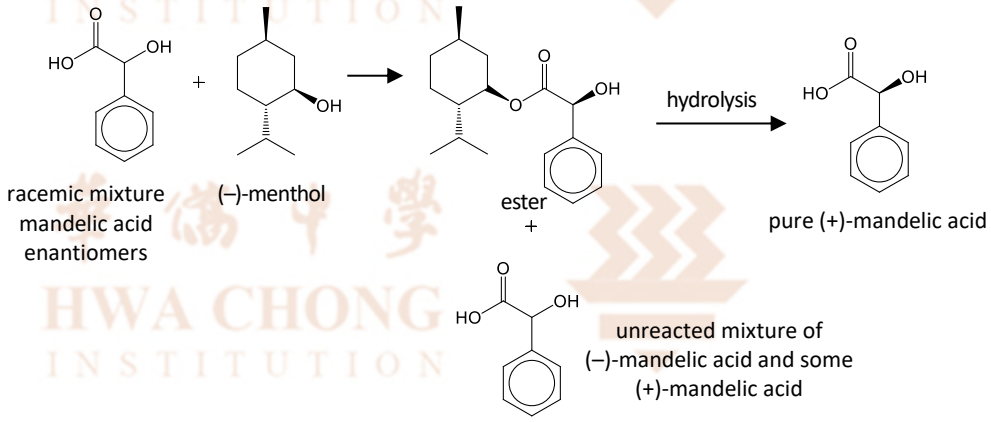


Figure 16. Reaction scheme in the kinetic resolution of mandelic acid

3.3 Counting the total number of stereoisomers

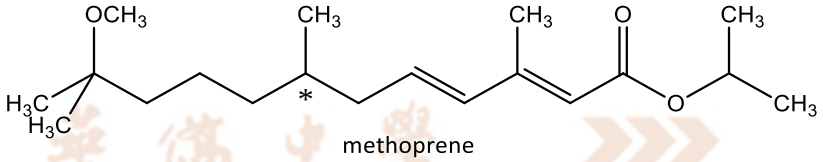
LO11.2(i): deduce the possible isomers for an organic molecule of known molecular formula
LO11.2(j): identify chiral centres and/or cis-trans isomerism in a molecule of given structural formula

Stereoisomers include *both cis–trans* isomers and enantiomers.

If a molecule has ***m*** chiral centres and ***n*** double bonds that can give rise to *cis–trans* isomers, the **maximum** number of stereoisomers it can have = $\mathbf{2}^{m+n}$.

The *actual* number of stereoisomers is determined by considering any **internal plane of symmetry** in the possible structures.

For example, in the methoprene molecule below, there is only one chiral centre, and both C=C double bonds can give rise to *cis-trans* isomerism. As such, the maximum number of possible stereoisomers for methoprene is $2^{(1+2)} = 8$. There is no internal plane of symmetry, so the actual total number is 8.



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Exercise 3.6

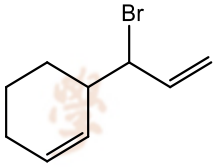
Consider a compound with structural formula $CH_3CH=CHCH(CH_3)CH_2CH_3$.

(a) What is the total number of stereoisomers?

(b) Draw the structure of each stereoisomer.

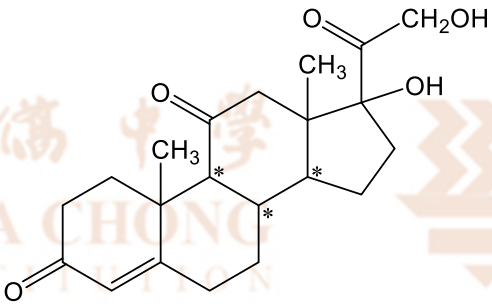
Exercise 3.7

(a) What is the total number of stereoisomers for the following compound?



A 2 **B** 3 **C** 4 **D** 8

(b) The drug cortisone has the formula shown.



In addition to those chiral centres marked by an asterisk(*), how many other chiral centres are present in the cortisone molecule?

A 0 **B** 1 **C** 2 **D** 3

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10 Alkanes

GUIDING QUESTIONS

- Why are alkanes generally unreactive, particularly towards polar reagents?
- Which class of reagents do alkanes react with and why?
- What type of reactions do alkanes undergo and why?
- How do alkanes react with halogens?
- What are the environmental concerns arising from the use of hydrocarbons?

LEARNING OUTCOMES

At the end of the chapter, you should be able to:

11.3 (a) explain the general unreactivity of alkanes, including towards polar reagents

11.3 (b) describe the chemistry of alkanes as exemplified by the following reactions of ethane:

(i) combustion

(ii) free-radical substitution by chlorine and by bromine

11.3 (c) describe the mechanism of free-radical substitution with particular reference to the initiation, propagation and termination reactions

11.3 (n) recognise the environmental consequences of:

(i) carbon monoxide, oxides of nitrogen and unburnt hydrocarbons arising from the internal combustion engine and of their catalytic removal

(ii) gases that contribute to the enhanced greenhouse effect

11.3 (o) recognise that petroleum, a chemical feedstock, is a finite resource and the importance of recycling

REFERENCES

1. Peter Cann and Peter Hughes, *Cambridge International AS and A level Chemistry*, Hodder Education, Chapter 13.
2. John McMurry, *Organic Chemistry*, 6th ed., Thomson/Brooks/Cole, Chapters 3, 5 and 10.
3. Jonathan Clayden, Nick Greeves and Stuart Warren, *Organic Chemistry*, 2nd Ed., Oxford University Press, Chapter 37.

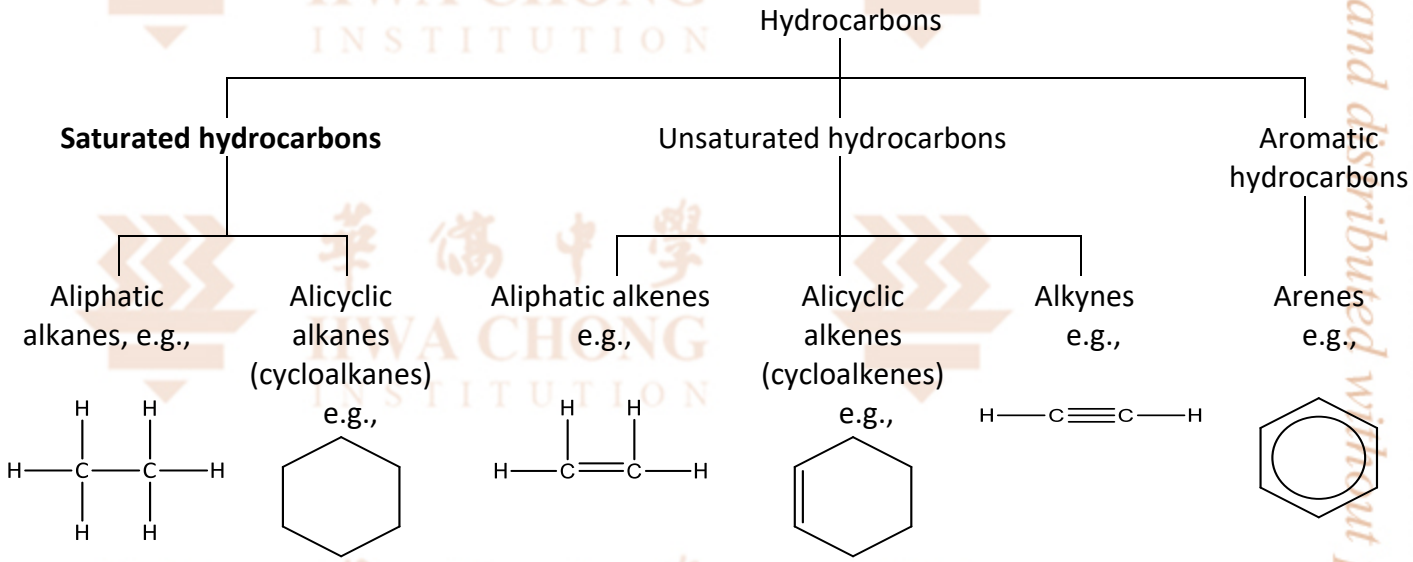
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1 INTRODUCTION

Alkanes are the simplest and least reactive of the homologous series found in organic chemistry.

- They are often described as saturated hydrocarbons:
  Hydrocarbon – contains only carbon and hydrogen
  Saturated – contains only single bonds (i.e. only C–C and C–H single bonds for alkanes), hence each carbon has four bonds.

The chart below describes different types of hydrocarbons and some examples of them.



- Alkanes contain only sp^3 hybridised carbon atoms.
- Aliphatic alkanes contain open chains of carbon atoms which may be straight–chain or branched.

  In straight–chain alkanes, the carbon atoms are connected in a continuous line, whereas in branched alkanes the carbon atoms may be connected to two or three other carbon atoms.

- Cycloalkanes contain closed rings of carbon atoms.

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2 NOMENCLATURE

LO11.1(a)(i)(part): interpret, and use the nomenclature, general formulae and displayed formulae of the following classes of compound: (i) hydrocarbons (alkanes, alkenes and arenes)

2.1 Straight-chain alkanes

Straight–chain alkanes are named according to the number of carbon atoms in their chain with an –***ane*** suffix.

Examples

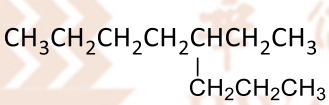
Number of carbons (*n*)	Name	Formula (C_nH_{2n+2})	Number of carbons (*n*)	Name	Formula (C_nH_{2n+2})
1	**Meth**ane	CH_4	6	**Hex**ane	C_6H_{14}
2	**Eth**ane	C_2H_6	7	**Hept**ane	C_7H_{16}
3	**Prop**ane	C_3H_8	8	**Oct**ane	C_8H_{18}
4	**But**ane	C_4H_{10}	9	**Non**ane	C_9H_{20}
5	**Pent**ane	C_5H_{12}	10	**Dec**ane	$C_{10}H_{22}$

Table 1. Names of straight-chain alkanes

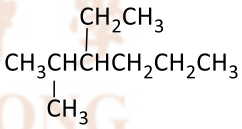
2.2 Branched (or substituted) alkanes

1. Locate the longest continuous chain of carbon atoms; this chain determines the parent name for the alkanes.
2. Number the longest chain beginning with the end of the chain nearer to the substituent, if any.
3. Use the numbers obtained by application of rule no. 2 to designate the location of the substituent group.
4. When two or more substituents are present, give each substituent a number corresponding to its location on the longest chain. Cite them in alphabetical order. The number prefixes *di-*, *tri-*, *tetra-*, etc. are ignored in alphabetizing (refer to point 6).
5. When two substituents are present on the same carbon atom, use that number twice.
6. When two or more substituents are identical, indicate this by the use of the prefixes di-, tri-, tetra- and so on.

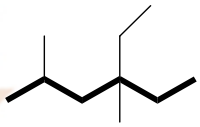
Examples



4–ethyloctane



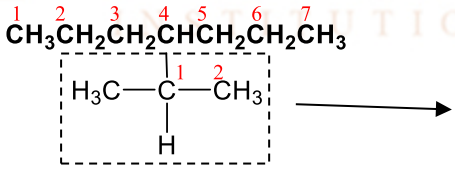
3–ethyl–2–methylhexane



4–ethyl–2,4–dimethylhexane

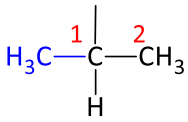
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In the case of a substituent also branching off, it is useful to treat the substituent separately.



4–(1–methylethyl)**heptane**

The substituent is named as it follows:



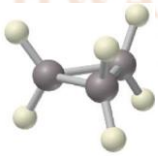
a (1–methylethyl) group

The carbon bonded to the parent chain is C1.

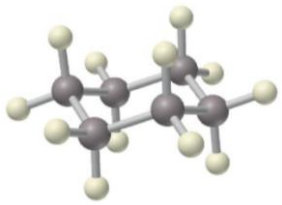
2.3 Cycloalkanes

To name a cycloalkane, add "*cyclo-*" as a prefix in front of the parent name of the corresponding alkane.

Examples



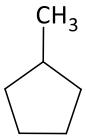
cyclopropane (C_3H_6)



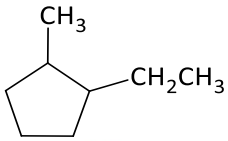
cyclohexane (C_6H_{12})

Substituted cycloalkanes are named by rules similar to those used for open–chain alkanes.

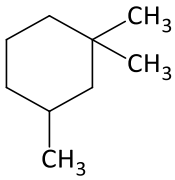
Examples



methylcyclopentane



1–ethyl–2–methylcyclopentane



1,1,3–trimethylcyclohexane

If there is just one substituent, no numbering is needed.

Exercise 2.1

(a) Write the general formula of aliphatic alkanes and cycloalkanes.

(b) Which class of compounds is isomeric with cycloalkanes?

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3 ISOMERISM

LO11.2(a): describe constitutional (structural) isomerism
LO11.2(d): deduce whether a given molecule is chiral based on the presence or absence of chiral centres and/or a plane of symmetry
LO11.2(i): deduce the possible isomers for an organic molecule of known molecular formula

3.1 Constitutional (structural) Isomerism

Alkanes can exhibit constitutional isomerism.

The number of constitutional isomers increases dramatically as the number of carbon atoms increases. For example, $C_{10}H_{22}$ has 75 and $C_{20}H_{42}$ has 366,319 constitutional isomers respectively.

Exercise 3.1 (Includes Worked Example)

Draw the skeletal formulae of all the alkanes with the molecular formula of

(a) C_5H_{12} (Worked Example)

With five C and twelve H atoms, the molecule will consist of single bonds only, just like a saturated (aliphatic) alkane with a general formula of C_nH_{2n+2}. Thus, we start with the straight chain pentane with five C atoms. Then, we rearrange the carbon chain by shortening it one carbon at a time and re-attaching this $-CH_3$ group to other non-terminal carbon atoms to form the various constitutional isomers with branched chains.

Answer



Note: Remember to draw the skeletal formulae as specified in the question.

(b) C_5H_{10}

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3.2 Enantiomerism

Apart from exhibiting constitutional isomerism, some alkanes can also exhibit enantiomerism.

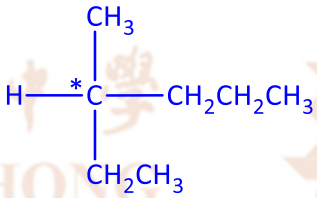
Exercise 3.2 (Worked Example)

Draw the structural formula of the alkane with the lowest M_r that can exhibit enantiomerism. Draw the mirror images of the enantiomers.

[J95/1/9(a) modified]

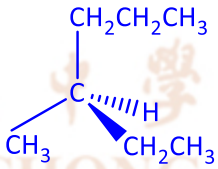
Answers

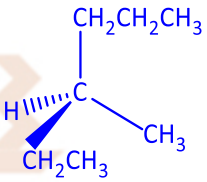
To exhibit enantiomerism, the molecule should have a central C atom as a chiral centre with four different groups attached to it. To obtain an alkane with the lowest M_r, start by drawing a hydrogen atom to the central C atom and increase the number of C atoms for each new group attached. Check that all four groups attached to the central C atom are different.



Next, draw the stereochemical formula of the molecule and its mirror image. The molecule and its mirror image are not superimposable on each other and are enantiomers.

Enantiomers:





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4 PHYSICAL PROPERTIES

LO2(m): describe, interpret and/or predict the effect of different types of structure and bonding on the physical properties of substances
LO2(n): suggest the type of structure and bonding present in a substance from given information

The electronegativity of carbon and hydrogen are 2.55 and 2.20 respectively. The C–H bond thus has a very small dipole moment (considered as a non-polar bond). The molecules of alkanes are therefore non–polar and are held together mainly by weak dispersion forces.

4.1 Physical state

At room temperature and pressure, the lower alkanes, from methane to butane are gases.
The C_5–C_{17} straight–chain alkanes are liquids while those with 18 or more carbon atoms are solids.

Formula	Name	State (at r.t.p)	M_r	Melting point /°C	Boiling point /°C	Density /g cm^{-3}	Remarks (FYI only)
CH_4	methane	gas	16	–182	–162	–	major component of natural gas
C_2H_6	ethane	gas	30	–183	–89	–	component of natural gas
C_3H_8	propane	gas	44	–188	–42	–	component of liquefied petroleum gas (LPG), bottled gas
C_4H_{10}	butane	gas	58	–138	0	–	component of LPG, cigarette lighters
C_5H_{12}	pentane	liquid	72	–130	36	0.63	component of petrol
C_6H_{14}	hexane	liquid	86	–95	69	0.66	
C_7H_{16}	heptane	liquid	100	–91	98	0.68	
C_8H_{18}	octane	liquid	114	–57	126	0.70	major component of petrol

Table 2. Physical properties of some alkanes

4.2 Boiling point

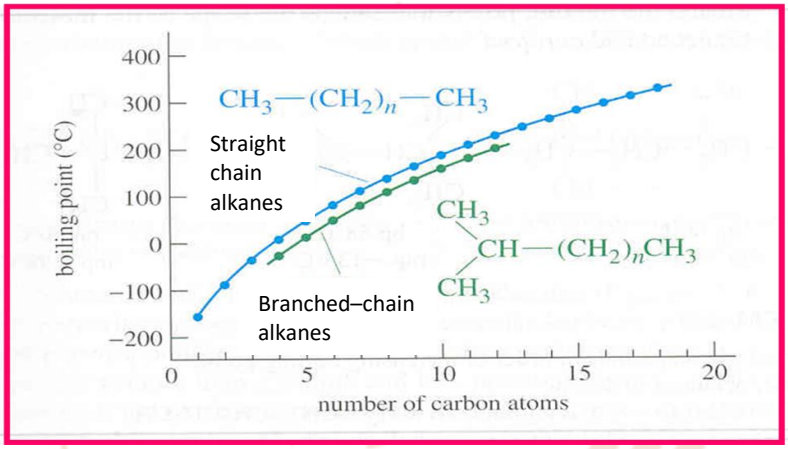
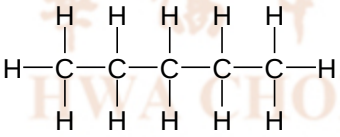


Figure 1. Boiling points of straight-chain and branched-chain alkanes

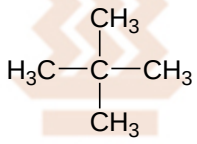
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The boiling point of alkanes increases regularly with increasing number of carbon atoms in the chain.

As the number of carbon atoms increases, the **number of electrons in the molecule increases**, hence **size of the electron cloud increases** leading to **stronger dispersion forces** between the molecules. Thus, **more energy is required to overcome** the stronger dispersion forces between the molecules.
Branched–chain alkanes have lower boiling points than the straight–chain alkanes with the same number of carbon atoms. Recall what you have learned in Topic 2 Chemical Bonding that explains this observation.



pentane
b.p. = 36 °C



2,2–dimethylpropane
b.p. = 9.5 °C





4.3 Melting point

The increase in melting point of alkanes is not as regular as that observed for their boiling points; this is because the dispersion forces between the molecules in a crystal depend not only on the size of the molecules but also on the arrangement of molecules in a solid crystal lattice. The table below illustrates the effect of structure on the melting point of four different C_6H_{14} isomers.

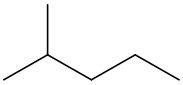
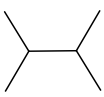
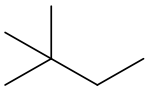
IUPAC Name	Structure	Boiling point / °C	Melting point / °C
Hexane		69	–95
2-methylpentane		60	–154
2,3-dimethylbutane		58	–135
2,2-dimethylbutane		50	–98

Table 3. Boiling and melting points of C_6H_{14} isomers

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4.4 Solubility

In order for dissolution to occur, the solute molecules and the solvent molecules should have favourable intermolecular forces of attraction.
Alkanes can form favourable dispersion forces with non-polar solvents such as benzene and tetrachloromethane. Hence they are soluble in non-polar solvents.

Alkanes can only form permanent dipole-induced dipole intermolecular forces with water, which are much weaker than the hydrogen bonding between water molecules themselves (as well as the dispersion forces between alkane molecules). Hence they are insoluble in water.

4.5 Density

Liquid alkanes are less dense than water and form an immiscible layer above water.

Their densities increase slightly with increasing number of carbon atoms present. This is because the increase in the strength of dispersion forces causes the alkane molecules to attract more closely together, resulting in a slightly smaller volume of the liquid. Since ρ = m/V, with a larger relative molecular mass, the density of the liquid increases.

4.6 Viscosity

Viscosity describes a fluid's internal resistance to flow and may be thought of as a measure of fluid friction. The viscosity of liquid alkanes increases with increasing number of carbon atoms present as the dispersion forces between the molecules increases. In addition, longer-chain alkanes have higher viscosity as the long molecules tend to "tangle up" with one another.

Exercise 4.1

The following are boiling points of various alkanes given in ^{o}C and at atmospheric pressure.

Butane	Pentane	Hexane
0.5 ^{o}C	36 ^{o}C	69 ^{o}C

(a) Explain why the boiling point of butane is lower than that of pentane.
(b) Draw the structure of 2,2-dimethylbutane and predict whether it would have a higher or lower boiling point than hexane.

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5 CHEMICAL PROPERTIES

LO11.3(a): explain the general unreactivity of alkanes, including towards polar reagents

The only two types of bonds contained in alkanes, C–C and C–H, are strong and non-polar. The C–C and C–H bonds are essentially non-polar due to similarity in electronegativities of the C and H atoms. Hence, alkane molecules do not contain any significant amount of positive or negative charge, and are unreactive towards polar reagents.

The net result is that alkanes have a fairly restricted set of reactions, namely: combustion and free radical substitution.

5.1 Combustion of alkanes

LO11.3(b): describe the chemistry of alkanes as exemplified by the following reactions of ethane: (i) combustion

Alkanes react with excess oxygen (complete combustion) to give carbon dioxide and water. The reaction is a highly exothermic process.

General equation $C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$

Example

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\quad \Delta H_c = -890 \text{ kJ mol}^{-1}$

$C_{20}H_{42}(s) + 30½\ O_2(g) \rightarrow 20CO_2(g) + 21H_2O(l)$ $\quad \Delta H_c = -13368 \text{ kJ mol}^{-1}$

Although the combustion of alkanes is highly exothermic, it also has a high activation energy. For example, a mixture of methane and oxygen is stable unless ignited by a spark. The reaction, once started, accelerates explosively due to large amount of heat liberated.

Alkanes only burn in the gaseous state. Liquid and solid alkanes must be vapourised before they will burn.

When they are burnt in a limited supply of oxygen (incomplete combustion), carbon (soot) and carbon monoxide are also formed and these have adverse environmental consequences.

Example

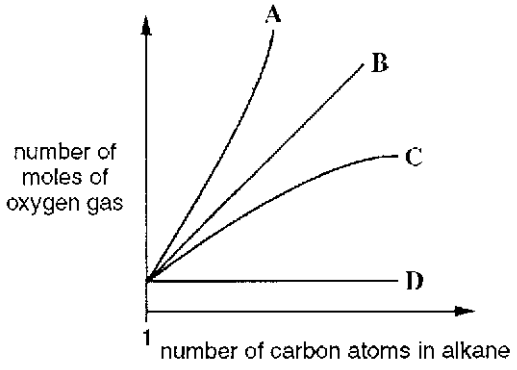
$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$

$CH_4 + O_2 \rightarrow C + 2H_2O$

Exercise 5.1

The complete combustion of alkanes to produce carbon dioxide and water is an important exothermic reaction. Which line on the graph shows the relationship between the number of carbon atoms in the alkane and the number of moles of oxygen gas needed for complete combustion of the alkane?

[J2003/I/23]



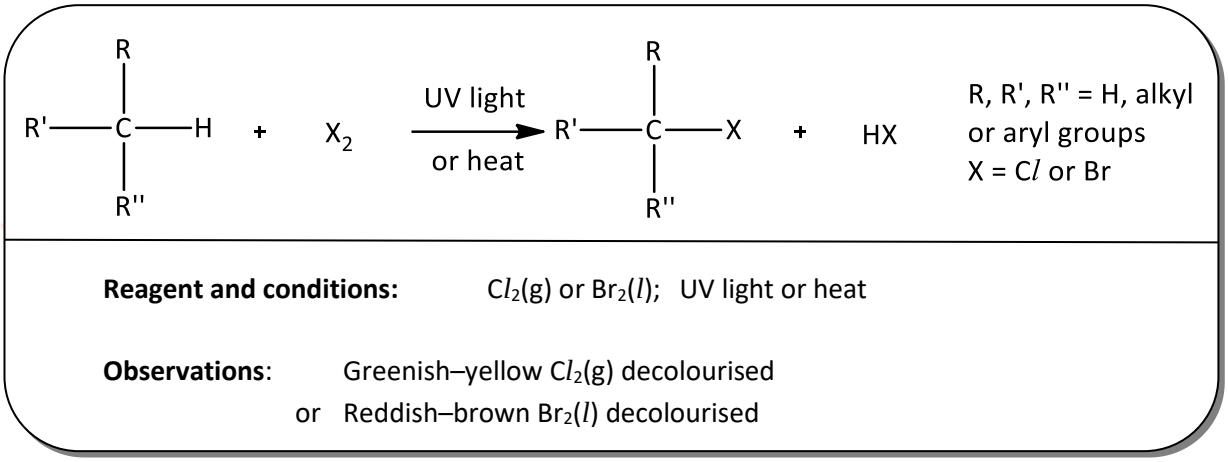
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5.2 Free radical substitution

LO11.3(b): describe the chemistry of alkanes as exemplified by the following reactions of ethane: (ii) free-radical substitution by chlorine and by bromine

Alkanes react with halogens (Cl_2 and Br_2) in the presence of ultraviolet light or heat to form halogenoalkanes (or alkyl halides). This type of reaction is known as free radical substitution, an example of non-polar reactions.

When initiated (started off) by the absorption of UV light or sunlight, the reaction is called a photochemical reaction. Nevertheless, remember that the free radical substitution can also be initiated if sufficient heat is supplied. In the reaction, one or more of the hydrogen atoms in the alkane can be substituted by the halogen atom(s).

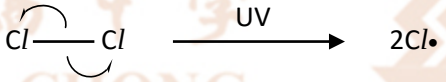


5.2.1 Mechanism of the free radical substitution of methane by chlorine

LO11.3(c): describe the mechanism of free-radical substitution with particular reference to the initiation, propagation and termination reactions

Step 1. Initiation

The C*l*–C*l* bond is **homolytically** broken to give chlorine free radicals (C*l*•). The energy required comes from the light absorbed or the heat supplied.



Exercise 5.2 (Worked Example)

Why are the C–H bonds in CH_4 unaffected during the initiation step?

Answer

The energy is insufficient to break the stronger C–H bond.
(From the Data Booklet, Bond Energy (C*l*–C*l*) = 242 kJ mol^{-1}; Bond Energy (C–H) = 410 kJ mol^{-1})

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Step 2. Propagation

The highly reactive chlorine radical collides with a methane molecule and abstracts a hydrogen atom to produce HC*l* and a methyl radical (•CH_3).

$$Cl\bullet + CH_4 \rightarrow HCl + \bullet CH_3 \qquad (1)$$

(Note: $\Delta H_{(1)}$ = B.E.$_{(C–H)}$ – B.E.$_{(HCl)}$ = 413 – 431 = **–18 kJmol^{-1}** which explains why HC*l* and •CH_3 are formed instead of C–C*l* and •H)

This methyl radical then reacts further with another molecule of Cl_2 in a second propagation step to yield the product chloromethane and **regenerate** a new chlorine radical.

$$\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet \qquad (2)$$

The chlorine radical formed can again react with another methane molecule as in step (1) and so on, making the radical a homogeneous catalyst. Thus, once the reaction has been initiated, it becomes a self–sustaining cycle of repeating steps (1) and (2), making the overall process a **chain reaction**.

Exercise 5.3

(a) Why is the free radical reaction known as a chain reaction?

(b) Explain why the reaction of alkanes with halogens requires only a flash of ultraviolet light rather than prolonged radiation. *[J88/II/2(c) modified]*

Step 3. Termination

Two radicals collide and combine to form a stable product in this stage. The possible products are:

$$Cl\bullet + C\bullet \rightarrow Cl_2$$
$$Cl\bullet + \bullet CH_3 \rightarrow CH_3Cl$$
$$\bullet CH_3 + \bullet CH_3 \rightarrow CH_3CH_3$$

When these reactions occur, radicals needed for the propagation steps are consumed. The reaction cycle is broken and the chain reaction is terminated.

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Exercise 5.4

(a) State the conditions used for the reaction between ethane and bromine.

$$C_2H_6 + Br_2 \rightarrow C_2H_5Br + HBr$$

(b) Why is this described as a *free–radical substitution* reaction?

(c) Write equations to show the mechanism for the above reaction.

[N2006/III/6(a) modified]

5.2.2 Formation of by–products

Halogenation of alkanes via free radical substitution may seem like a good method of obtaining halogenoalkanes at first, but in reality, the extent and the position of substitution is difficult to control.

A free radical is highly reactive and can react with almost any C–H bond present in the reaction mixture. In the presence of **excess halogen**, further substitutions of the product may occur resulting in a mixture of multi–substituted halogenoalkanes.

For example, chloromethane formed may further react with a chlorine radical to form dichloromethane:

$$CH_3Cl + Cl\bullet \rightarrow \bullet CH_2Cl + HCl$$

$$\bullet CH_2Cl + Cl_2 \rightarrow \underset{\text{dichloromethane}}{CH_2Cl_2} + Cl\bullet$$

Similarly, CH_2Cl_2 can undergo further chlorination to give $CHCl_3$ and CCl_4.

$$CH_4 \xrightarrow[UV]{Cl_2} CH_3Cl \xrightarrow[UV]{Cl_2} CH_2Cl_2 \xrightarrow[UV]{Cl_2} CHCl_3 \xrightarrow[UV]{Cl_2} CCl_4$$

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Exercise 5.5 (Includes Worked Example)

Suggest suitable reaction conditions for the substitution of methane by chlorine in UV light, so as to favour the production of

(a) chloromethane (Worked Example)

Answer

Excess methane and limited amount of chlorine.

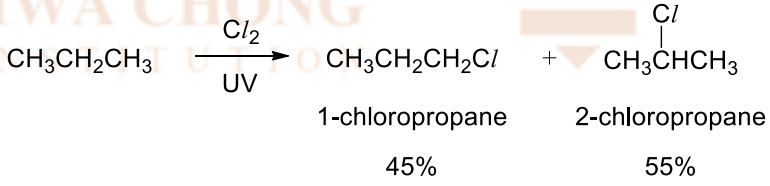
In this way, further substitution of the monochlorinated methane is limited as the probability of chlorine radicals reacting with a methane molecule is higher than the probability of chlorine radicals reacting with a monochlorinated methane molecule.

(b) tetrachloromethane.

5.2.3 Ratios of products formed when an alkane has non-equivalent hydrogen atoms

As all hydrogen atoms are susceptible to substitution, when an alkane contains 3 or more carbon atoms, isomeric products are formed depending on which H atom is substituted. The proportion of the isomers depends on the probability of the intermediates formed and the relative stability of the intermediates.

Let's look at the chlorination of propane: two monochlorinated products are possible and their experimental yields are shown in the equation below. How can we explain their ratios?



Before we examine their ratios, let's look at the classification of hydrogen atoms in alkanes and the stability of alkyl radicals.

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Classification of carbon and hydrogen atoms

Carbon atoms are classified depending on the number of other carbon atoms attached to it. Hydrogen atom is classified according to the carbon atom to which it is attached. For example, a hydrogen atom attached to a primary carbon atom is called a primary hydrogen (*Table 4*). In the following topics, we will use the same classification for radicals, carbocations, alcohols, amines, and so on.

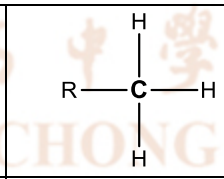
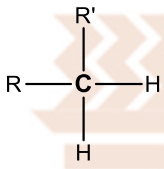
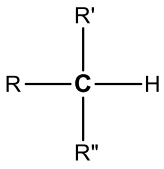
			
No. of alkyl groups attached	1	2	3
Type of carbon atom	Primary (1°)	Secondary (2°)	Tertiary (3°)
Type of hydrogen atom	Primary (1°)	Secondary (2°)	Tertiary (3°)

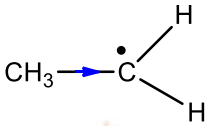
Table 4. Classification of carbon and hydrogen atoms

Stability of alkyl radicals

The alkyl groups attached to the carbon radical play a role in the stability of that carbon radical. **The more alkyl groups attached to the carbon radical – the more stable the radical** is and hence more easily it will be formed.



Reason: Alkyl groups are weakly electron-donating and can hence compensate for the electron deficiency experienced by carbon radicals (or carbocations, see *Alkenes*).

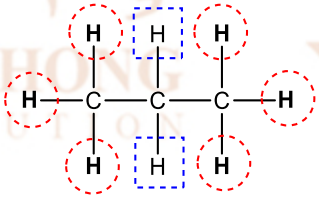


We can now use the abovementioned concepts to explain the **experimentally observed** ratio of the two monochlorination products formed from propane. There are two factors which affect the proportion of products formed:

1. *Ratio of different types of hydrogen atoms present in the alkane*

In the case of propane, the ratio of primary (H) hydrogens to secondary (H) hydrogens is 6:2. Therefore, based on probability only, there should be two types of monochlorinated products formed, 1–chloropropane and 2–chloropropane, and their ratio should be 6:2, or 3:1. (see next page)

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2. *Stability of each type of carbon radical intermediate present*

Propyl radical ($CH_2CH_2CH_3$), formed by the abstraction of a primary hydrogen atom, is however a primary radical and less stable than the secondary isopropyl radical CH_3CHCH_3, and hence it is less likely to form. So, formation of 1-chloropropane is less favoured.

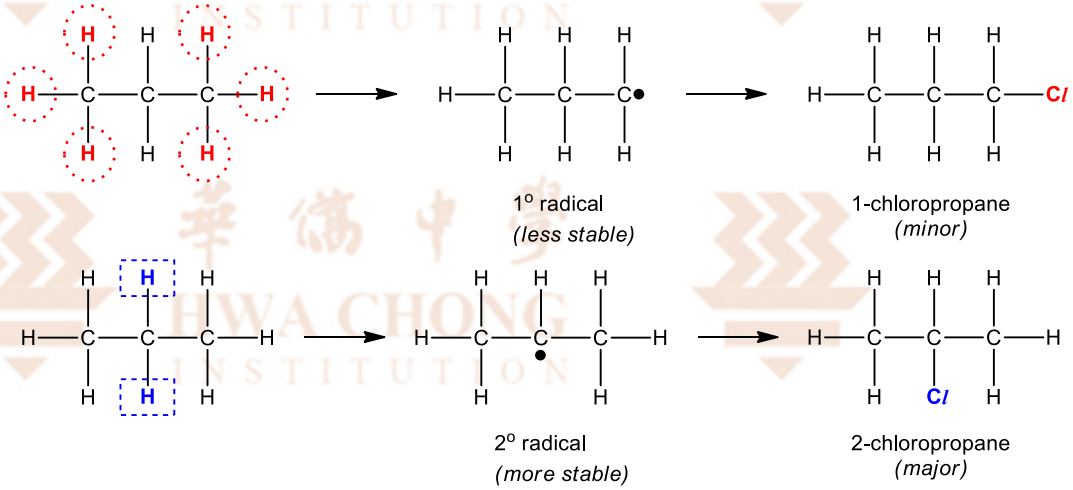


Figure 2. The formation of carbon radical intermediate and its subsequent chlorination

Hence, the actual ratio of 1–chloropropane:2–chloropropane cannot be 6:2. In fact, it is found to be 45:55 (or **nearly 1:1)**, which is due to both factors playing a role in the mechanism of the reaction.

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Exercise 5.6 (Includes Worked Example)

1. Pentane was reacted with limited chlorine in the presence of *uv* light. Assuming that only mono-chlorination takes place and the reaction occurs **at the same rate** at all carbon atoms, predict the ratio of the products obtained.

[HCl Prelim 2008/I/20]

	1-chloropentane	:	2-chloropentane	:	3-chloropentane
A	3	:	2	:	1
B	1	:	2	:	3
C	1	:	3	:	2
D	3	:	1	:	2

2. **Worked Example**

2-methylbutane, $CH_3CH_2CH(CH_3)_2$, undergoes free radical substitution with Cl_2 to give 4 mono-substituted products **A**, **B**, **C**, and **D**.

Type of Hydrogen	Relative Reactivity
Primary, 1°	1
Secondary, 2°	3.5
Tertiary, 3°	5

The following information will allow you to determine the structures of **A**, **B**, **C** and **D**.

- The ratio of the four products formed can be found by multiplying the relative reactivity of the hydrogen responsible for the formation of the product to the number of hydrogen atoms in the compound that can form that product.
- There is twice as much of **C** as compared to **A** in the product mixture.
- **B** and **C** are both optically active.

(i) Draw the structures of the 4 monochlorinated products and label each structure (**A**, **B**, **C** or **D**). Explain your answer.

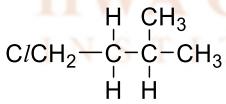
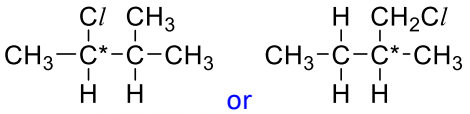
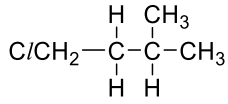
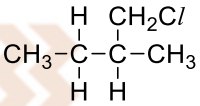
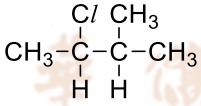
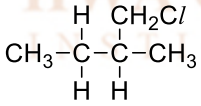
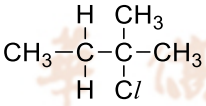
(ii) Predict the ratio of the four monochlorinated products by considering the above information.

[HCl Promo 2014/II/5]

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Answer

(i)

Structure		Explanation
	**A**	• Since **B** and **C** are optically active, they can only be:  • Since there is twice the amount of **C** as compared to **A**, the hydrogen atoms responsible for their formation should be from the -CH_3 groups. **A** must be  and **C** must be  • As a check, ratio of product **A** : **C** = 3 x 1° H : 6 x 1° H = 3 : 6
	**B**	
	**C**	
	**D**	

(ii) Ratio **A** : **B** : **C** : **D** = 1 × 3 : 3.5 × 2 : 1 × 6 : 5 × 1 = 3 : 7 : 6 : 5

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5.2.4 Reactivity of halogens with alkanes

The reactivity of halogens in the free radical substitution of alkanes decreases in the following order: $F_2 > Cl_2 > Br_2 > I_2$.

Reaction of methane with halogens

Fluorine gas	Reacts vigorously, even in the dark and at room temperature. Dangerously exothermic because of the low F–F bond energy and the high C–F bond energy.
Chlorine gas	Requires UV light or heat. Reaction is exothermic.
Bromine liquid	Requires UV light or heat. Reaction is slower than with chlorine.
Iodine solid	No reaction.

The ΔH of the reactions of methane with the halogens are shown below:

$$CH_4 + X_2 \rightarrow CH_3X + HX \qquad \Delta H_r$$

Halogen (X)	ΔH_r / kJ mol^{-1}	H–X bond energy / kJ mol^{-1}	C–X bond energy / kJ mol^{-1}	X–X bond energy / kJ mol^{-1}
F	–478	562	484	158
Cl	–117	431	340	244
Br	–43	366	280	193
I	+22	299	240	151

Table 5. Bond energies for calculation of ΔH_r

From the table, the trend in reactivity matches the trend in ΔH_r, which is calculated as the overall enthalpy change for both propagation steps. Recall Topic 5 Chemical Energetics for the calculation of ΔH_r by the use of bond energies of the bonds broken and formed.
The C–H bond is broken in the first propagation step (Step 1), whereas H–X is formed. The X–X bond is broken in the second propagation step (Step 2) and C–X bond is formed.

Step 1:	$CH_3–H + X\bullet \rightarrow \bullet CH_3 + H–X$	ΔH_1 = BE(C–H) – **BE(H–X)**
Step 2:	$\bullet CH_3 + X–X \rightarrow CH_3–X + X\bullet$	ΔH_2 = BE(X–X) – **BE(C–X)**
Overall reaction:	$CH_4 + X_2 \rightarrow CH_3X + HX$	$\Delta H_r = \Delta H_1 + \Delta H_2$

Exercise 5.7 (Worked Example)

Chloroalkanes and bromoalkanes can be made by the reaction of the corresponding halogen with alkanes, for example:

$$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$$

Suggest why it is **not** possible to make iodoalkanes by this method. *[N2010/III/1(c)]*

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Answer

Propagation: $I\bullet + CH_3CH_3 \rightarrow HI + \bullet CH_2CH_3$

$\bullet CH_2CH_3 + I_2 \rightarrow CH_3CH_2I + I\bullet$

The H–I bond formed in the first propagation step is very weak, such that this step becomes highly endothermic. ΔH_1 = BE(C–H) – BE(H–I) = 410 – 299 = +111 kJ mol^{-1}. For the second step, ΔH_2 = BE(X–X) – BE(C–I) = 151 – 240 = -89 kJ mol^{-1}. Hence, this final step is insufficiently exothermic to make up for the endothermic formation of the alkyl radical in the first step.

Note: recall from Chemical Energetics that ΔH = *BE(Broken) – BE(Formed)*

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6 ALKANES AS FUELS

Alkanes are found in crude oil and their main use is as fuels. A huge fraction of the energy we use comes from the combustion of alkanes. The gas in cookers, the petrol in cars, aviation fuel and diesel oil for powering ships and electric generators are all mixtures of alkanes.

6.1 Processing of crude oil

Fractional distillation (Background info)

- Crude oil is a mixture of many hundreds of hydrocarbons. It also contains some compounds containing sulfur and nitrogen. It is an important source of aliphatic and aromatic hydrocarbons.
- The first stage in the processing of crude oil is fractional distillation, carried out at atmospheric pressure.

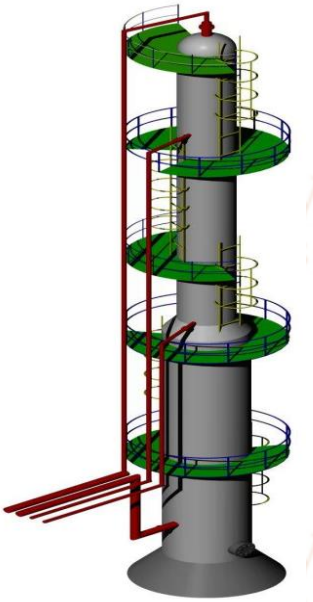


Figure 3. Model of a fractional distillation tower

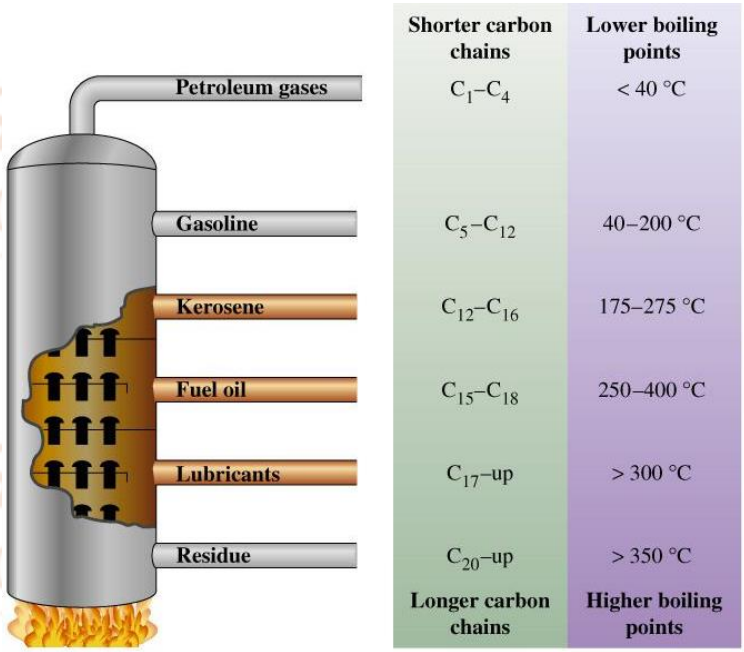


Figure 4. Fractional distillation of crude oil

Fraction	No. of C atoms	Boiling point range / °C	% in crude oil	Uses
Petroleum gas	1 – 4	< 40	2	Fuel, petrochemical feedstock
Gasoline	5 – 12	40 – 200	20	Fuel for petrol engines, petrochemical feedstock
Kerosene	12 – 16	175 – 275	13	Airplane fuel, can be cracked to give more gasoline
Gas oil	15 – 18	250 – 400	20	Fuel for diesel engines, can be cracked to give more gasoline
Residue	> 20	> 350	45	Lubricating oil, power station fuel, bitumen for roads, can be cracked to give more gasoline

Table 6. Fractions of crude oil and their uses

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LO 11.3(o): recognise that petroleum, a chemical feedstock, is a finite resource and the importance of recycling

Petroleum, a fraction of crude oil, is an important energy source. However, it is a finite resource (a resource that does not renew itself at a sufficient rate for sustainable economic extraction in meaningful human time-frames). The world has a limited supply of petroleum, and current estimations tell us that within the next few decades mankind will have completely depleted this valuable natural resource.

6.2 Importance of recycling



Recycling is a process to convert waste materials into new products to prevent waste of potentially useful materials, reduce the consumption of fresh raw materials, reduce energy usage, reduce air pollution (from incineration) and water pollution (from landfilling) by reducing the need for "conventional" waste disposal and lower greenhouse gas emissions as compared to plastic production. Recycling is a key component of modern waste reduction and is the third component of the "Reduce, Reuse and Recycle" waste hierarchy.

Recycling is very important as waste has a huge negative impact on the natural environment.

- Harmful chemicals and greenhouse gases are released from rubbish in landfill sites. Recycling helps to reduce the pollution caused by waste.
- Habitat destruction and global warming are some the effects caused by deforestation. Recycling reduces the need for raw materials so that the rainforests can be preserved.
- Huge amounts of energy are used when making products from raw materials. Recycling helps to preserve natural resources.

Recycling is essential to cities around the world and to the people living in them.

- No space for waste. Landfill sites are filling up fast.
- Reduce financial expenditure in the economy. Making products from raw materials costs much more than if they were made from recycled products.
- Preserve natural resources for future generations. Recycling reduces the need for raw materials; therefore preserving natural resources for the future.

6.3 Environmental consequences of the use of hydrocarbons

LO 11.3(n)(part): recognise the environmental consequence of: (i) carbon monoxide, oxides of nitrogen and unburnt hydrocarbons arising from the internal combustion engine and of their catalytic removal

6.3.1 Carbon monoxides and unburnt hydrocarbons

Carbon monoxide and unburnt hydrocarbons arise due to incomplete combustion of the fuel, which may be caused by various factors such as short reaction time in the internal combustion engine, poor maintenance of the engine and a lack of oxygen supply in the engine.

Carbon monoxide is a dangerous pollutant as it binds irreversibly with hemoglobin in blood by forming a stable complex and reduces the capacity of hemoglobin to transport oxygen. This causes drowsiness, headaches and is fatal above 2000 ppm. Being odorless, it gives no warning of its presence.

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Unburnt hydrocarbons by themselves cause little damage, but in the presence of sunlight, they react with oxygen, ozone and oxides of nitrogen to form ***photochemical smog*** (read Section 6.3.2 below).

6.3.2 Oxides of nitrogen

NO and NO_2, collectively known as NO_x, are formed inside the combustion chambers of motor vehicles. At the high temperature of combustion, atmospheric nitrogen and oxygen combine to form NO which is further oxidised to NO_2.

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$
$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

Oxides of nitrogen irritate lungs, cause bronchitis and pneumonia and lower resistance to respiratory infections. They often result in the formation of ***photochemical smog*** where the strong sunlight interacts with pollutant gas causing a complex series of photochemical reactions which produce a choking mixture of ozone, NO_x and other gases. Photochemical smog has a harmful effect on plants. It may also result in chest pains and breathing difficulties in children.

NO_2 dissolves in water to give a mixture of nitrous (HNO_2) and nitric (HNO_3) acids:

$$2NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq)$$

NO_2 also catalyses the formation of SO_3 from SO_2. SO_3 then dissolves in water to form H_2SO_4.

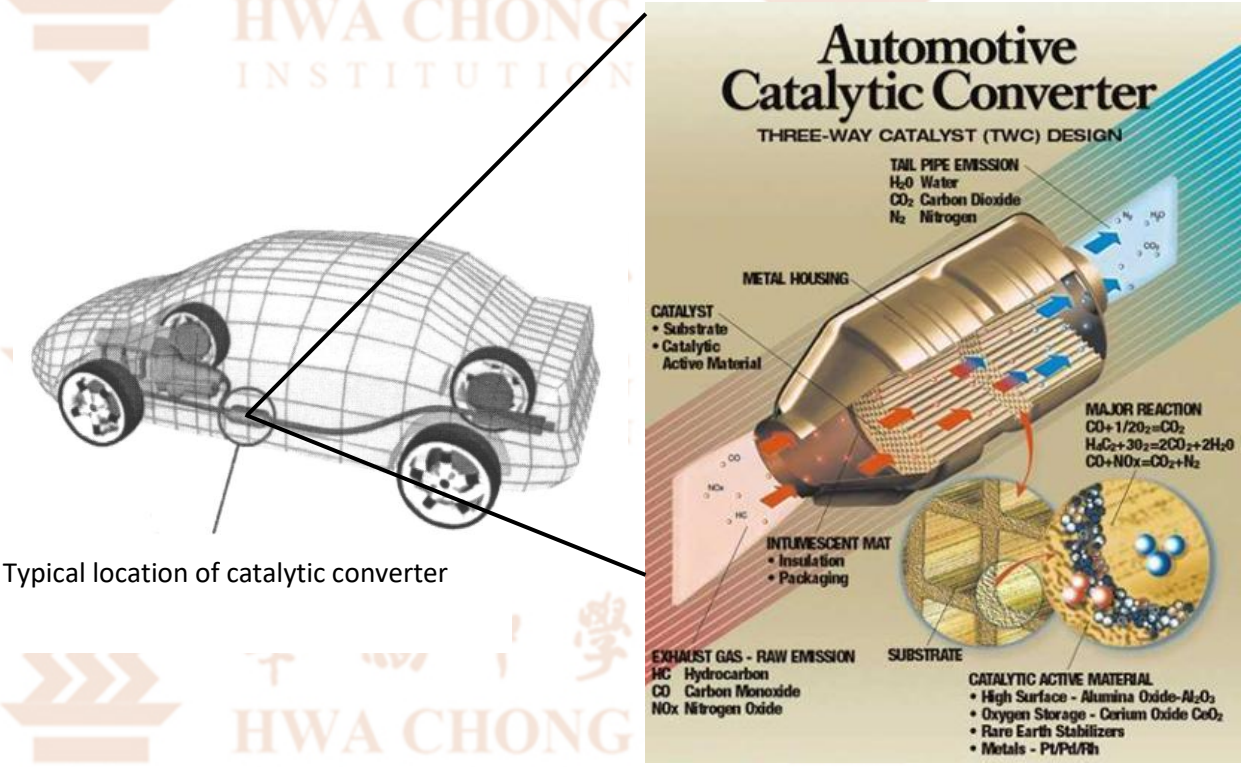
$$SO_2(g) + NO_2(g) \rightarrow SO_3(g) + NO(g)$$

HNO_3 and H_2SO_4 are strongly acidic. When they are present in rainwater, they produce ***acid rain***. Acid rain renders farm land unsuitable for cultivation (due to the acidity of the soil), causes corrosion of buildings and other man–made structures, and adversely affects marine lives (due to increased acidity of water). In addition, NO_2 can be easily regenerated by atmospheric oxygen:

$$NO(g) + ½\ O_2(g) \rightarrow NO_2(g)$$

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6.3.3 Catalytic converter



Typical location of catalytic converter

Figure 5. Expanded view of a catalytic converter

A catalytic converter removes pollutant gases from the exhaust by oxidising or reducing them. The exhaust gases pass through a converter containing an alloy of platinum or rhodium. The mechanism of the reaction is that of a heterogeneous catalyst reaction (recall Topic 6 Reaction Kinetics for the mechanism). The harmful gases are adsorbed onto the surface on the metals, go through a reaction and then the harmless gas products desorb from the surface.

Three main pollutants (CO, NO_x and unburnt hydrocarbons) are removed from exhaust gases by the catalytic converter. According to the following equations, these harmful gases are converted into less harmful CO_2, N_2 and water vapour.

$$2NO(g) + 2CO(g) \rightarrow N_2(g) + 2CO_2(g)$$

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

$$C_xH_y(g) + \left(x + \frac{y}{4}\right)O_2(g) \rightarrow xCO_2(g) + \frac{y}{2}H_2O(g)$$

However, catalytic converters only work with unleaded petrol because lead 'poisons' the catalyst in the converter (i.e. destroy their catalytic action).

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Exercise 6.1 (Includes Worked Example)

1. How are oxides of nitrogen formed in a car engine?
   A oxidation of nitrogen by ethanol in petrol
   B reaction of nitrogen with oxygen
   C oxidation of nitrogen by carbon dioxide
   D reaction of nitrogen compounds in petrol with oxygen *[N2001/III/19]*

2. **Worked example**
   The three-way catalytic systems which are fitted to the exhaust systems of cars remove nitrogen oxides, carbon monoxide and unburnt hydrocarbons. Oxidation and reduction are both involved.
   (a) State whether the catalysis is homogeneous or heterogeneous.
   (b) What reaction or reactions are catalysed by the reduction catalyst?
   (c) What reaction or reactions are catalysed by the oxidation catalyst?
   (d) Name a substance which poisons the catalyst and suggest a remedy for this poisoning.

Answer

(a) Heterogeneous catalysis. The nitrogen oxides, carbon monoxide and unburnt hydrocarbons are in the gaseous state while the catalyst is in the solid state.

(b) $2NO(g) + 2CO(g) \rightarrow N_2(g) + 2CO_2(g)$
NO(g) is reduced to $N_2(g)$.

(c) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

$$C_xH_y(g) + \left(x + \frac{y}{4}\right)O_2(g) \rightarrow xCO_2(g) + \frac{y}{2}H_2O(g)$$

CO(g) and the unburnt hydrocarbons $C_xH_y(g)$ are oxidised to $CO_2(g)$.

(d) Lead poisons the catalyst. Use unleaded petrol instead to remedy this poisoning.

6.3.4 Enhanced greenhouse effect

LO 11.3(n)(part): recognise the environmental consequence of: (ii) gases that contribute to the enhanced greenhouse effect

The "greenhouse effect" is the heating of the Earth due to the presence of greenhouse gases. It is named this way because of a similar effect produced by the glass panes of a greenhouse. Increase in the amount of greenhouse gases in the Earth's atmosphere enhances the greenhouse effect.

As concentration of greenhouse gases increases, there will be a greater proportion of radiation trapped in the atmosphere, resulting in an increase in global temperatures.

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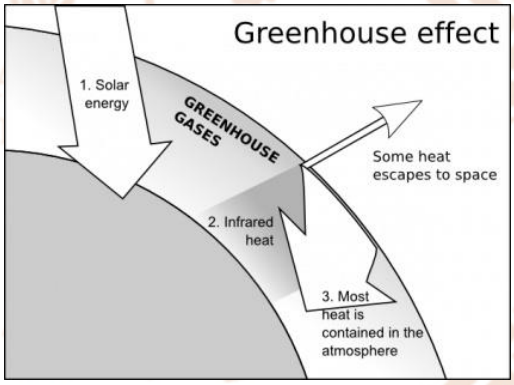


Figure 6. Illustration of greenhouse effect

What are greenhouse gases? http://www.ncdc.noaa.gov/oa/climate/gases.html

Many chemical compounds present in Earth's atmosphere behave as 'greenhouse gases'. These are gases which allow direct sunlight (relative shortwave energy) to reach the Earth's surface unobstructed. As the shortwave energy (that is in the visible and ultraviolet portion of the spectra) heats the surface, longer–wave (infrared) energy (heat) is re–radiated to the atmosphere. Greenhouse gases absorb this energy, thereby allowing less heat to escape back to space, and 'trapping' it in the lower atmosphere.

Many greenhouse gases occur naturally in the atmosphere, such as **carbon dioxide**, methane, water vapour, and nitrous oxide, while others are synthetic. Those that are man–made include the chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs), as well as sulfur hexafluoride (SF_6). Atmospheric concentrations of both the natural and man–made gases have been rising over the last few centuries due to the industrial revolution. As the global population has increased and our reliance on fossil fuels (such as coal, oil and natural gas) has been firmly solidified, so emissions of these gases have risen. While gases such as carbon dioxide occur naturally in the atmosphere, through our interference with the carbon cycle (through burning forest lands, or mining and burning coal), we artificially move carbon from solid storage to its gaseous state, thereby increasing atmospheric concentrations, making carbon dioxide a major greenhouse gas.

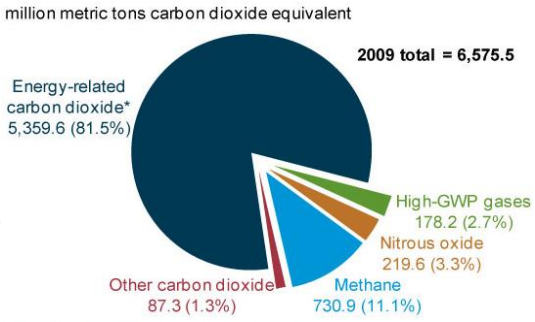


Figure 7. U.S. greenhouse gas emissions by gas, 2009

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6.3.5 Impact of Methane on the Environment

Methane is one of literally millions of compounds in the carbon cycle, but one of the most abundant. It is formed when carbon-containing compounds decompose in the absence of air (anaerobic conditions). The organisms that bring this about are called methanogens. Each year an estimated 5×10^{14} g of biologically produced methane is released into the atmosphere. This vast amounts of methane produced in the biosphere have been touted as a renewable, carbon neutral energy source. However, this also carries particular significance to the global climate because methane is a highly potent **greenhouse gas**, with a greenhouse factor ~30. Although present at much lower concentrations in the atmosphere than CO_2, methane currently accounts for ~20% of the radiative forcing of all greenhouse gases.

Exercise 6.2 (Worked Example)

Methane is burnt in power plants to produce heat which is used to generate electricity. This process produces an exhaust gas which contains $CO_2(g)$, $CO(g)$, steam and nitrogen oxides, ($NO_x(g)$). When $CO_2(g)$ is released into the atmosphere it causes an enhanced greenhouse effect.

(a) Describe what is meant by the term *enhanced greenhouse effect*.

(b) Name one environmental consequence which occurs when nitrogen oxides are released into the atmosphere. Ignore the effect of nitrogen oxides on human health.

[N2022/II/6(a),(b)]

Answer

(a) It refers to the increased temperatures on Earth's surface due to release of greenhouse gases from human activities, in addition to the natural greenhouse effect Earth has.

(b) Acid rain (which makes farm land unsuitable for cultivation / affects marine life).

Note: The question states to ignore effect on human health, so formation of photochemical smog which causes breathing difficulties is not the answer here.

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11 Alkenes

GUIDING QUESTIONS

- Which classes of reagents does alkenes react with and why? What types of reactions do alkenes undergo and why?
- How do alkenes react with electrophiles?
- What is the major product obtained when an unsymmetrical alkene reacts with hydrogen halide and why?

LEARNING OUTCOMES

Students should be able to:

11.3(d) explain the general reactivity of alkenes towards electrophilic reagents/electrophile

11.3(e) describe the chemistry of alkenes as exemplified, where relevant, by the following reactions of ethene:

(i) electrophilic addition of water/steam, hydrogen halides and halogens

(ii) reduction via catalytic hydrogenation (catalytic addition of hydrogen)

(iii) oxidation by cold, alkaline solution of manganate(VII) ions to form the diol

(iv) oxidation by hot, acidified solution of manganate(VII) ions leading to the rupture of the carbon-to-carbon double bond in order to determine the position of alkene linkages in larger molecules

11.3(f) describe the mechanism of electrophilic addition in alkenes, using bromine/ethene as an example

11.3(g) apply Markonikov's rule to the addition of hydrogen halides to unsymmetrical alkenes and explain the composition of products in terms of the stability of carbocation intermediates

REFERENCES

1. L. G. Wade, Jr (2012), *Organic Chemistry*, 8th Ed., Chapters 7 and 8.
2. Cann & Hughes (2015), *Chemistry,* Chapter 24.
3. J. McMurry (2010), *Organic Chemistry*, 8th Ed., Chapter 6 and 7.

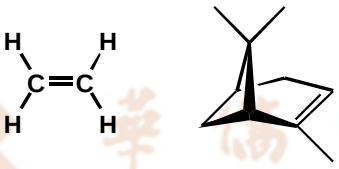
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1 INTRODUCTION

Alkenes are unsaturated hydrocarbons that contain at least one **carbon-carbon double bond**, C=C. Alkenes are said to be unsaturated because they have fewer than the maximum possible number of hydrogen atoms.

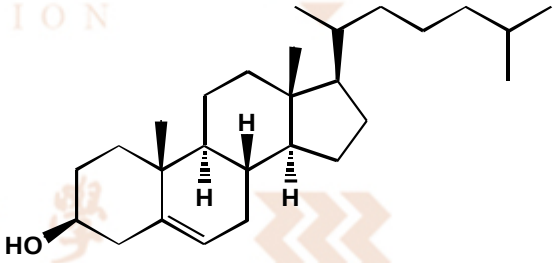
Alkenes occur abundantly in nature. Examples include:

- ethene, a gas responsible for the ripening of fruits;
- α-pinene, a major component of turpentine which is commonly used as paint solvent;
- cholesterol, a precursor for the synthesis of steroid hormones and vitamin D;
- β-carotene, the orange pigment responsible for the colour of carrots.

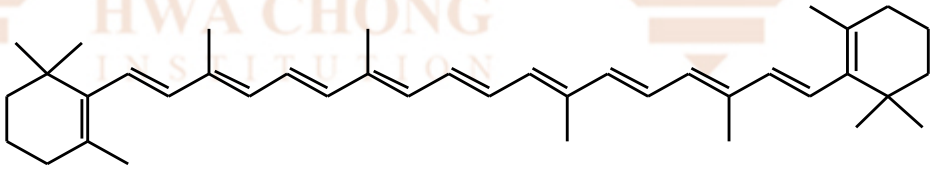


ethene

α-pinene



cholesterol



β-carotene

1.1 Nomenclature

Aliphatic alkenes containing only one carbon-carbon double bond have the general formula C_nH_{2n}, where n is the number of carbon atoms in the molecule. Do note that this general formula is not applicable for aliphatic alkenes containing more than one carbon-carbon double bond and alicyclic alkenes.

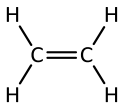
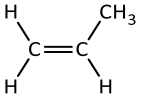
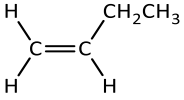
n	Name	Molecular Formula	Structural Formula
2	Ethene	C_2H_4	
3	Propene	C_3H_6	
4	But-1-ene	C_4H_8	

Table 1. Table showing some examples of alkenes

The number "1" in but-1-ene is used because the carbon-carbon double bond is on C1 and C2. What do you think is the structure of but-2-ene?

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The IUPAC rules for naming alkenes are similar to those for alkanes.

1. Find the **longest parent chain containing the double bond** and name the compound accordingly using the suffix -ene.

2. **Number the double bond from the end of the chain nearest to the double bond.** If the double bond is equidistant from the two ends, begin at the end nearer the first branch point. The number, followed by a hyphen, precedes the name of the parent chain.

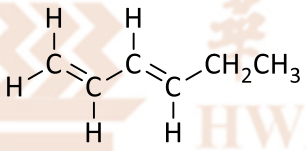
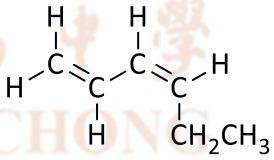
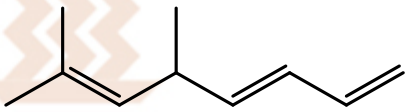
$CH_3CH_2CH=CH_2$	$CH_3CH_2CH_2CH=CHCH_3$	$CH_3CH(CH_3)CH=CHCH_2CH_3$
but-1-ene	hex-2-ene	2-methylhex-3-ene

3. **Number the substituents** according to their position in the chain **and list them alphabetically.**

4. If **more than one double bond is present**, indicate the position of each and use the suffixes -diene, -triene, -tetraene, and so on.

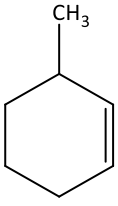
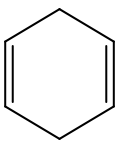
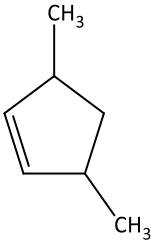
$CH_3CH_2CH=CHCH=CH_2$	$CH_2=C(CH_3)CH=CHCH_3$	$(CH_3)_2C=CHCH(CH_3)CH=CHCH=CH_2$
hexa-1,3-diene	2-methylpenta-1,3-diene	5,7-dimethylocta-1,3,6-triene

5. Stereochemical descriptors, such as *cis* and *trans*, are placed in front of the prefix, followed by a hyphen.

		
trans-hexa-1,3-diene	*cis*-hexa-1,3-diene	*trans*-5,7-dimethylocta-1,3,6-triene

Note: When drawing the stereochemical formula of *cis-trans* isomers, the geometry around each carbon of the C=C bond should be shown to be trigonal planar.

6. Cycloalkenes are named in a similar way. Number the cycloalkene so that the double bond is between C1 and C2 and the first substituent has as low a number as possible.

		
3-methylcyclohexene	cyclohexa-1,4-diene	3,5-dimethylcyclopentene

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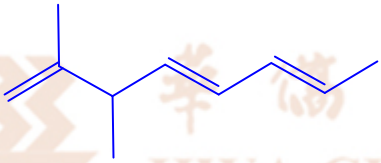
Exercise 1.1 (Worked Example)

Draw the structural formulae of

(a) 2,3-dimethylocta-1,4,6-triene

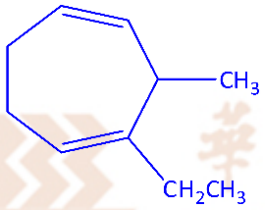
(b) 2-ethyl-3-methylcyclohepta-1,4-diene.

Answer:



(a)

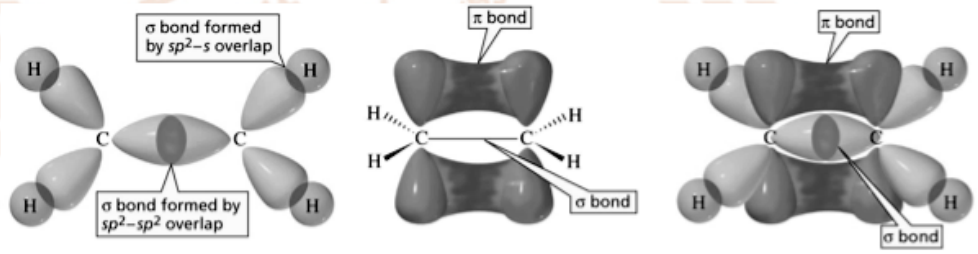
After drawing the main carbon chain with 8 carbon atoms, insert C=C between carbons 1 and 2, 4 and 5, as well as 6 and 7. Add the two dimethyl carbons on carbon 2 and carbon 3 as the last step.



(b)

A 7 membered ring must be established first before inserting C=C between carbons 1 and 2, as well as 4 and 5 on the ring. Add one ethyl group on carbon 2 and one methyl group on carbon 3 as stated by the locants.

1.2 Electronic structure of ethene



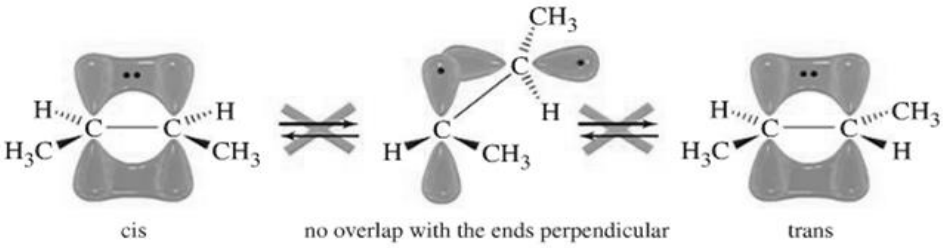
In Topic 2 Chemical Bonding, you have learnt the hybridisation, shape and bonding of ethene.

- The ethene molecule is trigonal planar with respect to each carbon atom.
- The carbon-carbon double bond in ethene is made up of one σ bond and one π bond. The carbons are sp^2-hybridised and have three equivalent sp^2 hybrid orbitals that lie in a plane at angles of 120° to one another. The carbons form a σ bond with each other by head-on overlap of sp^2 orbitals, as well as a π bond by side-on overlap of unhybridised *p* orbitals orientated perpendicular to the sp^2 plane. The π-electron cloud lies above and below the plane of the atoms.
- The C-H bonds are σ bonds formed by head-on overlap of sp^2 orbital of C and *s* orbital of H.

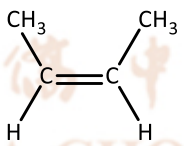
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1.3 *Cis-trans* isomerism in alkenes

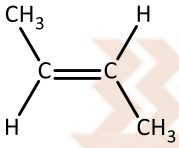
In Topic 9 Isomerism, you have learnt that *cis-trans* isomerism arises in alkenes due to **restricted rotation about the C=C bond** and **2 different groups attached to each C=C carbon atom**.



But-2-ene can exist as *cis*-but-2-ene and *trans*-but-2-ene as shown below. *Cis*-but-2-ene has the same groups on the **same side of the double bond**, whereas *trans*-but-2-ene has the same groups on the **opposite sides of the double bond**.

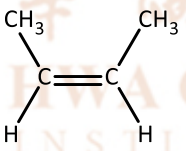


cis-but-2-ene
(*cis* isomer)

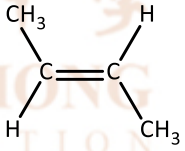


trans-but-2-ene
(*trans* isomer)

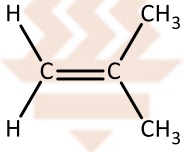
***Cis-trans* isomerism cannot exist if any one of the C=C carbons carries two identical groups.**
2-methylpropene is an example of a constitutional isomer of *cis*-but-2-ene and *trans*-but-2-ene.



cis-but-2-ene



trans-but-2-ene



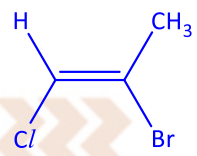
2-methylpropene

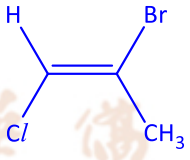
(constitutional isomer of the *cis* and *trans* isomers)

Cycloalkenes with **up to 7 carbon atoms** exist only as the "*cis* isomers". Cycloalkenes with **8 or more carbon atoms** can exist as *cis-trans* isomers.

Exercise 1.2 (Worked Example)
Draw the *cis-trans* isomers of (C*l*)CH=C(CH_3)Br.

Answer:





The shape and bond angles of 120° of sp^2 hybridised carbon atoms of alkene must be clearly shown in your drawing. In your syllabus, there is no need to assign which is the cis or trans isomer for alkenes with no same groups on each C of C=C.

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2 PHYSICAL PROPERTIES OF ALKENES

2.1 Boiling and melting points within the homologous series

The trend in the boiling and melting points within the homologous series indicate that as the number of carbon atoms increases, the boiling points increase correspondingly. This is due to the increase in number of electrons and hence the size of the electron cloud, leading to stronger dispersion forces between the molecules.

The trend in melting points is not as clear as the trend in boiling points as melting point also depends on how the molecules are packed in the solid lattice.

	Boiling point (°C)	Melting point (°C)
Ethene	–104	–169
Propene	–47	–185
But-1-ene	–6	–138
Pent-1-ene	30	–165

Table 2. Boiling and melting points of a few alkenes.

2.2 Physical properties of *cis-trans* isomers

Boiling point of *cis-trans* isomers

There can be differences in the boiling and melting points between the *cis* and *trans* isomers of alkenes e.g. 1,2-dichloroethene

Isomer	Boiling point (°C)	Melting point (°C)
cis-1,2-dichloroethene	60.3	–81
trans-1,2-dichloroethene	47.5	–50

Table 3. Boiling and melting points of cis- and trans- isomers of 1,2-dichloroethene

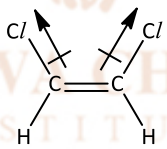
You will notice that:

- the *cis*-isomer has the higher boiling point;
- the *trans*-isomer has the higher melting point.

Between the *cis* and the *trans* isomer of disubstituted alkenes, **the *cis* isomer tend to have higher boiling points**. The reason for this is that *cis* isomers tend to be more polar. We shall use 1,2-dichloroethene as an example below:

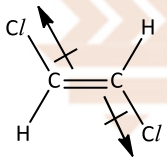
- In the *cis* isomer, the polar C–C*l* bonds result in dipole moments that do not cancel out, hence producing an overall dipole moment for the molecule. Thus, the *cis* isomer is polar and permanent dipole-permanent dipole interactions (on top of dispersion forces) exist between molecules.

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cis-1,2-dichloroethene

dipole moment ≠ 0



trans-1,2-dichloroethene

dipole moment = 0

- In the *trans* isomer, the two dipole moments cancel out such that the overall dipole moment for the molecule is zero. Hence, the *trans* isomer is non-polar and only dispersion forces exist between molecules.
- Hence, more energy is required to overcome the stronger forces of attraction between *cis* isomers, leading to a higher boiling point.

This effect is less noticeable for some alkenes, for example:

Isomer	Boiling Point (°C)
cis-but-2-ene	4
trans-but-2-ene	1
cis-pent-2-ene	37
trans-pent-2-ene	36

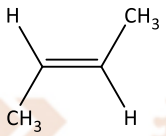
Table 4. Table showing the boiling points of some cis-trans isomers

Their similar boiling points can be understood from the fact that both isomers (in the case of *cis*-but-2-ene and *trans*-but-2-ene) contain the methyl group as a substituent and this is a relatively non-polar group such that the *cis* isomer is not much more polar than the *trans* isomer. The same reasoning can be applied to *cis*-pent-2-ene and *trans*-pent-2-ene.

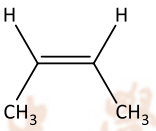
Exercise 2.1 (Worked Example)

Which of the following compounds has the highest boiling point?

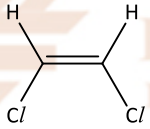
A



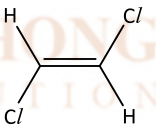
B



C



D



Answer: C

C-H bonds are generally considered non-polar due to small difference in electronegativity between the two atoms. Since **D** is a trans isomer, there is no net dipole moment. Being a cis isomer with polar C-Cl bond, **C** has a net dipole moment and permanent dipole-permanent dipole interactions between molecules, in addition to dispersion forces. Hence, **C** has the highest boiling point.

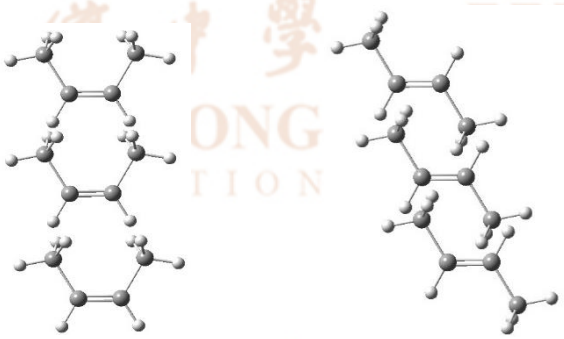
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Melting point of *cis*-*trans* isomers

Between the *cis* and the *trans* isomer of alkenes, **the *trans* isomer tend to have higher melting point**.

In order for the intermolecular forces of attraction to work well in a solid, the molecules must be able to pack together efficiently in the solid state.

- The *trans* isomer pack better than the *cis* isomer due to the higher symmetry of the trans isomer. The "U" shape of the *cis* isomer does not pack well compared to the straighter shape of the *trans* isomer.
- The better packing of the *trans* isomer in the solid state means that the dispersion forces work more effectively in holding the molecules together when compared to the *cis* isomer.
- Hence more energy is required to overcome the forces of attraction between *trans* isomer, leading to a higher melting point.



cis *trans*

2.3 Solubility

In order for dissolution to occur, the solute molecules and the solvent molecules should have favourable intermolecular forces of attraction.

Non-substituted alkenes can form favourable dispersion forces with non-polar solvents such as benzene and tetrachloromethane. Hence they are soluble in non-polar solvents.

Non-substituted alkenes can only form permanent dipole-induced dipole intermolecular forces with water, which are much weaker than the hydrogen bonding between water molecules themselves (as well as the dispersion forces between non-substituted alkene molecules). Hence they are insoluble in water.

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2.4 Density

Liquid alkenes are less dense than water and form an immiscible layer above water.

Their densities increase slightly with increasing number of carbon atoms present. This is because the increase in the strength of intermolecular dispersion forces causes the alkene molecules to attract more closely together, resulting in a slightly smaller volume of the liquid. Since ρ = m/V, with a larger relative molecular mass, the density of the liquid increases.

2.5 Viscosity

The viscosity of liquid alkenes increases with increasing number of carbon atoms present as the strength of dispersion forces between the molecules increases. In addition, straight-chain alkenes have higher viscosity as compared to branched alkenes.

3 PREPARATION OF ALKENES

Alkenes can be prepared by the following reactions:

- Elimination of hydrogen halide from halogenoalkanes (to be covered in Topic 15 Halogen Derivatives)

- Dehydration of alcohol (to be covered in Topic 16 Hydroxy Compounds)

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4 REACTIONS OF ALKENES

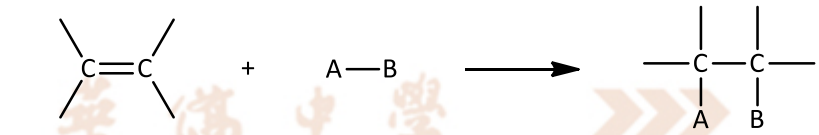
Reactivity of alkenes towards electrophilic reagents

LO11.3(d): explain the general reactivity of alkenes towards electrophilic reagents/electrophile

Even though C=C bond is stronger than C–C bond, alkenes are more reactive than alkanes. This is due to the electron-rich C=C. The π bond (electron cloud), which lies on the surface of the molecules, attracts **electrophiles**.

During reaction, the weaker π bond is broken instead of the σ bond in the C=C bond. In place, two strong bonds (C–A and C–B) are formed in the product, leaving the carbon atoms joined by a single bond. This typical reaction of alkenes is known as **electrophilic addition**.

The overall reaction for electrophilic addition of alkenes can be represented as:



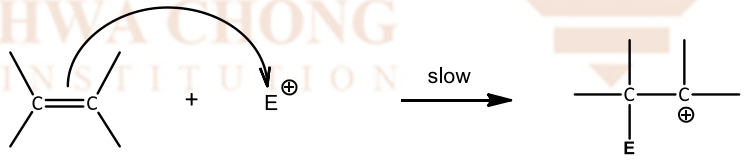
unsaturated alkene electrophile saturated product

Examples of electrophiles that react with alkenes include hydrogen halides and halogens.

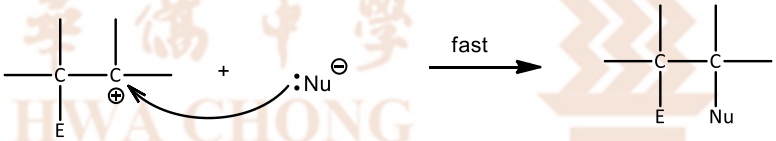
4.1 Electrophilic addition

4.1.1 General mechanism of electrophilic addition

Step 1: Initial attack by the π electrons of the C=C bond on the electrophile, forming a positively-charged carbocation intermediate.



Step 2: Subsequent attack of the unstable carbocation intermediate by nucleophile to generate a stable product.

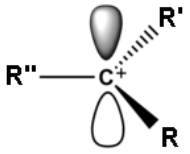


4.1.2 Carbocation intermediate

In electrophilic addition to alkenes, the carbocation is an important intermediate. Before studying the reactions of alkenes, we need to learn more about the structure and factors affecting the stability of carbocations.

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Structure



The central carbon atom is positively charged and sp^2 hybridised. The 3 substituents are arranged in a trigonal planar geometry around the central carbon atom. As the carbon atom has lost an electron, the unhybridised *p* orbital is empty.

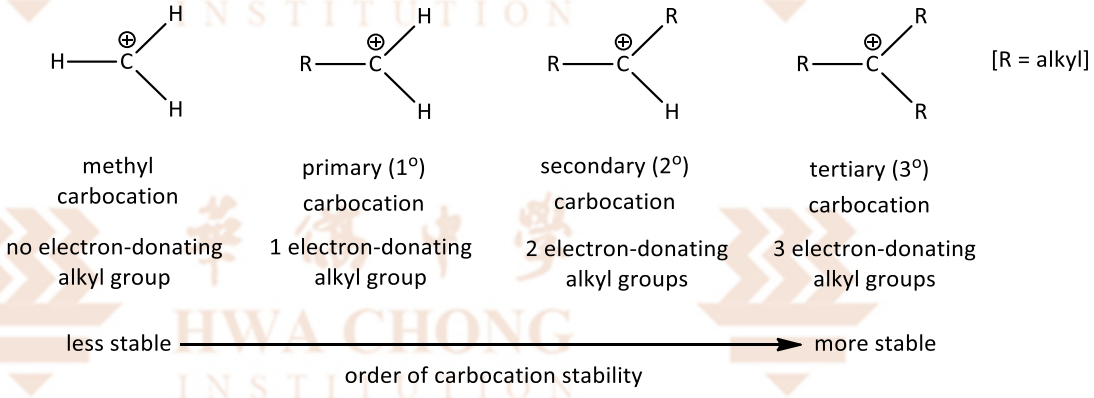
Due to the positive charge on the carbon atom, the carbon atom is electron-deficient and strongly attracts any **nucleophile** towards it. And because the geometry around the carbon atom is **planar**, the nucleophiles may **attack from either side of the plane**.

Stability

In general, organic species with a charge on it are less stable. Therefore, anything that disperses the charge would stabilise the species as a whole. Conversely, anything that intensifies the charge on it would destabilise it.

As mentioned earlier, the central carbon atom of the carbocation is positively charged. The 3 substituents bonded to it can affect the stability of the carbocation as a whole depending on whether they are electron donating or electron withdrawing.

Alkyl groups e.g. methyl ($-CH_3$) are considered **electron donating groups**. Therefore, the **more alkyl substituents the carbocation has, the more stable it would be, as the electron donating groups disperse the positive charge on the central carbon atom.**

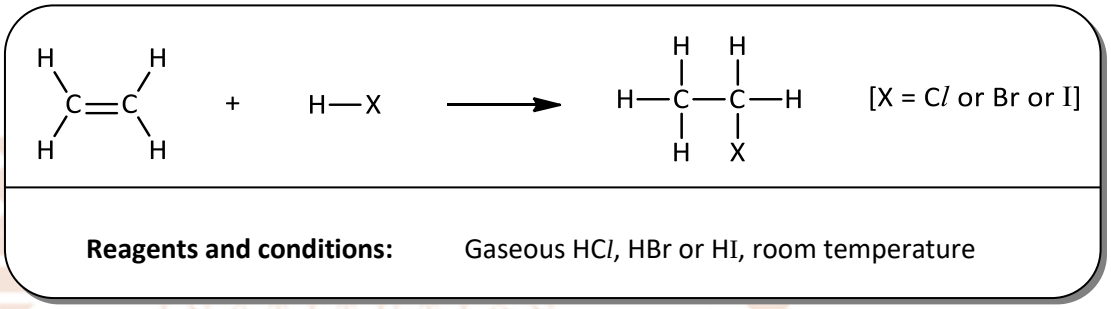


Conversely, **electron withdrawing substituents** like halogens would destabilise the carbocation as they **intensify** the positive charge on the central carbon atom.

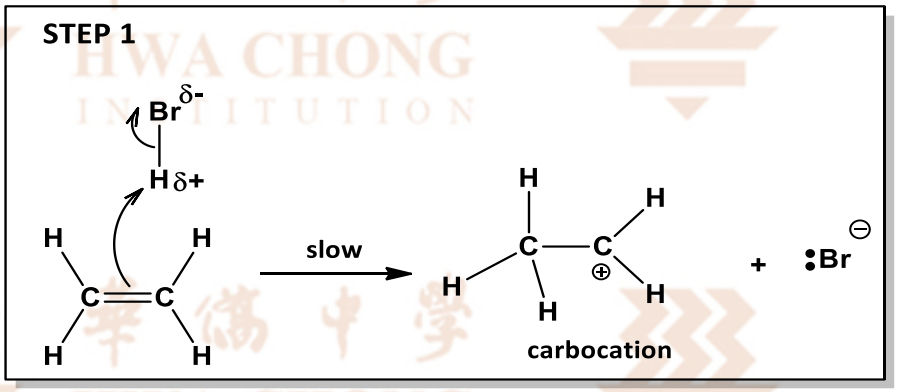
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4.1.3 Electrophilic addition of hydrogen halides (H-X)

LO11.3(e)(part): describe the chemistry of alkenes as exemplified, where relevant, by the following reactions of ethene: (i) electrophilic addition of water/steam, hydrogen halides and halogens



The general reaction mechanism of electrophilic addition applied to the reaction between ethene and HBr is illustrated as follows:

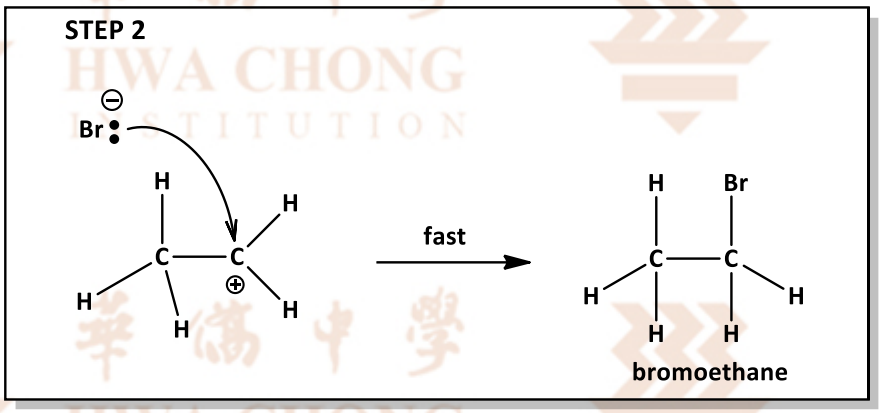


- This is the **rate-determining step** (involves breaking of the π bond).

- As the polar HBr molecule approaches the π electron cloud of ethene in the correct orientation, the high electron density of the π electron cloud "attacks" the electron deficient H atom on the HBr molecule. (*Note: arrow must show the direction of electron movement.)

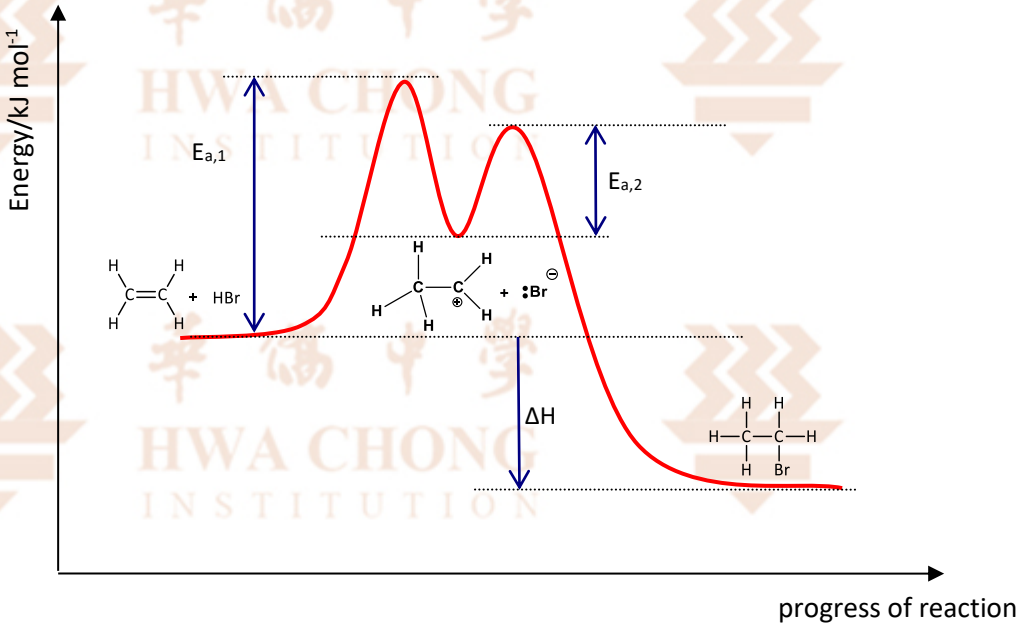
- The π bond in the C=C bond breaks, forming a new C–H bond. The H–Br bond undergoes heterolytic fission producing a **carbocation intermediate** and a bromide ion.

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- In the next step, the bromide anion acts as a nucleophile and attacks the unstable carbocation intermediate quickly as the negatively charged bromide ion is attracted to the positively charged carbon, forming a new C–Br bond. A stable product, bromoethane is formed.

The energy profile diagram of the electrophilic addition of hydrogen halide to ethene is as follows:



Exercise 4.1 (Worked Example)

Hydrogen bromide reacts with ethene to form bromoethane. What is the best description of the organic intermediate in this reaction?

A It contains carbon, hydrogen and bromine.
B It has a negative charge.
C It is an electrophile.
D It is a free radical. N97/III/Q23

Answer: **C**

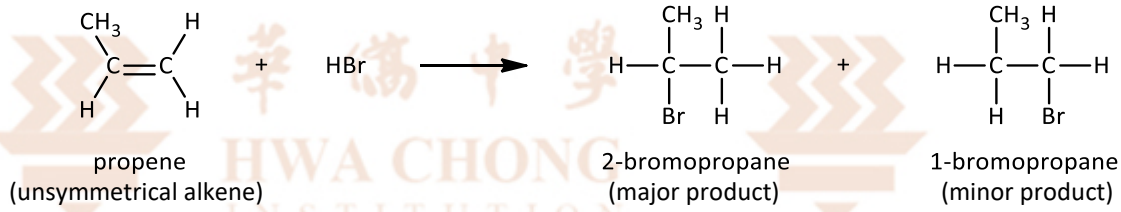
The organic intermediate formed is a carbocation. It is an electrophile because it has 6 electrons around the carbon atom, which is electron deficient.

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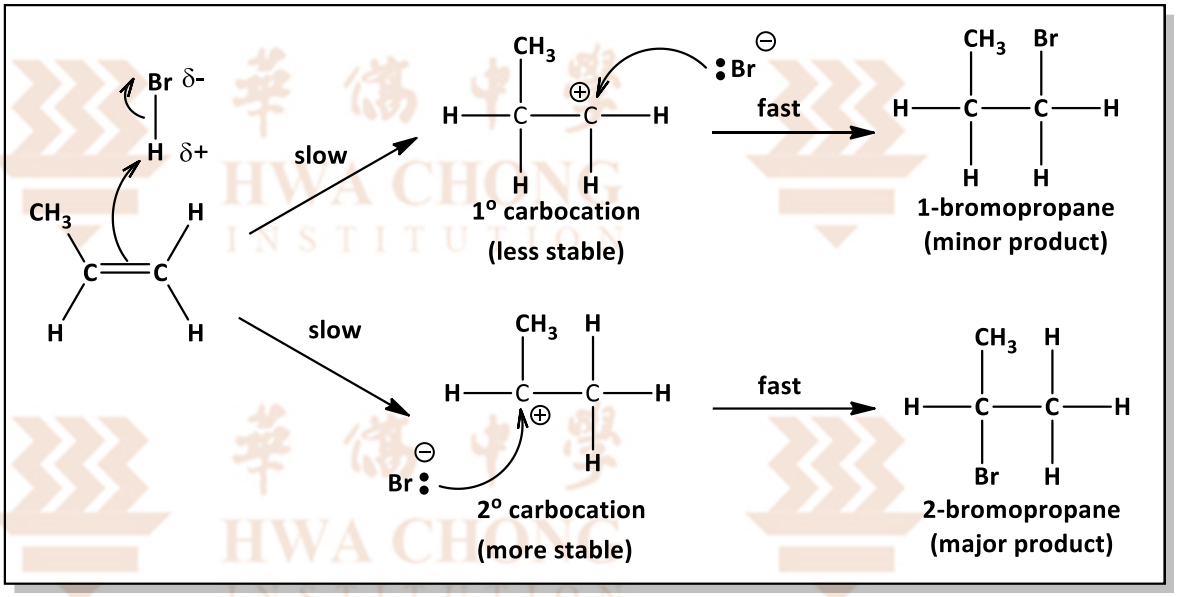
Addition to an unsymmetrical alkene

LO11.3(g): apply Markonikov's rule to the addition of hydrogen halides to unsymmetrical alkenes and explain the composition of products in terms of the stability of carbocation intermediates

When a hydrogen halide adds across the double bond of an **unsymmetrical alkene**, there are two possible products. One of them is preferred over the other. Why is this so?

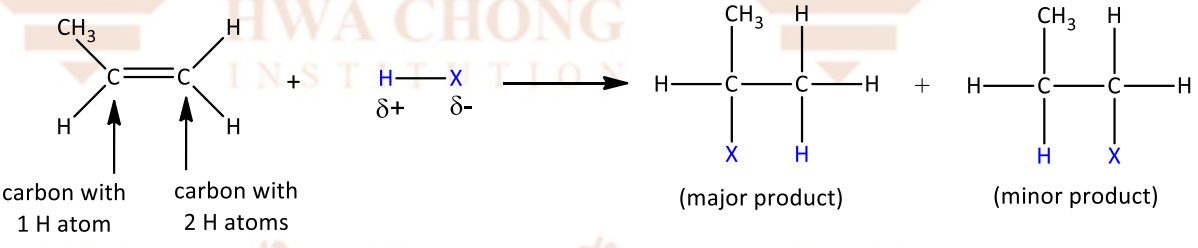


To explain this observation, we need to look at the 2 possible intermediates that generate each product.



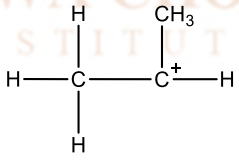
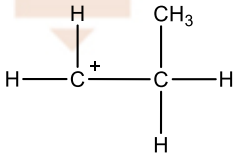
Markovnikov's rule

The Markovnikov's rule states that in the addition of HX to an alkene, the H atom adds to the C atom of the double bond that holds the greater number of H atoms. Reactions that follow this rule are said to follow Markovnikov orientation and give the Markovnikov product.

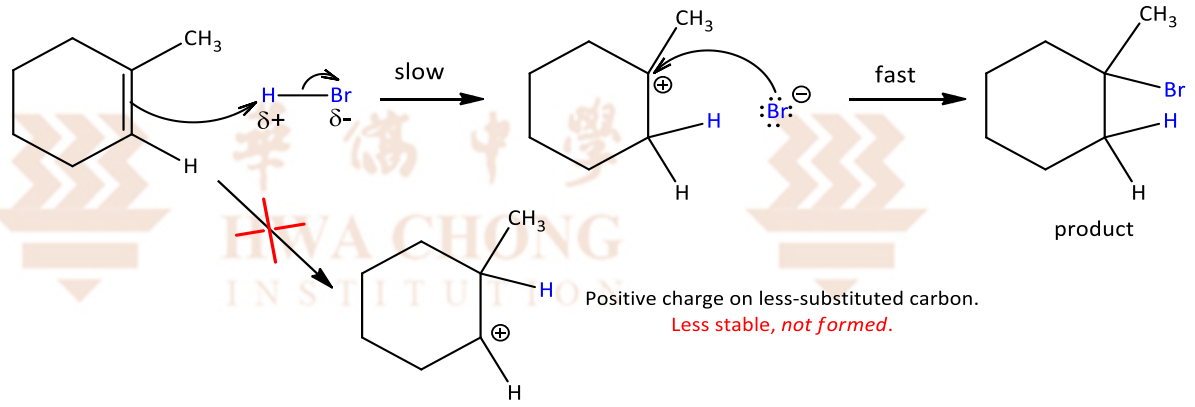


[X = Cl, Br or I]

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This observation is due to the stability of the carbocation intermediate formed. Since alkyl groups are electron-donating, they tend to disperse the positive charge on a cation, and thus stabilise it. The secondary carbocation  is more stable than  as the secondary carbocation has 2 electron-donating groups while the primary carbocation only has one. The more stable the carbocation, the lower the energy of the transition state that precedes it.

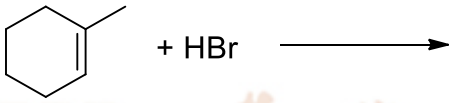
In an electrophilic addition to an alkene, the electrophile adds in such a way so as to generate the most stable carbocation intermediate. In short, in an electrophilic addition to an alkene, the electrophile adds to the less-substituted end of the double bond to give the more substituted (and therefore more stable) carbocation.



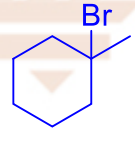
However, we are often interested in adding electrophiles other than H to the double bonds of alkenes. Markovnikov's rule can be extended to include a variety of other additions, based on the addition of the electrophile in such a way as to produce the most stable carbocation.

Exercise 4.2 (Worked Example)

Identify the major product of the following reaction:

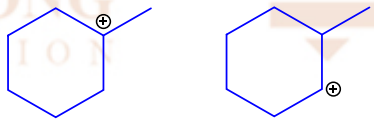


Answer:



(major)

There are two possible carbocations that can be formed:



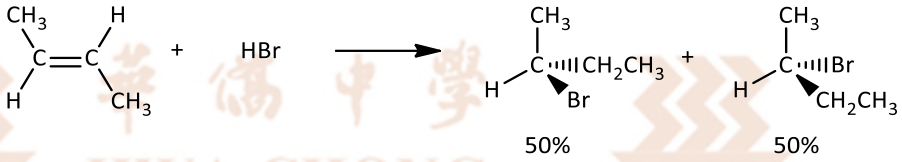
more stable

The carbocation on the left will be formed more preferably because there are three electron-donating alkyl groups attached to the electron deficient carbon. Thus, the major product will be formed from the more stable carbocation.

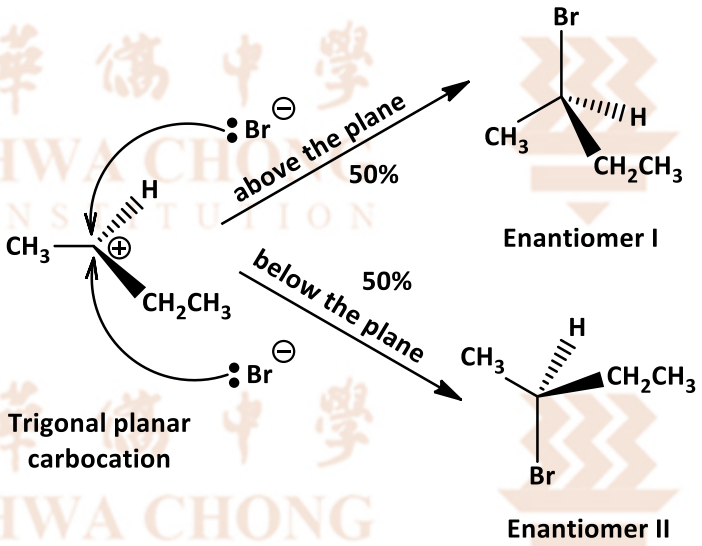
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Formation of a racemic mixture

When a hydrogen halide adds across the double bond of an alkene that produces an intermediate carbocation with 3 different groups attached to it, it produces **equal** amounts of 2 enantiomers, forming a **racemic mixture**.



This occurs because the geometry about the positively charged carbon is planar, hence it has equal chances of being attacked from the top or bottom by the bromide ion in the second step, thereby producing the two enantiomers in equimolar ratio.

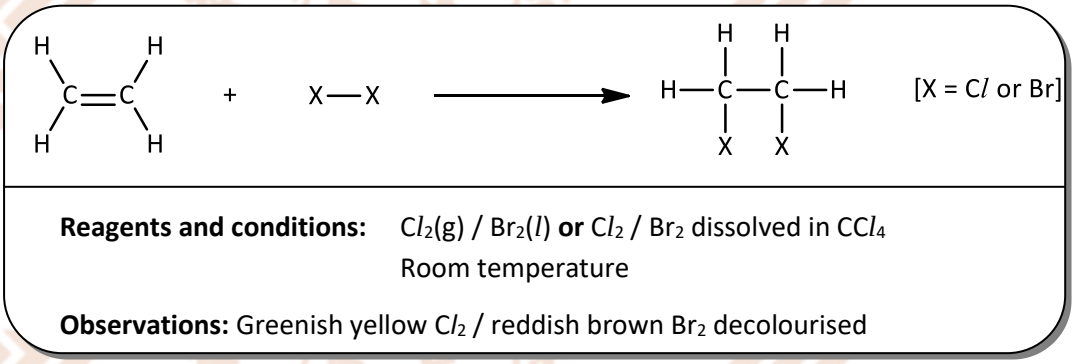


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4.1.4 Electrophilic addition of halogens (X_2)

LO11.3(e)(part): describe the chemistry of alkenes as exemplified, where relevant, by the following reactions of ethene:
(i) electrophilic addition of water/steam, hydrogen halides and halogens
LO11.3(f): describe the mechanism of electrophilic addition in alkenes, using bromine/ethene as an example

Alkenes also readily react with chlorine or bromine to form halogenoalkanes with two atoms of halogens attached to adjacent carbon atoms. The reaction with fluorine is very violent while iodine does not react with most alkenes.



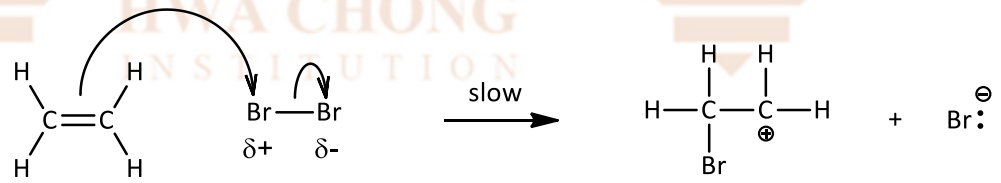
Reagents and conditions: Cl_2(g) / Br_2(l) **or** Cl_2 / Br_2 dissolved in CCl_4
Room temperature

Observations: Greenish yellow Cl_2 / reddish brown Br_2 decolourised

Electrophilic addition of halogens can occur in the presence of UV light but the reaction is usually carried out in the absence of UV light to prevent free radical substitution of the alkyl substituents on the alkene or of the product.

For the mechanism, we will use the electrophilic addition of Br_2 to ethene as an example. The mechanism takes place in two steps.

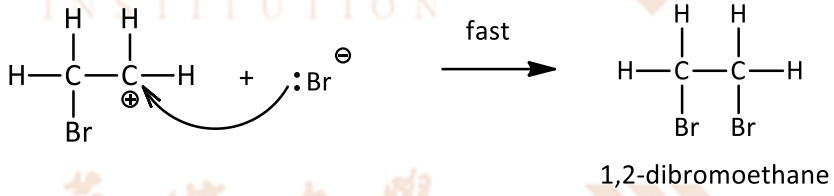
STEP 1



- As the non-polar Br_2 molecule approaches the π electron cloud of ethene, the high electron density of the π electron cloud polarises the electron cloud of the Br_2 molecule.
- The Br-Br bond undergoes heterolytic fission resulting in a bromide anion with the other bromine atom bonded to the alkene to form a positively charged carbocation intermediate.
- This is the rate-determining step as it involves breaking the π bond in ethene and Br-Br bond.

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STEP 2



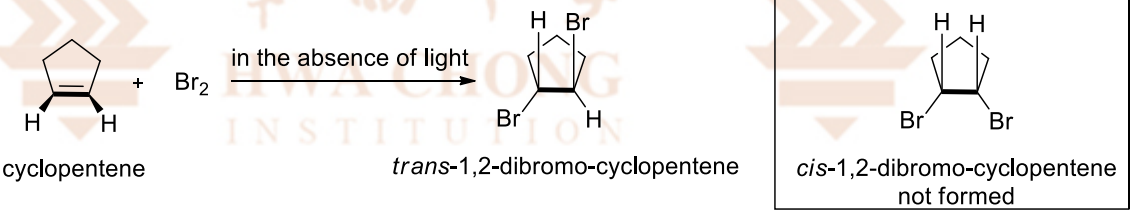
- In this step, the bromide anion acts as a nucleophile to attack the carbocation intermediate to form the product, 1,2-dibromoethane.

- This step is fast as it involves the reaction between oppositely charged species. The mutual electrostatic attraction results in the easy formation of the stable 1,2-dibromoethane.

For your information

Although the mechanism Section 4.1.4 is reasonable and follows that of the alkene reaction with hydrogen halides, studies have shown that it is not completely consistent with some observations.

For instance, it was observed in the reaction of bromine with cyclopentene, that only the *trans* product is formed rather than an expected mixture of *cis* and *trans* products if a planar carbocation intermediate was involved.



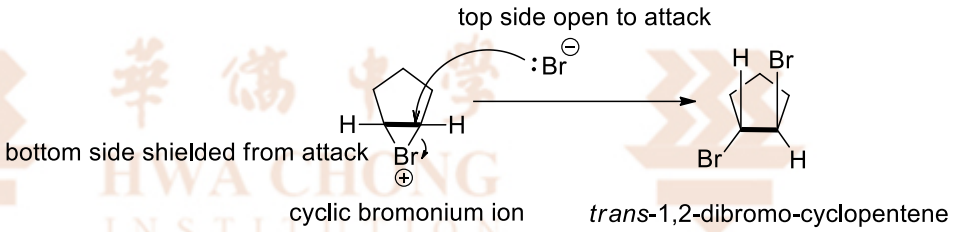
Hence, it was proposed that the intermediate in the mechanism was a cyclic three-membered bromonium ion during electrophilic addition of bromine on alkene.



cyclic bromonium ion

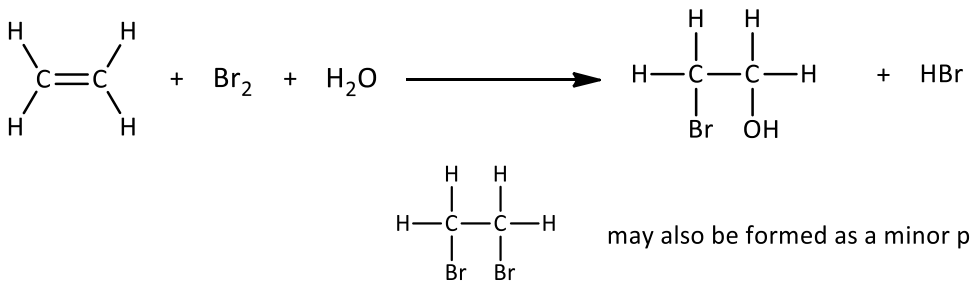
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This cyclic bromonium ion as an intermediate could explain the above observation because the second step of the mechanism (shown below) will then involve an S_N2 attack by bromide anion from the opposite side of the C–Br bond to be broken. The consequence of this S_N2 attack is the formation of a *trans* product in which the two Br atoms are on the opposite faces of the double bond. We shall look at S_N2 mechanism in greater detail in Topic 15 Halogen Derivatives.



4.1.5 Electrophilic addition of bromine water

LO11.3(e)(part): describe the chemistry of alkenes as exemplified, where relevant, by the following reactions of ethene: (i) electrophilic addition of water/steam, hydrogen halides and halogens

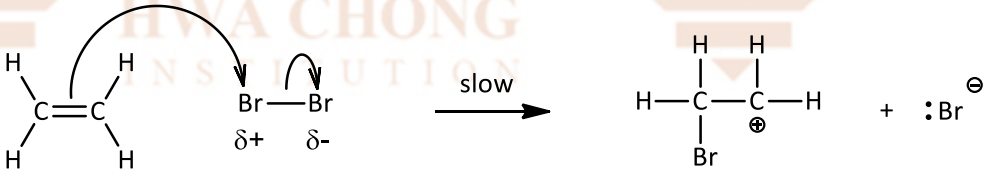


Reagents and conditions: Br_2(aq), room temperature

Observations: Yellow-orange Br_2(aq) decolourised (*distinguishing test)

Alkenes react with bromine water to form bromoalcohol (or bromohydrin) as the major product instead of the dibromo compound.

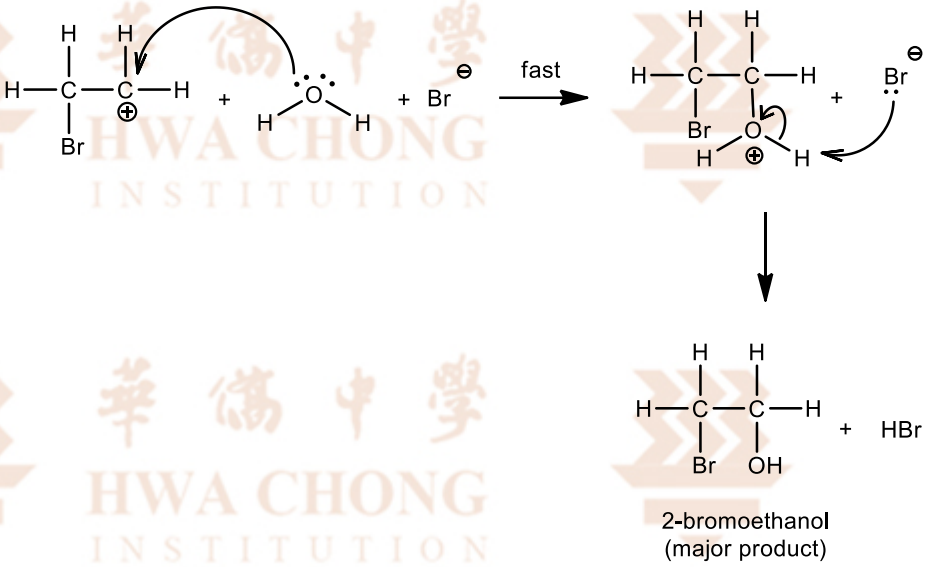
This is because the carbocation intermediate is susceptible to attack by any nucleophile present in the reaction mixture.



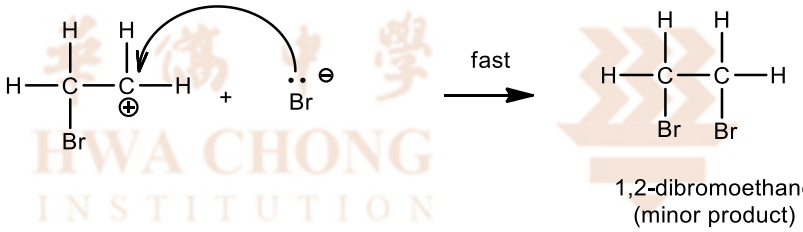
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In the case of bromine water, after forming the carbocation intermediate in the rate-determining step, the carbocation intermediate can be attacked by any nucleophile in the reaction mixture. So, both water and bromide ion can act as nucleophiles to attack the carbocation. The major product generally depends on which nucleophile is present in excess.

Scenario 1: Nucleophilic attack by water



Scenario 2: Nucleophilic attack by bromide ion

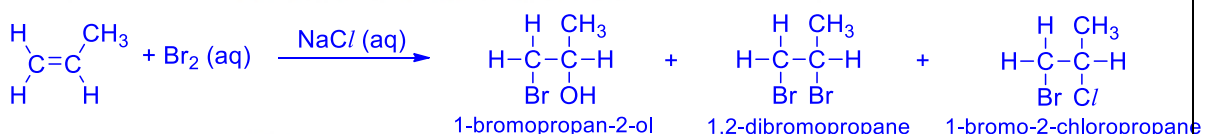


Water is present in a much higher concentration compared to the bromide ion and therefore attacks the intermediate preferentially in the second step of the reaction.

Exercise 4.3 (Worked Example)

Predict the products formed when propene reacts with bromine water that is contaminated by aqueous sodium chloride. Explain why it is not possible to obtain 1,2-dichloropropane.

Answer:



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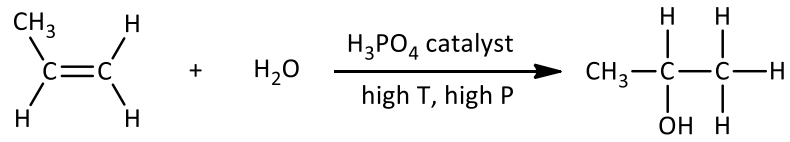
The first slow step of the reaction involves the electrophilic attack of Br_2. Thus the product will always have the addition of at least one Br atom. Also, there is no Cl^+ electrophile and hence the products cannot contain 2 *Cl* atoms.

Note that the only electrophile present is Br_2, in the presence of propene, bromine, water and sodium chloride.

4.1.6 Electrophilic addition of water/steam

LO11.3(e)(part): describe the chemistry of alkenes as exemplified, where relevant, by the following reactions of ethene: (i) electrophilic addition of water/steam, hydrogen halides and halogens

Alkenes react with steam (H_2O) to form alcohols. The addition of steam to alkenes is similar to that of hydrogen halides. Phosphoric acid is added as a catalyst.



Industrial method

Reagents and conditions: steam; H_3PO_4 catalyst
High temperatures and high pressures

Lab method

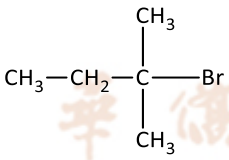
Reagents and conditions:
1. concentrated H_2SO_4, cold
2. H_2O

(Refer to Appendix for the mechanism)

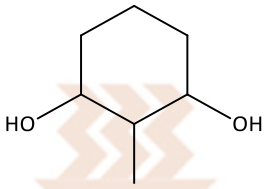
Exercise 4.4 (Worked Example)

What alkenes would you start with to prepare the following compounds?

(a)

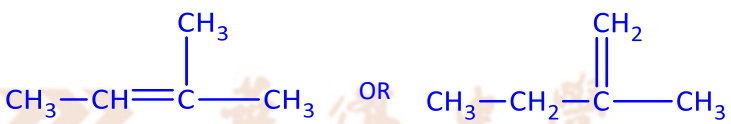


(b)



Answer:

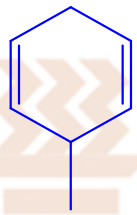
(a)



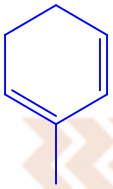
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By eliminating a bromine atom with a hydrogen atom on an adjacent C atom and establishing a C=C bond, two possible alkenes are possible starting reactants. Using HBr, the most stable carbocation intermediate would be preferably formed. In either cases, they result in the tertiary carbocation as the most stable intermediate, thus producing the compound as the major product.

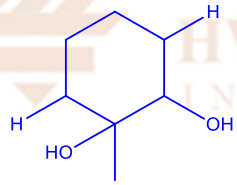
(b)



Eliminate the OH group with a hydrogen atom on an adjacent C atom (not attached to methyl group)



to establish two C=C bonds as shown in the answer. Note that would give a major product



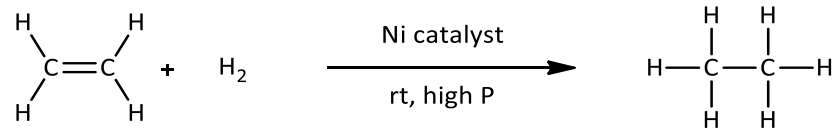
of instead as it forms a stable tertiary carbocation as the intermediate.

4.2 Reduction

LO11.3(e)(part): describe the chemistry of alkenes as exemplified, where relevant, by the following reactions of ethene: (ii) reduction via catalytic hydrogenation (catalytic addition of hydrogen)

Reduction via catalytic hydrogenation is often used to convert unsaturated alkenes to saturated alkanes. This process is commonly used in the food industry to produce margarine by converting unsaturated plant oil into the saturated soft margarine.

This is a form of heterogeneous catalysis. See Topic 6 Reaction Kinetics for the mechanism.



Reagents and conditions: H_2 gas; Ni catalyst
Room temperature and high pressure

Note: Platinum/Palladium catalyst at room temperature and pressure can also be used for this reduction.

H_2 gas with nickel catalyst is also able to reduce other functional groups and these reactions will be discussed in the later organic chemistry topics.

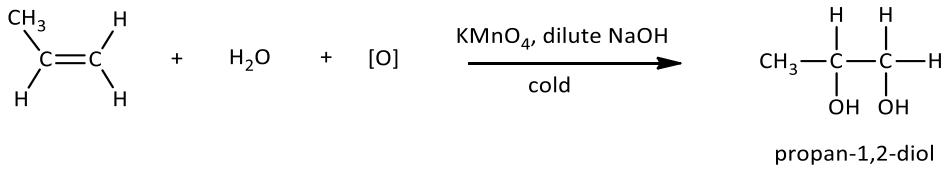
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4.3 Oxidation

4.3.1 Mild oxidation

LO11.3(e)(part): describe the chemistry of alkenes as exemplified, where relevant, by the following reactions of ethene: (iii) oxidation by cold, alkaline solution of manganate(VII) ions to form the diol

Cold alkaline potassium manganate(VII) can oxidise alkenes into the corresponding diols. The formation of diols from alkenes is considered as a type of mild oxidation.



propan-1,2-diol

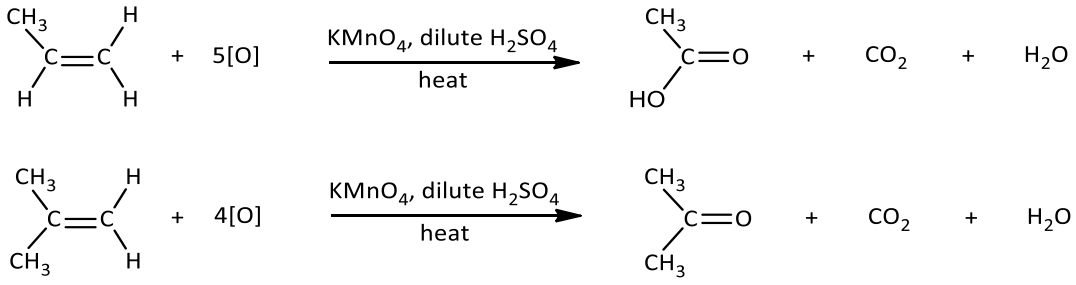
Reagents and conditions: $KMnO_4$, dilute NaOH, cold

Observations: Purple $KMnO_4$ is decolourised and a brown precipitate of MnO_2 is formed. (*distinguishing test)

4.3.2 Oxidative cleavage

LO11.3(e)(part): describe the chemistry of alkenes as exemplified, where relevant, by the following reactions of ethene: (iv) oxidation by hot, acidified solution of manganate(VII) ions leading to the rupture of the carbon-to-carbon double bond in order to determine the position of alkene linkages in larger molecules

Hot acidic potassium manganate(VII) can cleave the carbon-carbon double bond in alkenes to give carbonyl compounds and/or carboxylic acids as products. This oxidative cleavage of alkenes is considered as a type of strong oxidation.



Reagents and conditions: $KMnO_4$, dilute H_2SO_4, heat

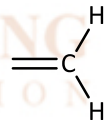
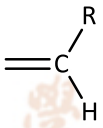
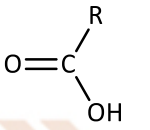
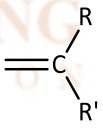
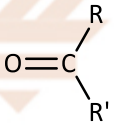
Observations: Purple $KMnO_4$ is decolourised. Note that effervescence of carbon dioxide is possible for selected alkenes as mentioned below.
(*distinguishing test)

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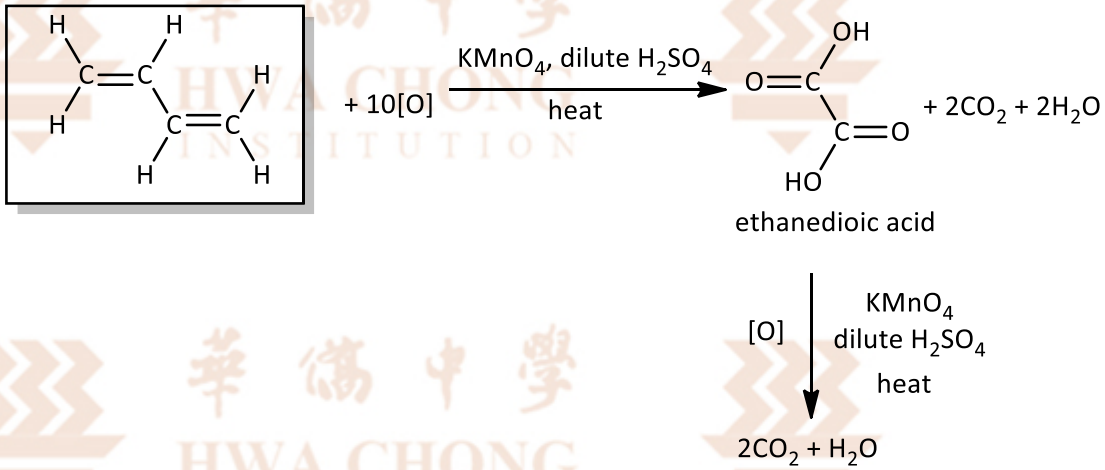
NOTE:

- Oxidation of alkenes CANNOT be carried out with potassium dichromate(VI).

Different substituents on the C=C carbon atoms give rise to different products upon oxidative cleavage. The table next page summarises the possible products arising from a different number of hydrogen atoms attached directly to the C=C carbon atoms.

No. of hydrogen atoms on carbon	Structure	Products after oxidative cleavage
2		CO_2 + H_2O
1		 carboxylic acid
0		 ketone

Special case of oxidative cleavage:



The special case of oxidative cleavage illustrated above should not be surprising as you have learnt about the redox titration of ethanedioic acid and potassium manganate(VII) under Topic 4 Reactions and Stoichiometry (try balancing the redox equation).

Usefulness of oxidative cleavage:

- Oxidative cleavage is a useful tool to establish the location of the alkene double bond in a hydrocarbon chain or ring.

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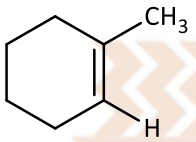
- Oxidative cleavage using hot acidified $KMnO_4$ can be used as a test to **distinguish between alkenes with terminal C=C double bonds (=CH_2) and those without**. Alkenes with terminal C=C double bonds would, upon oxidation, evolve carbon dioxide gas. This distinguishes between the alkenes.

Exercise 4.5 (Worked Example)

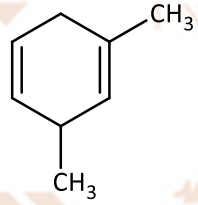
Write down the products of the following compounds undergoing oxidative cleavage.

(a) $(CH_3)_2C{=}CHCH{=}CH_2$

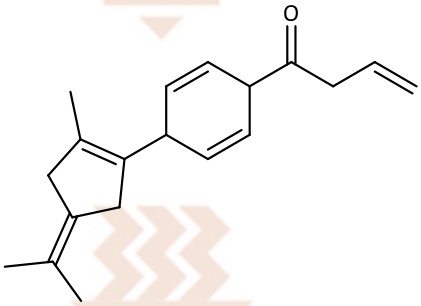
(b)



(c)

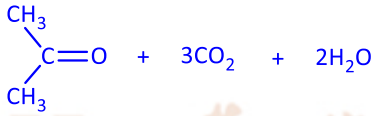


(d)

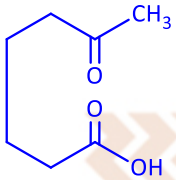


Answer:

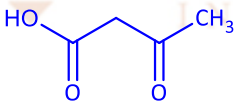
(a)

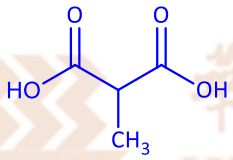


(b)

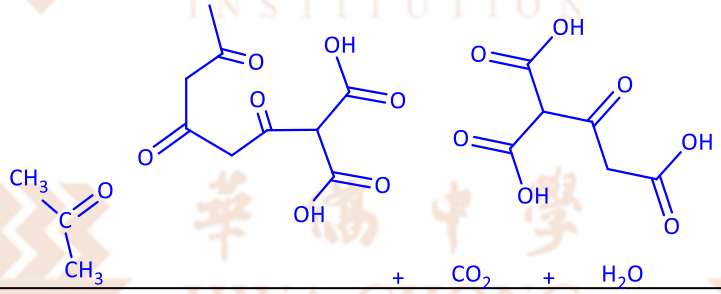


(c)





(d)



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Generic procedure for distinguishing test for alkenes

(a) Using acidified potassium manganate(VII), $KMnO_4$

1. To prepare acidified $KMnO_4$ solution, add 5 drops of $KMnO_4$(aq) to 1 cm^3 of dilute H_2SO_4 in a test tube.
2. To 1 cm^3 of the unknown, add 2 – 3 drops of the acidified $KMnO_4$ dropwise.
3. Shake well.
4. Warm in a water bath.

(b) Using aqueous bromine (bromine water)

1. To 1 cm^3 of the unknown in a test tube, add aqueous bromine dropwise.
2. Shake well.

Exercise 4.6 (Worked Example)

Refer to the above distinguishing test and answer the following questions.

(a) Why should the $KMnO_4$ be added dropwise?

(b) Why should the aqueous Br_2 be added dropwise?

Answer:

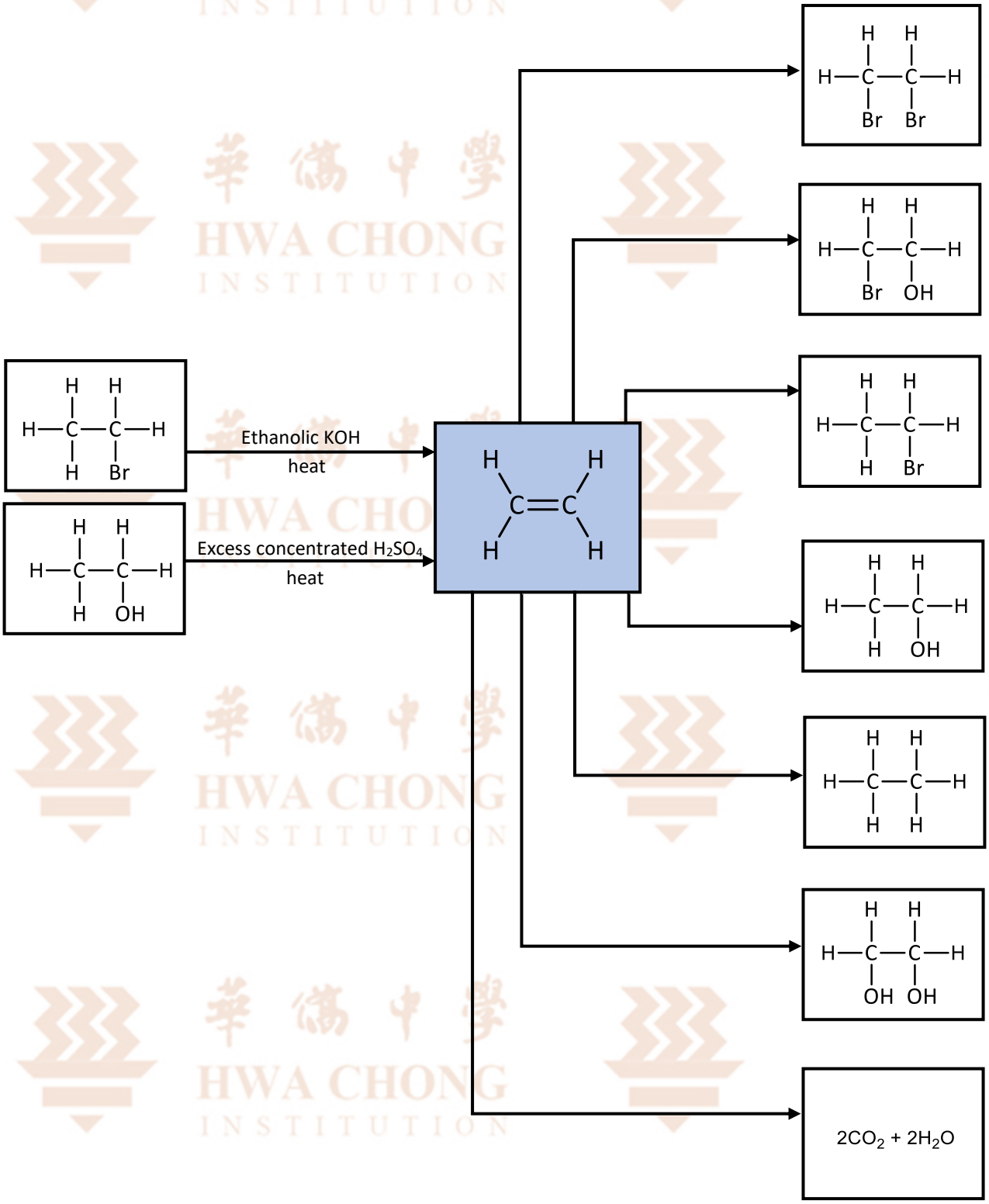
(a) If excess $KMnO_4$ is added, the decolourisation cannot be observed. Instead, the solution will remain purple.

(b) If excess aqueous Br_2 is added, the decolourisation cannot be observed. Instead, the solution will remain yellow-orange.

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Summary of reactions

Write the reagents and conditions needed for the conversions on the arrows below.



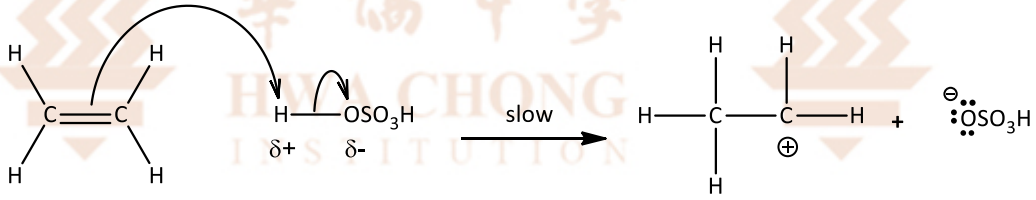
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APPENDIX

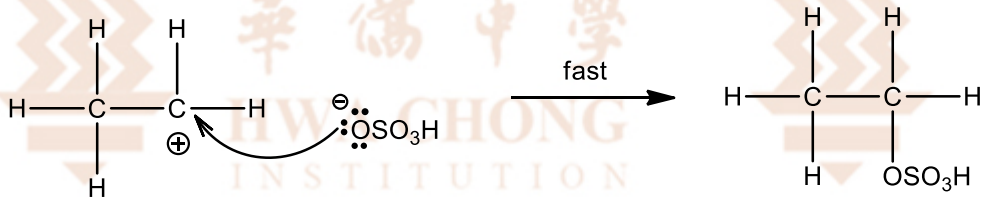
Electrophilic addition of water/steam mechanism:

Using ethene as an example, the mechanism for the acid-catalysed hydration of ethene is as follows:

Step 1: Protonation of the double bond to form a carbocation.



Step 2: Nucleophilic attack by $^{-}OSO_3H$ on carbocation to produce a hydrogensulfate.



The hydrogensulfate is then added to cold water. Water acts as a nucleophile to attack the hydrogensulfate. The $–OSO_3H$ group is substituted with –OH group, producing the alcohol and regenerating the sulfuric acid catalyst.



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12 Arenes

GUIDING QUESTIONS

- What determines the shape of benzene?
- How does the reactivity of benzene compare to that of alkene and why?
- Which class of reagents does benzene react with and why? What types of reactions does benzene undergo and why? How does benzene react with an electrophile?
- What types of reactions do the alkyl side-chains of arenes undergo and why?
- How does the substituent on mono-substituted arenes determine the reactivity towards, and the substitution position of an incoming electrophile?

LEARNING OUTCOMES

At the end of the chapter, you should be able to:

11.1(d) **describe** sp^3 hybridisation, as in ethane molecule, ***sp*²** **hybridisation, as in** ethene and **benzene** molecules, and *sp* hybridisation, as in ethyne molecule.

11.1(e) **explain the shapes of, and bond angles in**, the ethane, ethene, **benzene**, and ethyne molecules in relation to σ and π carbon-carbon bonds

11.1(f) **predict the shapes of, and bond angles in, molecules analogous to** the ethane, ethene, **benzene**, and ethyne molecules

11.3(h) explain, in terms of delocalisation of π electrons, the difference between benzene and alkene

(i) reactivity towards electrophiles

(ii) preference of benzene to undergo substitution rather than addition reaction

11.3(i) describe the chemistry of the benzene ring as exemplified by the following reactions of benzene and methylbenzene:

(i) electrophilic substitution reactions with chlorine and with bromine
(recognise the use of Lewis acid as catalysts)

(ii) nitration with concentrated nitric acid
(recognise concentrated sulfuric acid as a Bronsted-Lowry acid catalyst)

(iii) Friedel-Crafts alkylation with halogenoalkanes
(recognise the use of Lewis acid as catalysts)

11.3(j) (i) describe the mechanism of electrophilic substitution in arenes, using the mono-bromination of benzene as an example

(ii) describe the effect of the delocalisation of electrons in arenes in such reactions

11.3(k) describe the chemistry of the alkyl side-chain of benzene ring as exemplified by the following reactions of methylbenzene:

(i) free-radical substitution by chlorine and by bromine

(ii) complete oxidation to give benzoic acid

11.3(l) predict whether halogenation will occur in the side-chain or aromatic nucleus in arenes depending on reaction conditions

11.3(m) apply the knowledge of positions of substitution in the electrophilic substitution reactions of mono-substituted arenes

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REFERENCES

1. P. Cann & P. Hughes (2015), *Chemistry*, Chapter 25.
2. J. McMurry (2010), *Organic Chemistry*, Chapters 15-16.
3. M. B. Smith, J. March (2007), *March's Advanced Organic Chemistry*, Chapter 19.

1 INTRODUCTION (Background info)

Arenes are aromatic hydrocarbons that contain one or more benzene rings. The name "aromatic" originally referred to certain compounds that possessed pleasant smells, such as benzaldehyde (from cherries, peaches and almonds) and methylbenzene (from Tolu balsam). As chemists discovered more aromatic hydrocarbons, they found that other members of the group possess unpleasant smells and are extremely carcinogenic. Today, aromaticity is used to describe the **extra stability** of benzene and its structural relatives due to the **delocalisation of electrons**.

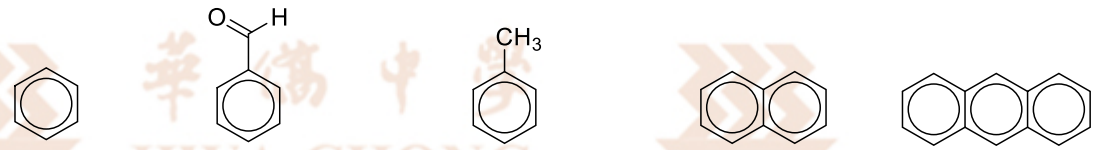
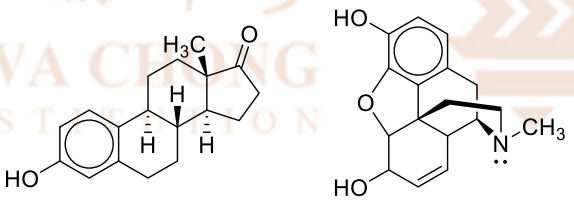


Figure 1. Examples of aromatic compounds.

Many compounds from natural sources as well as many synthetic drugs are aromatic in part. Similarly, each of the three aromatic amino acids phenylalanine, tryptophan, and tyrosine, also serve as the basic building blocks of proteins.



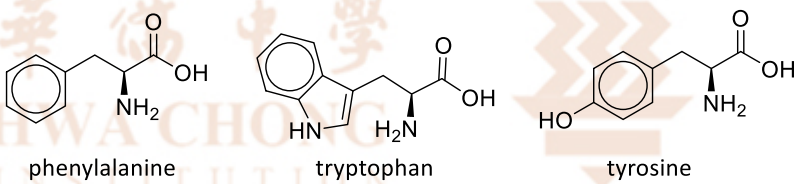


Figure 2. Examples of compounds containing aromatic rings.

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1.1 Nomenclature

LO 11.1(a)(i)part: interpret, and use the nomenclature of hydrocarbons (alkanes, alkenes and arenes)

1.1.1 Benzene

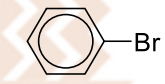
Benzene has a molecular formula of C_6H_6. The benzene ring is often represented using the skeletal formula as shown below.



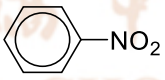
benzene

1.1.2 Mono-substituted benzenes

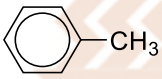
When one H atom of benzene is replaced by another atom or group of atoms comprising 6 carbon atoms or less, the benzene ring is considered the **parent** and a suffix – **benzene** is employed in naming.



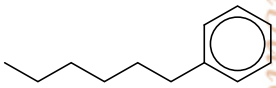
bromobenzene



nitrobenzene

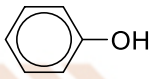


methylbenzene

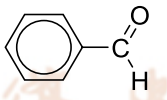


hexylbenzene

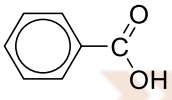
Some mono-substituted benzenes are more common such that their conventional names are used instead.



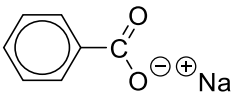
phenol



benzaldehyde

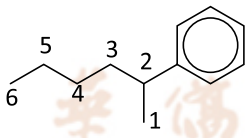


benzoic acid

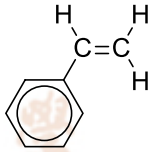


sodium benzoate

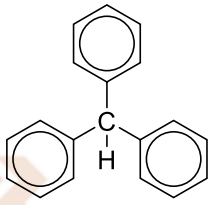
When the substituent is an alkyl group of more than 6 carbon atoms, or when it is too complex to be named conveniently as a prefix, benzene is considered as a **substituent** and named as a prefix – **phenyl**.



2-phenylhexane



phenylethene



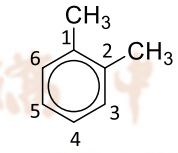
triphenylmethane

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1.1.3 Multi-substituted benzenes

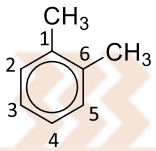
Multi-substituted benzenes are named by numbering the position of each substituent so that the lowest possible numbers are used.

E.g.



1,2-dimethylbenzene

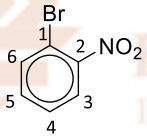
(CORRECT naming)



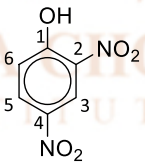
1,6-dimethylbenzene

(WRONG naming)

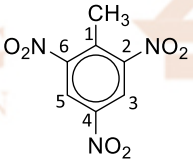
If the substituents are different, one of them is deemed the principal functional group (at position 1), in the order of precedence $–CO_2H$ > –OH > $–CH_3$ > –halogen > $–NO_2$. The rest of the substituents are named in alphabetical order.



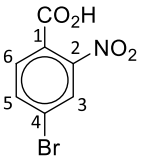
2-nitrobromobenzene



2,4-dinitrophenol



2,4,6-trinitromethylbenzene (TNT)

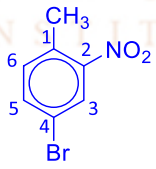


4-bromo-2-nitrobenzoic acid

Exercise 1.1 (Worked Example)

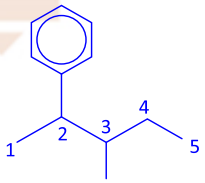
Draw the structure for each of the following compounds:

a) 4-bromo-2-nitromethylbenzene



Note: CH_3 as principal functional group
Br and NO_2 as substituents
in alphabetical order and lowest possible number

b) 3-methyl-2-phenylpentane



Note: pentane as principal functional group,
methyl and phenyl as substituents
in alphabetical order and lowest possible number

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2 PHYSICAL PROPERTIES AND USES OF BENZENE

Physical properties

Benzene is a **colourless liquid** at rtp. It is toxic and carcinogenic and should therefore be handled cautiously if used in the laboratory. It is highly volatile and flammable.

Melting and boiling points

Melting point: 5.5 °C; boiling point: 80 °C
Being a non-polar molecule, only a small amount of energy is required to overcome the **weak dispersion forces** between molecules; hence benzene has **low** melting and boiling points.

Solubility

Being a non-polar molecule, benzene is **insoluble** in (or immiscible with) polar solvents (e.g. water), but **soluble** in non-polar solvents (e.g. hexane, CCl_4). It could be used as a non-polar solvent.

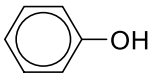
Uses

Prior to the 1920's, benzene was frequently used as an industrial solvent, especially for degreasing metal. As its toxicity became obvious, other solvents such as methylbenzene replaced benzene in most applications. By far, the largest use of benzene is as an **intermediate to make other chemicals**. The most widely produced derivatives of benzene are styrene (phenylethene), which is used to make polymers and plastics, phenol for resins and adhesives (via cumene i.e. isopropylbenzene), and cyclohexane, which is used in the manufacture of nylon.

Health effects

The major effect of benzene from chronic (long term) exposure is to the blood. Benzene causes harmful effects on the bone marrow and can cause a decrease in red blood cells leading to anaemia. Benzene is a known carcinogen to human beings. Long-term exposure to high levels of benzene in the air can cause leukaemia, cancer of the blood-forming organs.

Exercise 2.1 (Worked Example)

a) Explain the difference in the boiling point of phenol, 

(bp 182 °C) with that of benzene,  (bp 80 °C).

b) Explain, in terms of intermolecular forces and energy, why benzene is insoluble in water. (You may refer to Topic 2 Chemical Bonding for the discussion on solubility.)

(a) Phenol has stronger intermolecular hydrogen bonding (on top of dispersion forces) while benzene has weaker dispersion forces between the molecules.
More energy is needed to overcome the stronger intermolecular hydrogen bonding in phenol, resulting in a higher boiling point.

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(b) The energy released from the weaker permanent dipole-induced dipole interactions between water and benzene molecules is not sufficient to overcome the stronger hydrogen bonding between water molecules, and dispersion forces between benzene molecules.

3 BENZENE

3.1 Structure of benzene

LO 11.1(d)part: describe sp^2 hybridisation, as in benzene
LO 11.1(e)part: explain the shapes of, and bond angles in benzene in relation to σ and π carbon-carbon bonds
LO 11.1(f)part: predict the shapes of, and bond angles in, molecules analogous to benzene

In benzene, each carbon is bonded to two other carbons and one hydrogen. The geometry around **each carbon atom in benzene is trigonal planar with C–C–C bond angle of 120°**. Recall from Topic 2 Chemical Bonding where you learnt about the hybridisation of atomic orbitals. Each carbon atom in benzene is ***sp*² hybridised**. The mixing of one *s* orbital and two *p* orbitals gives three sp^2 hybrid orbitals oriented at 120° to one another for each carbon atom. One *p* orbital remains unhybridised, and this *p* orbital is arranged perpendicular to the three sp^2 hybrid orbitals as shown in Figure 3.

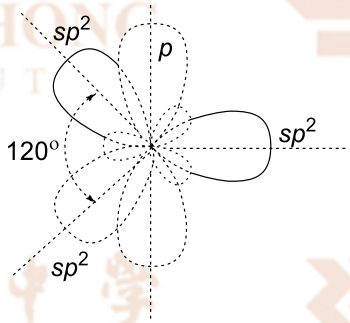


*Figure 3. Arrangement of sp^2 hybrid orbitals and unhybridised p orbital around **each carbon** in benzene.*

Overall, there are six C-C sigma (σ) bonds in benzene, each of which is formed from the head-on overlap of one sp^2 hybrid orbital of one carbon atom with one sp^2 hybrid orbital of the adjacent carbon atom. There are also six C-H single bonds, each of which is an *s*–sp^2 σ bond formed from head-on overlap of the 1*s* atomic orbital of H and the sp^2 hybrid orbital of C.

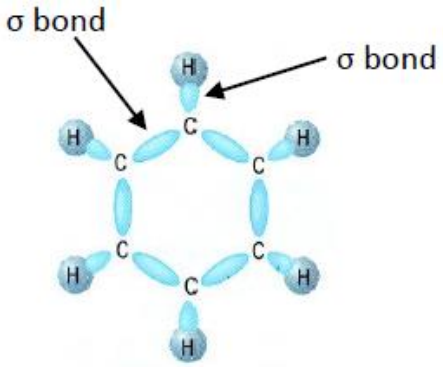


Figure 4. σ bonds between two carbon atoms and between carbon and hydrogen atoms in benzene.

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The remaining unhybridised *p* orbitals of the six carbon atoms are all parallel to one another due to the planarity of the benzene molecule. These *p* orbitals could overlap side-on as shown in Figure 5a to produce three π bonds between atoms 1 and 2, 3 and 4 and 5 and 6 of the ring, or just as likely, overlap as shown in Figure 5b to produce π bonds between atoms 2 and 3, 4 and 5 and 6 and 1 of the ring. In reality, **all six unhybridised *p* orbitals overlap side-on with each other equally** to produce two continuous rings of π electrons above and below the plane of the benzene ring, known as the **delocalised π electron cloud**, as shown in Figure 5c. The six electrons found in this delocalised π electron cloud are free to move throughout the entire π electron cloud, so the electrons are said to be delocalised.

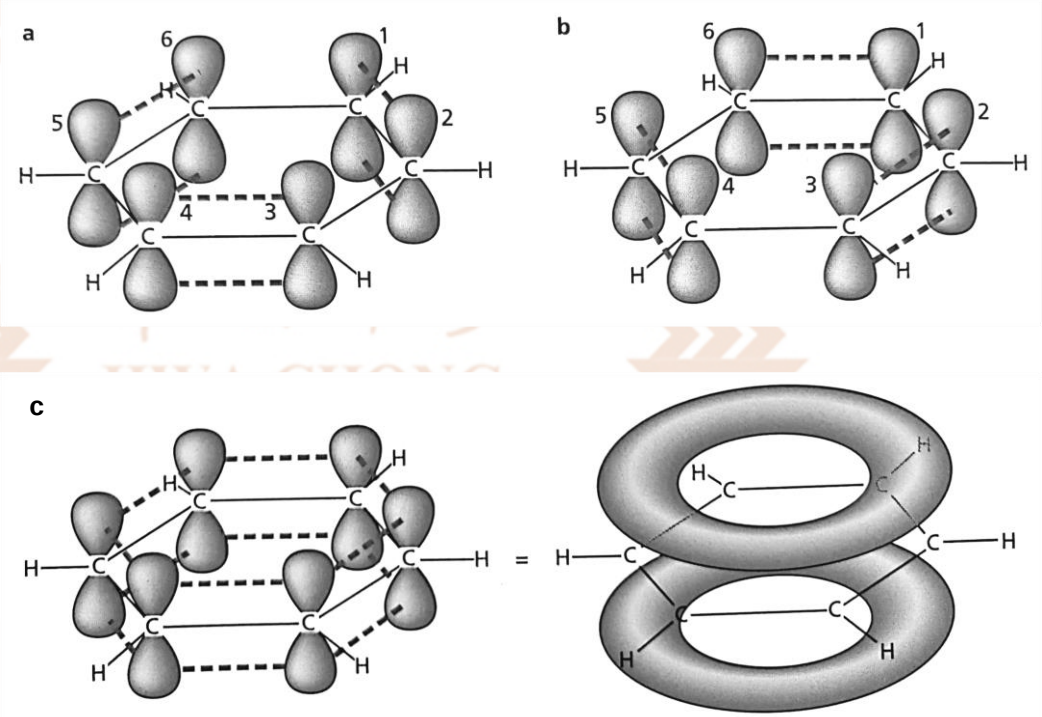


Figure 5. (a) and (b) Alternative views of bonding between carbon pairs in benzene. (c) The delocalised bonding in benzene.

3.2 Implications of π electron cloud delocalisation

The delocalised π electron cloud is responsible for the following physical and chemical properties of benzene:

i. It causes all carbon-carbon bond lengths to be equal, creating a planar, regular hexagonal shape.
ii. It prevents benzene from undergoing any of the typical addition reactions that alkenes show.

i. Carbon-carbon bond lengths and bond energies in benzene

Instead of three C=C double bonds and three C-C single bonds, X-ray measurements showed that all six carbon-carbon bonds of benzene are identical in length and intermediate between a C-C single bond length and a C=C double bond length. The carbon-carbon bond energy in benzene is also between that of a C-C single bond and a C=C double bond. (Note: When quoting the carbon-carbon

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bond energy for benzene from the *Data Booklet*, do refer to the specific bond energy between carbon atoms for benzene.)

carbon-carbon bond	bond length / nm	bond energy / kJ mol^{-1}
C–C bond	0.154	350
carbon-carbon bond in benzene	**0.139**	**520**
C=C bond	0.134	610

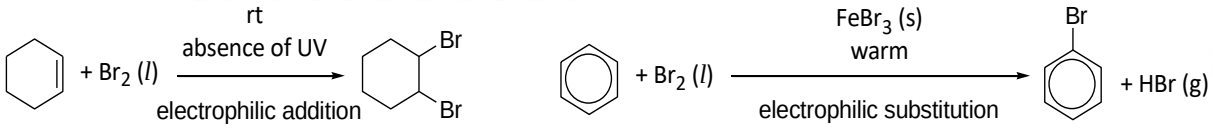
Table 1. Different types of carbon-carbon bond lengths and bond energies.

ii. Difference in reactivities of benzene versus alkenes

LO11.3(h): explain, in terms of delocalisation of π electrons, the difference between benzene and alkene: (i) reactivity towards electrophiles, (ii) preference of benzene to undergo substitution rather than addition reaction

Similar to electron-rich alkenes, the π electron cloud in benzene attracts electrophiles (electron-deficient species). However, the **delocalisation of electrons in the π electron cloud in benzene** results in **extra stability** of benzene (which is also known as resonance-stabilisation). As a result, the **π electron cloud in benzene is less susceptible to attack by electrophiles** compared to the C=C double bonds in alkenes. Hence, benzene requires **stronger electrophiles** to react as compared to alkenes. In addition, **benzene undergoes electrophilic substitution rather than electrophilic addition reactions** because electrophilic addition destroys the delocalised π electron cloud and this requires a significant amount of energy, which is highly unfavourable. Benzene preferentially undergoes electrophilic substitution reactions (where one or more hydrogen atoms is substituted by electrophiles) which **preserve its aromaticity**.

The following shows an example of the electrophilic addition in alkenes, and the electrophilic substitution in arenes. While electrophilic addition of cyclohexene using liquid bromine can be carried out at room temperature and without a catalyst, electrophilic substitution of benzene with liquid bromine requires warming, and $FeBr_3$ as a Lewis acid catalyst to generate strong electrophile Br^+ (to be discussed in Section 4.2).



The stabilisation energy of benzene (Application example)

We can get a quantitative idea of benzene's stability from the comparison of various enthalpy change of hydrogenation. The experimentally determined enthalpy change of hydrogenation of cyclohexene is −118 kJ mol^{-1}. The experimentally determined enthalpy change of hydrogenation of cyclohexa-1,4-diene is −232 kJ mol^{-1}, which is approximately twice of the experimentally determined enthalpy change of hydrogenation of cyclohexene. Hence the theoretical prediction for benzene's enthalpy change of hydrogenation, based on the model of 3 alternating C–C and C=C bonds (i.e. hypothetical cyclohexatriene), is –354 kJ mol^{-1} (−118 kJ mol^{-1} × 3). However, the experimentally determined enthalpy change of hydrogenation of benzene was found to be –205 kJ mol^{-1}. Hence, benzene is estimated to be more stable than the hypothetical cyclohexatriene by about 354 – 205 = 149 kJ mol^{-1}. The difference of 149 kJ mol^{-1} is known as the stabilisation energy.

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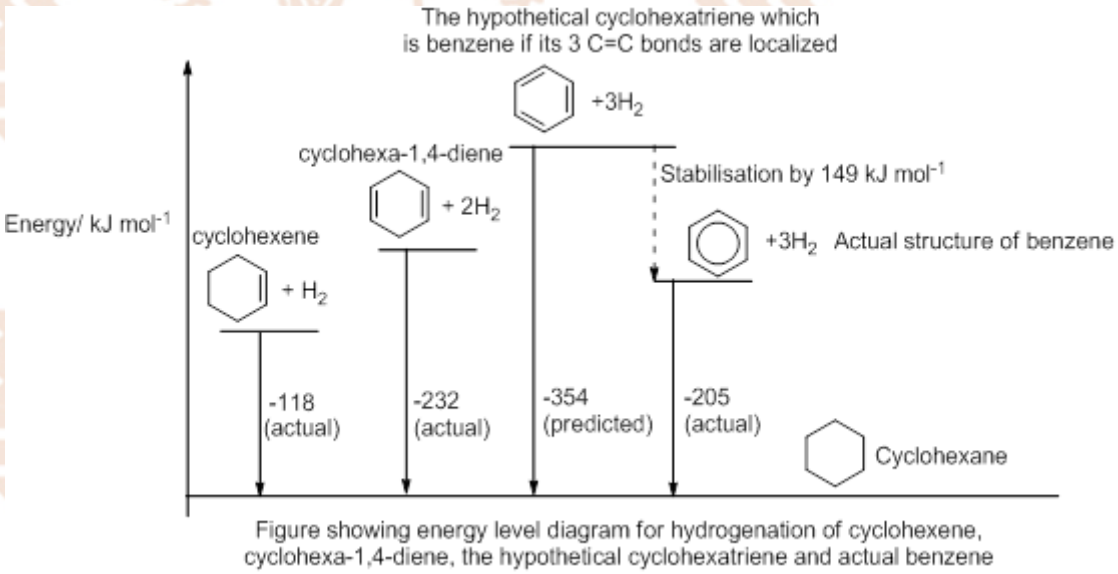


Figure showing energy level diagram for hydrogenation of cyclohexene, cyclohexa-1,4-diene, the hypothetical cyclohexatriene and actual benzene

Figure 6. Energy level diagram for hydrogenation of cyclohexene, cyclohexa-1,4-diene, the hypothetical cyclohexatriene and actual benzene.

Exercise 3.1 (Worked Examples)

(a) Consider cyclohexane, cyclohexene and methylbenzene, is methylbenzene the only compound that contains sp^2 hybridised carbon atoms? Explain your answer.

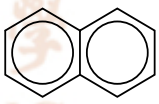
[Modified from PromoHCI09/I/16]

(b) Which property does benzene have as a consequence of the delocalised electrons present in the molecule?

A. It is a good conductor of electricity.
B. It is susceptible to attack by nucleophilic reagents.
C. Addition reactions of benzene take place more readily than substitution.
D. The carbon-carbon bond length is between that of a C–C bond and a C=C bond.

[PromoHCI09/I/19]

(c) Naphthalene is an aromatic compound with the following structure.

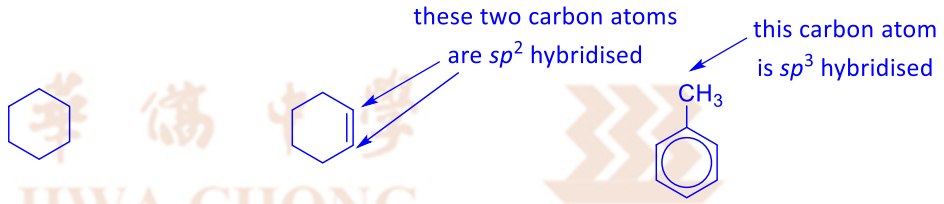


(i) How many π electrons does naphthalene have?
(ii) Is naphthalene a planar molecule? Explain your answer.
(iii) Draw all the hydrogen atoms on naphthalene.

[Modified from PrelimRI12/I/21]

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(a) No. Both cyclohexene and methylbenzene contain sp^2 hybridised carbon atoms.



cyclohexane

all carbon atoms
are sp^3 hybridised

cyclohexene

the rest of the carbon atoms
are sp^3 hybridised

methylbenzene

the rest of the carbon atoms
in the benzene ring
are sp^2 hybridised

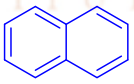
(b) Answer: D (Refer to Section 3.2); Teaching solutions: Benzene does not conduct electricity (The delocalised π electrons in benzene is "localised" in the π electron cloud within each benzene molecule, they are not free to move as charge carriers). Electron-rich benzene reacts with electrophiles (electron-deficient species), and not with nucleophiles (electron-rich species). Benzene undergoes substitution more readily than addition.

c(i) 10 π electrons

c(ii) Yes, all carbon atoms that make up the rings are sp^2 hybridised, and the geometry around each carbon atom in napthalene is trigonal planar with C–C–C bond angle of 120°.

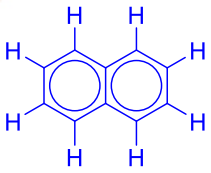
c(iii)

Suggested approach for c(i):
draw one resonance structure of napthalene



5 pi bonds means 10 pi electrons

Answer for c(iii):



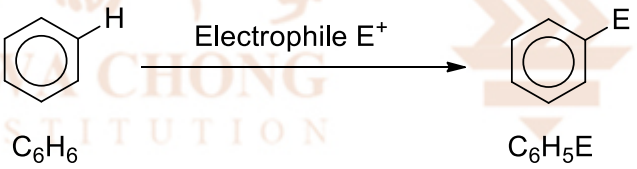
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4 REACTIONS OF BENZENE

4.1 Electrophilic substitution reaction

Aromatic compounds like benzene undergo electrophilic substitution reactions where a hydrogen atom bonded to the benzene ring is substituted by an electrophile.

The overall reaction for an electrophilic substitution can be represented as:



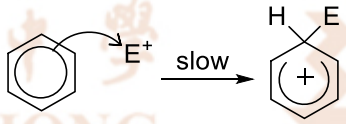
*unbalanced equation

Examples of electrophiles that can react with benzene include Br^+, NO_2^+ and R^+ (R = alkyl group). Unlike alkenes, the electrophiles that react with benzene are all positively charged, with a strong electron-attracting tendency.

4.1.1 General Mechanism

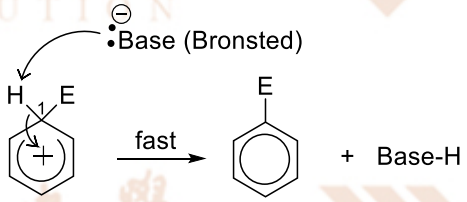
LO11.3(j)(i): describe the mechanism of electrophilic substitution in arenes, using the mono-bromination of benzene as an example
LO11.3(j)(ii): describe the effect of the delocalisation of electrons in arenes in such reactions

Step 1:



- Initial attack by the π electrons of the aromatic system on the electrophile forms a carbocation intermediate with a positive charge delocalised across five carbon atoms. Two of the six π electrons are used to form the bond to the electrophile, leaving only four π electrons delocalised across the five carbon atoms.
- The movement of two π electrons means that the stability conferred by the delocalisation of the six π electrons of the ring is disrupted, so this process has high activation energy. Hence, this is the **slow step** i.e. rate-determining step.

Step 2:

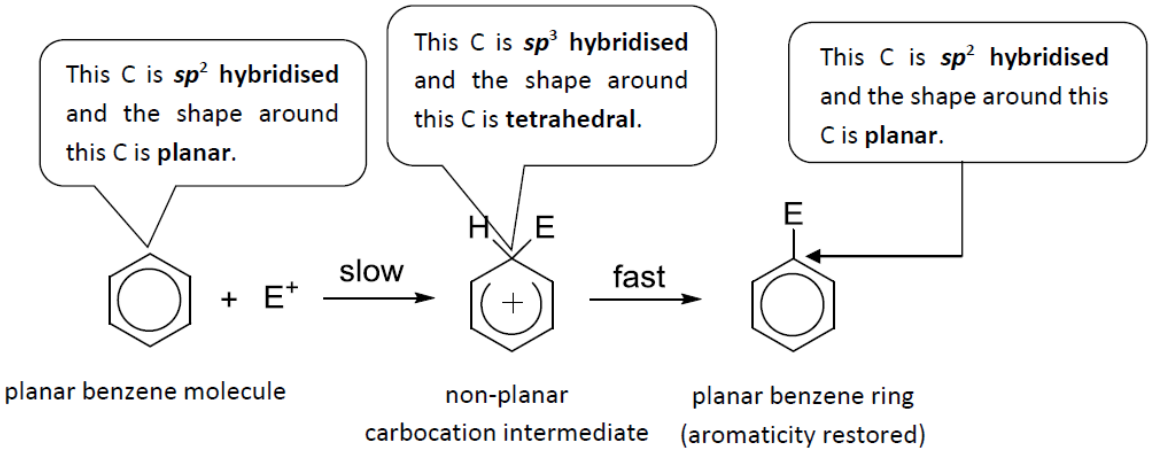


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- Unlike in alkenes where an anion 'adds on' to the carbocation intermediate, the proton i.e. H^+ on the carbon-1 of the benzene intermediate is removed by a Bronsted base, so as to reform the delocalised π system. A stable substitution product results, and aromaticity is restored.

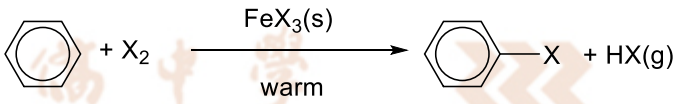
4.1.2 Shape of molecule and intermediate

The hybridisation and shape of the reacting carbon changes in each step of the mechanism.



4.2 Electrophilic substitution with chlorine or bromine (chlorination or bromination)

LO11.3(i)part: describe the chemistry of the benzene ring as exemplified by the following reactions of benzene: (i) electrophilic substitution reactions with chlorine and with bromine (recognise the use of Lewis acid as catalyst)



X = Cl	X = Br
Reagents & Conditions: Cl_2(g), $FeCl_3$(s) as Lewis acid catalyst, warm **OR** Cl_2(g), Fe(s), warm	**Reagents & Conditions**: Br_2(l), $FeBr_3$(s) as Lewis acid catalyst, warm **OR** Br_2(l), Fe(s), warm
Observations: decolourisation of greenish-yellow Cl_2(g) and white fumes of HCl(g)	**Observations**: decolourisation of reddish-brown Br_2(l) and white fumes of HBr(g)
Note • Fe(s) is **not** the Lewis acid catalyst for electrophilic substitution (see Note 5 below). • Aluminium analogues such as $AlCl_3$ (s), $AlBr_3$ (s), and Al (s) can also be used in place of their respective iron counterparts.	

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LO11.3(j)(i): describe the mechanism of electrophilic substitution in arenes, using the mono-bromination of benzene as an example

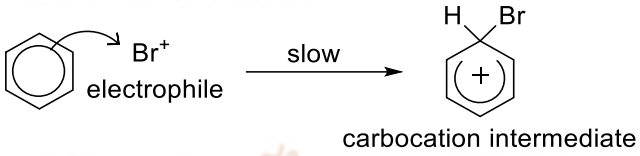
Mechanism: Electrophilic substitution

Formation of electrophile Br^+

$$FeBr_3 + Br_2 \longrightarrow \underset{\text{electrophile}}{Br^+} + [FeBr_4]^-$$

(Reaction between $FeBr_3$(s) and Br_2(l) generates a strong electrophile Br^+.)

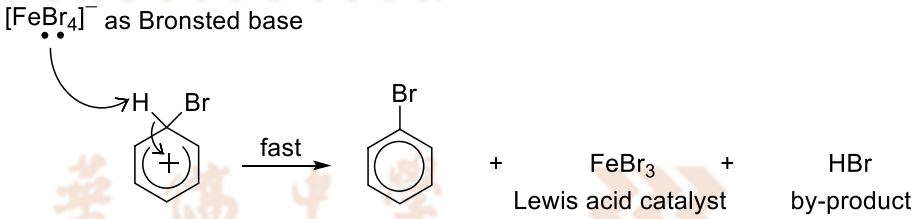
Step 1: Delocalised π electron cloud attacks the electrophile.



carbocation intermediate

(The delocalised π system is disrupted in this step thus it has fairly high activation energy. Notice that E_{A1} is larger than E_{A2} in Figure 7 as step 1 is the slow step.)

Step 2: The intermediate loses a proton and aromaticity is restored.



($[FeBr_4]^-$ acts as a Bronsted base and deprotonates the carbocation intermediate, producing the product bromobenzene, by-product HBr, and regenerating the Lewis acid catalyst $FeBr_3$.)

The energy profile diagram of bromination of benzene via electrophilic substitution is as follows:

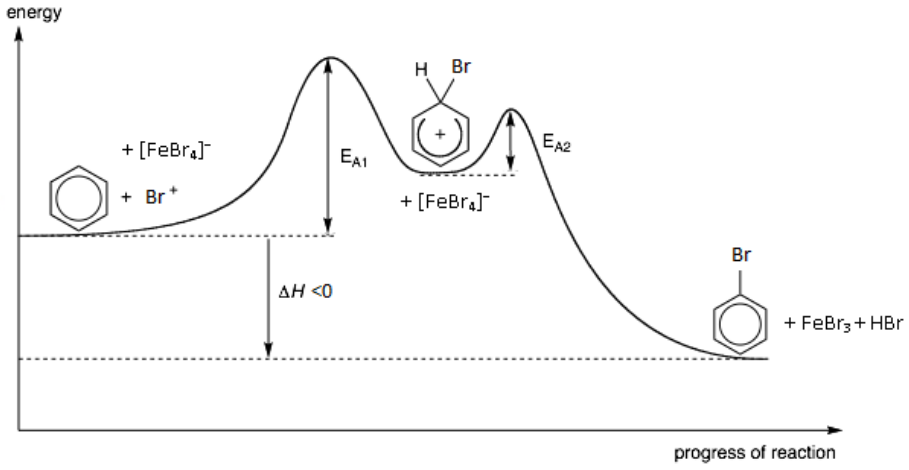


Figure 7. Energy profile diagram of bromination of benzene via electrophilic substitution.

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Note

1. Fe in $FeX_3(s)$ or A*l* in $AlX_3(s)$ are electron deficient and can accept a lone pair of electrons from the halogen X_2. Hence $FeX_3(s)$ or $AlX_3(s)$ are called the **Lewis acid** (electron pair acceptors) catalysts.

2. $FeX_3(s)$ or $AlX_3(s)$ catalyses the electrophilic substitution because they react with halogen X_2 (where X = C*l* or Br) to generate a **strong (positively charged) electrophile** (Cl^+ or Br^+).

$$FeCl_3 + Cl_2 \longrightarrow Cl^+ [FeCl_4]^-$$
$$FeBr_3 + Br_2 \longrightarrow Br^+ [FeBr_4]^-$$

3. In the **absence** of the Lewis acid catalyst, reaction between benzene and halogen **cannot** take place. This is because halogen molecule $Cl_2(g)$ or $Br_2(l)$ is a **weak electrophile**, unable to react with the resonance-stabilised benzene ring.

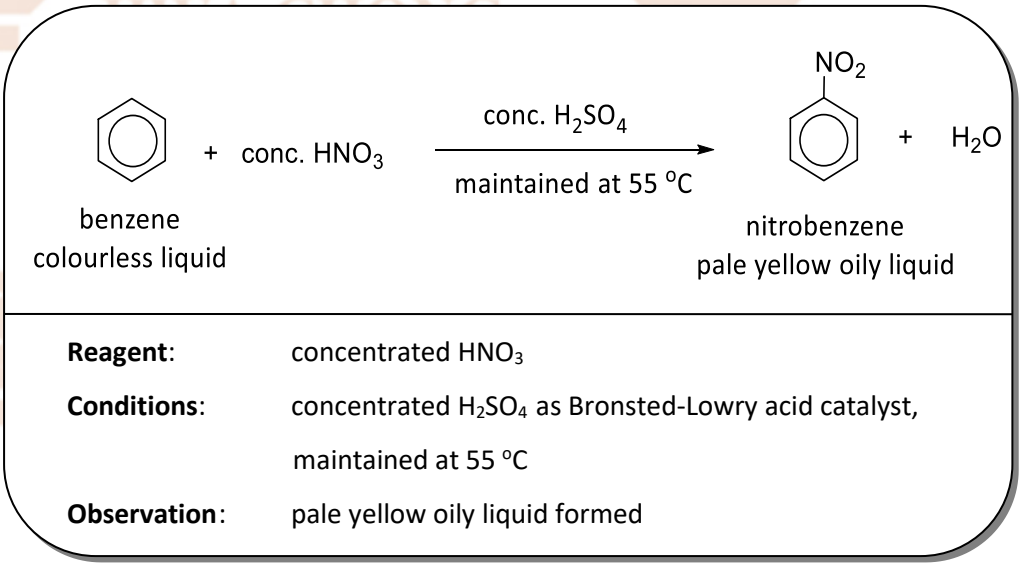
4. The reaction conditions must be **anhydrous**. This is because in the presence of water, $FeX_3(s)$ or $AlX_3(s)$ will accept lone pair of electrons from water and undergo hydrolysis instead, and hence can no longer accept lone pair of electrons from halogen X_2 to generate the strong electrophile X^+.

5. Fe(s) can also be used instead of $FeX_3(s)$. This is because when Fe(s) comes into contact with X_2, Lewis acid catalyst $FeX_3(s)$ is generated *in situ* according to the redox reaction shown below.

$$2Fe(s) + 3Cl_2(g) \longrightarrow 2FeCl_3(s)$$
$$2Fe(s) + 3Br_2(l) \longrightarrow 2FeBr_3(s)$$

4.3 Electrophilic substitution with concentrated nitric acid (nitration)

LO11.3(i)part: describe the chemistry of the benzene ring as exemplified by the following reactions of benzene: (ii) nitration with concentrated nitric acid (recognise concentrated sulfuric acid as a Brønsted-Lowry acid catalyst)



Reagent:	concentrated HNO_3
Conditions:	concentrated H_2SO_4 as Bronsted-Lowry acid catalyst, maintained at 55 °C
Observation:	pale yellow oily liquid formed

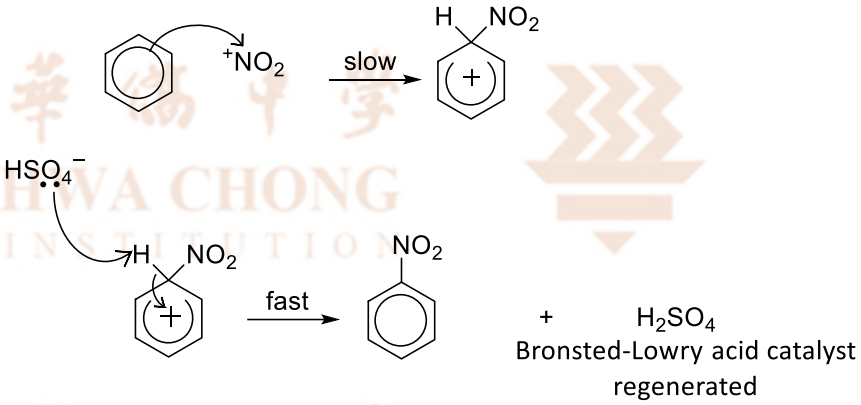
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Mechanism

Electrophilic substitution

$2H_2SO_4 + HNO_3 \longrightarrow {}^{+}NO_2 + H_3O^{+} + 2HSO_4^{-}$

electrophile



Note

1. Sulfuric acid is a **stronger Bronsted-Lowry acid** than nitric acid hence sulfuric acid protonates nitric acid, eventually generating strong electrophile nitronium ion NO_2^+.

Steps for generating NO_2^+ electrophile (background info)

Sulfuric acid protonates nitric acid

$H_2SO_4 + HNO_3 \longrightarrow HSO_4^- + H_2NO_3^+$

The protonated nitric acid loses a water molecule to give nitronium ion

$H_2NO_3^+ \longrightarrow H_2O + NO_2^+$

The water molecule lost is protonated by another molecule of sulfuric acid to give hydronium ion

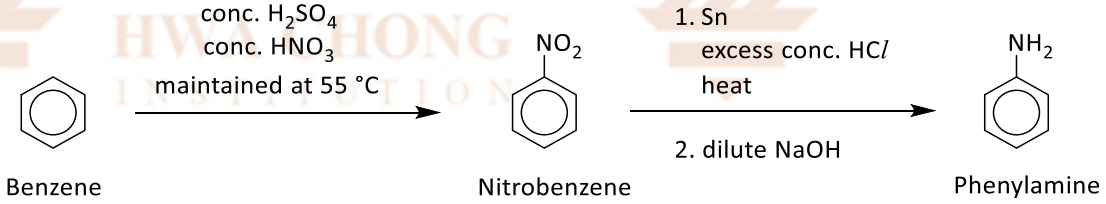
$H_2SO_4 + H_2O \longrightarrow HSO_4^- + H_3O^+$

Overall equation is therefore $2H_2SO_4 + HNO_3 \longrightarrow 2HSO_4^- + H_3O^+ + NO_2^+$

2. The reaction does not occur in the absence of concentrated sulfuric acid.

3. Under more rigorous conditions (e.g. higher temperature or prolonged heating), nitrobenzene can be further nitrated to give 1,3-dinitrobenzene or 1,3,5-trinitrobenzene. This is not ideal if the desired product is nitrobenzene.

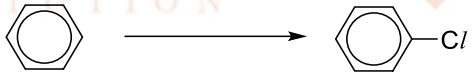
4. Nitration of benzene is an important first step on the way to a variety of compounds in organic synthesis. For example:



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Exercise 4.1 (Worked Example)

1. Which set of conditions will bring about the transformation shown below?



A $Cl_2(g)$ in the presence of UV
B $Cl_2(g)$ in the presence of $AlCl_3(aq)$
C $Cl_2(g)$ in the presence of Fe(s)
D Concentrated HCl with heat

[Modified from PrelimRI12/I/20]

Ans C.
Option A is incorrect. While the free radical substitution results in the hydrogen atom in benzene being substituted by the chlorine atoms, the C-H bond between a sp^2-hybridised carbon and a hydrogen in stronger in benzene than that of a sp^3-hybridised carbon in alkane. This will require an even more drastic condition for the reaction to occur.

Option B is incorrect as reaction conditions must be anhydrous (in the absence of moisture or water). Lewis acid catalyst $FeCl_3(s)$ is generated *in situ* from $Cl_2(g)$ and Fe(s).

A catalyst is required to be present in order to generate a positively charged electrophile for the stable benzene to react in Option D.

2. What is the main reason for adding concentrated sulfuric acid to concentrated nitric acid in the preparation of nitrobenzene?

$$C_6H_6(l) + HNO_3(l) \rightarrow C_6H_5NO_2(l) + H_2O(l)$$

A It acts as an inert solvent for the benzene and nitric acid.
B It removes protons from nitric acid, thus forming NO_3^- ions.
C It donates protons to the nitric acid, thus forming NO_2^+ ions.
D It removes the water, thus preventing equilibrium being established.

[J99/3/23]

Ans C. Conc. H_2SO_4 acts as a Bronsted-Lowry acid to protonate HNO_3 to generate strong electrophile NO_2^+ for electrophilic substitution to occur.

3. Will benzene decolourise liquid bromine when warmed in the presence of anhydrous iron(III) chloride? Explain your answer.

[Modified from PrelimVJC12/I/37]

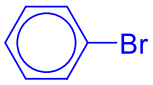
Yes. Electrophilic substitution will occur. Electrophile Br^+ is generated from $Br_2(l)$ and $FeCl_3(s)$ as shown below.

$$FeCl_3 + Br_2 \longrightarrow \underbrace{Br^+}_{\text{electrophile}} + [FeCl_3Br]^-$$

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4. Draw the organic product when benzene is warmed with Br*Cl* and anhydrous iron(III) chloride.

[Modified from PrelimTJC12/I/21]



Br is less electronegative than C*l*, hence Br*Cl* will react with $FeCl_3$ to give Br^+

$$FeCl_3 + \underset{\delta+}{Br}-\underset{\delta-}{Cl} \longrightarrow \underset{\text{electrophile}}{Br^+} + [FeCl_4]^-$$

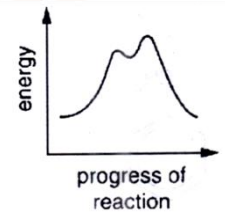
Exercise 4.2 (Worked Example)

The bromination of benzene in the presence of $AlBr_3$ can be represented by the following mechanism. The enthalpy change of reaction for the bromination of benzene is **–43 kJ mol^{-1}**.

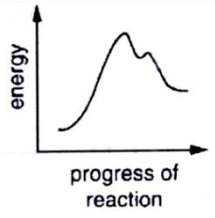
$$C_6H_6 + Br_2 \overset{AlBr_3}{\rightleftharpoons} C_6H_6Br^+ + AlBr_4^- \longrightarrow C_6H_5Br + HBr + AlBr_3$$

Which of the following reaction profiles correctly represents this mechanism?

A



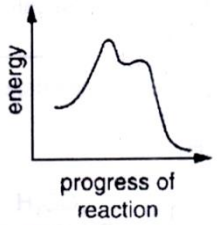
B



C



D

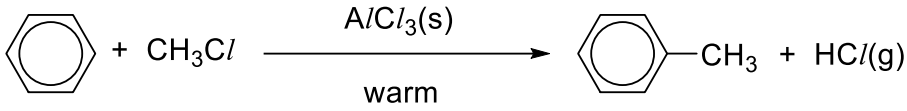


Option D is an energy profile diagram for an exothermic reaction. There are two steps in the electrophilic substitution mechanism hence we eliminate C because it has only one peak which implies that reaction is one step only. Activation energy for the first step is higher than the second step as aromaticity of the benzene ring is destroyed when the π electrons attack the electrophile.

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4.4 Electrophilic substitution with halogenoalkanes (Friedel-Crafts alkylation)

LO11.3(i)part: describe the chemistry of the benzene ring as exemplified by the following reactions of benzene: (iii) Friedel-Crafts alkylation with halogenoalkanes (recognise the use of Lewis acid as catalysts)



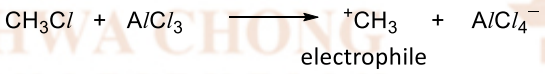
Reagent: chloroalkane

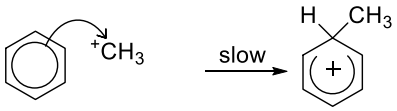
Conditions: $AlCl_3$(s) as Lewis acid catalyst, warm

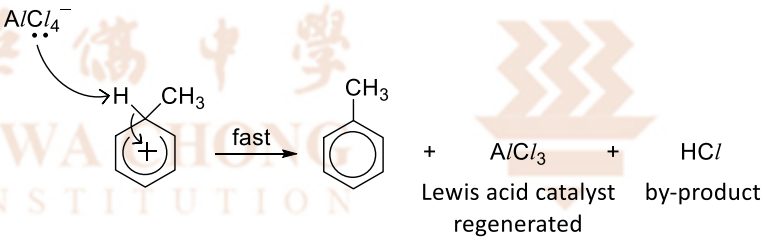
Observation: white fumes of HCl(g)

Mechanism

Electrophilic substitution







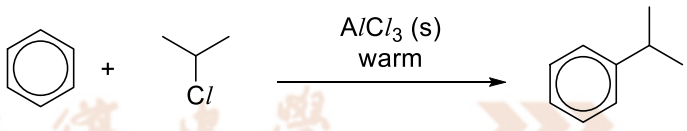
Note

1. Similar to electrophilic substitution using halogens, $AlCl_3$(s) acts as the **Lewis acid catalyst**.

2. Friedel-Crafts alkylation only works with **alkyl halides as reagents**, such as chloroalkane, bromoalkane and iodoalkane, and not aryl halides (e.g. chlorobenzene) as reagents. In Topic 15 Halogen Derivatives, you will learn that the C–X bond in aryl halides cannot be broken easily.

Exercise 4.3

Describe the mechanism for the following reaction scheme.



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5 METHYLBENZENE AND OTHER SUBSTITUTED BENZENES

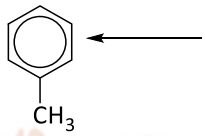
5.1 Structure and physical properties of methylbenzene

Methylbenzene (commonly known as toluene) is obtained when a methyl group ($–CH_3$) replaces one of the hydrogen atoms in benzene. It has the molecular formula C_7H_8.

Methylbenzene is a colourless liquid which is insoluble in water. It is relatively less toxic than benzene.

5.2 Overview of reactions of methylbenzene

For methylbenzene, reactions can occur either at the benzene ring or the methyl group (side chain):



benzene ring can undergo electrophilic substitution like
1. chlorination or bromination
2. nitration
3. Friedel-Crafts alkylation

(view section 5.3)

side chain can undergo side-chain reactions like
1. free radical substitution
2. side-chain oxidation

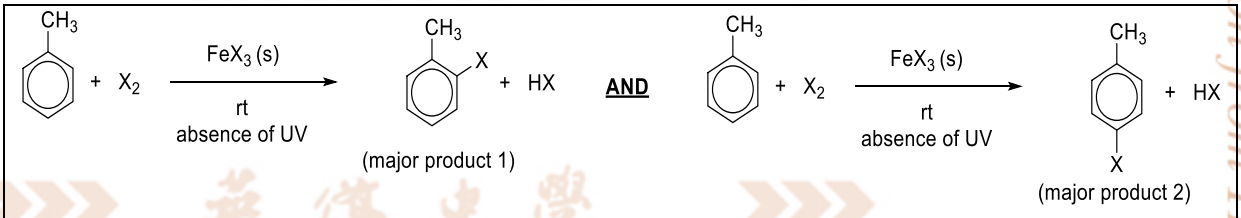
(view section 5.6)

5.3 Electrophilic substitutions of methylbenzene

5.3.1 Electrophilic substitution with chlorine or bromine

LO11.3(i)part: describe the chemistry of the benzene ring as exemplified by the following reactions of methylbenzene: (i) electrophilic substitution reactions with chlorine and with bromine (recognise the use of Lewis acid as catalyst)

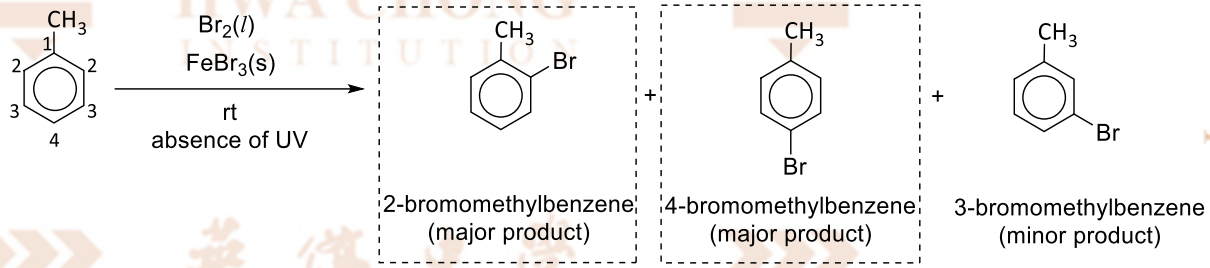
LO11.3(l): predict whether halogenation will occur in the side-chain or aromatic nucleus in arenes depending on reaction conditions



X = C*l*	X = Br
Reagents & Conditions: Cl_2(g), $FeCl_3$(s) as Lewis acid catalyst, rt and absence of UV	**Reagents & Conditions**: $Br_2(l)$, $FeBr_3$(s) as Lewis acid catalyst, rt and absence of UV
Observations: decolourisation of greenish-yellow Cl_2(g) and white fumes of HC*l* (g)	**Observations**: decolourisation of reddish-brown $Br_2(l)$ and white fumes of HBr (g)
Note: Room temperature and absence of UV prevent free radical substitution on alkyl side chain.	

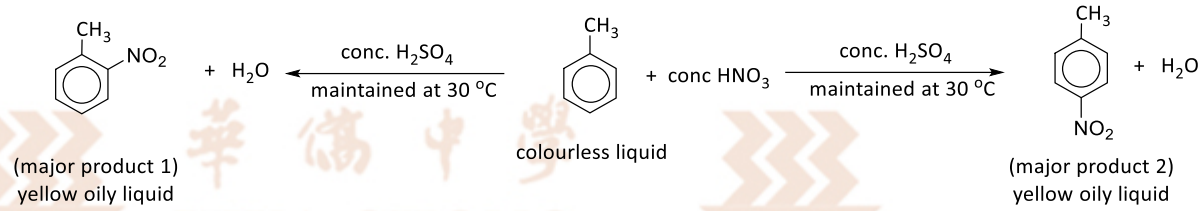
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Section 5.5 will explain why the major products below are obtained.



5.3.2 Electrophilic substitution with concentrated nitric acid

LO11.3(i)part: describe the chemistry of the benzene ring as exemplified by the following reactions of methylbenzene: (ii) nitration with concentrated nitric acid (recognise concentrated sulfuric acid as a Brønsted-Lowry acid catalyst)



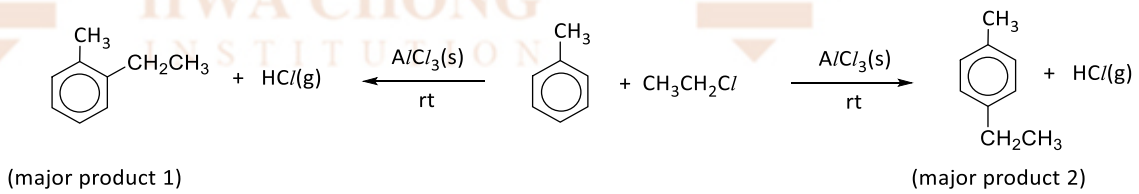
Reagent: Concentrated HNO_3

Conditions: Concentrated H_2SO_4 as Bronsted-Lowry acid catalyst, maintained at 30 °C

Observation: Yellow oily liquid formed

5.3.3 Electrophilic substitution with halogenoalkanes (Friedal-Crafts alkylation)

LO11.3(i)part: describe the chemistry of the benzene ring as exemplified by the following reactions of methylbenzene: (iii) Friedel-Crafts alkylation with halogenoalkanes (recognise the use of Lewis acid as catalysts)



Reagent: chloroalkane

Conditions: $AlCl_3$(s) as Lewis acid catalyst, rt

Observation: white fumes of HCl(g)

Notice that the reaction conditions and possible products in the electrophilic substitution of methylbenzene are slightly different from benzene. This is because the methyl group has changed the reactivity of the benzene ring and it also determines the substitution of the incoming group.

Sections 5.4 and 5.5 explain the effects of substituents on the benzene ring.

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5.4 Substituent effect on the reactivity of the benzene ring towards electrophilic substitution

LO11.1(c)part: interpret, and use the following terminology associated with organic reactivities: (i) delocalisation (ii) electronic effect (electron-donating and electron-withdrawing effect)

Electron-donating groups increase the electron density in the benzene ring. On the other hand, **electron-withdrawing** groups decrease the electron density in the benzene ring

From Topic 8 Introduction to Organic Chemistry, electron-donating and electron-withdrawing effects can occur through:

(i) σ bonds via **inductive effect**

(ii) a π electron cloud via **delocalisation**

Inductive effect

The inductive effect arises from the polarisation of electron density in a bond due to the **electronegativity** of nearby atoms.

- **Electron-withdrawing groups via inductive effect**

  These groups, e.g. –OH, $–NH_2$, –C*l*, **inductively withdraw electron density from the benzene ring** via the σ bond, because O, N and the halogens are more electronegative than the C atom in the benzene ring:



  Other examples include: –OR, –NHR, $–NR_2$, $–CHO$, $–COR$, $–CO_2H$, $–CO_2R$, $–NO_2$, and –CN etc.

- **Electron-donating groups via inductive effect**

  Alkyl groups (e.g. $–CH_3$, $–CH_2CH_3$) **inductively donate electron density into the benzene ring** via the σ bond. The reason is due to hyperconjugation which will not be covered here.

Delocalisation

Delocalisation occurs when ***p* orbitals on 3 or more adjacent atoms overlap**, forming a **π electron cloud**. For substituents with a *p* orbital on the atom joined to the benzene ring, the *p* orbital can overlap with the π electron cloud of the ring.

- **Electron-donating groups via delocalisation**

  These groups have a **lone pair of electrons in the *p* orbital** of the **atom directly joined to the benzene ring**, and can therefore **donate the lone pair of electrons into the benzene ring** via delocalisation. Examples include: –OH, –OR, $–NH_2$, $–NR_2$, –C*l*, –Br, and –I.

  In phenol below, the *p* orbital on the O atom joined to the benzene ring can overlap with the π electron cloud of the ring, enabling the lone pair of electrons on O to be donated into the π system.

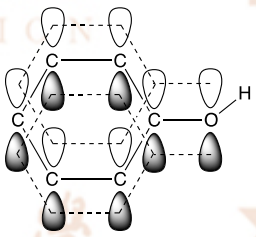


Figure 8. Delocalisation of the lone pair of electrons on O atom into the benzene ring in phenol.

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- **Electron-withdrawing groups via delocalisation**
  In these groups, the atom directly joined to the benzene ring forms double/triple bonds to electronegative atoms like O or N. Hence **electron density in the benzene ring is drawn away** by these electronegative atoms via delocalisation. Examples include: –CHO, $–COCH_3$, $–CO_2H$, $–CO_2CH_3$, $–NO_2$, –CN etc.

  In benzaldehyde below, the carbon directly bonded to benzene ring forms a double bond with an electronegative O atom. The *p* orbitals on C and O of the aldehyde group overlap with the π electron cloud of the benzene ring. The O atom draws electron density away from the aldehyde carbon *as well as* from the π electron cloud of the benzene ring.

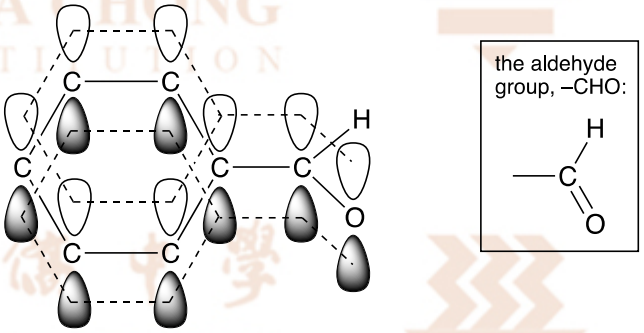


Figure 9. Electron density in the π electron cloud of benzene drawn away by electronegative O atom of –CHO group.

<u>Overall effect on reactivity of benzene ring</u>

Inductive effect and delocalisation do not necessarily act in the same direction. When two effects are opposing e.g. –OH group is electron-withdrawing via inductive effect but electron-donating via delocalisation, the stronger effect dominates.

- Substituents that are **overall electron-donating** towards the benzene ring will **increase the electron density of the benzene ring**, making it **more reactive towards electrophilic attack**. We call them **<u>activating</u> groups**.

- Substituents that are **overall electron-withdrawing** from the benzene ring will **decrease the electron density of the benzene ring**, making it **less reactive towards electrophilic attack**. We call them **<u>deactivating</u> groups**.

Table 2 summarises the **<u>overall</u>** electron-donating or electron-withdrawing effect of substituents on the reactivity of the benzene ring in the A-Level syllabus.

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substituent	via inductive effect	via delocalisation	overall effect on benzene ring
–OH, –OR –NH_2, –NHR, –NR_2 –NHCOR	weakly withdrawing	strongly donating	strongly electron-donating ⇒ strongly activating
–alkyl	weakly donating	–	weakly electron-donating ⇒ weakly activating
–C*l*, –Br, –I	strongly withdrawing	weakly donating*	electron-withdrawing ⇒ deactivating
–CHO, –COR, –CO_2H, –CO_2R, –NO_2, –CN, –NH_3^+	strongly withdrawing	strongly withdrawing	strongly electron-withdrawing ⇒ strongly deactivating

Table 2. Effect of substituents via inductive effect and delocalisation, and their overall effect on reactivity of the benzene ring.

*The electron-donating effect of –C*l* via delocalisation of lone pair of electrons is not significant because the overlap between the 3*p* orbital of C*l* atom with the 2*p* orbitals of the carbon atoms in the benzene ring is not effective due to large difference in size of the 3*p* and 2*p* orbitals. Hence the halogens are overall electron-withdrawing (mainly due to inductive effect) and deactivating **when attached to the benzene ring**.

In contrast, the 2*p*–2*p* overlap between O or N atoms with carbon atom is much more effective so the electron-donating effect of –OH and –NH groups via delocalisation of lone pair of electrons is much stronger. Hence –OH and –NH groups are overall electron-donating (mainly due to delocalisation) and activating **when attached to the benzene ring**.

Activating groups present on the benzene ring means **<u>milder conditions</u>** (e.g. lower temperatures, no need for catalysts, dilute concentrations etc.) are required for electrophilic substitution to take place, compared to benzene. Deactivating groups, on the other hand, will require more vigorous conditions.

Compare the reaction conditions required for benzene and methylbenzene to undergo electrophilic substitution in Table 3.

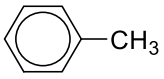
Reaction conditions	Benzene 	Methylbenzene 
Bromination	$Br_2(l)$, $FeBr_3$(s), **warm**	$Br_2(l)$, $FeBr_3$(s), **r.t.**
Nitration	conc. HNO_3, conc. H_2SO_4 maintained at **55 °C**	conc. HNO_3, conc. H_2SO_4 maintained at **30 °C**
Alkylation	chloroalkane, A*l*Cl_3(s), **warm**	chloroalkane, A*l*Cl_3(s), **r.t.**

Table 3. Reaction conditions required for electrophilic substitution of benzene, methylbenzene.

Since the –CH_3 group is activating, the conditions required for it to undergo electrophilic substitution are milder compared to those for benzene. If higher temperatures are used, more than one substitution could occur, resulting in multi-substituted products and reducing the yield of the desired monosubstituted product.

In later topics, we will also learn the different conditions required for phenol and phenylamines to undergo electrophilic substitution.

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5.5 Substituent effect on the position of the incoming electrophile of monosubstituted arenes

LO11.3(m): apply the knowledge of positions of substitution in the electrophilic substitution reactions of monosubstituted arenes

When methylbenzene undergoes electrophilic substitution with E^+ (electrophile), three possible mono-substituted compounds could be formed:

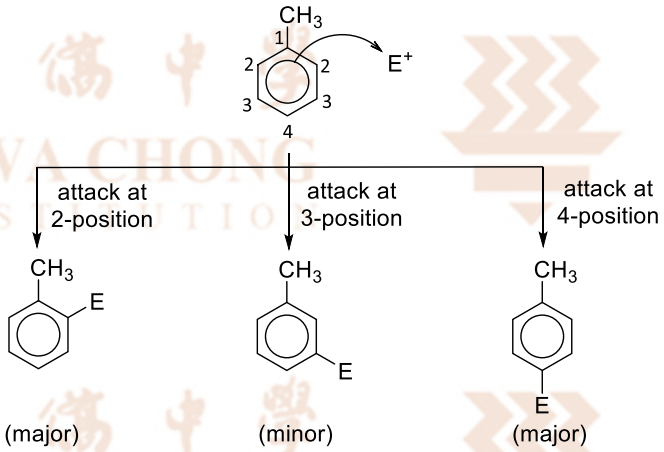


Figure 10. Three possible mono-substituted products: 2-and 4-substitution is favoured in this case (major products).

The position of the incoming group, E, is determined by the **nature of the substituent or group already bonded to the ring** (i.e. $-CH_3$ in this case), and not by the nature of E.

Activating groups (like $-CH_3$) favour 2- and 4- substitution, we call them **2,4-directing** groups. **Deactivating** groups favour 3-substitution, we call them **3-directing** groups. An exception is the halogens. The reasons are explained at the end of the chapter (not in syllabus). Table 4 summarises the effects on both reactivity and position of substitution by the group already on the benzene ring in the A-Level syllabus (also in the *Data Booklet*).

Substituent on benzene ring / Effect on	–alkyl –OH, –OR $-NH_2$, –NHR, $-NR_2$ –NHCOR	–Cl, –Br, –I	–CHO, –COR $-CO_2H$, $-CO_2R$ $-NH_3^+$ $-NO_2$, –CN
Reactivity of ring compared to benzene	activated	deactivated	deactivated
Position of incoming group E	2- and/or 4-	2- and/or 4-	3-

Table 4. Effects on reactivity and position of incoming electrophile by substituents.

What happens if there are **two** groups already bonded to the benzene ring?

- If both groups **direct to the same position on the ring**, then substitution will occur at that position.
- If each group directs the incoming electrophile to a different position, the major product follows the directing effect of the **more strongly activating** group.
- Further substitution rarely occurs between the two groups in 1,3-disubstituted benzene rings as this site is too sterically hindered.

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Other combinations may result in a **mixture of products** with no clear major product. This situation is not ideal as the reaction will give poor yields of the desired product.

Exercise 5.1 (Worked Examples)

1. Draw the structures of the major organic products in each of the following reactions.

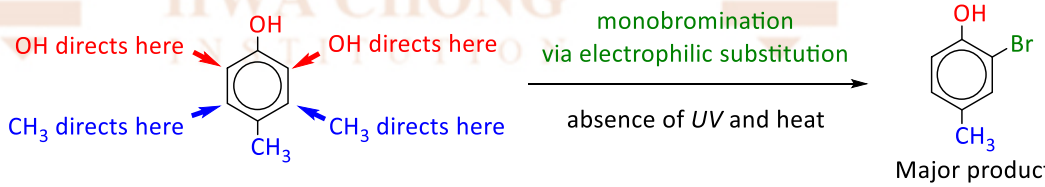
(a) mononitration of 4-methylbenzaldehyde



Major product

Comments:
CH_3 is 2,4-directing, but 4-position (with reference to CH_3) is occupied, hence CH_3 only direct incoming electrophile to 2-position (with reference to CH_3). CHO is 3-directing, since both substituents directs the incoming electrophile to the same position the major product is a result of substitution at that position.

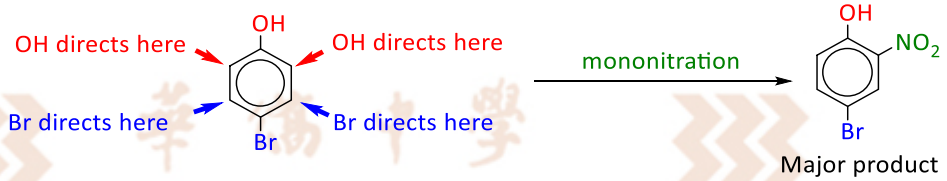
(b) monobromination of 4-methylphenol



Major product

Comments:
Both OH and CH_3 are 2,4-directing,
but 4-positions (with reference to each substituent) are occupied,
hence they only direct incoming electrophile to 2-positions (with reference to each substituent),
but **OH is more activating than CH_3**,
hence the major product is due to the OH directing the incoming electrophile
to 2-position with reference to OH

(c) mononitration of 4-bromophenol



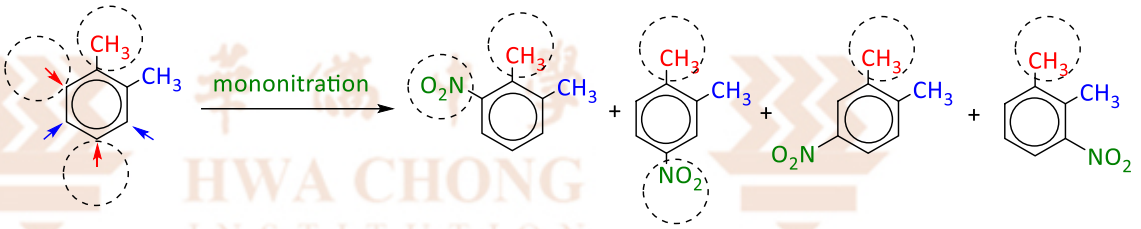
Major product

Comments:
Both OH and Br are 2,4-directing,
but 4-positions (with reference to each substituent) are occupied,
hence they only direct incoming electrophile to 2-positions (with reference to each substituent),
but **OH is strongly activating whereas Br is deactivating**,
hence the major product is due to the OH directing the incoming electrophile
to 2-position with reference to OH

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2. In the mononitration of 1,2-dimethylbenzene, a mixture of several products is obtained. Draw these products and explain why there is no one major product.

1,2-dimethylbenzene has two similarly activating groups which direct the incoming group to all 4 different positions on the benzene ring. Hence there is no clear major product.



Exercise 5.2

Draw the structures of the major organic products in each of the following reactions:

1. monochlorination of nitrobenzene

2. mononitration of bromobenzene

3. monobromination of 4-hydroxybenzoic acid

4. mononitration of 4-aminomethylbenzene

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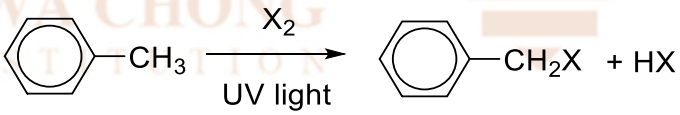
5.6 Side-chain reactions of methylbenzene

LO11.3(k): describe the chemistry of the alkyl side-chain of benzene ring as exemplified by the following reactions of methylbenzene: (i) free-radical substitution by chlorine and by bromine, (ii) complete oxidation to give benzoic acid

5.6.1 Free Radical Substitution

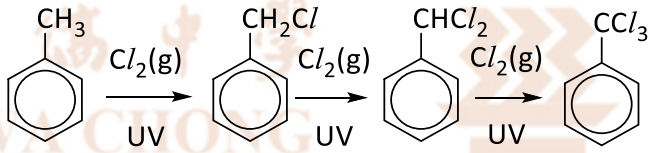
LO11.3(l): predict whether halogenation will occur in the side-chain or aromatic nucleus in arenes depending on reaction conditions

During the side-chain halogenation, methylbenzene and other alkylbenzenes undergo free-radical substitution with chlorine or bromine in the presence of UV light or heat. The alkyl side chain reacts like an alkane (Recall from Topic 10 Alkanes).



X = C*l*	X = Br
Reagents and conditions: Cl_2(g), UV light or heat	**Reagents and conditions:** Br_2(*l*), UV light or heat
Observation: greenish-yellow Cl_2(g) decolourises slowly	**Observation:** reddish brown Br_2(*l*) decolourises slowly
Note: To preferably obtain product of monohalogenation on the alkyl side chain, limited Cl_2(g) or excess alkylbenzene is usually employed.	

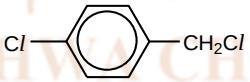
More than one chlorine or bromine atom can be incorporated onto the alkyl side chain if **excess** Cl_2(g) or Br_2(*l*) is used. For example:



Exercise 5.3 (Worked Examples)

a) Why must the synthesis of 2-bromomethylbenzene from methylbenzene be carried out in the absence of light and without heat?

b) Chlorine was passed into methylbenzene under reflux in the presence of aluminium chloride.

The compound 

was found to be present in the product. How is the mechanism for the formation of this product best described?

A electrophilic and free-radical substitution
B electrophilic and nucleophilic substitution
C nucleophilic and free-radical substitution
D nucleophilic substitution only

[N94/4/19]

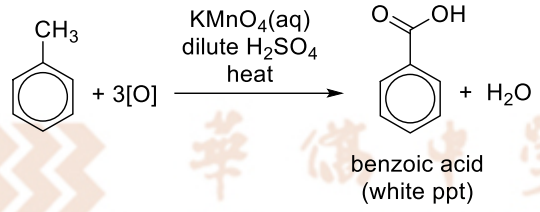
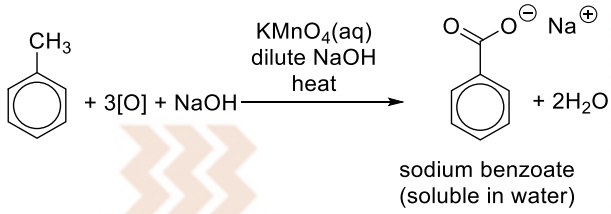
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(a) To prevent free radical substitution on the alkyl side-chain of methylbenzene which occurs in the presence of light or heat.

(b) Ans: A. $AlCl_3$ is present as Lewis acid catalyst for methylbenzene to undergo electrophilic substitution with chlorine. Under reflux conditions, the methyl side-chain may undergo free radical substitution with chlorine too.

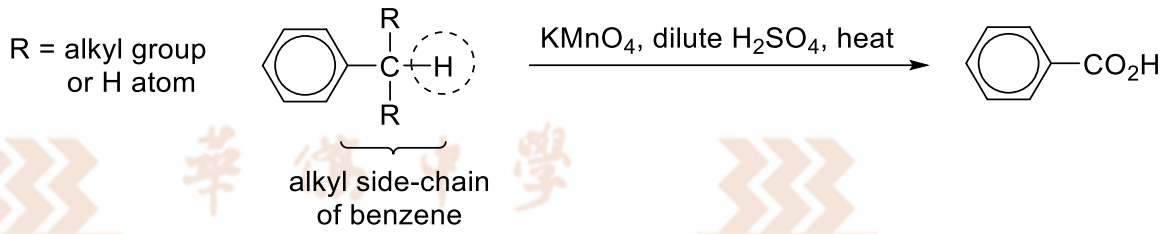
5.6.2 Side-Chain Oxidation

When particular alkylbenzenes are heated with aqueous potassium manganate(VII) in the presence of dilute H_2SO_4 or dilute NaOH, oxidation of the side chain occurs. Depending on whether acidic or alkaline conditions are used, the alkyl side-chain may be oxidised to benzoic acid or a benzoate salt.

	
Reagents and conditions: $KMnO_4$(aq), dilute H_2SO_4, heat	**Reagents and conditions:** $KMnO_4$(aq), dilute NaOH, heat
Observations: purple $KMnO_4$(aq) decolourises and white precipitate of benzoic acid is formed	**Observations:** purple $KMnO_4$(aq) decolourises and brown precipitate of manganese dioxide, MnO_2(s) is formed

Note: To write the balanced equation using [O], balance the H atoms using H_2O first, then O atoms using [O].

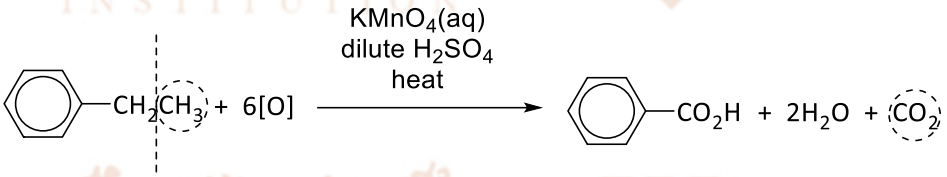
For an alkyl side-chain of benzene ring to undergo oxidation, the carbon atom just next to the benzene ring must possess at least one hydrogen atom as shown below.



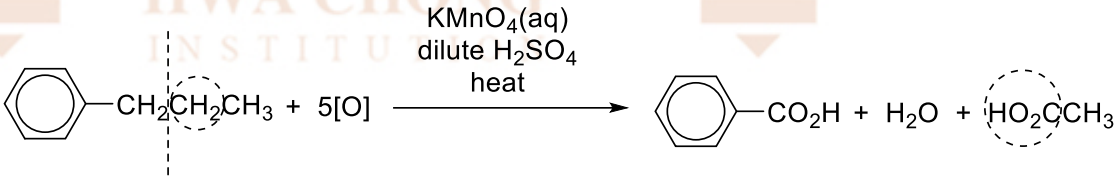
Regardless of the length of the alkyl side-chain, the carbon next to the benzene ring will be oxidised to $–CO_2H$ in acidic medium or $–CO_2^-$ in alkaline medium if it bears at least one H atom.

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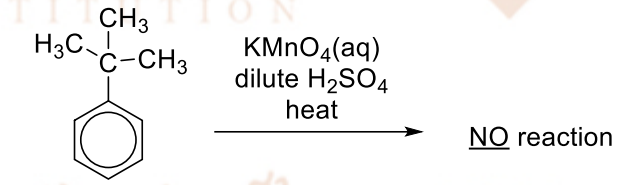
For example, ethylbenzene undergoes side-chain oxidation in acidic medium producing benzoic acid. The second carbon in the side-chain is oxidised to CO_2(g).



If the side-chain consists of a propyl group, the products after oxidation in acidic medium will consist of benzoic acid and the rest of the side-chain gets oxidised to a carboxylic acid.



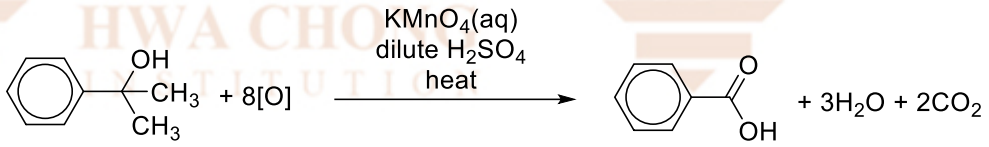
When there are three alkyl substituents attached to the C atom beside the benzene ring, the alkylbenzene will <u>not</u> undergo side-chain oxidation. For example, tert-butylbenzene does not react with hot acidified $KMnO_4$ as the C atom adjacent to the benzene ring does not possess any H atom.

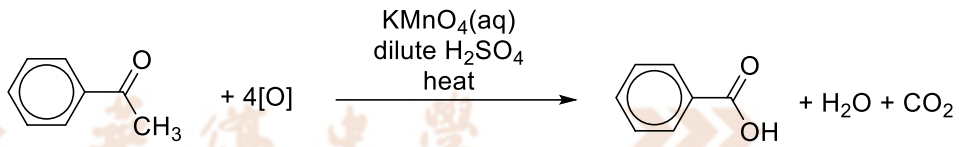


tert-butylbenzene

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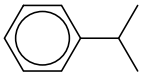
OTHER CASES OF SIDE-CHAIN OXIDATION (Application examples)

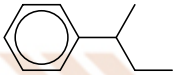


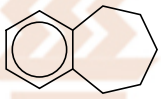


[2009/P2/4c and 2003/P3/7]

Exercise 5.4

1. Write a balanced equation for the side-chain oxidation of  in acidic medium.

2. Write a balanced equation for the side-chain oxidation of  in acidic medium.

3. Write a balanced equation for the side-chain oxidation of  in dilute NaOH.

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6 DISTINGUISHING TESTS

Bromine in tetrachloromethane can be used as a **distinguishing test to differentiate between alkenes and arenes**. For example: 1-methylcyclohexene and benzene.

Procedure for distinguishing test between 1-methylcyclohexene and benzene as example

1. Add bromine in tetrachloromethane **dropwise with shaking** to 1 cm^3 of each compound in separate test tubes.

Observations
Benzene: Br_2 in CCl_4 remains reddish-brown
1-methylcyclohexene: Reddish-brown Br_2 in CCl_4 decolourises

Note

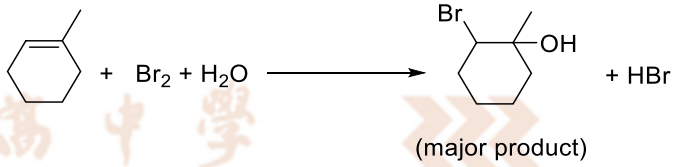
- Bromine in tetrachloromethane is usually employed instead of liquid bromine because it is easier to handle than liquid bromine which is a volatile liquid at rtp that constantly gives rise to toxic bromine gas.
- In the presence of light, both electrophilic addition and free radical substitution occur to 1-methylcyclohexene. However, free radical substitution is **not** usually used as a distinguishing test.

Aqueous bromine can also be used as a **distinguishing test to differentiate between alkenes and arenes**. For example: 1-methylcyclohexene and benzene.

Procedure for distinguishing test between 1-methylcyclohexene and benzene as example

1. Add aqueous bromine **dropwise with shaking** to 1 cm^3 of each compound in separate test tubes.

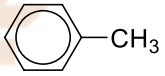
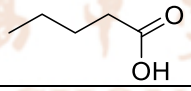
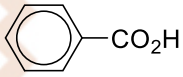
Observations
Benzene: Br_2(aq) remains yellow-orange
1-methylcyclohexene: Yellow-orange Br_2(aq) decolourises

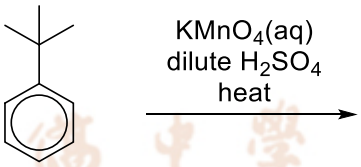
Equation: 

Note:
The difference between aqueous bromine and bromine in tetrachloromethane is that in the presence of light, free radical substitution does not occur with the use of aqueous bromine.

Heating with aqueous potassium manganate(VII) and dilute H_2SO_4 can be used as a **distinguishing test to differentiate between certain alkenes and certain alkylbenzenes, and between certain alkylbenzenes**. For example: hexene and methylbenzene, and methylbenzene and *tert*-butylbenzene.

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	Hexene	Methylbenzene
Structure		
Physical appearance at rtp	Colourless liquid	Colourless liquid
Reagents and conditions	$KMnO_4$(aq) Dilute H_2SO_4 Heat	$KMnO_4$(aq) Dilute H_2SO_4 Heat
Type of reaction	Oxidative cleavage	Side chain oxidation
Organic product		
Observations	Effervescence of CO_2(g) and purple $KMnO_4$(aq) decolourises No white ppt	Purple $KMnO_4$(aq) decolourises, and white ppt of benzoic acid No effervescence



tert-butylbenzene
(colourless liquid at rtp)

NO reaction

Observations: $KMnO_4$(aq) remains purple. No white ppt.

Procedure for distinguishing test between methylbenzene and *tert*-butylbenzene as example

1. Add 5 drops of $KMnO_4$(aq) to 1 cm^3 of dilute H_2SO_4 in a test tube.
2. To 1 cm^3 of each compound in separate test tubes, add 2–3 drops of the $KMnO_4$(aq)/H_2SO_4(aq) mixture **dropwise with shaking**. Warm this test tube in a water bath for a few minutes.

Observations
Methylbenzene: Purple $KMnO_4$(aq) decolourises, and white ppt of benzoic acid forms
tert-butylbenzene: $KMnO_4$(aq) remains purple. No white ppt.

Exercise 6.1
Suggest a simple chemical test to distinguish between each of the following pairs of compounds. State the reagents and conditions required, and expected observations for each compound.

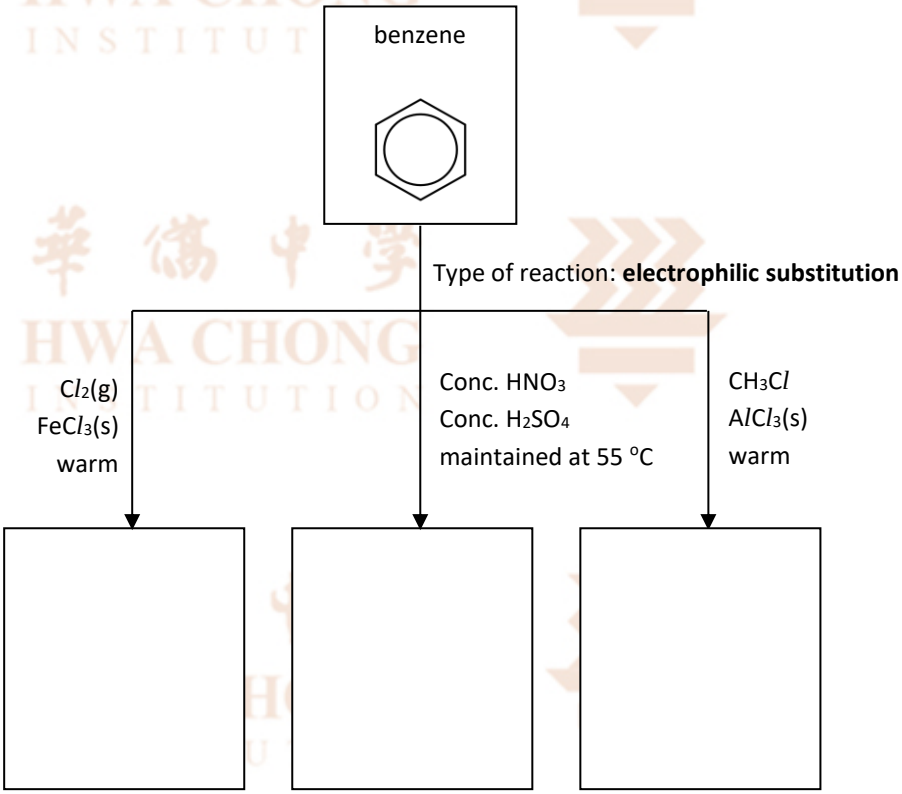
a) 1-methylcyclohexene and methylbenzene, both appears as colourless liquid

b) Benzene and methylbenzene, both appears as colourless liquid

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Summary of reactions of benzene

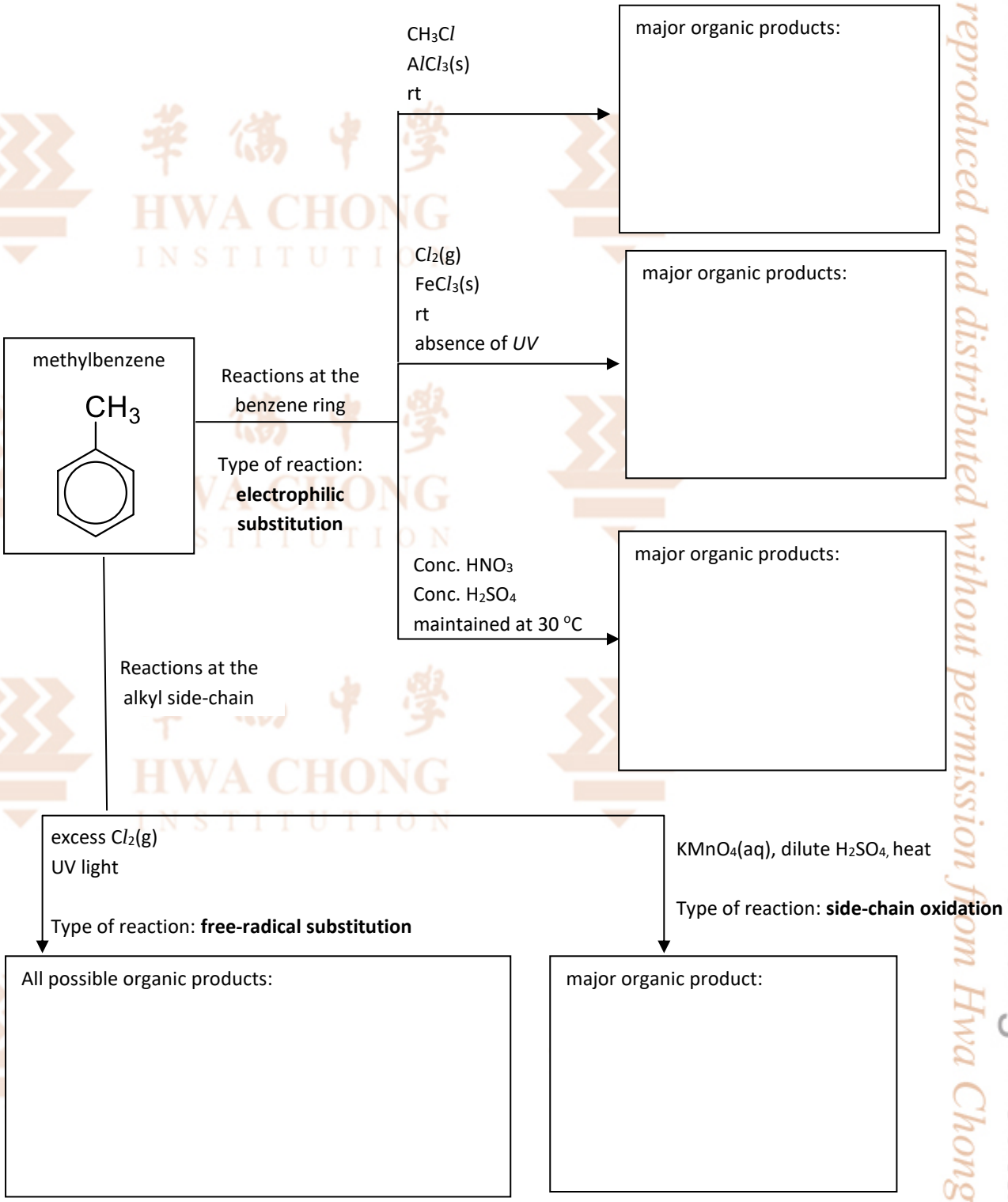
Fill in the boxes with the correct compounds.



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Summary of reactions of methylbenzene

Fill in the boxes with the correct compounds.



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Reasons for directing effects of substituents (Background Info)

2,4-directing groups

Activating groups and halogens are 2,4-directing. The reason can be explained by the stability of the carbocation intermediates. The fundamental principle is that **"A more stable carbocation is formed faster than a less stable one"**.

Consider the nitration of methylbenzene in the following example. NO_2^+ can be added to methylbenzene at 2-, 3- or 4-position to give three carbocation intermediates as shown in the following figure. The carbocation intermediates formed from 2- and 4-substitution are stabilised more than the intermediate formed from 3-substitution. This is because carbocation intermediates formed from 2- and 4-substitution each have resonance structures where the positive charge is on the methyl-substituted carbon. These carbocation intermediates are stable tertiary carbocations that are stabilised by the electron-donating methyl substituent by inductive effect (see the box). The carbocation intermediates formed from 2- and 4-substitution are therefore more stable and form faster, giving rise to higher product yields of 2-nitromethylbenzene and 4-nitromethylbenzene than 3-nitromethylbenzene.

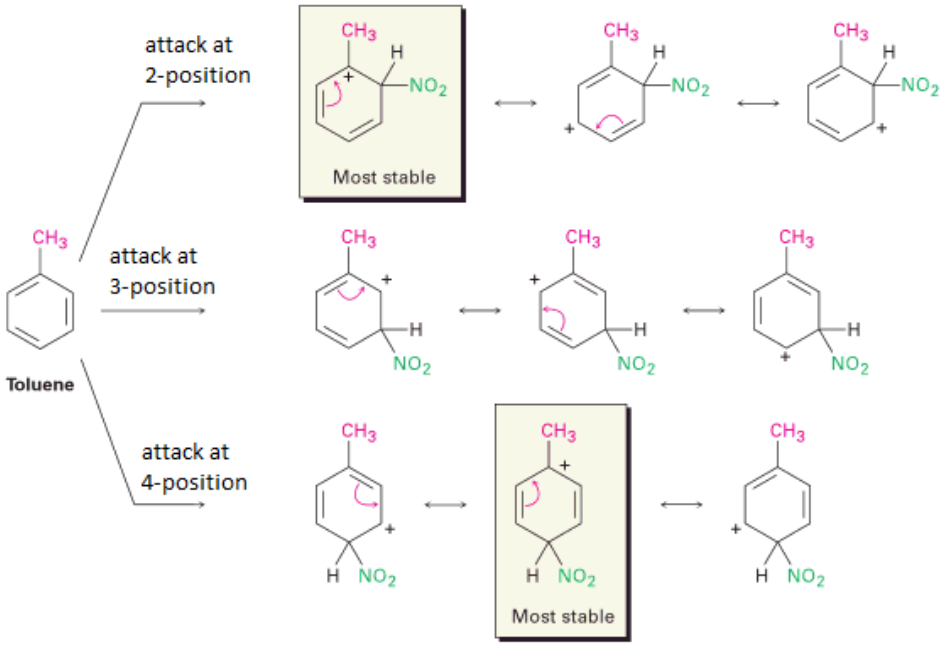


Figure 11. Carbocation intermediates in the nitration of methylbenzene. Note: It is more convenient to use one of the resonance structures of toluene for illustration.

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Consider the nitration of phenol in the following example. The carbocation intermediates formed from 2- and 4-substitution are more stable than the intermediate formed from 3-substitution. This is because carbocation intermediates formed from 2- and 4-substitution each have resonance structures where the positive charge is dispersed by the OH substituent via delocalisation of lone pair of electrons from O atom.

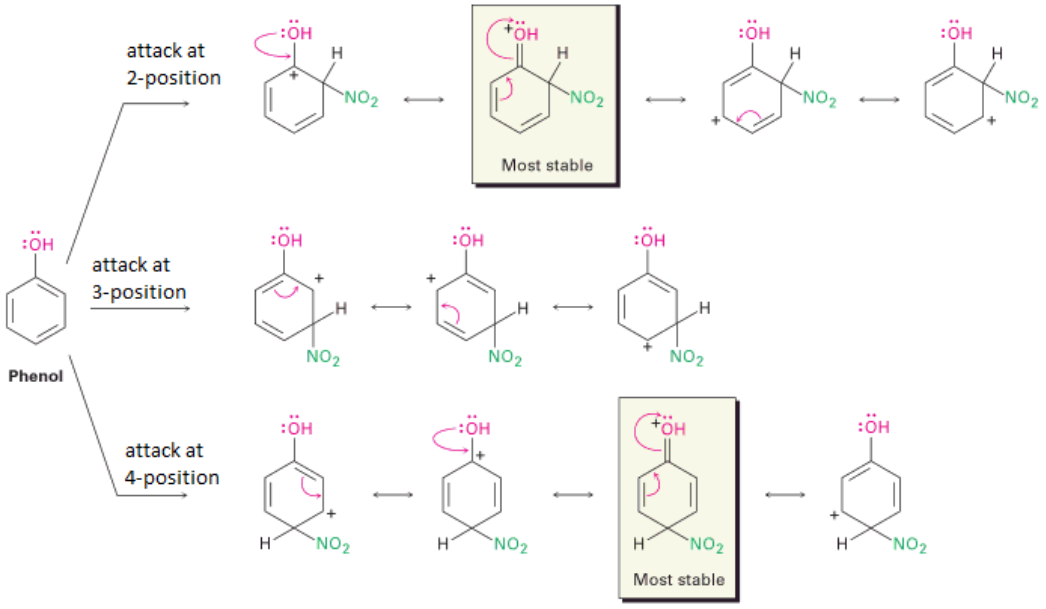


Figure 12. Carbocation intermediates in the nitration of phenol. Note: It is more convenient to use one of the resonance structures of phenol for illustration.

Consider the nitration of chlorobenzene in the following example. The carbocation intermediates formed from 2- and 4-substitution are more stabilised than the intermediate formed from 3-substitution. This is because carbocation intermediates formed from 2- and 4-substitution each have resonance structures where the positive charge is dispersed by the C*l* substituent via delocalisation of lone pair of electrons from C*l* atom.

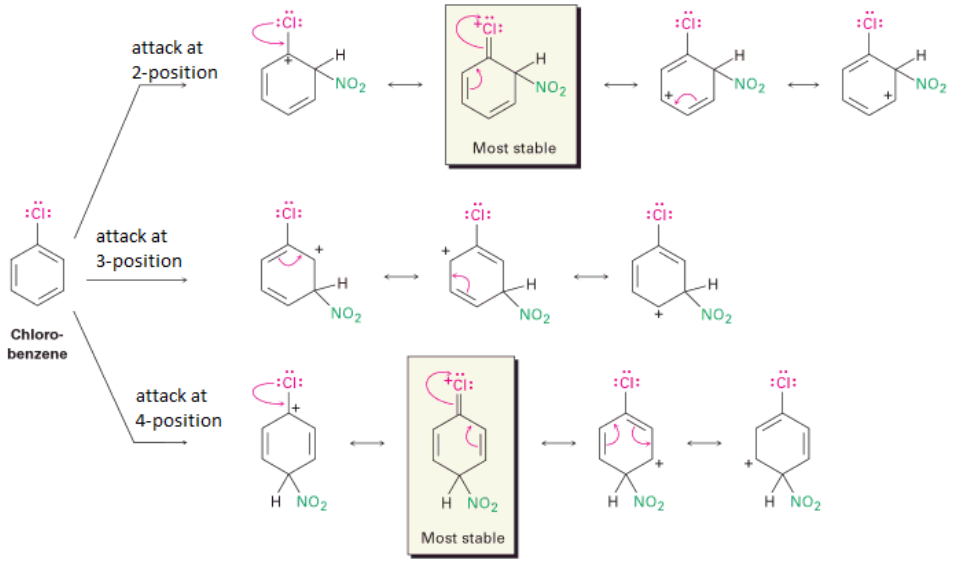


Figure 13. Carbocation intermediates in the nitration of chlorobenzene. Note: It is more convenient to use one of the resonance structures of chlorobenzene for illustration.

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3-directing groups

Deactivating groups (with the exception of halogens) are 3-directing. Consider the nitration of benzaldehyde in the following example. The carbocation intermediates formed from 3-substitution is more stable than the intermediate formed from 2- and 4-substitution. This is because carbocation intermediates formed from 2- and 4-substitution each have resonance structures where the positive charge is on the carbon bearing the deactivating group. These carbocation intermediates will be destabilised by the electron-withdrawing deactivators by inductive effect and delocalisation. (See the box)

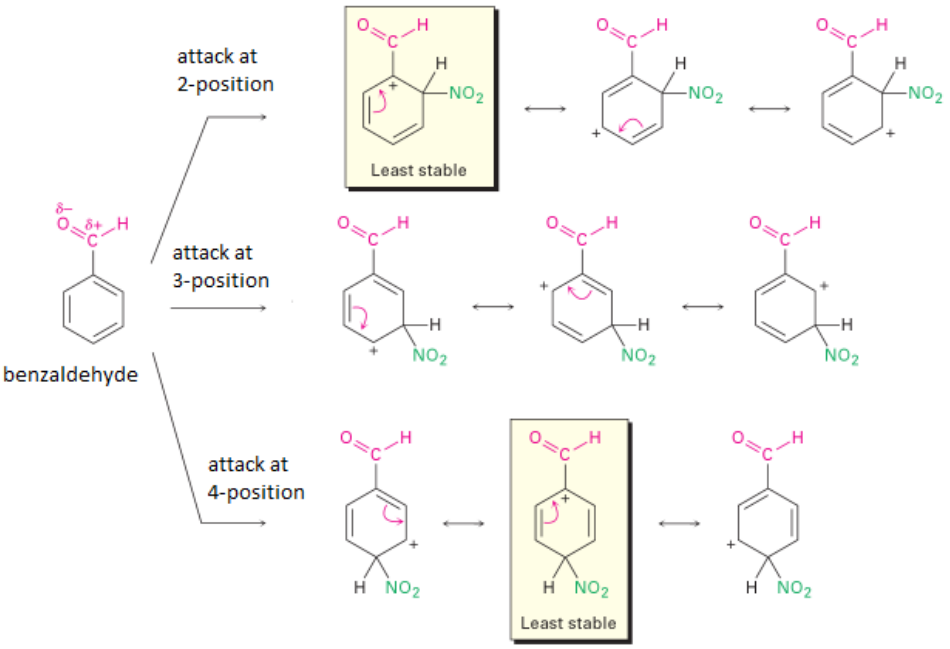


Figure 14. Carbocation intermediates in the nitration of benzaldehyde. Note: It is more convenient to use one of the resonance structures of benzaldehyde for illustration.

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13 Chemistry of the Aqueous Solution: Solubility Equilibria

GUIDING QUESTIONS

- What is a saturated solution?
- What is solubility and solubility product? How are they related?
- What and why does precipitation take place?

LEARNING OUTCOMES

Students should be able to:

10.2(a) show understanding of, and apply, the concept of solubility product, K_{sp}

10.2(b) calculate K_{sp} from concentrations and vice versa

10.2(c) discuss the effects on the solubility of ionic salts by the following:

(i) common ion effect

(ii) formation of complex ion, as exemplified by the reactions of halide ions with aqueous silver ions followed by aqueous ammonia

REFERENCES

1. Martin S. Silberberg, *Chemistry: The molecular nature of Matter and Change*. 3rd Edition, McGraw Hill, Chapter 18
2. Graham C. Hill and John S. Holman, *Chemistry in Context*, second Edition, ELBS, Chapter 22

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1 INTRODUCTION

LOOKING BACK

In Topic 7 Chemical Equilibrium, we learnt the concept of dynamic equilibrium and the Le Chatelier's principle. In this topic, we will apply this knowledge to the dynamic equilibrium that exists between an undissolved solute and its dissolved ions in solution, when the rate of precipitation and dissolution is equal, and use the Le Chatelier's principle to explain the factors that affect the solubility of a salt.

Equilibria involving ions in aqueous solution are important in industrial, analytical and biological processes. The dissolving and precipitating of ionic compounds in aqueous solution are phenomena that occur both within us and around us. For example, the dissolving of enamel on teeth in acidic solutions causes tooth decay; the precipitation of certain salts in our kidneys produces kidney stones; the precipitation of calcium carbonate from underground water forms stalactites and stalagmites inside caves. The principles and characteristics of these heterogeneous equilibria in aqueous solutions are very similar to those in other systems in chemical equilibria.

In this extension topic, we will explore the **solubility equilibria** of sparingly soluble ionic compounds.

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2 SOLUBILITY AND SATURATED SOLUTIONS

DEFINITION

Solubility of a salt is the number of moles (or mass) of solute (salt) that can be dissolved in **1 dm^3 of a given solvent (e.g. water)** to form a **saturated solution** at a given temperature.

For example, the solubility of NaC*l* in water at 25 °C is 357 g dm^{-3} or 6.102 mol dm^{-3}.
This is the maximum amount of NaC*l* that can be dissolved in water to give a saturated solution at that temperature.

- **Units of solubility:** mol dm^{-3} (molar solubility) or g dm^{-3}

Ionic compounds with low solubility are said to be **sparingly soluble**. The table below summarises some ionic compounds with very high solubility ('soluble') and very low solubility ('insoluble').

Ions	Solubility
NO_3^-	All nitrates are soluble
Cl^-, Br^-, I^-	All halides are soluble except Ag^+ and Pb^{2+}
SO_4^{2-}	All sulfates are soluble except Pb^{2+}, Ba^{2+} and Ca^{2+}
CO_3^{2-}	All carbonates are insoluble except Na^+, K^+ and NH_4^+
O^{2-}	All oxides are insoluble except Na^+ and K^+
OH^-	All hydroxides are insoluble except Na^+ and K^+

As a solute begins to dissolve in a solvent, the concentration of the solute particles in the solution increases. But this cannot occur infinitely, most solutes have a finite (limited) solubility in a particular solvent at a particular temperature. For the sparingly soluble salts, they reach equilibrium with relatively little solute dissolved.

When this upper limit is reached, the solution is said to be **saturated** at that temperature, and no more solute will dissolve in the saturated solution.

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3 SOLUBILITY EQUILIBRIA AND SOLUBILITY PRODUCT, K_{sp}

LO 10.2(a): show understanding of, and apply, the concept of solubility product, K_{sp}

When increasing quantities of a sparingly soluble ionic salt are added to water, a saturated solution will eventually be formed. Upon addition of excess solute, a dynamic **equilibrium** is set up, in which there is simultaneous dissolution of the excess undissolved solute and precipitation of the solute from the ions in the solution. These two processes take place at the same rate. Ions in the saturated solution are at equilibrium with the excess undissolved solute:

$$MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$$

Now, consider a mixture containing a saturated aqueous solution of silver chloride and some undissolved silver chloride. The system is at **equilibrium**:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

We can write:

$$K_c = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

However, [AgC*l*] represents the 'concentration' of a pure solid, and is therefore a constant.

Therefore,

$$K_c \times [AgCl] = [Ag^+][Cl^-]$$
$$\Rightarrow K_{sp} = [Ag^+][Cl^-]$$

The new constant, K_{sp}, is called the **solubility product** of AgC*l*.

Units of K_{sp} of AgC*l*: $mol^2\ dm^{-6}$

DEFINITION

Solubility product, K_{sp}, of a sparingly soluble salt is the product of the molar concentrations of the constituent ions in a **saturated solution**, raised to the appropriate powers **at a given temperature**.

Note: Appropriate power refers to the stoichiometric coefficient of the substance in the balanced equation for the reaction.

- The concept of solubility product is valid only for sparingly soluble salts. For soluble salts such as NaC*l*, $CuSO_4$ and $AgNO_3$, the use of the K_{sp} concept is inappropriate.

- As such, for sparingly soluble salts, the numerical value of K_{sp} is always very small, rarely exceeding 10^{-4} and can be as low as 10^{-40}.

- Like other equilibrium constants, the value of K_{sp} changes only with temperature.

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- Using the general formula A_xB_y for a sparingly soluble salt, the solubility equilibrium is:

$$A_xB_y(s) \rightleftharpoons xA^{y+}(aq) + yB^{x-}(aq)$$

and the general expression for solubility product is given by:

$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

where $[A^{y+}]$ and $[B^{x-}]$ are concentrations of ions(in mol dm^{-3}) in a saturated solution.

Exercise 3.1 (Worked Example)

Write an expression for the solubility product of each of the following salts and state its units:

(a) PbI_2 (b) Ag_2CO_3 (c) $Ca_3(PO_4)_2$

(a) $K_{sp} = [Pb^{2+}][I^-]^2$ mol^3 dm^{-9}

(b) $K_{sp} = [Ag^+]^2[CO_3^{2-}]$ mol^3 dm^{-9}

(c) $K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$ mol^5 dm^{-15}

Exercise 3.2

Write an expression for the solubility product of each of the following salts and state its units:

(a) $FeCO_3$ (b) SrF_2 (c) Hg_2SO_4

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An experimental investigation on the solubility product of $AgBrO_3$ at 16 °C

$$AgBrO_3(s) \rightleftharpoons Ag^+(aq) + BrO_3^-(aq)$$

Different initial volumes of $AgNO_3(aq)$ and $KBrO_3(aq)$, both of initial concentrations of 0.10 mol dm^{-3}, were added to 200 cm^3 of distilled water at 16 °C. The $[Ag^+]$ and $[BrO_3^-]$ at equilibrium were determined and shown in the table below:

Initial vol. of 0.10 mol dm^{-3} $AgNO_3$ / cm^3	Initial vol. of 0.10 mol dm^{-3} $KBrO_3$ / cm^3	$[Ag^+]$ at equilibrium / mol dm^{-3}	$[BrO_3^-]$ at equilibrium / mol dm^{-3}	$[Ag^+]_{eqm} \times [BrO_3^-]_{eqm}$ / $mol^2\ dm^{-6}$
40	10	0.0144	0.0024	3.45×10^{-5}
30	20	0.0081	0.0041	3.32×10^{-5}
25	25	0.0058	0.0058	3.36×10^{-5}
20	30	0.0042	0.0082	3.44×10^{-5}
10	40	0.0033	0.0102	3.37×10^{-5}

It is important to note that the product of the equilibrium concentrations of $Ag^+(aq)$ and $BrO_3^-(aq)$ in all 5 sets of experiments were almost constant.

$[Ag^+][BrO_3^-]$ = constant at a given temperature = 3.39×10^{-5} $mol^2\ dm^{-6}$ at 16 °C

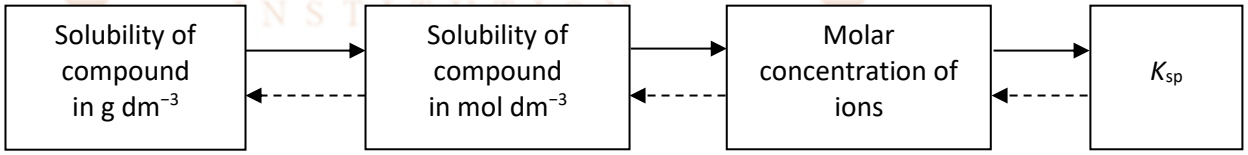
This value of $[Ag^+][BrO_3^-]$ is the solubility product of $AgBrO_3$ at 16 °C.

In other words, this value of K_{sp} of $AgBrO_3$ at 16 °C is independent of the amount of Ag^+ and BrO_3^- added to the solution, provided that a saturated solution is obtained. (i.e. some undissolved $AgBrO_3$ is in contact with the solution.)

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4 SOLUBILITY VS SOLUBILITY PRODUCT

LO 10.2(b): calculate K_{sp} from concentrations and vice versa



- Solubility and solubility product are different.
- K_{sp} can be calculated from the solubility of the salt and vice versa.

4.1 Calculation of K_{sp} from solubility

Exercise 4.1 (Worked Example)

The solubility of silver chloride is 1.46×10^{-3} g dm^{-3} at 18 °C. What is the solubility product of silver chloride at this temperature? (M_r of AgCl is 143.5)

Molar solubility of AgCl = $(1.46 \times 10^{-3}) \div 143.5 = 1.0174 \times 10^{-5}$ mol dm^{-3}

	AgCl (s)	⇌	Ag^+(aq)	+	Cl^- (aq)
$[\ ]_{eqm}$ /mol dm^{-3}			1.017×10^{-5}		1.017×10^{-5}

$K_{sp} = [Ag^+][Cl^-] = (1.017 \times 10^{-5})^2 = 1.04 \times 10^{-10}$ mol^2 dm^{-6}

4.2 Calculation of solubility from K_{sp}

Exercise 4.2

A suspension of solid $Mg(OH)_2$ in water is sold as "milk of magnesia" to alleviate minor stomach disorders by neutralising stomach acid. The $[OH^-]$ is too low to harm the mouth and throat, but the suspension dissolves in the acidic stomach juices.

Find the solubility of $Mg(OH)_2$ in mol dm^{-3} and in g dm^{-3}, given the numerical value of K_{sp} of $Mg(OH)_2$ is 6.30×10^{-10}. (M_r of $Mg(OH)_2$ is 58.3)

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Determining the solubility product of a sparingly soluble compound

Scenario:

To plan an experiment to determine a value of the solubility product K_{sp} of a sparingly soluble salt, and to investigate how the solubility will be affected by the presence of a common ion (see section 6.1).

Approach:

This experiment is in two parts: part 1, preparing the saturated solution(s), and part 2, determining the amount of dissolved solid (usually by titration).

Part 1: To prepare a saturated solution of the sparingly soluble compound, take into consideration the following characteristics of heterogeneous equilibria:

$$MX\,(s) \rightleftharpoons M^+(aq) + X^-(aq).$$

- To establish an equilibrium, the saturated solution must also contain excess (undissolved) solid. If you are not required to determine the mass of the dissolved solid gravimetrically, there is no need to weigh the amount of solid added accurately, so long as there is undissolved solid in the saturated solution. At this stage, this is called a suspension because it contains undissolved solid.
- Like all reversible reactions, it takes time to reach equilibrium. Therefore the suspension is shaken in stoppered bottles / conical flasks, or stirred in beakers with a glass rod, and then allowed to stand for a while (about 5 – 10 min), at the end of which, the excess solid settles to the bottom.
- Solubility and K_{sp} values are dependent on temperature, so the temperature of the suspension must be maintained (usually by a water bath or thermostat), and be recorded.
- To investigate the effect of a common ion (see section 6.1), you may be required to set up several (usually five) different saturated solutions with different starting concentrations of the common ion.

Part 2: To determine the amount of dissolved solid, a titration procedure is often carried out. For example, standard hydrochloric acid will be used to titrate the saturated solution if X^- is OH^-. However, before this titration is carried out, the suspension must be filtered to remove the undissolved solid. To prevent the introduction of water which will dilute the saturated solution, it is critical that the filtration is carried out using dry filter funnel, dry filter paper, and the filtrate is collected in a dry conical flask.

Generic procedure for determining solubility

1. Measure (volume) of (solvent) into a conical flask, using a measuring cylinder.
2. Add (solid) to the conical flask and swirl. Continue adding (solid) until no more can dissolve.
3. Stopper the flask and shake.
4. Leave the flask to stand in a water bath maintained at 25 °C for (a suitable time) .
5. Filter the suspension into a dry conical flask, using dry filter funnel and dry filter paper.
6. Pipette 25 cm^3 of the filtrate (saturated solution) into another conical flask.
7. (titration procedure).

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5 IONIC PRODUCT

DEFINITION

The **ionic product (IP)** of a **sparingly soluble** salt is the product of the molar concentrations of the constituent ions in the solution, raised to the appropriate powers.

For example $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

The ionic product of AgCl is therefore given by: IP of AgCl = $[Ag^+][Cl^-]$

- IP has the same mathematical expression as K_{sp}.
- IP can take on any value and is only numerically equal to K_{sp} in saturated solutions.
- Unlike K_{sp} which applies only in saturated solutions and at equilibrium, IP is applicable in unsaturated solutions as well as in theoretical terms at the instant of mixing (or the instant before precipitation occurs). Refer to the following exercises.

Exercise 5.1 (Worked Example)

1.00×10^{-3} mol dm^{-3} solution of Ca^{2+} is mixed with an equal volume of 1.00×10^{-3} mol dm^{-3} solution of SO_4^{2-} at 25.0 °C. No precipitation of $CaSO_4$ occurs. Calculate the ionic product of $CaSO_4$ in the resulting solution.

After mixing, the concentration of each ion is halved since final volume has doubled

$[Ca^{2+}] = [SO_4^{2-}] = (1.00 \times 10^{-3}) \div 2 = 5.00 \times 10^{-4}$ mol dm^{-3}

$IP = [Ca^{2+}][SO_4^{2-}] = (5.00 \times 10^{-4})^2 = 2.50 \times 10^{-7}$ mol^2 dm^{-6}

(note: K_{sp} value of $CaSO_4$ is 4.93×10^{-5})

5.1 Using K_{sp} and IP to predict the occurrence of precipitation

- The value of IP indicates the direction in which the solubility reaction will occur. The idea of IP and K_{sp} is analogous to that of Q_c and K_c.
- When IP < K_{sp}, the forward reaction (dissolution of the salt) occurs. When IP > K_{sp}, the backward reaction (precipitation of the salt) occurs. Relate this to what you learnt in Topic 7 Chemical Equilibria about Q_c and K_c.
- Hence, the value of IP allows us to predict if precipitation would occur when two solutions are mixed.
- When two solutions are mixed, precipitation may or may not occur depending on:
  (a) concentration of ions after mixing
  (b) K_{sp} of the salt present

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Consider the sparingly soluble salt $BaSO_4$, $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

$$IP = [Ba^{2+}][SO_4^{2-}]$$

Context	Adding solid $BaSO_4$ in small amounts into pure water.	Mixing a solution of $Ba^{2+}(aq)$ and a solution of $SO_4^{2-}(aq)$
IP vs K_{sp}	When does the solution become saturated?	Will there be precipitation?
IP < K_{sp} Forward reaction occurs.	The solution is **not** saturated. $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$ More $BaSO_4$ can dissolve in the solution until IP = K_{sp}.	**No** precipitation occurs.
IP = K_{sp} At equilibrium	The solution is saturated. No more $BaSO_4$ can dissolve. The solution contains the **maximum** amount of Ba^{2+} and SO_4^{2-}. Upon further addition of solid, IP remains equal to K_{sp}. Undissolved solid is present in equilibrium with the saturated solution.	The **first trace** of precipitate just **appears**. (or is just about to appear)
IP > K_{sp} Backward reaction occurs.		Precipitation of $BaSO_4$ **occurs**. $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$ Equilibrium shifts to the left, forming the precipitate <u>until</u> IP = K_{sp}.

Exercise 5.2 (Worked Example)

Will a precipitate form when 0.100 dm^3 of 3.00×10^{-3} mol dm^{-3} $Pb(NO_3)_2(aq)$ is added to 0.400 dm^3 of 5.00×10^{-3} mol dm^{-3} $Na_2SO_4(aq)$? (numerical value of K_{sp} of $PbSO_4$ is 1.60×10^{-8})

The insoluble salt that may be produced is $PbSO_4$.

$[Pb^{2+}] = 3.00 \times 10^{-3} \times (0.1 \div 0.5) = 6.00 \times 10^{-4}$ mol dm^{-3}

$[SO_4^{2-}] = 5.00 \times 10^{-3} \times (0.4 \div 0.5) = 4.00 \times 10^{-3}$ mol dm^{-3}

Ionic Product of $PbSO_4$ $= [Pb^{2+}][SO_4^{2-}] = (6.00 \times 10^{-4})(4.00 \times 10^{-3})$

$= 2.40 \times 10^{-6}$ mol^2 $dm^{-6} > 1.60 \times 10^{-8}$ mol^2 dm^{-6}

Since IP > K_{sp}, precipitation occurs and white precipitate of $PbSO_4$ forms.

Exercise 5.3

$Ca(NO_3)_2(s)$ is added to a 2.00×10^{-4} mol dm^{-3} solution of $MgSO_4$. What is the minimum $[Ca^{2+}]$ before a precipitate of $CaSO_4$ can be formed? (numerical value of K_{sp} of $CaSO_4$ is 2.40×10^{-5})

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5.2 Selective Precipitation of Ions

- Selective precipitation is the separation of ions in an aqueous solution by using a reagent that forms a precipitate with one or a few of the other ions but not all.

- Ions can be separated from each other based on the different solubilities of their salts.

Exercise 5.4

In a solution, $[Ag^+] = 1.00 \times 10^{-2}$ mol dm^{-3} and $[Pb^{2+}] = 2.00 \times 10^{-2}$ mol dm^{-3}. NaCl(s) is added to this solution.

(numerical value of K_{sp} of AgCl is 1.80×10^{-10}, numerical value of K_{sp} of $PbCl_2$ is 1.60×10^{-5})

(i) What is the minimum concentration of Cl^- necessary for each salt to be precipitated?

(ii) Which salt precipitates first?

(iii) How can Ag^+ be separated from Pb^{2+}? Find the % of Ag^+ left in the solution. Is the separation effective?

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6 FACTORS AFFECTING SOLUBILITY

6.1 Common Ion Effect

LO 10.2(c)(i): discuss the common ion effect on the solubility of ionic salts

Consider a mixture of solid calcium fluoride and its aqueous ions in a saturated solution:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\ F^-(aq)$$

If a water-soluble solute containing the **common ion** Ca^{2+} or F^- is added, e.g. adding $CaCl_2$(aq) or NaF(aq), by Le Chatelier's Principle, the position of equilibrium will shift to the left to decrease $[Ca^{2+}]$ or $[F^-]$. Less CaF_2 will dissolve, reducing the solubility of CaF_2.

Exercise 6.1

The numerical value of K_{sp} of AgCl is 2.00×10^{-10} at 25 °C.

(i) What is the solubility of AgCl?

(ii) Calculate the solubility of AgCl in 0.100 mol dm^3 NaCl (aq).

Comments on the data:

- When a saturated solution is obtained by dissolving the pure salt in water, the concentrations of the ions are in the ratio determined by the stoichiometry of the salt.
- Solubility of AgCl decreases in the presence of Cl^-, the common ion (2.00×10^{-9} mol dm^{-3} in (ii) < 1.40×10^{-5} mol dm^{-3} in (i)). This is known as the **common ion effect**.
- In other words, the solubility of a sparingly soluble salt **decreases** in the presence of a second solute that contains a common ion.

6.2 Formation of complex ion:

LO 10.2(c)(ii): discuss the effects on the solubility of ionic salts by formation of complex ions, as exemplified by the reactions of halide ions with aqueous silver ions followed by aqueous ammonia

Some metal ions can accept electron pairs from neutral molecules or anions to form **complex ions**.

Example 1:

When NaOH(aq) is added to a solution containing Al^{3+}, a white precipitate of $Al(OH)_3$ is formed. This precipitate dissolves in excess NaOH to form the complex ion $[Al(OH)_4]^-$. Such complex ions are soluble in water.

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Explanation:
Initially, when NaOH(aq) is added to a solution containing Al^{3+}, since K_{sp} of $Al(OH)_3$ is very low, IP easily exceeds K_{sp}.

Precipitate starts forming when IP = K_{sp} and equilibrium exists between some $Al(OH)_3$(s) and its ions.

$$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq) \quad \text{----------(1)}$$

In excess NaOH, the complex ions $[Al(OH)_4]^-$ are formed.

$$Al^{3+}(aq) + 4OH^-(aq) \rightleftharpoons [Al(OH)_4]^-(aq) \text{ ----------(2)}$$

- Formation of the complex ions removes Al^{3+} from the solution, hence $[Al^{3+}]$ decreases.
- This shifts the position of equilibrium in (1) to the right to produce more Al^{3+}, and the white precipitate of $Al(OH)_3$ dissolves.
- Complex ion formation **increases** the solubility of a sparingly soluble salt.

Example 2:
When $AgNO_3$(aq) is added to a solution containing halide ions, (X^-), silver halide (other than silver fluoride), is precipitated. When this reaction is followed up by adding NH_3(aq), AgCl dissolves in both dilute and concentrated NH_3, AgBr does not dissolve in dilute aqueous NH_3, but dissolves in concentrated NH_3, while AgI does not dissolve in both dilute and concentrated NH_3.

The table below summarises the reaction of the halide ions with aqueous silver nitrate and the subsequent solubility of the silver halides in dilute and concentrated ammonia.

Halide ion		F^- (aq)	Cl^- (aq)	Br^- (aq)	I^- (aq)
Reaction with $AgNO_3$ (aq)		No ppt	White ppt	Cream ppt	Yellow ppt
Solubility of AgX	**(i) in dilute NH_3**	–	Soluble	Partially soluble	Insoluble
	(ii) in conc. NH_3	–	Soluble	Soluble	Insoluble
K_{sp} of AgX/ mol^2 dm^{-6}		–	1.80×10^{-10}	5.40×10^{-13}	8.50×10^{-17}

Explanation:

Initially, when $AgNO_3$(aq) is added to a solution containing halide ion (X^-), since the numerical values of the K_{sp} of AgX are very low, IP easily exceeds K_{sp}, hence AgX is formed.

Precipitates starts forming and equilibrium exists between the AgX and its ions.

$$AgX\ (s) \rightleftharpoons Ag^+\ (aq) + X^-\ (aq) \quad \text{---------- (1)}$$

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The subsequent addition of ammonia results in the formation of the stable diammine silver(I) complex, $[Ag(NH_3)_2]^+$.

$$Ag^+ (aq) + 2NH_3 (aq) \rightleftharpoons [Ag(NH_3)_2]^+ (aq) \text{ --------- (2)}$$

Addition of NH_3 shifts the position of equilibrium (2) to the right, causing $[Ag^+]$ to decrease (and the value of ionic product, $[Ag^+][X^-]$, to decrease). The decrease in $[Ag^+]$ causes the position of equilibrium (1) to shift to the right, hence **increasing** the solubility of AgX. The solubility of the silver halides in ammonia depends on the K_{sp} of the silver halides. For the AgX solid to dissolve completely in ammonia, the ionic product must decrease to $\leq K_{sp}$.

The K_{sp} values of silver halides decrease in the order: AgC*l* > AgBr > AgI.

For AgC*l*, when dilute NH_3 is added, the precipitate **dissolves completely** because the addition of dilute NH_3 is sufficient to lower $[Ag^+]$ such that the ionic product becomes **smaller** than K_{sp} of AgC*l*.

For AgBr, K_{sp} is lower, so the addition of dilute NH_3 is not sufficient to lower $[Ag^+]$ till the ionic product becomes smaller than K_{sp} of AgBr. Hence, AgBr **does not dissolve completely** in dilute NH_3. However, when **concentrated** NH_3 is used, it will sufficiently lower $[Ag^+]$ such that the ionic product becomes **smaller** than K_{sp} and the precipitate **dissolves completely**.
For AgI, the value of K_{sp} is extremely low, thus the addition of either dilute or concentrated NH_3 is not sufficient to lower $[Ag^+]$ such that the ionic product becomes smaller than K_{sp} of AgI. Hence AgI precipitate remains when dilute or concentrated NH_3 is added.

Exercise 6.2 (Worked Example)
Explain why the solubility of PbC*l*$_2$ decreases in dilute HC*l* but increases in concentrated HC*l*.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq) \text{ ----------(1)}$$

In dilute HC*l*, the common ion $[Cl^-]$ causes the position of equilibrium in (1) to shift to the left to lower $[Cl^-]$, hence less PbC*l*$_2$ dissolves.

$$Pb^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [PbCl_4]^{2-}(aq) \text{ ----------(2)}$$

In concentrated HC*l*, Pb^{2+} will form a water soluble complex, $[PbCl_4]^{2-}$, with excess Cl^-.
Formation of the complex ion removes Pb^{2+} from solution.

The position of equilibrium in (1) shifts to the right to produce more Pb^{2+}, and PbC*l*$_2$ dissolves (i.e. solubility of PbC*l*$_2$ increases).

6.3 Effects of pH

Changes to the pH of a solution may affect the solubility of a sparingly soluble salt **containing either Brønsted acids or bases**. A Brønsted acid is a proton donor whereas a Brønsted base is a proton acceptor. The Brønsted acid-base theory was introduced briefly in Topic 4 Reactions & Stoichiometry.

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DEFINITIONS

The pH of a solution is the negative logarithm to base ten of the molar concentration of hydrogen ion, i.e. $pH = -\lg [H^+]$

The pOH of a solution is the negative logarithm to base ten of the molar concentration of hydroxide ion, i.e. $pOH = -\lg [OH^-]$

i.e. $[H^+] = 10^{-pH}$ and $[OH^-] = 10^{-pOH}$

Also, at 25 °C, pH + pOH = 14 (refer to Topic 14 Acid-base Equilibria).
For example, a sparingly soluble salt, magnesium hydroxide, $Mg(OH)_2$, dissolves in aqueous solution according to the equation below.

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

Addition of a strong Brønsted acid like HC*l* (which will decrease pH) will neutralise the OH^- to form water. The removal of OH^- lowers $[OH^-]$. According to the Le Chatelier's Principle, the position of the above equilibrium will shift to the right to offset the decreased $[OH^-]$, more $Mg(OH)_2$ dissolves.

Thus, the solubility of $Mg(OH)_2$ increases when the pH of the solution decreases.
Therefore, the solubility of a sparingly soluble salt containing **basic** anions **increases** as $[H^+]$ **increases** (i.e. pH **decreases**).

Exercise 6.3

A saturated solution of $Mg(OH)_2$ has a pH of 10.52.
(The numerical value of K_{sp} of $Mg(OH)_2$ is 1.80×10^{-11})

(i) Calculate the solubility of $Mg(OH)_2$ in this solution. (1.64×10^{-4} mol dm^{-3})

(ii) Calculate the solubility of $Mg(OH)_2$ if the saturated solution in (i) is mixed with a solution maintained (i.e. buffered) at pH 9.00. (0.180 mol dm^{-3})

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7 APPLICATION AND RELEVANCE TO REAL-LIFE CONTEXTS

The following examples illustrate the relevance of the K_{sp} concept to a range of phenomena and contexts.

- Daily life
  In regions with hard water (that contains calcium and magnesium ions), mineral deposits can sometimes be seen on cooking dishes or in bathtubs. These deposits are caused by the precipitates of calcium/magnesium ions in the hard water. These deposits can make hard water unsuitable for many uses. Thus, variety of ways can be used to reduce the hardness of water, for example, by the addition of sodium carbonate.

- Health
  Kidney stones are a biological example of how the concept of solubility is experienced in our lives. A kidney stone is usually made up of a salt of calcium, commonly ethanedioate or phosphate. Thus people who are prone to kidney stones have to limit or avoid eating foods with high ethanedioate content (e.g. spinach, peanuts and sweet potatoes). A possible approach to treating kidney stones is to drink a large amount of water so as to flush out the kidney stones from the urinary tract.

Looking ahead:
The concepts learnt about the dynamic equilibrium of a saturated solution will be useful when we explore the chemistry of inorganic compounds in further topics (such as in Inorganic Qualitative Analysis experiments and Topic 22 Chemistry of the Transition Elements). For example, the Le Chatelier's principle, common ion effect and the formation of metal complex ions will be applied to explain the precipitation and dissolution of metal salts in inorganic reactions.

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14 Chemistry of Aqueous Solutions: Acid-Base Equilibria

GUIDING QUESTIONS:

- What is a strong or weak acid/base?
- How can the strength of acids and bases be represented and determined?
- What is the relationship between concentration of acid (base), pH (pOH) and strength of acid (base)?
- What are buffers? How do buffers work? How can the pH of buffers be determined?
- What are the changes in pH during acid-base titrations? How can these pH changes be explained?

LEARNING OUTCOMES

Students should be able to:

4(b) show understanding of, and apply the Brønsted-Lowry theory of acids and bases, including the concept of conjugate acids and conjugate bases (Refer to Topic 4 Reactions and Stoichiometry for the Brønsted-Lowry theory of acids and bases)

5(e)(v) describe and explain the reactions of the chlorides with water (for NaCl; $MgCl_2$; $AlCl_3$; $SiCl_4$; PCl_5) (Refer to Topic 21 Chemical Periodicity for the reactions of NaCl, $MgCl_2$, $SiCl_4$, PCl_5 with water)

10.1(a) explain qualitatively the differences in behaviour between strong and weak acids and bases in terms of the extent of dissociation

10.1(b) explain the terms pH; K_a; pK_a; K_b; pK_b; K_w and apply them in calculations, including the relationship $K_w = K_aK_b$

10.1(c) calculate $[H^+(aq)]$ and pH values for strong acids, weak monobasic (monoprotic) acids, strong bases, and weak monoacidic bases [Calculations involving weak acids/bases will **not** require solving of quadratic equations]

10.1(d) describe the changes in pH during acid-base titrations and explain these changes in terms of the strengths of the acids and bases

10.1(e) explain the choice of suitable indicators for acid-base titrations, given appropriate data

10.1(f) **(i)** explain how buffer solutions control pH

(ii) describe and explain their uses, including the role of H_2CO_3/HCO_3^- in controlling pH in blood

10.1(g) calculate the pH of buffer solutions, given appropriate data

REFERENCES

1. Peter Cann & Peter Hughes, *Cambridge International AS and A Level Chemistry*, Hodder Education, Chapters 6 & 22
2. Martin S. Silberberg, *Chemistry – The Molecular Nature of Matter & Change*, McGraw Hill, Chapter 18 & 19

LOOKING BACK

In Topic 4 Reactions and Stoichiometry, we learnt to define acids and bases according to three models: Arrhenius Theory, Brønsted-Lowry Theory and Lewis Theory of acids and bases. In this topic, we shall use the Brønsted-Lowry Theory in our understanding of acids and bases and apply the concept of equilibrium learnt from Topic 7 Chemical Equilibria specifically to acid–base systems.

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1 INTRODUCTION

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. In this topic, we will examine equilibria involving acids and bases and study the pH of solutions containing strong acids and bases, weak acids and bases, salts and buffers.

Recall from Topic 4 Reactions and Stoichiometry that, according to the **Brønsted-Lowry Theory of acids and bases**:

- An acid is a proton-donor and a base is a proton-acceptor.
- An acid-base reaction therefore involves a transfer of a proton from an acid to a base.

1.1 Conjugate Acid-Base pair

LO 4(b): show understanding of, and apply the Brønsted-Lowry theory of acids and bases, including the concept of conjugate acids and conjugate bases

Consider the following acid-base reaction:

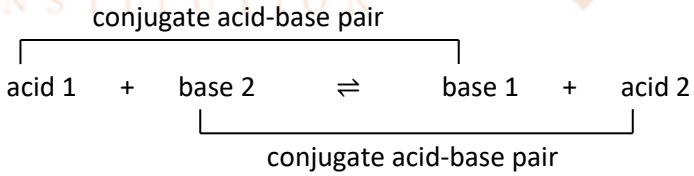
$$\underset{\text{acid}}{CH_3CO_2H} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{conjugate base}}{CH_3CO_2^-} + \underset{\text{conjugate acid}}{H_3O^+}$$

In the forward reaction:
CH_3CO_2H acts as a Brønsted acid, donating a proton to the Brønsted base, H_2O.

In the reverse reaction:
$CH_3CO_2^-$ acts as a Brønsted base, accepting a proton from the Brønsted acid, H_3O^+, to re-form the Brønsted acid, CH_3CO_2H.

- CH_3CO_2H and $CH_3CO_2^-$ form a conjugate acid-base pair;
- H_2O and H_3O^+ form another conjugate acid-base pair.

In general,



- **A conjugate acid-base pair constitutes two species which differ from each other by one proton.**
- An acid after donating a proton forms its conjugate base.
- A base after accepting a proton forms its conjugate acid.
- In any acid-base reaction, there are two conjugate acid-base pairs.

Exercise 1.1

Identify the conjugate acid-base pairs in each of the following reactions:

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

HNO_3 (acid) / NO_3^- (conjugate base) & NH_3 (base) / NH_4^+ (conjugate acid)

2. $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

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1.2 Strong and Weak Acids and Bases

LO 10.1(a): explain qualitatively the differences in behaviour between strong and weak acids and bases in terms of the extent of dissociation

A **strong Brønsted acid** is a **proton-donor** that **dissociates or ionises <u>completely</u>** in water to give H_3O^+. It donates a proton more readily compared to the H_3O^+ ion.

e.g. HCl + H_2O → Cl^- + H_3O^+
strong acid conjugate base

- The conjugate base of a strong acid has a very low tendency to accept a proton.
- The reverse reaction is negligible ∴ single–headed arrow (→).
- Other examples of strong acids: HNO_3, HBr, HI, $HClO_3$, $HClO_4$, H_2SO_4

A **weak Brønsted acid** is a **proton-donor** that **dissociates <u>partially</u>** in water to give H_3O^+. It donates a proton less readily compared to the H_3O^+ ion.

e.g. CH_3CO_2H + H_2O ⇌ $CH_3CO_2^-$ + H_3O^+
weak acid conjugate base

- The conjugate base of a weak acid ($CH_3CO_2^-$) has a tendency to accept a proton.
- CH_3CO_2H and $CH_3CO_2^-$ is a conjugate acid-base pair that differ by one proton.
- The reverse reaction occurs to some extent ∴ double–headed arrow (⇌).
- A mixture of mainly undissociated CH_3CO_2H molecules and the ions exists in solution.
- Other examples of weak acids: H_2SO_3, HNO_2, H_2CO_3, H_2S, HF, HCN, most organic acids

A **strong Brønsted base** is a **proton-acceptor** that **dissociates or ionises <u>completely</u>** in water to give OH^-.

e.g. $NaOH \rightarrow Na^+ + OH^-$

- Other examples of strong bases: KOH, $Ba(OH)_2$

A **weak Brønsted base** is a **proton-acceptor** that **dissociates or ionises <u>partially</u>** in water to give OH^-.

e.g. $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

- Other examples of weak bases: hydrazine N_2H_4, amines such as CH_3NH_2, $C_6H_5NH_2$

The <u>strength</u> of an acid (or base) is *different* from the <u>concentration</u> of the acid (or base).
Strength of an acid (or base) refers to the extent of its dissociation at equilibrium.
Concentration of an acid (or base) refers to the no. of moles of acid (or base) dissolved in 1 dm^3 of solution.

Exercise 1.2
Match each acid on the left with the correct description on the right.

0.001 mol dm^{-3} HNO_3	•	• concentrated but weak acid
4.0 mol dm^{-3} CH_3CO_2H	•	• dilute but strong acid
0.001 mol dm^{-3} $CH_3CH_2CO_2H$	•	• dilute and weak acid

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2 CALCULATIONS INVOLVING ACIDS AND BASES

LO 10.1(b)part: explain the terms pH; K_w and apply them in calculations

2.1 Definition of pH and pOH

The concentration of H^+ and OH^- in an aqueous solution is usually quite small. Hence it is more convenient to express the concentration of $H^+(aq)$ in terms of its negative logarithm to base 10.

$$\mathbf{pH = -lg\,[H^+(aq)]}$$

where symbol 'p' means '$-\log_{10}$'

Hence, $$\mathbf{[H^+(aq)] = 10^{-pH}}$$

E.g. for 0.01 mol dm^{-3} HC*l*, $[H^+(aq)] = 10^{-2}$ mol dm^{-3} and pH = 2.

Note:
pH is a measure of the (total) concentration of H^+ in a solution. It is not a measure of the strength of the acid unless the two acids being compared have the same initial concentration (see Section 2.8).

Similarly, the concentration of $OH^-(aq)$ is commonly expressed in terms of its negative logarithm to base 10.

$$\mathbf{pOH = -lg\,[OH^-(aq)]}$$

and $$\mathbf{[OH^-(aq)] = 10^{-pOH}}$$

E.g. for 0.01 mol dm^{-3} NaOH, $[OH^-(aq)] = 10^{-2}$ mol dm^{-3} and pOH = 2.

2.2 Ionic product of water, K_w

Pure water conducts electricity slightly, due to the very slight self-ionisation or autoionisation of water which produces trace concentrations of ions.

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

A simpler way of representing the equilibrium is:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The equilibrium constant, K_c, for the reaction is given by:

$$K_c = \frac{[H^+][OH^-]}{[H_2O]}$$

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$[H_2O]$ = 55.6 mol dm^{-3} (water has density 1.00 g cm^{-3}, so 1 dm^3 of water has mass of 1000 g. Since molar mass of water is 18.0 g mol^{-1}, therefore 1000 g (1 dm^3) of water contains 1000/18.0 = 55.6 mol of water.)

The extent of self-ionisation of water is very small compared to the concentration of water (55.6 mol dm^{-3}), hence $[H_2O]$ is almost constant.

Therefore, $K_c \times [H_2O] = [H^+][OH^-]$

or $\boxed{K_w = [H^+][OH^-]}$

where K_w is known as the **ionic product of water**. The value of K_w depends only on temperature. It is always a constant at constant temperature.

Taking –lg on both sides of equation:

$$-\lg K_w = (-\lg [H^+]) + (-\lg [OH^-])$$

$\boxed{pK_w = pH + pOH}$ * remember the symbol 'p' means '$-\log_{10}$'

Hence, we can determine the value of pH, given K_w value at the specified temperature and the pOH value, and vice versa.

2.3 Relationship between $[H^+(aq)]$, $[OH^-(aq)]$ and pH

In pure water as well as *any* aqueous solution, the following equilibrium exists:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

where K_w always = $[H^+][OH^-]$ and pK_w = pH + pOH.

When $[H^+(aq)] = [OH^-(aq)]$ ➔ *neutral* solution
$[H^+(aq)] > [OH^-(aq)]$ ➔ *acidic* solution
$[H^+(aq)] < [OH^-(aq)]$ ➔ *alkaline* solution

At **25°C,** $K_w = 1.00 \times 10^{-14}$ **mol^2 dm^{-6}** (value is given in the *Data Booklet*)

And so $pK_w = pH + pOH = 14$

Hence at 25° C, the pH of acidic, basic and neutral solutions can be calculated as follows:

Table 1. Summary of $[H^+]$, $[OH^-]$, pH and pOH of acidic, basic and neutral solution at 25 °C

Type of solution	$[H^+]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	pH	pOH
Neutral	$= 1.0 \times 10^{-7}$	$= 1.0 \times 10^{-7}$	= 7.00	= 7.00
Acidic	$> 1.0 \times 10^{-7}$	$< 1.0 \times 10^{-7}$	< 7.00	> 7.00
Basic	$< 1.0 \times 10^{-7}$	$> 1.0 \times 10^{-7}$	> 7.00	< 7.00

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Like other equilibrium constants, the **value of K_w depends *only* on <u>temperature</u>**:

Table 2. K_w values and $[H^+]$ of water at different temperatures

Temperature / °C	K_w / mol^2 dm^{-6}	$[H^+] = [OH^-] = \sqrt{K_w}$ / mol dm^{-3}
0	1.5×10^{-15}	3.9×10^{-8}
10	3.0×10^{-15}	5.5×10^{-8}
25	1.0×10^{-14}	1.0×10^{-7}
40	3.0×10^{-14}	1.7×10^{-7}
60	9.5×10^{-14}	3.1×10^{-7}

Exercise 2.1

With reference to the above data in Table 2, state whether the following statements are true or false.

(i) The ionic dissociation of water, $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$, is an endothermic process.

(ii) When water is heated, the concentration of $H^+(aq)$ increases.

(iii) When water is heated, the concentration of $OH^-(aq)$ increases.

(iv) In pure water, the concentration of $H^+(aq)$ is higher than that of $OH^-(aq)$ at 60 °C.

(v) Water remains a neutral liquid at 60 °C.

(vi) The pH of pure water at temperatures greater than 25 °C is greater than 7.

2.4 pH of Strong Acid / Strong base solutions

LO 10.1(c)part: calculate $[H^+(aq)]$ and pH values for strong acids, strong bases

Strong acids and strong bases are fully dissociated, hence

$[H^+]$ = [strong monobasic acid] and $[H^+] = 2 \times$ [strong dibasic acid]

Similarly, $[OH^-]$ = [strong monoacidic base] and $[OH^-] = 2 \times$ [strong diacidic base]

<u>Note</u>: If the concentration of the acid or base is 10^{-7} mol dm^{-3} or lower, the contribution of H^+ or OH^- from auto-ionisation of H_2O becomes significant. We should then take into consideration the contribution of H^+ or OH^- from auto-ionisation of H_2O in the calculation (See Exercise 2.2 Q3).

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Exercise 2.2 (Worked Example)

1. An aqueous solution contains 1.0×10^{-5} mol dm^{-3} of hydrogen iodide (a strong acid). Calculate the concentration of H^+ in mol dm^{-3}, and hence the pH of this solution at 25 °C.

$HI(aq) \rightarrow H^+(aq) + I^-(aq)$
$[H^+] = [HI] = \underline{1.00 \times 10^{-5} \text{ mol dm}^{-3}}$
$pH = -\lg [H^+] = -\lg (1.0 \times 10^{-5}) = \underline{5.00}$

2. An aqueous solution contains 0.010 mol dm^{-3} of $Ba(OH)_2$ (a strong base) and 0.050 mol dm^{-3} of KOH. Calculate the pH of this solution at 25 °C.

$Ba(OH)_2(aq) \rightarrow Ba^{2+}(aq) + 2OH^-(aq)$
$KOH(aq) \rightarrow K^+(aq) + OH^-(aq)$ Note: KOH is also a strong base
Total $[OH^-] = 2 \times 0.010 + 0.050 = 0.070$ mol dm^{-3}
$pOH = -\lg [OH^-] = 1.15$
$pH = 14 - pOH = \underline{12.8}$

3. An aqueous solution contains 1×10^{-8} mol dm^{-3} of HNO_3. Calculate the pH of this solution.

$HNO_3 (aq) \rightarrow H^+ (aq) + NO_3^- (aq)$
$H_2O (l) \rightleftharpoons H^+ (aq) + OH^- (aq)$ (auto–ionisation of water)
Hence, $[H^+] \approx 10^{-8} + 10^{-7} = 1.1 \times 10^{-7}$ mol dm^{-3}
$pH = -\lg (1.1 \times 10^{-7}) = \underline{6.96}$

Note:
$[H^+]$ from water = 10^{-7} mol dm^{-3} is an approximation.
As the concentration of the acid is lower than 10^{-7} mol dm^{-3}, the contribution of H^+ from auto-ionisation of H_2O becomes significant.

Exercise 2.3

1. An aqueous solution contains 0.10 mol dm^{-3} of calcium hydroxide (a strong base). Calculate the concentration of OH^- in mol dm^{-3}, and hence the pH of this solution at 25 °C.

{$[OH^-] = 0.20$ mol dm^{-3}, pH = 13.3}

2. Solution *X* contains HC*l*, it has pH 2.2. Solution *Y* has the same volume as solution *X*. Solution Y contains HNO_3 and has pH 1.6. The two solutions are mixed. Calculate the pH of the resulting solution.

[1.80]

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2.5 Acid Dissociation Constant (K_a) and Base Dissociation constant (K_b)

LO 10.1(b)part: explain the terms K_a; pK_a; K_b; pK_b and apply them in calculations, including the relationship $K_w = K_aK_b$

2.5.1 Acid Dissociation Constant (K_a)

A weak acid HA dissociates **partially** in water to give H_3O^+.

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

In dilute aqueous solution, $[H_2O]$ is almost constant (at 55.6 mol dm^{-3}). The equilibrium constant may be written as:

$$\boldsymbol{K_a} = \frac{\boldsymbol{[H^+]_{eqm}[A^-]_{eqm}}}{\boldsymbol{[HA]_{eqm}}} \quad \text{mol dm}^{-3}$$

and $\boldsymbol{pK_a = -\lg K_a}$

- For strong acids, e.g. HC*l*, K_a is very large and not used.
- The value of K_a indicates the **extent** to which the weak acid dissociates in water at the specified temperature.
- To compare the strength of two weak acids, compare their K_a values.
- At the same temperature, **larger K_a (smaller pK_a) ⇒ stronger acid**.
- Like other equilibrium constants, the value of K_a depends <u>only</u> on temperature.

Table 3. Some weak acids and their K_a values at 25 °C

Acid dissociation equilibrium reaction	K_a /mol dm^{-3}
$CH_3CO_2H + H_2O \rightleftharpoons CH_3CO_2^- + H_3O^+$	1.8×10^{-5}
$HCO_2H + H_2O \rightleftharpoons HCO_2^- + H_3O^+$	1.8×10^{-4}
$C_6H_5CO_2H + H_2O \rightleftharpoons C_6H_5CO_2^- + H_3O^+$	6.5×10^{-5}
$HCN + H_2O \rightleftharpoons CN^- + H_3O^+$	4.9×10^{-10}

2.5.2 Base Dissociation Constant (K_b)

A weak base dissociates **partially** in water to give OH^-.

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

In dilute aqueous solution, $[H_2O]$ is almost constant (at 55.6 mol dm^{-3}). The equilibrium constant may be written as:

$$\boldsymbol{K_b} = \frac{\boldsymbol{[BH^+]_{eqm}[OH^-]_{eqm}}}{\boldsymbol{[B]_{eqm}}} \quad \text{mol dm}^{-3}$$

and $\boldsymbol{pK_b = -\lg K_b}$

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- For strong bases, e.g. NaOH, K_b is very large and not used.
- The value of K_b indicates the **extent** to which the weak base dissociates in water at the specified temperature.
- To compare the strength of two weak bases, compare their K_b values.
- At the same temperature, **larger K_b (smaller pK_b) ⇒ stronger base**.
- The value of K_b depends <u>only</u> on temperature.

Table 4. Some weak bases and their K_b values at 25 °C

Base Dissociation equilibrium reaction	K_b /mol dm^{-3}
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	4.4×10^{-4}
$CH_3CO_2^- + H_2O \rightleftharpoons CH_3CO_2H + OH^-$	5.6×10^{-10}

- In aqueous solution, the two large classes of weak bases are nitrogen-containing molecules such as NH_3 and amines (e.g. $CH_3CH_2NH_2$), and the anions or conjugate bases of weak acids (e.g. ethanoate ion, $CH_3CO_2^-$).

2.5.3 Relationship between K_a, K_b and K_w for conjugate acid-base pairs

Consider the weak acid, CH_3CO_2H, and its conjugate base, $CH_3CO_2^-$.

$CH_3CO_2H \rightleftharpoons CH_3CO_2^- + H^+$

$$K_a = \frac{[CH_3CO_2^-][H^+]}{[CH_3CO_2H]} \quad \text{——————————} (1)$$

$CH_3CO_2^- + H_2O \rightleftharpoons CH_3CO_2H + OH^-$

$$K_b = \frac{[CH_3CO_2H][OH^-]}{[CH_3CO_2^-]} \quad \text{——————————} (2)$$

(1) × (2), $K_a \times K_b = [H^+]\,[OH^-] = K_w$

Therefore, **for any conjugate acid–base pair,**

$$\boxed{K_a \times K_b = K_w}$$

Taking –lg on both sides of equation:

$$(-\lg K_a) + (-\lg K_b) = -\lg K_w$$

$$\boxed{pK_a + pK_b = pK_w}$$ * remember the symbol 'p' means '$-\log_{10}$'

Hence, we can determine the value of K_a of an acid, given the K_b value of its conjugate base and vice versa.

From $K_a \times K_b = K_w$, we see that for a conjugate acid-base pair,
as the strength of the acid decreases (smaller K_a),
the strength of its conjugate base increases (larger K_b) and vice versa.

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2.6 Degree of dissociation

The **fraction** of molecules which is **ionised** into ions in water is called the degree of dissociation, α.

For an acid,

$$\alpha = \frac{\text{amount ionised}}{\text{initial amount}} = \frac{[\text{acid}]_{\text{dissociated}}}{[\text{acid}]_{\text{initial}}}$$

In general, for a strong acid or strong base, α is close to 1
for a weak acid or weak base, $\alpha \ll 1$

2.7 pH of Weak Acid / Weak Base Solutions

*LO 10.1(c)part: calculate $[H^+(aq)]$ and pH values for weak monobasic (monoprotic) acids, and weak monoacidic bases [Calculations involving weak acids/bases will **not** require solving of quadratic equations]*

Since weak acids and weak bases dissociate **partially** in water, $[H^+]$ or $[OH^-]$ in the solution will be **lower than** the initial concentration of the weak acid or weak base.

We use K_a or K_b to calculate the $[H^+]$ or $[OH^-]$ in the solution at equilibrium.

Exercise 2.4 (Worked Example)

1. Find **(a)** the pH and **(b)** the degree of dissociation of a solution of ethanoic acid, CH_3CO_2H, of concentration 0.1 mol dm^{-3}. [Given: K_a of CH_3CO_2H = 1.8 × 10^{-5} mol dm^{-3}]

(a)

	HA	⇌	H^+	+	A^-
Initial conc	0.1				
Change	$-x$		$+x$		$+x$
Eqm conc	$0.1-x$		x		x

Important note:
$[H^+]_{eqm} = [A^-]_{eqm}$ is true only if the solution contains only weak acid HA (i.e. all H^+ ions and A^- ions present in the solution come only from the dissociation of HA and there are no added H^+ ions or A^- ions). This equation cannot be used for calculations involving buffer solutions (see Section 4.4).

$$K_a = \frac{[H^+]_{eqm}[A^-]_{eqm}}{[HA]_{eqm}} = \frac{x^2}{0.1-x} \approx \frac{x^2}{0.1} \quad \text{(assume } x \ll 0.1\text{)}$$

$$x = [H^+] = \sqrt{1.8 \times 10^{-5} \times 0.1} = 1.34 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{pH} = -\lg(1.34 \times 10^{-3}) = 2.87$$

Note:
Solving quadratic equations is not required for Chemistry 'A' Levels. The assumption ($x \ll 0.1$) is valid since a weak acid only dissociates partially. Without the approximation, $[H^+]$ would have been 1.33 × 10^{-3} mol dm^{-3}. The difference is insignificant because it is within the limits of the accuracy to which the data is given.

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(b) $\alpha = (1.34 \times 10^{-3})/0.1 = 1.34 \times 10^{-2}$ (or 1.34% dissociated)

Exercise 2.5

Calculate (a) the pH and (b) the degree of dissociation of a solution of 0.125 mol dm^{-3} aqueous ammonia at 298 K.

[Given K_b for ammonia = 1.78×10^{-5} mol dm^{-3} at 298 K]

[(a) 11.2 ; (b) 1.19×10^{-2} or 1.19%]

Exercise 2.6 (Worked Example)

Caffeine, $C_8H_{10}N_4O_2$, a stimulant found in coffee and tea, is a weak base.

$$C_8H_{10}N_4O_2 + H_2O \rightleftharpoons (C_8H_{11}N_4O_2)^+ + OH^-$$

At 25 °C, a 0.020 mol dm^{-3} caffeine solution has a pH of 11.5.

(a) Write the K_b expression of caffeine and calculate its value at 25 °C.

$$K_b = \frac{[C_8H_{11}N_4O_2^+][OH^-]}{[C_8H_{10}N_4O_2]}$$

pOH = 14 – pH = 14 – 11.5 = 2.5 $\therefore$ $[OH^-] = 10^{-2.5} = 3.162 \times 10^{-3}$ mol dm^{-3}

$$K_b = \frac{(3.162 \times 10^{-3})^2}{0.020 - 3.162 \times 10^{-3}} = \underline{5.94 \times 10^{-4} \text{ mol dm}^{-3}}$$

Note: If $[H^+]$ at equilibrium is known, the assumption $[H^+] << [HA]$ should **not** be made in the calculations.

(b) Calculate the degree of dissociation, α for caffeine at 25 °C.

$$\alpha = \frac{3.162 \times 10^{-3}}{0.020} = \underline{0.158}$$

Exercise 2.7

The pH of a weak acid, HA, of concentration 0.100 mol dm^{-3} was found to be 3.0.

Calculate the K_a and pK_a of the acid.

[$K_a = 1.01 \times 10^{-5}$ mol dm^{-3}, pK_a = 5.00]

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2.8 Strength of Acids and Bases

LO 10.1(a): explain qualitatively the differences in behaviour between strong and weak acids and bases in terms of the extent of dissociation

The strength of an acid (or base):

- is a measure of **how readily** the acid (or base) donates its proton (or accepts a proton).
- depends on its **structure** (refer to Organic Chemistry Topic 16 Hydroxy Compounds, Topic 18 Carboxylic Acids for acid strengths of different phenols and carboxylic acids, as well as Topic 19 Nitrogen Compounds to compare the basic strength of amines)
- is indicated by its K_a **(or** K_b**)** value [see Section 2.5.1 and 2.5.2]
- is *different* from the concentration of the acid (or base) [see Exercise 2.4]

Are pH or degree of dissociation, α, reliable indicators of the strength of an acid (or base)?

Exercise 2.8

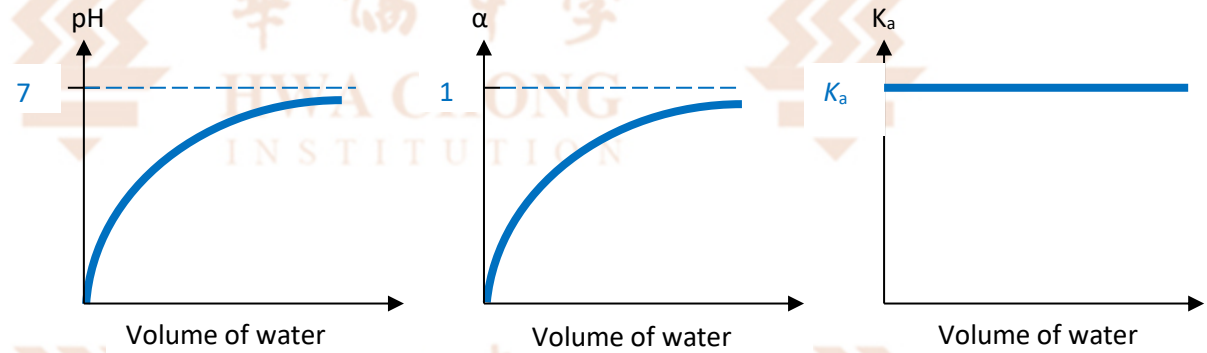
In **Exercise 2.4**, the pH and the degree of dissociation of a solution of ethanoic acid of concentration 0.1 mol dm^{-3} were found to be: pH: …… degree of dissociation, α: ……

[Given: K_a of $CH_3CO_2H = 1.8 \times 10^{-5}$ mol dm^{-3}]

Now, find **(a)** the pH and **(b)** the degree of dissociation of ethanoic acid of concentration 0.001 mol dm^{-3}. How have the pH and α been affected by the dilution?

[(a) 3.87; (b) 0.134 or 13.4%]

The diagrams below show how the values of pH, α and K_a for a weak acid vary with dilution (i.e. volume of water increases) at a constant temperature:



(pH → 7 as dilution → ∞) **(α → 1 as dilution → ∞)**

K_a does not vary with concentration. It is a constant at constant temperature. Therefore K_a is the best indicator of the strength of a weak acid.

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Exercise 2.9

Each of the following reactions contains two Brønsted acids and two Brønsted bases. Suggest with brief reasoning which is the stronger acid and which is the stronger base.

(a) (worked example)

$NH_3(aq)$ + $H_2O(l)$ ⇌ $NH_4^+(aq)$ + $OH^-(aq)$ $K_c = 3.2 \times 10^{-7}$

weaker base — weaker acid — stronger acid — stronger base

K_c is very small, this suggests that the position of equilibrium lies very much to the left.
So NH_4^+ is a better proton donor than H_2O, OH^- is a better proton acceptor than NH_3.

(b) $C_6H_5O^-$ + CH_3CO_2H ⇌ C_6H_5OH + $CH_3CO_2^-$ $K_c = 1.3 \times 10^5$

Note:
From part **(b)**, we see that the stronger acid is able to protonate the conjugate base of the weaker acid.
Strong acids (e.g. HC*l*) are often used to liberate the weak acids (e.g. CH_3CO_2H) from their salt (e.g. $CH_3CO_2^-Na^+$).

HC*l* (aq) + $CH_3CO_2^-$(aq) → Cl^-(aq) + CH_3CO_2H(aq)
stronger acid — conjugate base — weaker acid

3 pH OF SALT SOLUTIONS

LO 4(b): show understanding of, and apply the Brønsted-Lowry theory of acids and bases, including the concept of conjugate acids and conjugate bases
LO 10.1(b): explain the terms pH; K_a; pK_a; K_b; pK_b; K_w and apply them in calculations, including the relationship $K_w = K_aK_b$
*LO 10.1(c)part: calculate $[H^+(aq)]$ and pH values for weak monobasic (monoprotic) acids, and weak monoacidic bases [Calculations involving weak acids/bases will **not** require solving of quadratic equations]*

An ionic salt may be prepared from a reaction between an aqueous acid and an aqueous base.
E.g. KC*l* may be prepared from KOH(aq) and HC*l* (aq).

Salt hydrolysis is a reaction in which ions of a salt react with water to produce OH^- or H_3O^+ ions.

3.1 Salt derived from a strong acid and a strong base

Ions in salts derived from a strong acid and a strong base (e.g. NaC*l*, KNO_3) **do not** undergo salt hydrolysis. Hence the resulting solution is neutral ⇒ pH = 7 at 25 °C.

However, ions in salts derived from weak acids/bases, as well as metal cations with high charge density, could undergo hydrolysis to result in acidic or alkaline solutions (pH less/greater than 7 at 25 °C).

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3.2 Salt derived from a weak acid and a strong base

- Consider $CH_3CO_2^-Na^+$ which is derived from the salt of CH_3CO_2H and NaOH.
- CH_3CO_2H is a weak acid so its conjugate base **$CH_3CO_2^-$ is a stronger base than water**. $CH_3CO_2^-$ undergoes **hydrolysis** forming OH^- ions.

$$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + \mathbf{OH^-(aq)}$$

- Hence $[OH^-] > [H_3O^+]$ and the salt solution of $CH_3CO_2^-Na^+$ is alkaline.
- **At 25 °C, pH of a solution of $CH_3CO_2^-Na^+$ is > 7**.

Note:

- $CH_3CO_2^-$ (aq) is a stronger base than water so is able to accept a proton from water.
- However, it is still a weak base (K_b of $CH_3CO_2^- = 5.6 \times 10^{-10}$ mol dm^{-3}). Hence a reversible arrow '⇌' is used in the salt hydrolysis equation.
- The cation Na^+ does not undergo hydrolysis due to its low charge density.

3.3 Salt derived from a strong acid and a weak base

- Consider $NH_4^+Cl^-$ which is derived from the salt of HC*l* and NH_3.
- NH_3 is a weak base so its conjugate acid **NH_4^+ is a stronger acid than water**. NH_4^+ undergoes **hydrolysis** forming H_3O^+ ions.

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + \mathbf{H_3O^+(aq)}$$

- Hence $[H_3O^+] > [OH^-]$ and the salt solution of NH_4Cl is acidic.
- **At 25 °C, pH of a solution of NH_4Cl is < 7**.

Note:

- NH_4^+ is a stronger acid than water so is able to donate a proton to water. (see Exercise 2.9)
- However, it is still a weak acid (K_a of $NH_4^+ = 5.56 \times 10^{-10}$ mol dm^{-3}). Hence a reversible arrow '⇌' is used in the salt hydrolysis equation.
- The anion Cl^- (derived from strong acid HC*l*) is a weaker base than water and so does not hydrolyse.

3.4 Salt derived from a weak acid and a weak base

E.g. $CH_3CO_2^-NH_4^+$

- Both cation and anion hydrolyse.
- pH of the salt solution depends on K_a of the acid (cation) and K_b of the base (anion)

If K_a(cation) > K_b(anion) → salt solution is acidic

K_a(cation) = K_b(anion) → salt solution is neutral

K_a(cation) < K_b(anion) → salt solution is basic

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3.5 Salt containing an aqueous metal cation with high charge density

LO 5(e)(iv)part: describe and explain the reactions of the chlorides with water (for $AlCl_3$)

Consider the ionic compound, aluminium nitrate $Al(NO_3)_3$. When it dissolves in water, the Al^{3+} and NO_3^- ions are separated and surrounded by water molecules.

$$Al(NO_3)_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3NO_3^-(aq)$$

The Al^{3+} cations are coordinated to water molecules through dative (co–ordinate) bonds to form the complex ion, $[Al(H_2O)_6]^{3+}$.

The Al^{3+} ion is **small and highly charged**, so it has **high charge density**. It **withdraws sufficient electron density from the O–H bonds of the coordinated H_2O molecules, weakening the O–H bonds**. When one O–H bond breaks, a proton is released:

$$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + \mathbf{H_3O^+(aq)}$$

We call this a **hydrolysis** reaction. Observe that $[Al(H_2O)_6]^{3+}$ is acting as a weak Brønsted acid. Since $[H_3O^+] > [OH^-]$, $Al^{3+}(aq)$ is **acidic and pH < 7 at 25 °C**.

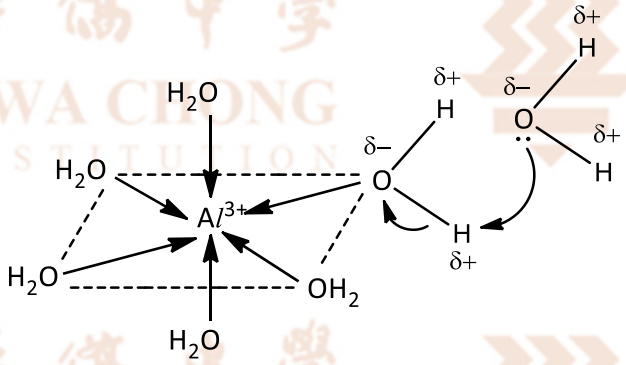


Figure 1. $[Al(H_2O)_6]^{3+}$ acting as an acid, donating a proton to another H_2O molecule

Other metal cations like Fe^{3+} and Cr^{3+} also form complex ions with water which undergo the hydrolysis reaction to produce an acidic solution.

Table 5. Formula of the complex ions of Fe^{3+}, Cr^{3+} and Al^{3+} with water and their K_a values

Metal ion	Complex ion formed with water	K_a / mol dm^{-3} (at 25 °C)
Fe^{3+}	$[Fe(H_2O)_6]^{3+}(aq)$	6×10^{-3}
Cr^{3+}	$[Cr(H_2O)_6]^{3+}(aq)$	1×10^{-4}
Al^{3+}	$[Al(H_2O)_6]^{3+}(aq)$	1×10^{-5}

Exercise 3.1

State whether the following solutions are acidic, alkaline or neutral. Write an equation, including state symbols, for any hydrolysis reaction.

(a) KBr(aq)

(b) $Na_2CO_3(aq)$

(c) $CH_3NH_3^+Cl^-(aq)$

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(d) (worked example)

$NH_4HS(aq)$, given: K_b of $NH_3 = 1.8 \times 10^{-5}$ mol dm^{-3}

K_{a1} of $H_2S = 9 \times 10^{-8}$ mol dm^{-3} (H_2S is a weak diprotic acid)

K_{a1} : $H_2S(aq) \rightleftharpoons HS^-(aq) + H^+(aq)$

Both ions undergo hydrolysis:

$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$ ——(1)

$HS^-(aq) + H_2O(l) \rightleftharpoons H_2S(aq) + OH^-(aq)$ ——(2)

K_a of $NH_4^+ = K_w / K_b$ of $NH_3 = 10^{-14} / (1.8\times10^{-5}) = 5.6 \times 10^{-10}$ mol dm^{-3}

K_b of $HS^- = K_w / K_a$ of $H_2S = 10^{-14} / (9\times10^{-8}) = 1.1 \times 10^{-7}$ mol dm^{-3}

Since K_b of HS^- > K_a of NH_4^+, (2) occurs to a larger extent than (1).

Thus, resultant $[OH^-] > [H_3O^+]$. The salt solution is **alkaline**.

(e) (worked example) $FeCl_3(aq)$

Acidic (Fe^{3+} is a metal cation with high charge density. The complex ion $[Fe(H_2O)_6]^{3+}(aq)$ undergoes hydrolysis.)

$[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq)$

3.6 Calculations of pH of salt solutions

The pH of salt solutions can be calculated using the following general strategy:

1. Determine whether the ions in the salt undergoes hydrolysis in water by considering the strength of acid and base from which the salt is derived
2. Write an equation for any hydrolysis that takes place in water to produce H_3O^+ or OH^- ions.
3. Calculate $[H_3O^+]$ or $[OH^-]$ using the K_a or K_b of the ion that undergoes hydrolysis in water.

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Exercise 3.2 (Worked Example)

Calculate the pH of 0.10 mol dm^{-3} $CH_3CO_2^-$ Na^+(aq) at 25°C.

K_a value for ethanoic acid is 1.8×10^{-5} mol dm^{-3}.

	$CH_3CO_2^-$	+ H_2O ⇌	CH_3CO_2H	+ OH^-	(salt hydrolysis)
Initial conc / mol dm^{-3}	0.10				
Change / mol dm^{-3}	$-x$		$+x$	$+x$	
Eqm conc / mol dm^{-3}	$0.10 - x$		x	x	

$$K_b\,(CH_3CO_2^-) = \frac{K_w}{K_a\,(CH_3CO_2H)} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

$$K_b = \frac{x^2}{0.10 - x} \quad \text{(from ICE table)}$$

$$5.56 \times 10^{-10} \approx \frac{x^2}{0.10} \quad \text{(assuming } x \ll 0.10\text{)}$$

$[OH^-] = x = 7.45 \times 10^{-6}$ mol dm^{-3}

pOH $= -\lg [OH^-] = 5.13$

∴ pH = 14−pOH = <u>8.87</u> (relationship in section 2.3)

Exercise 3.3 (Worked Example)

Calculate the pH of 0.450 mol dm^{-3} ammonium chloride at 298 K.

(Given K_b for ammonia = 1.78×10^{-5} mol dm^{-3})

	NH_4^+	+ H_2O ⇌	NH_3	+ H_3O^+
Initial conc / mol dm^{-3}	0.450			
Change / mol dm^{-3}	$-x$		$+x$	$+x$
Eqm conc / mol dm^{-3}	$0.450 - x$		x	x

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

$$\frac{10^{-14}}{1.78 \times 10^{-5}} = \frac{x^2}{0.450 - x} \approx \frac{x^2}{0.450} \quad \text{(assume } x << 0.450\text{)}$$

$$x = [H_3O^+] = \sqrt{\frac{10^{-14}}{1.78 \times 10^{-5}} \times 0.450} = 1.59 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\text{pH} = -\lg\left(1.59 \times 10^{-5}\right) = 4.80$$

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4 BUFFER SOLUTIONS

4.1 Definition of Buffer solutions

LO 10.1(f)(i): explain how buffer solutions control pH

A *buffer solution* is one that is able to **resist pH changes** upon addition of a **small amount** of **acid or base**.

A buffer (usually) consists of two species which make up a **conjugate acid-base pair of a weak acid or base** – one species acts as weak Brønsted acid and the other species acts as weak Brønsted base. An example is a mixture of ethanoic acid (CH_3CO_2H) and ethanoate ion ($CH_3CO_2^-$).

Exercise 4.1

Using your knowledge of strong and weak acids and bases and your understanding of conjugate acid-base pairs, suggest whether each of the following mixtures can act as a buffer solution.

1. $NaHCO_3$ and Na_2CO_3
2. CH_3CO_2H and NaC*l*
3. HNO_3 and $NaNO_3$

4.2 Preparing a Buffer (Background info)

4.2.1 Mixing a weak acid and its conjugate base

Consider a buffer consisting of **a weak acid**, CH_3CO_2H, **and its conjugate base**, $CH_3CO_2^-$ ions

Ethanoic acid is a weak acid and dissociates partially.

$$CH_3CO_2H(aq) \rightleftharpoons CH_3CO_2^-(aq) + H^+(aq) \quad \text{——————————(1)}$$

Adding sodium ethanoate (completely soluble in water) to this solution adds a lot of extra ethanoate ions.

$$CH_3CO_2^-Na^+(aq) \rightarrow CH_3CO_2^-(aq) + Na^+(aq)$$

According to Le Chatelier's Principle, the position of equilibrium (1) shifts further to the left (i.e. the dissociation of ethanoic acid is suppressed). Similarly, hydrolysis of the ethanoate ion in water is suppressed by the presence of the ethanoic acid.

The solution now contains the following:

- large reservoir of un-ionised **ethanoic acid**;
- large reservoir of **ethanoate ions** from the sodium ethanoate;

and can act as a **buffer** solution.

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4.2.2 Mixing a weak base and its conjugate acid

Consider a buffer consisting of **a weak base**, aqueous NH_3 and **its conjugate acid**, NH_4^+ ions

Ammonia is a weak base and ionises partially.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad \text{——————————(2)}$$

Adding ammonium chloride (completely soluble) to this solution adds a lot of extra ammonium ions.

$$NH_4^+Cl^-(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

In a similar explanation to Section 4.2.1, the solution now contains a large reservoir of un-ionised **ammonia** and a large reservoir of **ammonium ions** from the ammonium chloride, and can act as a **buffer** solution.

Note: Buffer solutions with pH < 7 (at 25 °C) may be referred to as 'acidic' buffers while buffer solutions with pH > 7 (at 25 °C) may be referred to as 'alkaline' buffers.

4.2.3 Partial neutralisation of a weak acid (or weak base)

Another way to prepare a buffer is to form one of the species by *partial neutralisation* of the other species. For example, the ethanoic acid/ethanoate buffer can be prepared by mixing suitable amounts of ethanoic acid and NaOH. The key is to add less NaOH than is required for complete neutralisation, such that the OH^- ions will react with part of the total ethanoic acid present to produce the ethanoate ions needed, at the same time leaving some ethanoic acid behind, to give a mixture consisting of *both* ethanoic acid and ethanoate ions.

This method is based on the same chemical process that occurs when a weak acid is titrated with a strong base (see Section 5.1.2) or when a weak base is titrated with a strong acid (see Section 5.1.3).

Exercise 4.2 (Worked Example)

Which combination of substance, when mixed, would **not** give a buffer solution?

A 25 cm^3 of 0.1 mol dm^{-3} HC*l* and 50 cm^3 of 0.1 mol dm^{-3} NH_3
B 25 cm^3 of 0.1 mol dm^{-3} NaOH and 25 cm^3 of 0.2 mol dm^{-3} NH_4^+
C 25 cm^3 of 0.2 mol dm^{-3} HC*l* and 25 cm^3 of 0.1 mol dm^{-3} $CH_3CO_2^-$
D 25 cm^3 of 0.1 mol dm^{-3} NaOH and 25 cm^3 of 0.2 mol dm^{-3} CH_3CO_2H

Ans: C

A	NH_3 is in excess. ($NH_3 + H^+ \rightarrow NH_4^+$) After all HC*l* reacts with NH_3, resulting mixture consists of unreacted NH_3 (weak base) and NH_4^+ (conjugate acid) formed. Hence the resulting mixture is a buffer.

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B	NH_4^+ is in excess. ($NH_4^+ + OH^- \rightarrow NH_3 + H_2O$) After all NaOH reacts with NH_4^+, resulting mixture consists of NH_3 (weak base) formed and unreacted NH_4^+ (conjugate acid). Hence the resulting mixture is a buffer.
C	HC*l* is in excess. ($CH_3CO_2^- + H^+ \rightarrow CH_3CO_2H$) After all $CH_3CO_2^-$ reacts with HC*l*, the resulting mixture consists of unreacted HC*l* and CH_3CO_2H formed. This mixture does not consist of a conjugate acid-base pair of a weak acid or base and is **not** a buffer.
D	CH_3CO_2H is in excess. ($CH_3CO_2H + OH^- \rightarrow CH_3CO_2^- + H_2O$) After all NaOH reacts with CH_3CO_2H, the resulting mixture consists of unreacted CH_3CO_2H (weak acid) and $CH_3CO_2^-$ (conjugate base) formed. Hence the resulting mixture is a buffer.

4.3 Explaining Buffer Action

LO 10.1(f)(i): explain how buffer solutions control pH

How does the buffer consisting of large reservoirs of CH_3CO_2H *and its conjugate base* $CH_3CO_2^-$ *resist pH changes on addition of small amount of acid or base?*

(i) When a small amount of **H^+** is added to this buffer, the H^+ ions **react with** the large reservoir of the **$CH_3CO_2^-$ (conjugate base)**:

$$CH_3CO_2^- + H^+ \rightarrow CH_3CO_2H$$

The added H^+ ions are removed and $[CH_3CO_2H]$ increases slightly and $[CH_3CO_2^-]$ decreases slightly.

As the original amounts of CH_3CO_2H and $CH_3CO_2^-$ are large compared to the amount of H^+ ions added, the ratio $[CH_3CO_2^-]$ / $[CH_3CO_2H]$ remains almost constant.

Since $K_a = [H^+][CH_3CO_2^-]$ / $[CH_3CO_2H]$, and K_a is a constant, so $[H^+]$ and pH remains almost constant.

(ii) When a small amount of **OH^-** is added to this buffer, the OH^- ions **react with** the large reservoir of the un–ionised **CH_3CO_2H molecules**:

$$CH_3CO_2H + OH^- \rightarrow CH_3CO_2^- + H_2O$$

The added OH^- ions are removed and $[CH_3CO_2H]$ decreases slightly and $[CH_3CO_2^-]$ increases slightly.

As the original amounts of CH_3CO_2H and $CH_3CO_2^-$ are large compared to the amount of OH^- ions added, the ratio $[CH_3CO_2^-]$ / $[CH_3CO_2H]$ remains almost constant.

Since $K_a = [H^+][CH_3CO_2^-]$ / $[CH_3CO_2H]$, and K_a is a constant, so $[H^+]$ and pH remains almost constant.

Note: Buffer action equations are written with single (non-reversible) arrows.

Exercise 4.3

How does a buffer solution containing NH_3(aq) and NH_4Cl(aq) resist changes in pH when small amounts of acid or alkali are added?

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4.4 Calculating pH of Buffer solutions

LO 10.1(g): calculate the pH of buffer solutions, given appropriate data

4.4.1 pH of buffer consisting of weak acid HA and its conjugate base A^-

In a buffer consisting of HA and its conjugate base A^-, the following equilibrium exists:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

and $$K_a = \frac{[H^+]_{eqm}[A^-]_{eqm}}{[HA]_{eqm}}$$

As the presence of excess $A^-(aq)$ suppresses the dissociation of HA,

$[HA]_{eqm} \approx [HA]_{initial}$ (since α is very small)

$[A^-]_{eqm} \approx [A^-]_{initial}$ (since $[A^-]_{\text{from HA}}$ is very small)

therefore $$\boldsymbol{K_a} \approx \frac{[H^+]_{eqm}[A^-]_{initial}}{[HA]_{initial}} = \frac{\mathbf{[H^+]_{eqm}[conjugate\ base]}}{\mathbf{[acid]}}$$

and $$\boxed{\mathbf{[H^+] = K_a \times \frac{[acid]}{[conjugate\ base]}}}$$

Hence pH of the buffer can be found easily.

Important note:
In this case of the buffer, $\mathbf{[H^+] \neq [A^-]}$ since the solution consists of *significant* amounts of HA and A^- and the A^- ions do not just come from the weak acid dissociation of HA alone, unlike in a solution of pure weak acid HA (see Exercise 2.4).

Alternatively, to find pH of a buffer, take –lg on both sides of boxed equation,

$$-\lg[H^+] = -\lg K_a - \lg\frac{[acid]}{[conjugate\ base]}$$

$$\boxed{pH = pK_a + \lg\frac{[conjugate\ base]}{[acid]}}$$ **Henderson–Hasselbalch Equation**

4.4.2 pH of buffer consisting of weak base and its conjugate acid

In a similar manner as above, the pOH and pH of this buffer can be found using:

$$\boxed{\mathbf{[OH^-] = K_b \times \frac{[base]}{[conjugate\ acid]}}}$$ or $$\boxed{\mathbf{pOH = pK_b + \lg\frac{[conjugate\ acid]}{[base]}}}$$

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Exercise 4.4 (Worked Example)

Calculate the pH of a solution consisting of **0.010** mol of ethanoic acid and **0.010** mol of sodium ethanoate dissolved in 1 dm^3 of water. (K_a of ethanoic acid = 1.8×10^{-5} mol dm^{-3})

$[CH_3CO_2H] = 0.010$ mol dm^{-3}
$[CH_3CO_2^-] = 0.010$ mol dm^{-3}

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]}$$

$$1.8 \times 10^{-5} = \frac{[H^+]\,(0.010)}{0.010}$$

$[H^+] = 1.8 \times 10^{-5}$ mol dm^{-3}

$\therefore$ pH = $-\lg [H^+]$ = 4.74

Note: $pK_a = -\lg K_a = 4.74$
In Section 4.5, you will observe that pH = pK_a when [weak acid] = [conjugate base].

Application Example

Calculate the change in pH when 1 cm^3 of a 1.00 mol dm^{-3} NaOH is added to 1 dm^3 of
(a) water; **(b)** the buffer solution in Exercise 4.2 above.

(a) No. of moles of NaOH added = $1 \div 1000 \times 1.00 = 0.001$

$[OH^-] = (0.001 \div 1001 \times 1000)$
$= 9.99 \times 10^{-4}$ mol dm^{-3}

Note: Remember to divide by the new total volume as volume of solution has changed upon adding aq. NaOH.

pOH = 3.00 $\therefore$ pH = 11.0

Change in pH = 11.0 – 7 = +4 units

(b) $CH_3CO_2H + OH^- \rightarrow CH_3CO_2^- + H_2O$

No. of moles of NaOH added = 0.001

Strategy: Decide which buffer component removes the added NaOH, then work out the new concentration of each buffer component.

After the reaction,

$[CH_3CO_2^-] = (0.010 + 0.001) / V$
$[CH_3CO_2H] = (0.010 - 0.001) / V$

Tip: The new total volume of the solution can just be denoted as V, as this would cancel in the K_a expression.

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+]\,(0.010 + 0.001) / V}{(0.010 - 0.001) / V}$$

$[H^+] = 1.47 \times 10^{-5}$ mol dm^{-3}

$\therefore$ pH = $-\lg [H^+] = 4.83$

Change in pH = 4.83 – 4.74= +0.09 units

From the above calculation, we can see that a buffer solution resists pH changes much better than water, when a small amount of strong base is added.

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4.5 Buffer Capacity (Background info)

The capacity of a buffer is the quantity of H_3O^+ or OH^- it can remove before its pH changes drastically. A buffer should have **high** [weak acid] and [conjugate base], or **high** [weak base] and [conjugate acid], to provide a large reservoir of the relevant components. The **more concentrated** the components of a buffer, the greater the buffer capacity.

Buffer capacity also depends on the **ratio** of [weak acid] and [conjugate base], or **ratio** of [weak base] and [conjugate acid]. For example, if a buffer contains a much higher proportion of the weak acid compared to its conjugate base, then it is more effective in resisting changes in pH on addition of OH^- as compared to the addition of H_3O^+. It can be shown that the **most effective buffer** has

$$\frac{[\text{conjugate base}]}{[\text{acid}]} = 1 \quad \text{or} \quad \frac{[\text{conjugate acid}]}{[\text{base}]} = 1$$

LO 10.1(d): describe the changes in pH during acid-base titrations and explain these changes in terms of the strengths of the acids and bases

Using the boxed equations in Section 4.4.1 and 4.4.2, it follows that, for this most effective buffer,

pH = pK_a (for acidic buffer) or pOH = pK_b (for alkaline buffer)

This buffer is said to have the ***maximum buffer capacity*** and it can most effectively resist a change in pH in either direction (i.e. when either acid or base is added).

4.6 Effective Buffer Range (Background info)

The further the buffer-component concentration ratio is from 1, the less effective the buffering action (i.e., lower buffer capacity).

In practice, a buffer is no longer effective when
[acid]/[conjugate base] or [base]/[conjugate acid] > 10/1 or < 1/10.

Since $\log_{10}(10/1) = +1$ and $\log_{10}(1/10) = -1$,

for an acidic buffer, $[H^+] = K_a \times \frac{[\text{acid}]}{[\text{conjugate base}]} \Rightarrow$ **effective buffer pH range = p$K_a \pm 1$**

for an alkaline buffer, $[OH^-] = K_b \times \frac{[\text{base}]}{[\text{conjugate acid}]} \Rightarrow$ **effective buffer pOH range = p$K_b \pm 1$**

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Exercise 4.5 (Worked Example)

Which of the following acids would be the best choice to combine with its sodium salt to make a solution buffered at pH 4.25?

For your choice, calculate the ratio of the conjugate base to the acid concentrations required to attain the desired pH.

Acid	pK_a
chlorous acid ($HClO_2$)	1.95
nitrous acid (HNO_2)	3.34
methanoic acid (HCO_2H)	3.74
hypochlorous acid (HClO)	7.54

The best choice is methanoic acid because the desired pH (4.25) is closest to and is within 1 unit of its pK_a value (3.74 ± 1).

$$K_a = \frac{[H^+][\text{conjugate base}]}{[\text{acid}]}$$

$$10^{-3.74} = \frac{10^{-4.25}\,[\text{conjugate base}]}{[\text{acid}]}$$

$$\therefore \quad \frac{[\text{conjugate base}]}{[\text{acid}]} = 3.24$$

Check: Ratio is between 0.1 and 10 (effective range)

4.7 Buffer System in Human Blood

LO 10.1(f)(ii): describe and explain uses of buffer solutions, including the role of H_2CO_3/HCO_3^- in controlling pH in blood

The pH of our blood must be kept constant at about 7.4 since enzymes operate only within a narrow pH range. Blood contains large amounts of the weak acid carbonic acid, **H_2CO_3** (an aqueous solution of CO_2), and its conjugate base, **HCO_3^-** ions (bicarbonate). Together they help maintain the pH of blood at 7.4. If blood pH falls below 6.8 or rises above 7.8, one can become sick or die. The bicarbonate neutralises excess acids in the blood while the carbonic acid neutralises excess bases.

The following equilibria operate in the H_2CO_3/HCO_3^- buffer system:

$$H^+(aq) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H_2O(l) + CO_2(g)$$

When H^+ is added to the blood as a result of metabolic processes, the following reaction occurs

$$H^+(aq) + HCO_3^-(aq) \rightarrow H_2CO_3(aq)$$

The amount of HCO_3^- (relative to the amount of CO_2) decreases; however, the amount of the change is small compared to the large amount of HCO_3^- present in the blood.

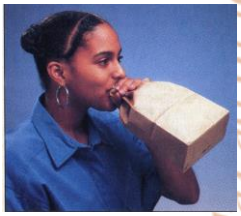
When OH^- is added, it is removed by the carbonic acid.

$$H_2CO_3(aq) + OH^- \rightarrow HCO_3^-(aq) + H_2O(l)$$

Or $$CO_2(aq) + OH^-(aq) \rightarrow HCO_3^-(aq)$$

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If blood pH rises above about 7.45, you can suffer from a condition called *alkalosis*. This can arise from hyperventilation or oxygen deficiency at high altitude. It can lead to over excitability of the central nervous system, muscle spasms and death. One way to treat alkalosis is to breathe into a paper bag. The CO_2 exhaled is recycled into the body. *Can you explain how that helps?*



pH Regulation During Exercise : a tutorial on buffer in the body

http://www.chemistry.wustl.edu/~edudev/LabTutorials/CourseTutorials/bb/Buffer/Buffers.pdf

Exercise 4.6

The main buffering agent in blood plasma is the carbon dioxide/hydrogen carbonate system.

$$H_2O + CO_2 \rightleftharpoons H^+ + HCO_3^- \qquad K_a = 7.90 \times 10^{-7} \text{ mol dm}^{-3}$$

(a) Explain how the system above acts as a buffer when
(i) H^+ ions, **(ii)** OH^- ions
are added to the blood plasma.

(b) The pH of normal blood plasma is 7.40. Use the data above to calculate the ratio $[HCO_3^-]/[CO_2]$ and hence deduce whether blood has a greater capacity for absorbing H^+ or OH^- ions.

(c) Using the above buffer system, briefly explain why strenuous exercise leads to an increase rate of breathing.

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5 ACID-BASE TITRATIONS

LO 10.1(d): describe the changes in pH during acid–base titrations and explain these changes in terms of the strengths of the acids and bases

5.1 Acid-Base Titration Curves

During an acid-base titration, for example when a base is added from the burette into an acid placed in a conical flask, the pH of the solution in the conical flask changes. Before the point of complete neutralisation, the acid is in excess while after the point of complete neutralisation, the base is in excess. A salt is also formed in the process. The pH of the solution depends on the species present in the conical flask after neutralisation of the acid by the base. These changes in pH can be monitored by measuring the pH of the solution using a pH meter as the base is added to the acid.

A ***titration curve*** is a graph of pH against the volume of the titrant added and it shows how the pH changes during a titration.

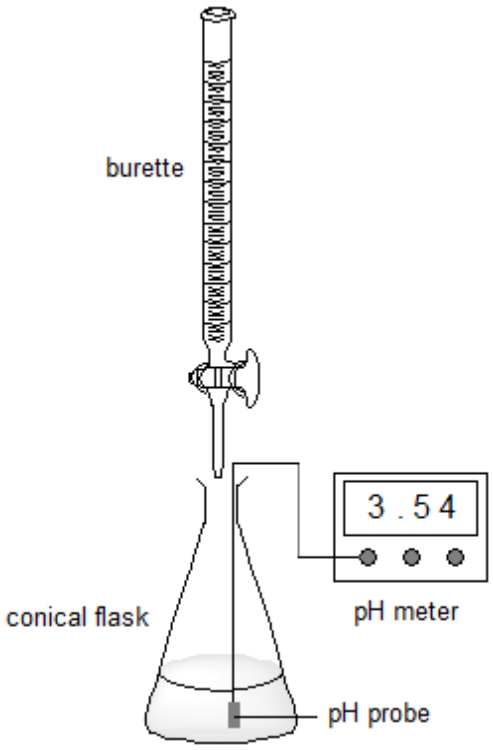


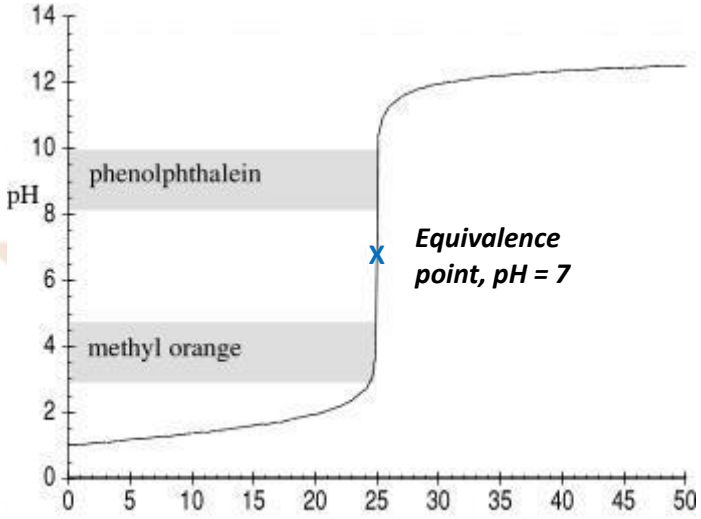
Figure 2. Monitoring pH changes during a titration with a pH meter

Four types of acid-base titration curves are shown on the following pages. Note that in all of them, the acid is in the conical flask while the base is added from the burette. To calculate the pH of the solution at various points of the curve, you will need to apply the concepts you have learnt earlier on calculation of pH involving strong acid / base, weak acid / base, salt solutions and buffer solutions.

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5.1.1 Strong Acid – Strong Base Titration

Consider addition of 0.10 mol dm^{-3} NaOH to 25.0 cm^3 of 0.10 mol dm^{-3} HC*l*.



Features of the curve:

- **At V_{NaOH} = 0 cm^3**
  Initial pH = pH of 0.10 mol dm^{-3} HC*l* = –lg 0.10 = 1
  HC*l* is a strong acid (fully dissociated in water), so $[H^+]$ = [HC*l*].

- **At 0 < V_{NaOH} < 25 cm^3**
  pH gradually rises as an increasing amount of H^+ is neutralised by the NaOH added.

- **At V_{NaOH} = 25 cm^3**
  Equivalence point is reached. This is the point where the acid is completely neutralised by the base.
  pH = 7 as the salt formed does not undergo hydrolysis.

  Suitable indicator:
  methyl orange, screened methyl orange, phenolphthalein, thymol blue, thymolphathalein

  Note the sharp pH change near equivalence point (see parts **(c)** and **(e)**).

- **At V_{NaOH} > 25 cm^3**
  There is excess NaOH present in the solution. As NaOH is a strong base, $[OH^-]$ is high, hence pH is high (exact value depends on [NaOH] that is in excess).

[Worked example] Determine the pH of the solution in the conical flask at the point when each of the following volumes of NaOH is added.

(a) 0.00 cm^3

Since HC*l* is a strong acid, it dissociates completely.
$[H^+]$ = 0.10 mol dm^{-3}
$\therefore$ pH = –lg (0.10) = 1.00

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(b) 12.50 cm^3 (This is called the **half–neutralisation** or **half–equivalence point**.)

No. of moles of NaOH added = $12.50 \times 10^{-3} \times 0.10 = 1.25 \times 10^{-3}$ mol
Initial no. of moles of HC*l* = $25.0 \times 10^{-3} \times 0.10 = 2.50 \times 10^{-3}$ mol
∴ HC*l* is in excess.

No. of moles of HC*l* remaining = $2.50 \times 10^{-3} - 1.25 \times 10^{-3} = 1.25 \times 10^{-3}$ mol

$$\therefore [HCl] \text{ remaining} = \frac{1.25 \times 10^{-3}}{(25.0 + 12.50) \times 10^{-3}} = 0.0333 \text{ mol dm}^{-3}$$

∴ pH = –lg (0.0333) = 1.48

(c) 24.90 cm^3

No. of moles of HC*l* remaining = $2.50 \times 10^{-3} - 2.49 \times 10^{-3} = 1.00 \times 10^{-5}$ mol

$$\therefore [HCl] \text{ remaining} = \frac{1.00 \times 10^{-5}}{(25.0 + 24.90) \times 10^{-3}} = 2.00 \times 10^{-4} \text{ mol dm}^{-3}$$

∴ pH = $-\lg (2.00 \times 10^{-4}) = 3.70$

(d) 25.00 cm^3 (This is called the **equivalence point**.)

At this point, HC*l* is completely neutralised by NaOH. The only species present at this point is NaC*l*. Since NaC*l* does not undergo hydrolysis in water, pH at this point = 7

(e) 25.10 cm^3

No. of moles of NaOH added = $25.10 \times 10^{-3} \times 0.10 = 2.51 \times 10^{-3}$ mol
Initial no. of moles of HC*l* = $25.0 \times 10^{-3} \times 0.10 = 2.50 \times 10^{-3}$ mol
∴ NaOH is in excess.

No. of moles of NaOH unreacted = $2.51 \times 10^{-3} - 2.50 \times 10^{-3} = 1.00 \times 10^{-5}$ mol

$$\therefore [NaOH] \text{ remaining} = \frac{1.00 \times 10^{-5}}{(25.0 + 25.10) \times 10^{-3}} = 2.00 \times 10^{-4} \text{ mol dm}^{-3}$$

∴ pOH = $-\lg (2.00 \times 10^{-4}) = 3.70$
pH = 14 – 3.70 = 10.3

(f) 50.00 cm^3

No. of moles of NaOH unreacted = $5.00 \times 10^{-3} - 2.50 \times 10^{-3} = 2.50 \times 10^{-3}$ mol

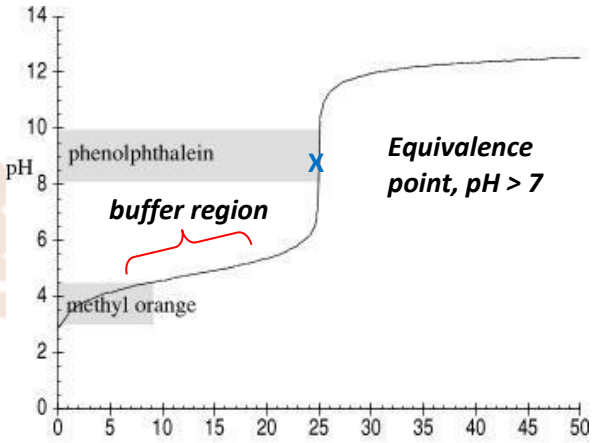
$$\therefore [NaOH] \text{ remaining} = \frac{2.50 \times 10^{-3}}{(25.0 + 50.00) \times 10^{-3}} = 0.0333 \text{ mol dm}^{-3}$$

∴ pOH = –lg (0.0333) = 1.48
pH = 14 – 1.48 = 12.5

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5.1.2 Weak Acid – Strong Base Titration

Consider addition of 0.10 mol dm^{-3} NaOH to 25.0 cm^3 of 0.10 mol dm^{-3} CH_3CO_2H



Features of the curve:

• **At V_{NaOH} = 0 cm^3** Initial pH = pH of 0.10 mol dm^{-3} CH_3CO_2H pH is not equal to 1.0 as CH_3CO_2H is a weak acid (only ionises partially in water).	*Calculation of pH of the solution in the conical flask when V_{NaOH} = 0 cm^3.* K_a of $CH_3CO_2H = 1.8 \times 10^{-5}$ mol dm^{-3} $K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]} = \frac{x^2}{0.10 - x}$ assume x << 0.10, therefore: $[H^+] = x = \sqrt{1.8 \times 10^{-5} \times 0.10}$ $= 1.34 \times 10^{-3}$ mol dm^{-3} pH = $-$lg $(1.34 \times 10^{-3}) = 2.87$
• **At 0 <V_{NaOH} < 25 cm^3** 1. Once the NaOH is added and some acid is neutralised, the solution contains a mixture of weak acid and its conjugate base ⇒ a **buffer solution** forms. 2. The pH at the initial part of the titration curve and the part immediately before complete neutralisation changes more sharply as these lie outside the effective buffer range of the buffer. 3. The **maximum buffer capacity** occurs when half of the number of moles of acid is neutralised at V_{NaOH} = 12.50 cm^3 (where [acid] = [conjugate base]). At this point, **pH = pK_a** of the weak acid.	*Calculation of pH of the solution in the conical flask when V_{NaOH} = 12.50 cm^3* ηNaOH added = 1.25×10^{-3} mol Initial η$CH_3CO_2H = 2.50 \times 10^{-3}$ mol ∴ CH_3CO_2H is in excess. The salt formed and the excess weak acid forms a buffer. ηCH_3CO_2H left = 1.25×10^{-3} mol η$CH_3CO_2^-$ formed = 1.25×10^{-3} mol $[H^+] = \frac{K_a[CH_3CO_2H]}{[CH_3CO_2^-]}$ $= \frac{1.8 \times 10^{-5} \times (1.25 \times 10^{-3} / 37.50 \times 10^{-3})}{1.25 \times 10^{-3} / 37.50 \times 10^{-3}}$ $= 1.8 \times 10^{-5}$ mol dm^{-3} ∴ pH = pK_a = 4.74

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- **At V_{NaOH} = 25 cm^3**

Suitable indicator: phenolphthalein or thymol blue or thymolphthalein

The sharp change in pH in the curve near equivalence point occurs over a smaller pH range compared to the previous strong acid–strong base titration.

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Equivalence point is reached.

pH > 7 as the anion undergoes **hydrolysis** to produce OH^-:

$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)$

Calculation of pH of the solution in the conical flask when V_{NaOH} = 25.00 cm^3

$\eta CH_3CO_2^-$ formed = 2.50×10^{-3} mol

$[CH_3CO_2^-] = \frac{2.50 \times 10^{-3}}{25.0+25.0} \times 1000 = 0.0500$ mol dm^{-3}

$K_b = \frac{[CH_3CO_2H][OH^-]}{[CH_3CO_2^-]} = \frac{x^2}{0.05 - x} = \frac{1.00 \times 10^{-14}}{1.80 \times 10^{-5}}$

Assume x << 0.05,

$[OH^-] = x = 5.27 \times 10^{-6}$ mol dm^{-3}

pH = 14 – pOH = 14 + lg (5.27×10^{-6}) = 8.72

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- **At V_{NaOH} > 25 cm^3**

There is excess NaOH present in the solution. As NaOH is a strong base, $[OH^-]$ is high and hence pH is high (exact value depends on [NaOH] in excess).

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Calculation of pH of the solution in the conical flask when V_{NaOH} = 30.00 cm^3

ηNaOH added = 3.00×10^{-3} mol

Initial ηCH_3CO_2H = 2.50×10^{-3} mol

$\therefore$ NaOH is in excess.

ηNaOH unreacted = 5.00×10^{-4} mol

[NaOH] remaining = $\frac{5.00 \times 10^{-4}}{55.00 \times 10^{-3}}$

= 0.00909 mol dm^{-3}

pOH = −lg(0.00909) = 2.04

pH = 14 – pOH = 12.0

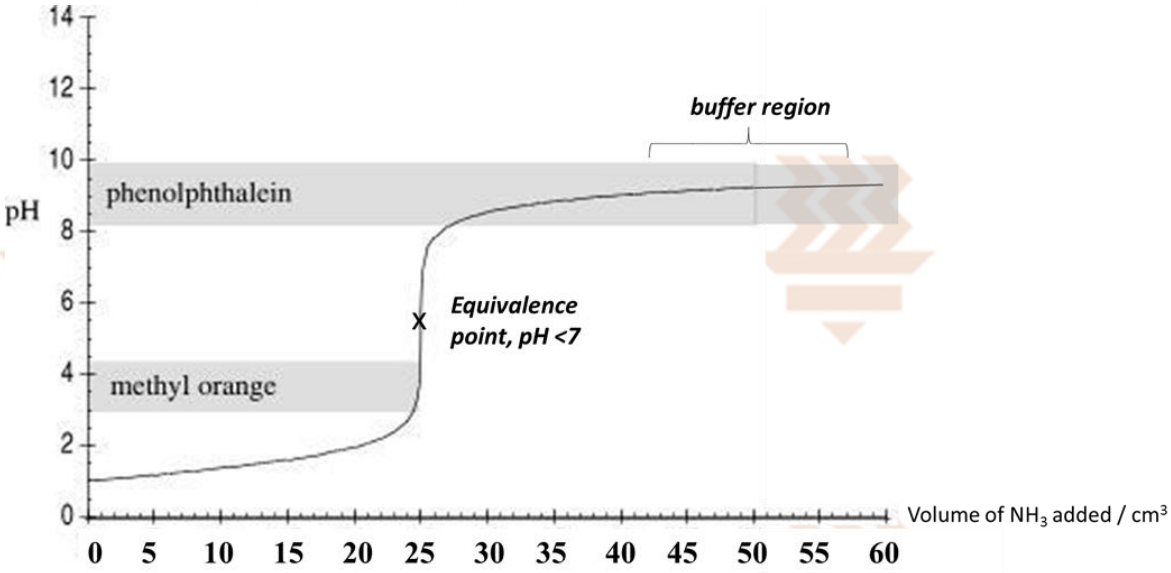
Note: OH^- from hydrolysis of $CH_3CO_2^-$ is insignificant compared to OH^- from unreacted strong base NaOH.

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5.1.3 Strong Acid – Weak base Titration

Consider addition of 0.10 mol dm^{-3} NH_3 to 25.0 cm^3 of 0.10 mol dm^{-3} HC*l*.



Features of the curve:

- **At $V_{weak\ base}$ = 0 cm^3**
  Initial pH = pH of 0.10 mol dm^{-3} HC*l* = –lg 0.10 = 1
  HC*l* is a strong acid (fully dissociated in water).

- **At 0 < $V_{weak\ base}$ < 25 cm^3**
  pH gradually rises as increasing amount of H^+ is neutralised by added weak base. However, no buffer is formed as there is no weak base present in excess in the conical flask.

- **At $V_{weak\ base}$ = 25 cm^3**
  Equivalence point is reached. pH < 7 as the cation undergoes **hydrolysis** to produce H_3O^+:

  $$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

  Suitable indicator: methyl orange or screened methyl orange

- **At $V_{weak\ base}$ > 25 cm^3**
  There is excess weak base present. The solution contains a mixture of weak base and its conjugate acid ⇒ a **buffer solution** forms.

Exercise 5.1

(a) With reference to the above example, determine the pH of the solution in the conical flask at the point when 12.50 cm^3 of NH_3 is added. (K_b of NH_3 = 1.8 × 10^{-5} mol dm^{-3})

(b) Calculate the pH at equivalence point.

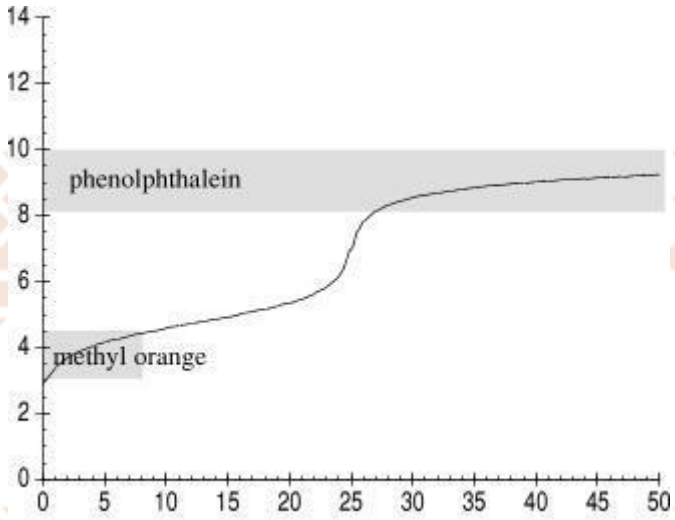
(c) What is volume of NH_3 added when maximum buffer capacity occurs? What is the pH at this point?

[(a) 1.48, (b) 5.28, (c) Volume of NH_3 at maximum buffer capacity = 50.00 cm^3, pH = 9.26]

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5.1.4 Weak Acid – Weak Base titration

Consider addition of 0.10 mol dm^{-3} NH_3 to 25.0 cm^3 of 0.10 mol dm^{-3} CH_3CO_2H



Features of the curve:

- **At $V_{weak\ base}$ = 0 cm^3**
  Initial pH = pH of 0.10 mol dm^{-3} CH_3CO_2H
  pH is not equal to 1.0 as CH_3CO_2H is a weak acid (only ionises partially in water).

- **At 0 < $V_{weak\ base}$ < 25 cm^3**
  Once the weak base is added and some acid is neutralised, the solution contains a mixture of weak acid and its conjugate base ⇒ a buffer solution forms.

- **At $V_{weak\ base}$ = 25 cm^3**
  Equivalence point is reached. **There is no sharp change in pH, hence no suitable indicator can be used, a pH meter may be used to help detect the equivalence point**.
  Both the cation and anion undergo hydrolysis (see Section 3.4).

- **At $V_{weak\ base}$ > 25 cm^3**
  There is excess weak base present in the solution together with its conjugate acid ⇒ another buffer region is formed.

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5.1.5 Titration Curves involving polyprotic acids or bases

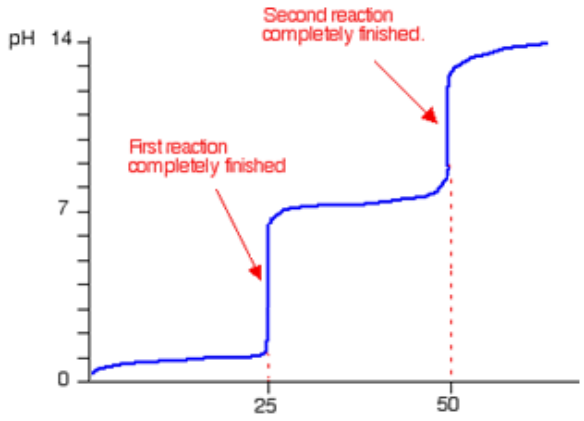
Polyprotic acids have more than one ionisable proton. The successive K_a values may differ by several orders of magnitude. This means the first H^+ is lost more easily than subsequent ones. (Why?)

E.g. $H_2SO_3(aq) + H_2O(l) \rightleftharpoons HSO_3^-(aq) + H_3O^+(aq)$ $\quad K_{a1} = 1.4 \times 10^{-2}$ mol dm^{-3}

$HSO_3^-(aq) + H_2O(l) \rightleftharpoons SO_3^{2-}(aq) + H_3O^+(aq)$ $\quad K_{a2} = 6.5 \times 10^{-8}$ mol dm^{-3}

In a titration of H_2SO_3, we can assume that all the H_2SO_3 molecules will lose one H^+ ion before any of the HSO_3^- ions loses its H^+.

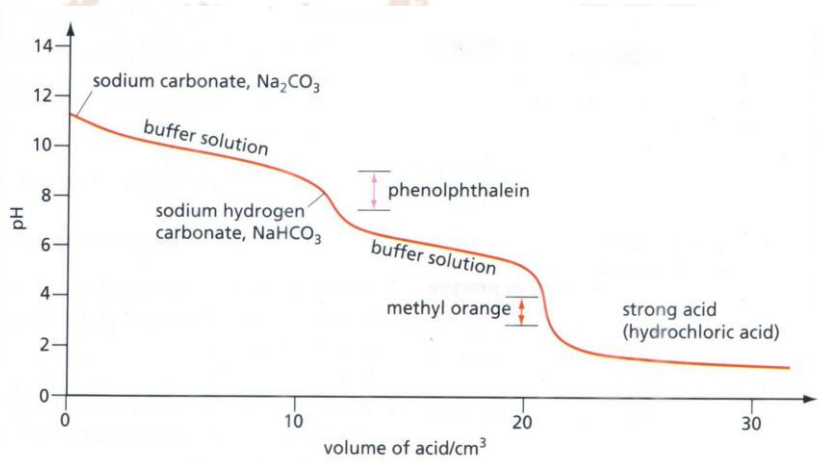
$$H_2SO_3 \xrightarrow{OH^-} HSO_3^- \xrightarrow{OH^-} SO_3^{2-}$$



Note that the titration curve usually has **two steep portions**, which corresponds to **two equivalence points**.

A similar curve is also obtained for a titration involving a mixture of two acids with an appreciable difference in K_a values (or a mixture of 2 bases with an appreciable difference in K_b values). In practice, we can observe the two separate end–points with the proper choice and use of two different indicators.

Consider the titration of sodium carbonate with dilute HC*l*.



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There are 2 stages in the titration:

$CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq)$ ——————————(1)

$HCO_3^-(aq) + H^+(aq) \rightarrow H_2O(l) + CO_2(g)$ ——————————(2)

The first rapid change in pH for reaction (1) occurs at pH = 8.5. Therefore a suitable indicator for the first equivalence point is phenolphthalein.

The second rapid change in pH for reaction (2) occurs at pH = 3.5. Therefore a suitable indicator for the second equivalence point is methyl orange.

To observe the two end–points separately, phenolphthalein is first added. Methyl orange is added only after the first equivalence point is reached.

If methyl orange is used at the start of the experiment, only one end–point is observed and the titre obtained is twice that obtained with phenolphthalein.

Exercise 5.2 (Worked Example)

A 25.0 cm^3 portion of a solution containing sodium carbonate and sodium hydrogencarbonate needed 22.50 cm^3 of a solution of hydrochloric acid of concentration 0.100 mol dm^{-3} to decolourise phenolphthalein. On addition of methyl orange, a further 28.50 cm^3 of the acid was needed to turn this indicator orange. Calculate the concentration of sodium carbonate and sodium hydrogencarbonate in the solution.

With phenolphthalein indicator:

$Na_2CO_3(aq) + HCl(aq) \rightarrow NaHCO_3(aq) + NaCl(aq)$ ——————————(1)

No of moles of HCl used = $0.100 \times 0.0225 = 2.25 \times 10^{-3}$
No of moles of $Na_2CO_3 = 2.25 \times 10^{-3}$

$[Na_2CO_3] = 2.25 \times 10^{-3} / 0.025 = 0.0900$ mol dm^{-3}

With methyl orange indicator:

$NaHCO_3(aq)$ + $HCl(aq) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g)$

(from original $NaHCO_3$ and the $NaHCO_3$ formed in (1))

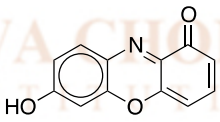
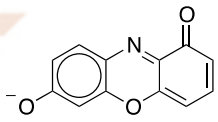
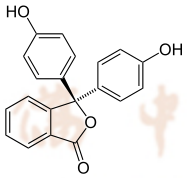
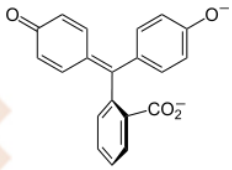
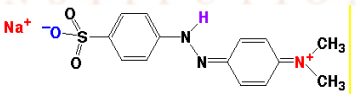
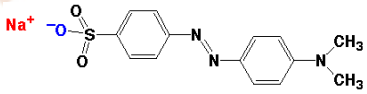
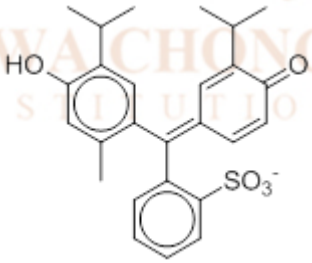
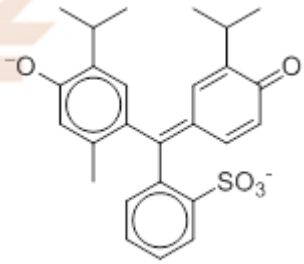
No of moles of HCl used = $0.100 \times 0.0285 = 2.85 \times 10^{-3}$
No of moles of HCl used for $NaHCO_3$ formed from $Na_2CO_3 = 2.25 \times 10^{-3}$
No of moles of HCl used for original $NaHCO_3 = 2.85 \times 10^{-3} - 2.25 \times 10^{-3} = 0.60 \times 10^{-3}$

$[NaHCO_3]$ in the original solution = $0.60 \times 10^{-3} / 0.025 = 0.0240$ mol dm^{-3}

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5.2 Acid-Base Indicators (Background Info)

An acid-base indicator is a weak aqueous acid whose acid form, HIn, is a different colour from its ionised form (or conjugate base form), In^-. As such, it shows different colours in solutions of different pH.

General equation	HIn(aq) acid form (colour 1)	⇌	$H^+(aq)$ +	$In^-(aq)$ ionised form (colour 2)
litmus	 red	⇌	$H^+(aq)$ +	 blue
Phenolphthalein	 colourless	⇌	$H^+(aq)$ +	 pink
Methyl orange	 red	⇌	$H^+(aq)$ +	 yellow
Thymol blue	 yellow	⇌	$H^+(aq)$ +	 blue

At different pH values, the proportion of HIn to In^- is different, giving rise to different colours.

For litmus:

- In acidic solutions, $[H^+]$ is high. The position of equilibrium lies on the left. Predominant form of litmus is HIn, so the solution will appear red.
- In alkaline solutions, $[OH^-]$ is high so $[H^+]$ is low. The position of equilibrium lies on the right. Predominant form of litmus is In^-. Hence the solution will appear blue.

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5.3 Working pH Range of Indicators (Background info)

For most indicators, the predominant form must be at least **10 times** more concentrated than the other form for its colour to be distinguished from the other coloured form.

Since for an indicator, $HIn\ (aq) \rightleftharpoons H^+\ (aq) + In^-\ (aq)$
The dissociation constant of an indicator, K_{In}, will be:

$$K_{In} = \frac{[H^+][In^-]}{[HIn]}$$

Taking –lg on both sides and rearranging,

$$pH = pK_{In} + \lg \frac{[In^-]}{[HIn]}$$

For litmus:
If the ratio of $[In^-]/[HIn] \geq 10/1$, i.e. **$pH \geq pK_{In} + 1$**, the solution appears blue.

If the ratio of $[In^-]/[HIn] \leq 1/10$, i.e. **$pH \leq pK_{In} - 1$**, the solution appears red.

Therefore, the litmus changes from red to blue over a pH range of

$$pH = pK_{In} - 1 \quad \text{to} \quad pH = pK_{In} + 1$$

That is, the **working range** of an indicator (i.e. pH range where a marked colour change occurs) is approximately **$pK_{In} \pm 1$**.

Colours of common indicators for acid-base titrations

Table 6 Some common indicators and their working pH range

Indicators	pH working range	Colour in acidic region	Colour in basic region
methyl orange	3.1 – 4.4	red	yellow
screened methyl orange	3.0 – 4.6	violet	green
bromothymol blue	6.0 – 7.6	yellow	blue
phenolphthalein (not used in lab)	8.0 – 9.6	colourless	pink
thymol blue*	8.0 – 9.6	yellow	blue
thymolphthalein*	9.3 – 10.5	colorless	blue

*can be used as an alternative indicator in place of phenolphthalein to indicate end point of weak acid-strong base titration

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5.4 Choice of Indicators

LO 10.1(e): explain the choice of suitable indicators for acid–base titrations, given appropriate data

During an acid-base titration, one solution is run into the other in the presence of an indicator.

- **End-point**: the point in a titration at which the indicator changes colour when 1 drop of excess titrant is added.

- **Equivalence point**: the point in a titration at which the exact number of moles of acid and base react completely.

The end-point tells us the equivalence point **only when a suitable indicator is used**.

- The indicator must have a **distinct colour change**.
- The **working pH range** of the indicator must **coincide with the rapid pH change at the equivalence point** for the titration.

The rapid pH change for the titration depends on the strengths of acid and alkali used. Either the acid or the alkali, or both, may be strong or weak, so that there are four possible combinations.

Table 7. Suitable indicators for different types of titration

Type	suitable indicator
strong acid – strong alkali	methyl orange or phenolphthalein or thymol blue
strong acid – weak alkali	methyl orange
weak acid – strong alkali	Phenolphthalein or thymol blue
weak acid – weak alkali	no suitable indicator

Exercise 5.3

A 25.0 cm^3 solution containing 0.120 mol dm^{-3} of lactic acid is titrated with aqueous NaOH of concentration 0.100 mol dm^{-3}. The pH at the equivalence point was found to be 8.29.

The table below lists the working ranges of some acid-base indicators. Suggest which of the following indicators can be used for this titration and explain your choice.

Indicator	Working range	Low pH color	High pH color
Bromophenol blue	3.0 – 4.6	yellow	purple
Thymol blue	8.0 – 9.6	yellow	blue
Naphtholphthalein	7.3 – 8.7	colorless	green-blue

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Planning Questions involving Acid-Base Equilibria

Using the concepts in this chapter, you may be asked to plan experiments involving acid-base equilibria. Some examples are as follows.

1. Determination of pK_a of a weak acid or pK_b of a weak base. (See 2013 HCI JC2 BT2 Paper 2 Q1 in "Examples of Acid-Base Equilibria Planning Qns" on Chemistry Google Site)
2. Preparation of a specific buffer for a particular purpose. (See 2011 HCI JC2 BT2 Paper 2 Q1 in "Examples of Acid-Base Equilibria Planning Qns" on Chemistry Google Site)

LOOKING AHEAD

Acidity of organic acids and phenols as well as basicity of amines will be covered under organic carboxylic acids, phenols and amines. The charges in an amino acid is also related to pH of solution.

Salt hydrolysis due to high charge density of cations will be covered in the chapters on Transition Elements and Periodicity.

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Acid-Base Equilibria – Summary

Concept	Application
A Brønsted acid is a proton donor. A Brønsted base is a proton acceptor.	To identify if a molecule or an ion is behaving as an acid or a base given an equation or vice versa
$\mathbf{pX = -\log_{10} X}$ $\Rightarrow$ $X = 10^{-pX}$	To define quantities such as pH, pOH, pK_w, pK_a and pK_b
$\mathbf{K_w = [H^+][OH^-]} = 1 \times 10^{-14}$ (at 25°C) K_w shows the relationship between $[H^+]$ and $[OH^-]$ in **any** aqueous solutions.	To calculate $[H^+]$ or $[OH^-]$ given the value of the other. In pure water, $[H^+] = [OH^-] = 1 \times 10^{-7}$ (at 25°C)
$\mathbf{pK_w = pH + pOH}$ = 14 (at 25°C)	To calculate pH from pOH, or vice versa
For any <u>conjugate</u> acid–base pair, $\mathbf{K_a \times K_b = K_w}$ pK_a + pK_b = pK_w = 14 (at 25 °C)	To calculate K_a from K_b, or vice versa. You use this equation when you need one of these K values but have the other.
$HA \rightleftharpoons H^+ + A^-$ $\mathbf{K_a} = \dfrac{[H^+]_{eqm}[A^-]_{eqm}}{[HA]_{eqm}}$	To calculate the pH of a • weak acid, $\mathbf{K_a} \approx \dfrac{[H^+]^2_{eqm}}{[HA]_{initial}}$ • buffer, $\mathbf{K_a} \approx \dfrac{[H^+]_{eqm}[salt]_{initial}}{[acid]_{initial}}$ To compare the *strength* of weak acids. The larger the K_a value, the stronger the acid.
$B + H_2O \rightleftharpoons BH^+ + OH^-$ $\mathbf{K_b} = \dfrac{[BH^+]_{eqm}[OH^-]_{eqm}}{[B]_{eqm}}$	To calculate the pH of a • weak base, $\mathbf{K_b} \approx \dfrac{[OH^-]^2_{eqm}}{[B]_{initial}}$ • buffer, $\mathbf{K_b} \approx \dfrac{[OH^-]_{eqm}[salt]_{initial}}{[base]_{initial}}$ To compare the *strength* of weak bases. The larger the K_b value, the stronger the base.
Salt hydrolysis – a reaction in which ions react with water to form acidic or alkaline solutions e.g. $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ $CH_3CO_2^- + H_2O \rightleftharpoons CH_3CO_2H + OH^-$	To explain why the pH of a salt derived from • strong acid and weak base (e.g. NH_4Cl) is < 7 • weak acid and strong base (e.g. CH_3CO_2Na) is > 7

<u>Checklist for pH calculations</u>

Do you know how to calculate the pH of a solution containing each of the following?

- ✓ a strong acid or strong base
- ✓ a weak acid or weak base
- ✓ a salt such as CH_3CO_2Na or NH_4Cl
- ✓ a buffer

Using the above, can you sketch a titration curve, and mark the various key points on the curve (initial pH, equivalence point, buffer with maximum capacity)

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15 Halogen Derivatives

GUIDING QUESTIONS

Halogenoalkanes

- How are halogenoalkanes synthesised?
- Which classes of reagents do halogenoalkanes react with and why? What types of reactions do halogenoalkanes undergo and why?
- How do halogenoalkanes react with nucleophiles? What are the factors which determine the mechanism of nucleophilic substitution?
- How does the reactivity compare between different halogenoalkanes?

Halogenoarenes

- How are halogenoarenes synthesised?
- How does the reactivity of a halogenoarene compare with that of a halogenoalkane towards nucleophilic reagents?

LEARNING OUTCOMES

Students should be able to:

11.4(a) recall the chemistry of halogenoalkanes as exemplified by:
- **(i)** the following nucleophilic substitution reactions of bromoethane: hydrolysis; formation of nitriles; formation of primary amines by reaction with ammonia
- **(ii)** the elimination of hydrogen bromide from 2-bromopropane

11.4(b) describe and explain the mechanisms of nucleophilic substitutions in halogenoalkanes:
- **(i)** S_N1, in terms of stability of the carbocation intermediates
- **(ii)** S_N2, in terms of steric hindrance in the halogenoalkanes

11.4(c) explain the stereochemical outcome in nucleophilic substitution involving optically active substrates:
- **(i)** inversion of configuration in S_N2 mechanism
- **(ii)** racemisation in S_N1 mechanism

11.4(d) interpret the different reactivities of halogenoalkanes, with particular reference to hydrolysis and to the relative strengths of the C–Hal bonds

11.4(e) explain the unreactivity of chlorobenzene compared to halogenoalkanes towards nucleophilic substitution, in terms of the delocalisation of the lone pair of electrons on the halogen and steric hindrance

11.4(f) suggest characteristic reactions to differentiate between
- **(i)** different halogenoalkanes
- **(ii)** halogenoalkanes and halogenoarenes

e.g. hydrolysis, followed by testing of the halide ions

11.4(g) explain the uses of fluoroalkanes and fluorohalogenoalkanes in terms of their relative chemical inertness

11.4(h) recognise the concern about the effect of chlorofluoroalkanes (CFCs) on the ozone layer
[the mechanistic details of how CFCs deplete the ozone layer are **not** required]

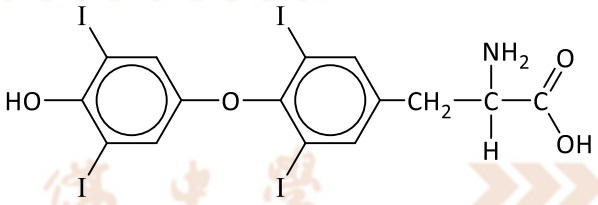
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REFERENCES

1. Peter Cann and Peter Hughes. Chemistry for Advanced Level. John Murray (Publishers) Ltd. Chapter 25.
2. John McMurry. Organic Chemistry. Brooks/Cole. Chapters 10-11.

1 INTRODUCTION

There are only a few naturally-occurring organic halogen compounds. One example is thyroxine, a hormone secreted by the thyroid gland.



thyroxine

Synthetic halogen compounds have a variety of commercial applications such as insecticides, herbicides, dry-cleaning agents and degreasers, fire-extinguishing chemicals, and polymers. However, many chlorinated hydrocarbons are suspected to be carcinogenic and are being replaced by other compounds.

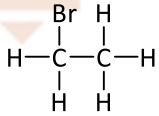
Organic halogen compounds are often used as intermediates in organic synthesis; they are readily formed from common materials and can easily be transformed into many different functional groups.

Two main types of halogen compounds will be discussed: **halogenoalkanes** and **halogenoarenes**.

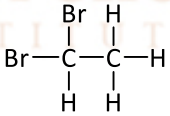
1.1 Halogenoalkanes (alkyl halides)

They are alkanes with one or more H atoms replaced by the halogen atom, F, C*l*, Br or I.

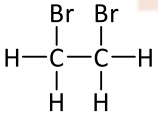
In IUPAC nomenclature, the halogen is considered as a substituent of the hydrocarbon. These compounds are therefore named using the prefixes, fluoro-, chloro-, bromo- and iodo-. Some examples are given below.



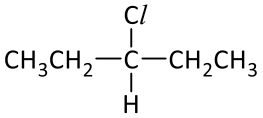
bromoethane



1,1-dibromoethane



1,2-dibromoethane



3-chloropentane

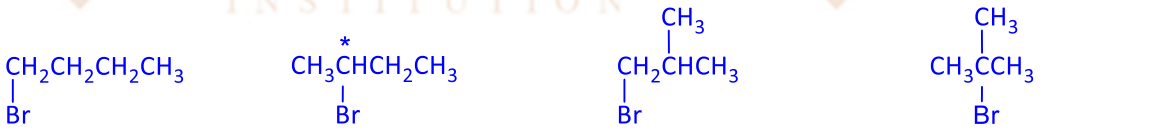
Halogenoalkanes may show constitutional isomerism and enantiomerism. For example, there are five isomers with the molecular formula, C_4H_9Br.

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Exercise 1.1 (Worked Example)

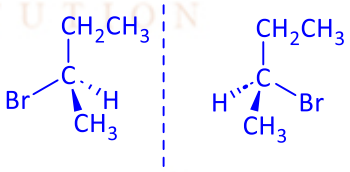
(a) Draw the five isomers (constitutional and enantiomers) with the molecular formula, C_4H_9Br.

(b) Give the IUPAC names of the four constitutional isomers.



1-bromobutane 2-bromobutane 1-bromo-2-methylpropane 2-bromo-2-methylpropane

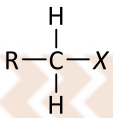
2-bromobutane has a pair of enantiomers:



mirror plane

Total five isomers, two of which are a pair of enantiomers.

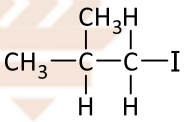
Halogenoalkanes are classified as **primary**, **secondary** or **tertiary**, depending on how many alkyl groups are attached to the halogenated carbon (the carbon atom that is joined to the halogen atom, *X*).

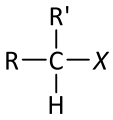


Primary halogenoalkanes

In a primary halogenoalkane, the halogenated carbon is only attached to **one** alkyl group or one other carbon atom.

e.g. CH_3CH_2Br $CH_3CH_2CH_2Cl$

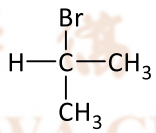


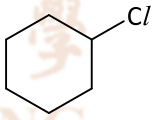


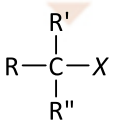
Secondary halogenoalkanes

In a secondary halogenoalkane, the halogenated carbon is attached to **two** alkyl groups or two other carbon atoms.

e.g.



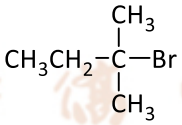


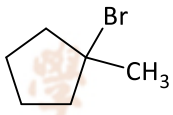


Tertiary halogenoalkanes

In a tertiary halogenoalkane, the halogenated carbon is attached to **three** alkyl groups or three other carbon atoms.

e.g.

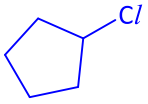
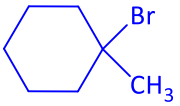




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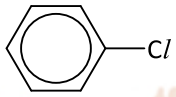
Exercise 1.2 (Worked Example)

Draw the structural formulae of the halogenoalkanes in the table and classify them as primary, secondary or tertiary.

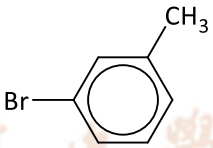
Name	Structural formula	Classification (primary, secondary or tertiary)
3-chloropropene	$CH_2=CHCH_2Cl$	primary
chlorocyclopentane		secondary
1-bromo-1-methylcyclohexane		tertiary

1.2 Halogenoarenes (aryl halides)

These compounds have a halogen atom attached directly to a benzene ring.

e.g. 

chlorobenzene



1-bromo-3-methylbenzene

1.3 Physical Properties of Halogenoalkanes

Halogenoalkanes are generally colourless liquids with sweetish smells. They are immiscible with and denser than water. Boiling points of halogenoalkanes are higher than those of their corresponding alkanes (alkanes with the same number of carbon atoms). For the same alkyl group, the boiling point increases in the order: chloroalkane < bromoalkane < iodoalkane.

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Exercise 1.3 (Worked Example)

The boiling points of some organic compounds are given below.

Compound	Structural formula	Name	Boiling point /°C
A	$CH_3CH_2CH_3$	propane	−42
B	$CH_3CH_2CH_2Cl$	1-chloropropane	47
C	$CH_3CH_2CH_2Br$	1-bromopropane	71
D	$CH_3CH_2CH_2I$	1-iodopropane	102

Note that the main intermolecular forces in halogenoalkanes are dispersion forces (also called instantaneous dipole-induced dipole attractions). The difference in permanent dipole-permanent dipole attractions is not as significant as dispersion forces and does not explain the observed boiling point trend.

Explain each of the following.

(a) The boiling point of compound *B* is higher than that of *A*.

Both compounds are simple covalent molecules.

B has more electrons than *A* *or* larger electron cloud, so *B* forms stronger dispersion forces between its molecules.

In addition, there is some amount of permanent dipole-permanent dipole attractions for *B*.

Thus, more energy is needed to overcome stronger intermolecular attractions between *B* molecules during boiling (than between *A* molecules). Therefore *B* has higher boiling point.

(b) The boiling point increases in the order, $B < C < D$.

All three compounds are simple covalent molecules.

The number of electrons for the molecule increases in the order, $B < C < D$
or the size of electron cloud for the molecule increases in the order, $B < C < D$.

So intermolecular dispersion forces increase in strength in the same order.

Energy needed to overcome intermolecular attractions increases in the same order. Thus, boiling point increases in the same order.

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2 PREPARATION OF HALOGENOALKANES AND HALOGENOARENES

Halogenoalkanes can be prepared from:

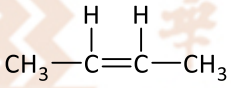
- Free radical substitution of alkanes but would give a mixture of halogenated alkanes (unable to control the position of substitution and how many H atoms become substituted) (Topic 10 Alkanes)
- Electrophilic addition on alkenes (Topic 11 Alkenes)
- Nucleophilic substitution of alcohols (to be covered in Topic 16 Hydroxy Compounds)

Halogenoarenes can be prepared from:

- Electrophilic substitution of arenes (Topic 12 Arenes)

Exercise 2.1

Draw the structure of the organic compound in each of the following boxes.

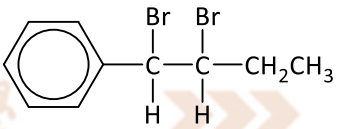


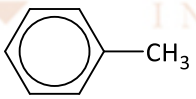
HBr →

(i)

(ii)

Br_2 in CCl_4 →





Cl_2, $FeCl_3$ catalyst →

(iii)

+

(iv)

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3 REACTIONS OF HALOGENOALKANES

Halogenoalkanes undergo two types of reactions: **nucleophilic substitution** and **elimination**.

3.1 Nucleophilic Substitution Reactions

Halogenoalkanes are fairly reactive compounds, owing largely to the polarity of the C–X bond. Halogens are more electronegative than carbon, so the carbon-halogen bond is polar. The electron-deficient carbon atom has a partial positive charge which causes it to be attractive to **nucleophiles**.

During reaction, the halogen atom in the halogenoalkane can be substituted by a nucleophile e.g. OH^-, CN^- and NH_3. This reaction typical of halogenoalkanes is called **nucleophilic substitution**.

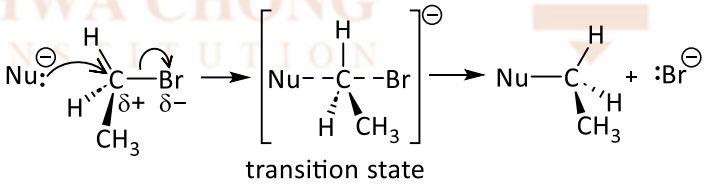
The overall reaction for nucleophilic substitution can be represented as:



3.1.1 General mechanisms of nucleophilic substitution mechanisms

Nucleophilic substitution reactions can proceed by either an S_N1 or S_N2 mechanism. Generally, primary halogenoalkanes undergo nucleophilic substitution via the one-step mechanism S_N2 while tertiary halogenoalkanes undergo reactions via the two-step mechanism S_N1. Secondary halogenoalkanes may react via either mechanism.

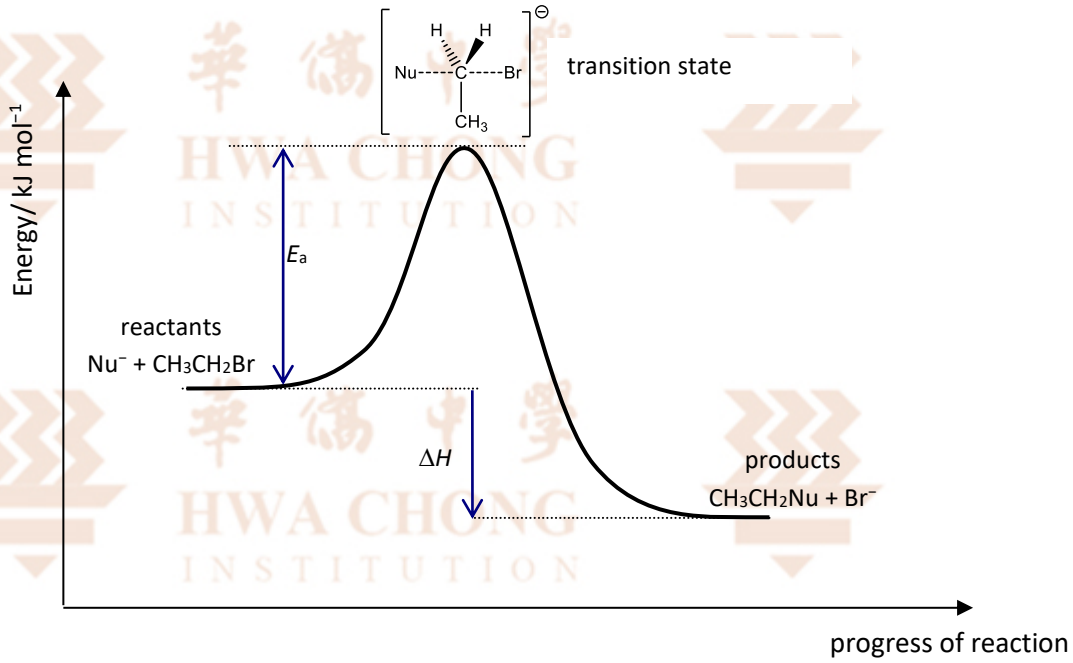
- **S_N2 mechanism (bimolecular nucleophilic substitution)**



- The C–Br bond in bromoethane is **polar** due to the difference in electronegativity between the carbon and bromine atoms.
- The **nucleophile** attacks the partially positively charged carbon atom from the side opposite to the bromine atom. The nucleophile donates its lone pair to the electron-deficient carbon so that a bond begins to form between the nucleophile and the carbon atom.
- At the same time, the C–Br bond is simultaneously weakened and begins to break. Both the bonding electrons in the C–Br bond are donated to the Br atom to form Br^-.
- An unstable, activated complex called a **transition state** is formed where the entering nucleophile and the leaving Br^- ion are partially bonded to the same carbon atom. Bond breaking and bond forming occur simultaneously. This is a **one-step mechanism**.

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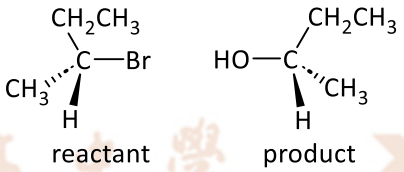
- Rate = k[RBr][Nu^-]
- The mechanism is known as S_N2 (**bimolecular** nucleophilic substitution), because two species are involved in the rate determining step of the mechanism.
- The energy profile or reaction pathway diagram for the S_N2 mechanism is given below.



Stereochemistry

LO 11.4(c)(i) explain the stereochemical outcome in nucleophlic substitution involving optically active substrates: inversion of configuration in S_N2 mechanism

If the original R*X* molecule is chiral, the stereochemistry at the electron-deficient carbon will be **inverted** after the substitution reaction (see below).

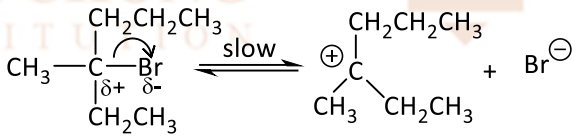


If the reaction occurs purely through the S_N2 mechanism, only one of the enantiomers will be formed as the product. There will not be a mixture of two enantiomers. As a result, the product obtained through the S_N2 mechanism will be optically active, if there is a chiral carbon present.

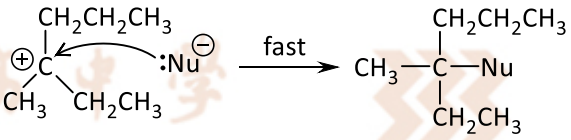
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- **S_N1 mechanism (unimolecular nucleophilic substitution)**

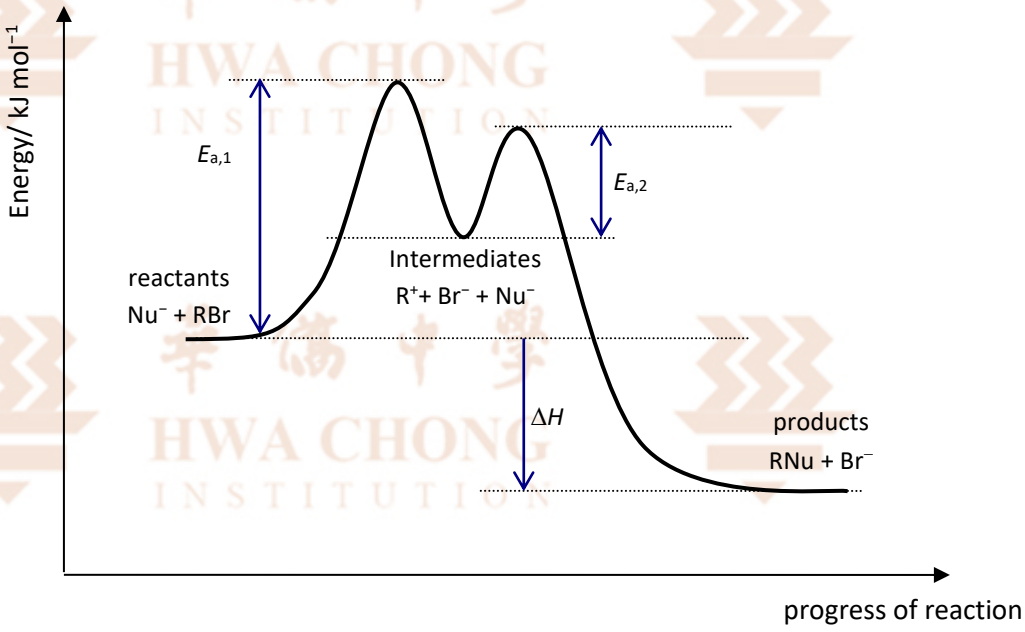
STEP 1



STEP 2



- The C–Br bond in 3-bromo-3-methylhexane is **polar** due to the difference in electronegativity between the carbon and bromine atom.
- In the first step, heterolytic fission of the C–Br bond occurs, giving a **carbocation intermediate** and a bromide ion. The electron-donating alkyl groups help to stabilise the carbocation intermediate.
- In the second step, the highly reactive carbocation is readily attacked by the **nucleophile** to form the product.
- This is a **two-step mechanism**.
- Rate = k[RBr]
- The mechanism is known as S_N1 (**unimolecular** nucleophilic substitution) because only one species is involved in the rate determining step of the mechanism.
- The energy profile or reaction pathway diagram for the S_N1 mechanism is given below.

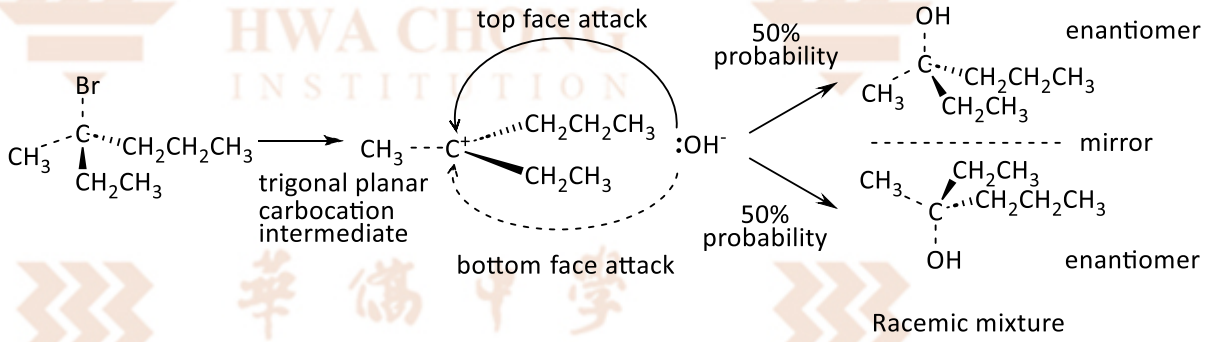


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Stereochemistry

LO 11.4(c)(ii) explain the stereochemical outcome in nucleophilic substitution involving optically active substrates: racemisation in S_N1 mechanism

Since the carbocation is **trigonal planar** with respect to the electron-deficient carbon, the nucleophile is able to attack from the top and bottom face of the carbocation with **equal probability**. If the addition of the nucleophile results in a chiral product, a **racemic mixture** is formed in this mechanism as both mirror image enantiomers are formed in equal quantities.



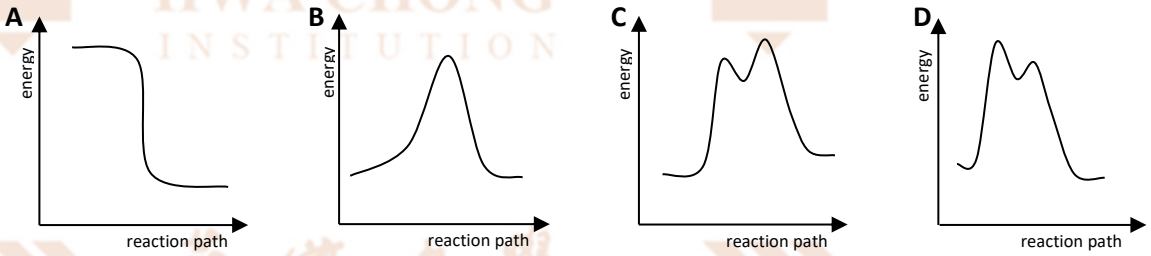
Exercise 3.1 (Worked Example)

A possible reaction of hydrolysis of 2-chloro-2-methylpropane is as shown.

$$(CH_3)_3C{-}Cl \xrightarrow{slow} (CH_3)_3C^+ + Cl^-$$

$$(CH_3)_3C^+ + OH^- \xrightarrow{fast} (CH_3)_3C{-}OH$$

Which diagram represents the reaction profile for this mechanism? Hint: Consider the bond energies.



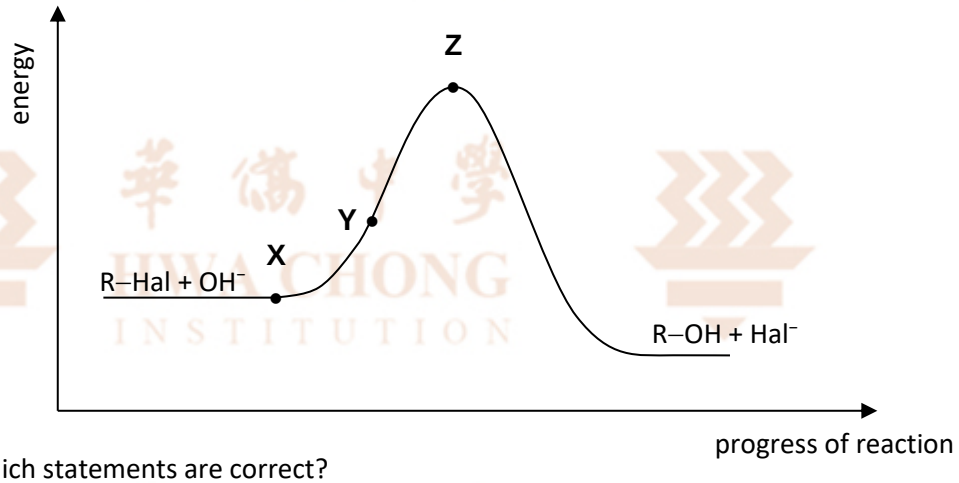
Ans: D

Remarks: This is a two-step mechanism (S_N1 mechanism) and thus there should be two peaks on the reaction profile. Since the C–O bond formed is stronger than the C–*Cl* broken (check bond energy data from *Data Booklet*), the overall reaction (chloroalkane + OH^- → alcohol + Cl^-) is exothermic and thus the energy of the (final) products should be lower than that of the (starting) reactants.

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Exercise 3.2 (Worked Example)

Halogenoalkanes react with aqueous alkali. One mechanism has the energy profile shown below.



Which statements are correct?

1 The reaction is an example of nucleophilic substitution.

2 Between **X** and **Z** the C–Hal bond will be lengthening.

3 The energy difference between **X** and **Y** represents the activation energy.

Ans: Options 1 and 2 are correct.

For Option 2, as the C–Hal bond breaks, the C–Hal lengthens and then breaks.

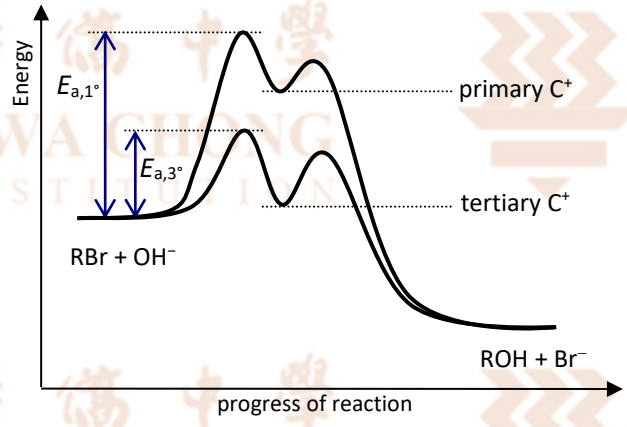
For Option 3, the energy difference bet. **X** and **Z** represents the activation energy and not **X** and **Y**.

Effect of structure of the halogenoalkane on the relative rates of S_N1 and S_N2

LO11.4(b)(i) describe and explain the mechanism of nucleophilic substitution in halogenoalkanes:S_N1 in terms of stability of the carbocation intermediate

- **S_N1 in terms of stability of the carbocation intermediates**

  Alkyl groups donate electrons to the carbocations and help to stabilise them. As such, the stability of carbocations increases in the order primary < secondary < tertiary. As the carbocation becomes more stable, the activation energy for the reaction leading to it decreases. See the figure below for the reaction profiles for the S_N1 mechanism for a primary vs. a tertiary bromoalkane:



We therefore expect that the **rate of S_N1 will increase in the order primary < secondary < tertiary**.

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LO 11.4(b)(i) describe and explain the mechanism of nucleophilic substitution in halogenoalkanes: S_N2 in terms of steric hindrance of the halogenoalkanes

- **S_N2 in terms of the steric hindrance of the halogenoalkane**

  A tertiary halogenoalkane has three alkyl groups attached to the halogenated carbon, while a primary halogenoalkane has only one alkyl group attached to the halogenated carbon. Alkyl groups could 'hinder' or 'block' the attack of a nucleophile on the halogenated carbon in a S_N2 mechanism. **The rate of S_N2 will increase in the order tertiary < secondary < primary.**

- **Overall, we expect primary halogenoalkanes to undergo nucleophilic substitution predominantly via the S_N2 mechanism, tertiary halogenoalkanes predominantly via the S_N1 mechanism, and secondary halogenoalkanes to react via either mechanism.**

- There are exceptions to the preference in mechanism due to the same electronic and steric considerations (and information would be provided in the question for you to make the conclusion).

  E.g. 1-chloro-2,2-dimethylpropane, $(CH_3)_3CCH_2Cl$, despite being a primary halogenoalkane, is practically inert to substitution by the S_N2 mechanism because of steric hindrance.

  On the other hand, (chloromethyl)benzene, despite being a primary halogenoalkane, favours substitution by the S_N1 mechanism due to stabilisation of the carbocation intermediate by delocalisation of the positive charge into the benzene ring.

Exercise 3.3
Bromoethane, CH_3CH_2Br, reacts with sodium methoxide, $CH_3O^-Na^+$, to form $CH_3CH_2OCH_3$.
Name and describe the mechanism for the reaction.

Relative rates of nucleophilic substitution in terms of the strength of the C–halogen bond

LO 11.4(d) interpret the different reactivities of halogenoalkanes, with particular reference to hydrolysis and to the relative strengths of the C–Hal bonds

In comparing the reactivity between different halogenoalkanes, there is one main factor at work:

Strength of the C–*X* bond

The ease of nucleophilic substitution in halogenoalkanes depends on the ease of breaking the C–*X* bond. As the size of the halogen atom increases, the **C–*X* bond length increases** and the **bond strength decreases**, and hence nucleophilic substitution takes place more readily. The C–F bond is very strong, so fluoroalkanes are extremely unreactive and do not undergo nucleophilic substitution.

Compound	C–*X* bond length /nm	Bond energy /kJ mol^{-1}
CH_3F	13.9	+485
CH_3Cl	17.8	+340
CH_3Br	19.3	+280
CH_3I	21.4	+240

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LO 11.4(a)(i) recall the chemistry of halogenoalkanes as exemplified by the following nucleophilic substitution reactions of bromoethane: hydrolysis; formation of nitriles; formation of primary amines by reaction with ammonia

3.1.2 Nucleophilic substitution with OH^- to form alcohols

$$R\text{–}X + OH^-(aq) \rightarrow R\text{–}OH + X^- \qquad X = Cl, Br \text{ or } I$$

Reagents and conditions: dilute NaOH, heat

This reaction is also known as alkaline hydrolysis.

3.1.3 Nucleophilic substitution with CN^- to form nitriles

$$R\text{–}X + CN^- \rightarrow R\text{–}CN + X^-$$

Reagents and conditions: ethanolic KCN, heat

The lone pair of electrons is donated by the C atom of CN^-.
This reaction serves to increase the length of the carbon chain by one C atom, and is known as a step-up reaction.

The nitrile formed can be used in the synthesis of carboxylic acids (via hydrolysis) and amines (via reduction) as shown below.

Acidic hydrolysis of nitriles

$$R\text{–}CN + H^+ + 2H_2O \rightarrow RCO_2H + NH_4^+$$

Reagents and conditions: dilute H_2SO_4, heat

Alkaline hydrolysis of nitriles

$$R\text{–}CN + OH^- + H_2O \rightarrow RCO_2^- + NH_3$$

Reagents and conditions: dilute NaOH, heat

Reduction of nitriles

$$R\text{–}CN + 4[H] \rightarrow RCH_2NH_2$$

Reagents and conditions: $LiAlH_4$ in dry ether or
$H_2(g)$, Ni catalyst, high P

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3.1.4 Nucleophilic substitution with NH_3 to form amines

$$R\text{–}X + NH_3 \rightarrow R\text{–}NH_2 + HX$$

Reagents and conditions: ethanolic concentrated NH_3, heat in sealed tube

(the sealed tube is to prevent the ammonia from escaping)

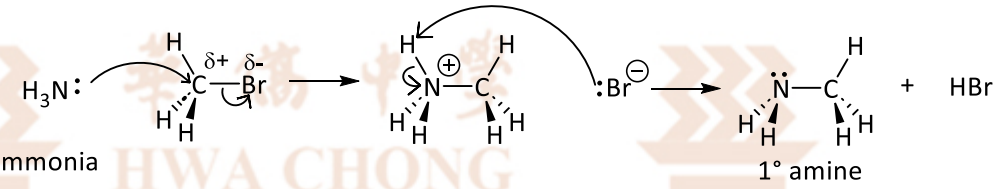
("ethanolic concentrated NH_3" means a concentrated solution of NH_3 in ethanol.)

A primary amine is formed in the above reaction. Like ammonia, this primary amine possesses a lone pair of electrons on the N atom. The electron-donating alkyl group makes the amine more nucleophilic than ammonia. If an excess of halogenoalkane is present, the amine can readily react with the halogenoalkane to form a secondary amine. Further reactions can then occur to form more substituted amines:

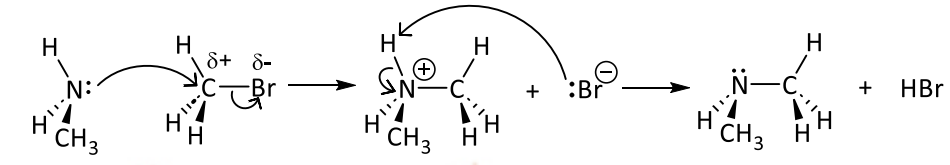
$$RX + RNH_2 \rightarrow R_2NH + HX \quad \text{(secondary amine formed)}$$
$$RX + R_2NH \rightarrow R_3N + HX \quad \text{(tertiary amine formed)}$$
$$RX + R_3N \rightarrow R_4N^+X^- \quad \text{(quaternary ammonium salt formed)}$$

The following mechanisms show how primary and secondary amines may be formed from the nucleophilic substitution of a halogenoalkane, using ammonia and bromomethane as an example:

Ammonia as the nucleophile can react with bromomethane to form methylamine (primary amine):



If excess bromomethane is present, the 1° amine reacts with the bromomethane:



The formation of the different amines when excess halogenoalkane is used causes the yield of the primary amine to decrease, and also makes the separation of products difficult. As such, to obtain the primary amine as the main product and avoid the further reactions described above, **excess ammonia** should be used.

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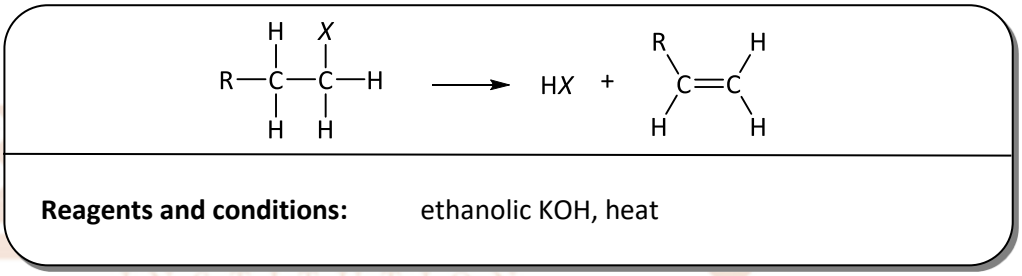
Exercise 3.4

The previous mechanisms showed how a side product, the secondary amine, can be formed from the reaction between ammonia and excess bromomethane. Suggest mechanisms to show how the tertiary amine $(CH_3)_3N$ and quarternary ammonium salt $(CH_3)_4N^+Br^-$ may be formed in further reactions with excess bromomethane.

3.2 Elimination

LO 11.4(a)(ii) recall the chemistry of halogenoalkanes as exemplified by the elimination of hydrogen bromide from 2-bromopropane

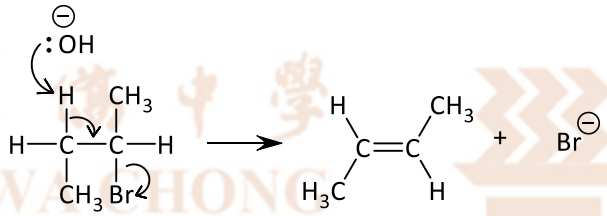
Halogenoalkanes take part in elimination reactions resulting in the formation of alkenes.



When KOH is dissolved in ethanol, the OH^- behaves more as a base than a nucleophile. It is able to remove a hydrogen ion from the **carbon atom adjacent to the C–*X***, causing the C–*X* to break, forming an alkene.

The same reagent (hydroxide ion) can therefore carry out two different types of reaction (nucleophilic substitution or elimination) when reacted with the same halogenoalkane. Both reactions do in fact occur at the same time, but the significance of substitution versus elimination varies, depending on the solvent, the nucleophile and the halogenoalkane used.

<u>Elimination (E2) mechanism</u> (For your information only)



The ease of elimination reactions depends on the strength of the C–*X* bond. The weaker the C–*X* bond, the more readily the halogenoalkane undergoes elimination.

More than one alkene can be formed when the carbon bonded to the halogen has more than one adjacent carbon atom with hydrogen atom(s) bonded to it. Both constitutional and *cis-trans* isomers may be formed.

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Exercise 3.5

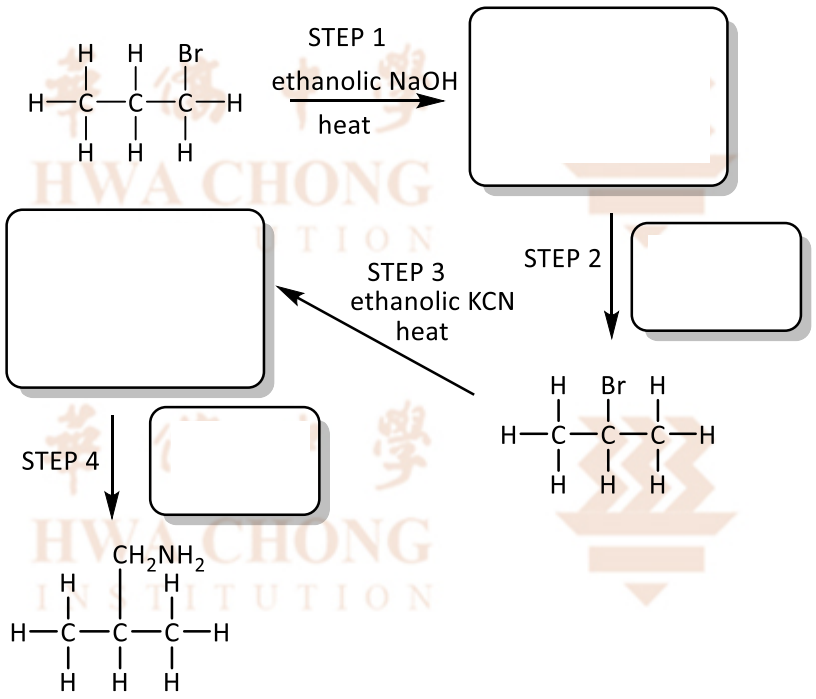
Draw the structural formulae of the three alkenes formed when 2-bromobutane undergoes elimination with hot ethanolic NaOH.

For your information only:

The major product is the alkene with the largest number of alkyl groups attached to the double-bonded carbon atoms. This is known as *Saytzeff's* rule. (Also spelt *Zaitsev* in some books.) Based on *Saytzeff's* rule, the major product for the above reaction is but-2-ene.

Exercise 3.6

Fill in the boxes with the correct reagents and structures of compounds in the reaction scheme.



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4 REACTIONS OF HALOGENOARENES

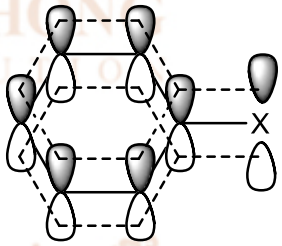
LO 11.4(e) explain the unreactivity of chlorobenzene compared to halogenoalkanes towards nucleophilic substitution in terms of the delocalisation of the lone pair of electrons on the halogen and steric hindrance

4.1 Reactivity of Halogenoarenes

Halogenoarenes are very much less susceptible to nucleophilic substitution than halogenoalkanes.

Reasons:

1. The lone pair of electrons on the halogen atom delocalises into the benzene ring.



As a result, there is **partial double bond character** in the C–*X* bond, so its bond length is shorter and bond strength is stronger than that in the corresponding halogenoalkane. The C–*X* bond in halogenoarenes is very difficult to break.

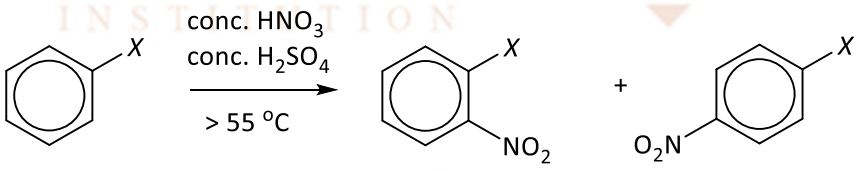
2. Sterically, the rear side of the C–X bond in halogenoarenes is blocked by the benzene ring. Also, the π-electron cloud of the benzene ring will repel the lone pair of electrons of an incoming nucleophile, rendering attack of the nucleophile difficult.

Hence, nucleophilic substitution of halogenoarenes cannot be achieved by the same reagents and conditions used for halogenoalkanes, and is only possible under very vigorous conditions.

4.2 Electrophilic Substitution on the Benzene Ring of Halogenoarenes

The halogenoarenes undergo electrophilic substitution on the benzene ring similar to other arenes. [See Topic 12 Arenes]

However, halogenoarenes are less susceptible to electrophilic substitution as the halogen substituent is deactivating. The halogen substituent is also 2,4-directing. An example of such a reaction is given below.

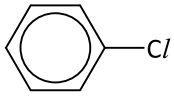
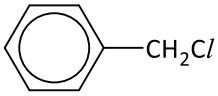


X = C*l*, Br & I
X is deactivating and 2,4-directing

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Exercise 4.1

State whether the following reactions take place in the respective halogen-containing compounds.

Compound	CH_3CH_2Cl		
Delocalisation of electrons	No	In the benzene ring as well as over to the chlorine atom	Within benzene ring only
Nucleophilic substitution			
Elimination			
Electrophilic substitution			

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5 DISTINGUISHING TESTS FOR HALOGENOALKANES

LO 11.4(f)(i) suggest characteristic reactions to differentiate between different halogenoalkanes

5.1 Comparing Colour of Ag*X* Precipitate

The general method for distinguishing between the type of halogen substituents present in halogenoalkanes is to compare the colour of the silver halide precipitates that are formed after the compound undergoes nucleophilic substitution by hydroxide ion. The test involves 3 steps.

Step 1: Add **NaOH(aq)** and heat. [Reaction: R*X* + OH^- → ROH + X^-]
Step 2: Add **excess dilute HNO_3**. [Removes unreacted OH^- so that brown Ag_2O ppt will not be formed in the next step]
Step 3: Add **$AgNO_3$(aq)** and observe the colour of precipitate formed. [$Ag^+(aq) + X^-(aq) \rightarrow AgX(s)$]

The expected observations (for the positive tests) are given in the table below. Sometimes, the colours of AgC*l* and AgBr are difficult to differentiate. We can follow up by adding NH_3(aq); AgC*l* dissolves in dilute aqueous NH_3 while AgBr does not.

	chloroalkane, RC*l*	bromoalkane, RBr	iodoalkane, RI
Colour of precipitate formed	white	cream	yellow
Identity of precipitate	AgC*l*	AgBr	AgI
Solubility of precipitate in NH_3 solution	dissolves in dilute aqueous NH_3	dissolves in concentrated NH_3	insoluble even in concentrated NH_3
	$AgX + 2NH_3 \rightarrow [Ag(NH_3)_2]^+ + X^-$ (Colourless complex ion) [Reasons for the solubility are discussed in Topic 13 Solubility Equilibria]		

5.2 Comparing Rate of Formation of Ag*X* Precipitate

The three different halogenoalkanes can also be distinguished using ethanolic $AgNO_3$. In this method, the rates of the formation of the silver halide precipitates will be different. The identity of the halogenoalkane can also be determined from the colour of the Ag*X* precipitate formed.

	chloroalkane, RC*l*	bromoalkane, RBr	iodoalkane, RI
Add 1 cm^3 of the organic compound in a test tube. Add 1 cm^3 of ethanolic $AgNO_3$ and place the test tube in a hot water bath.	white ppt (AgC*l*) formed in a longer time compared to RBr	cream ppt (AgBr) formed in a longer time compared to RI	yellow ppt (AgI) formed almost immediately

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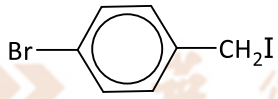
Explanation of the difference in the rate of formation of Ag*X* precipitate:

The C–*X* bond must break in a nucleophilic substitution reaction to give the halide ion. In this reaction, the nucleophile is ethanol. Bond strength decreases in the order C–C*l* > C–Br > C–I, as shown by the bond energies, +340, +280 and +240 kJ mol^{-1} obtained from the *Data Booklet*.

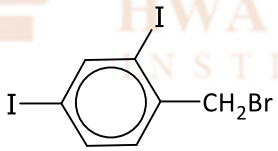
In this mechanism, the C–*X* is broken in the rate-determining step. Hence the stronger the C–*X* bond, the higher the activation energy of the rate-determining step, and hence a slower rate. The weaker the C–*X* bond, the easier and more readily it breaks to give the halide ion and the Ag*X* precipitate forms more quickly.

Exercise 5.1 (Worked Example)

A liquid *L* gave a pale yellow precipitate when shaken for some time with cold ethanolic silver nitrate. Which compound could *L* be?

1 

2 $CH_3CH_2CH_2I$

3 

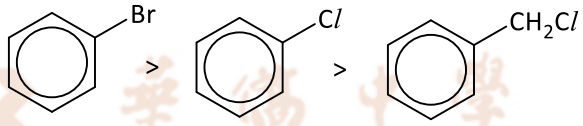
Ans: Options 1 and 2 are correct.
Remarks: Halogenoalkanes (i.e. chloroalkane, bromoalkane, iodoalkane groups) undergo nucleophilic substitution.
Halogenoarenes (i.e. chlorobenzene, bromobenzene, iodobenzene) less susceptible to nucleophilic substitution as explained in Section 4.1.

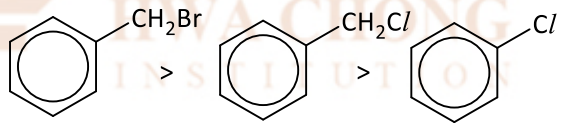
Exercise 5.2 (Worked Example)

Which sequence shows the correct order of **decreasing** ease of hydrolysis?

A $CH_3CH_2Cl > CH_3CH_2Br > CH_3CH_2I$

B $(CH_3)_2CHCl > (CH_3)_2CHI > (CH_3)_2CHBr$

C 

D 

Ans: D
Remarks: Ease (and rate) of nucleophilic substitution decreases in the order,
iodoalkane group > bromoalkane group > chloroalkane group
(look at bond energy data from *Data Booklet*, weaker C–halogen bond ⇒ easier to break)
Halogenoarenes – no nucleophilic substitution / very difficult to undergo nucleophilic substitution

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6 HALOGENOALKANES AND THE ENVIRONMENT

6.1 Uses of Halogenoalkanes

LO 11.4(g) explain the uses of fluoroalkanes and fluorohalogenoalkanes in terms of their relative chemical inertness

Halogenoalkanes are used as refrigerants, aerosol propellants and fire extinguishers.

Fluoroalkanes are less reactive than chloroalkanes due to the high bond energy of the C–F bond. They are more useful in certain applications where their inertness are required, such as non-stick coating on pots and pans and as taps and stoppers in laboratory glassware like burettes and standard flasks. The commercial name for polytetrafluoroethene is Teflon®.

Chlorofluorocarbons (CFCs), often known by the trade name 'Freons', are used as refrigerants, aerosol propellants and in fire extinguishers.

These compounds have some useful properties:
(1) they are inert and non-flammable
(2) they are non-toxic
(3) they are compounds that liquefy under pressure and therefore vapourise readily when that pressure is released
(4) they are odourless

6.2 Effect of CFCs on the Ozone Layer

*LO 11.4(h) recognise the concern about the effect of chlorofluoroalkanes (CFCs) on the ozone layer [the mechanistic details of how CFCs deplete the ozone layer are **not** required]*

Depletion of the ozone layer

Chlorofluorocarbons (CFCs) in aerosol sprays deplete the ozone (O_3) layer and expose us to ultraviolet radiation from the sun. The O_3 layer absorbs ultraviolet rays and is vital in screening the earth from excess ultraviolet radiation. Too much exposure to ultraviolet radiation causes skin cancer and widespread crop failure.

Due to the strength of C–F and C–C*l* bonds, fluoroalkanes and CFCs are stable molecular entities under ambient conditions, which exhibit low toxicity, low reactivity, and low flammability. However, this lack of reactivity also provides CFCs a lifespan that can exceed 100 years, giving them time to diffuse into the stratosphere, where the strong UV radiation will cleave the weaker C–C*l* bond (bond energies: C–C*l* = +340 vs. C–F = +485 kJ mol^{-1}) homolytically to generate reactive C*l*• radicals, which will catalyse the decomposition of ozone into oxygen, leading to depletion of the ozone layer.

$$CF_3Cl + uv \rightarrow Cl\bullet + \bullet CF_3$$

In the stratosphere, oxygen atoms are produced when O_2 absorbs UV light at 250 nm wavelength.

$$O_2 \rightarrow 2O$$

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Once oxygen atoms form, they can react with oxygen molecules to produce ozone, which by absorption of ultraviolet light, decompose to re-form oxygen atoms and oxygen molecules. An equilibrium is set up between the two processes.

Natural ozone formation : $O + O_2 \rightarrow O_3$
Natural ozone depletion : $O_3 \rightarrow O + O_2$
Chlorine atoms (radicals) disrupt the equilibrium by acting as a homogeneous catalyst for the destruction of ozone:

$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$ ----------**(1)**
$ClO\bullet + O \rightarrow Cl\bullet + O_2$ ----------**(2)**

As shown by equations **(1)** and **(2)**, the chlorine atoms are regenerated, and in the process remove the oxygen atoms needed to make more ozone by the natural ozone formation reaction. (You are **not** required to memorise the above mechanistic details i.e. mechanism equations of how CFCs deplete the ozone layer.)

Measures to protect the ozone layer

- Reduce use of CFCs in industrial and household applications. Since 1987, at the Montreal Protocol, the use of CFCs has been increasingly banned in an increasing number of countries.
- Substitutes such as hydrocarbons, hydrofluorocarbons or fluorocarbons have been used in place of CFCs. For example, some aerosols use propane or butane as propellant instead of CFCs. However, alkanes are highly flammable and pose a fire hazard.

Exercise 6.1 (Worked Example)
Chlorofluorocarbons (CFCs) have been widely used in aerosol sprays, refrigerators and in making foamed plastics, but are now known to destroy ozone in the upper atmosphere.

Which of the following compounds will **not** destroy ozone, and therefore can be used as a replacement for CFCs?

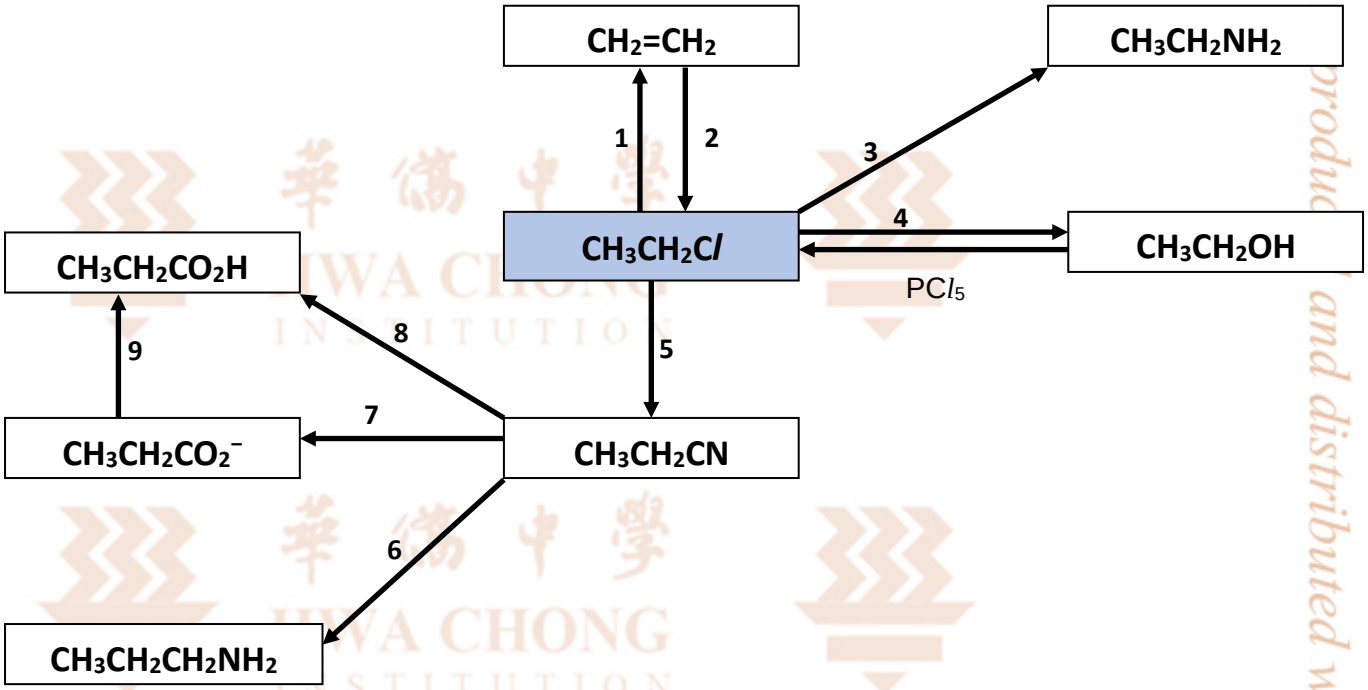
A $CHBr_3$
B CCl_3CBr_3
C $CHClFCClF_2$
D $CH_3CH_2CH_2CH_3$

Ans: D
Remarks: A, B and C are incorrect as they contain the weaker C–Cl and C–Br bonds which can be broken by UV light to form Cl• and Br• radicals

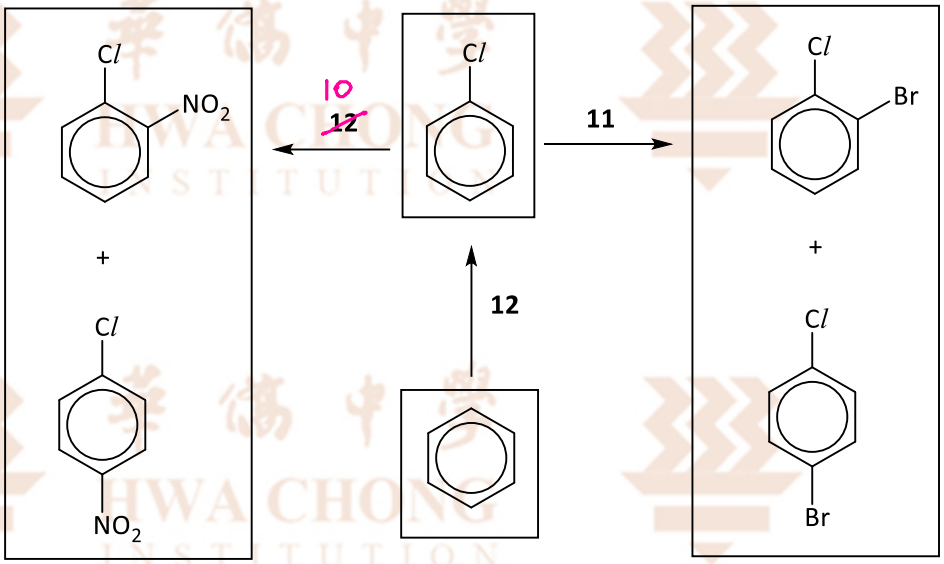
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State the reagents and conditions needed for the conversions on the arrows below.

Summary of reaction of halogenoalkanes



Summary of reaction of halogenoarenes



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16 Hydroxy Compounds

GUIDING QUESTIONS

- How are alcohols synthesised?
- Which classes of reagents do alcohols react with and why? What types of reactions do alcohols undergo and why?
- Which classes of reagents do phenols react with and why? What types of reactions do phenols undergo and why?
- How does the reactivity of phenol compare to benzene towards electrophiles?
- How do we compare the relative acidity of hydroxy compounds?

LEARNING OUTCOMES

Students should be able to:

11.5(a) recall the chemistry of alcohols, exemplified by ethanol:
- (i) combustion
- (ii) nucleophilic substitution to give halogenoalkanes
- (iii) reaction with sodium
- (iv) oxidation to carbonyl compounds and carboxylic acids
- (v) dehydration to alkenes

11.5(b) suggest characteristic distinguishing reactions for the different classes of alcohols (primary, secondary and tertiary alcohols), e.g. mild oxidation

11.5(c) deduce the presence of a $CH_3CH(OH)$– group in an alcohol from its reaction with alkaline aqueous iodine to form tri-iodomethane

11.5(d) recall the chemistry of phenol, as exemplified by the following reactions:
- (i) with bases
- (ii) with sodium
- (iii) nitration of, and bromination of, the aromatic ring

11.5(e) explain the relative acidities of water, phenol and ethanol in aqueous medium (interpret as Brønsted–Lowry acids)

REFERENCES

1. Cann, P.; Hughes, P. *Cambridge International AS and A Level Chemistry;* Hodder Education: London, 2015; pp 281–293, 432–439.
2. McMurry, J. *Organic Chemistry,* 6th ed.; Brooks/Cole: Belmont, CA, 2004; pp 587–638.
3. Bailey, P. S.; Bailey, C. A. *Organic Chemistry – A Brief Survey of Concepts and Applications,* 6th ed.; Prentice Hall: Upper Saddle River, NJ; 2000.

LOOKING BACK

In Topic 4 Reactions and Stoichiometry, we discussed various definitions of acids and bases. In Topic 14 Acid-Base Equilibria, we further learnt that the strength of weak acids and bases can be indicated by the equilibrium constants K_a and K_b. In our continuation of organic chemistry, we will see the application of the above acid-base concepts in the context of relatively weak organic acids (e.g. alcohols, phenols and carboxylic acids) and organic bases (e.g. amines). Fundamental concepts in Introduction and Isomerism (e.g. types of reactions, polar/non-polar mechanisms, delocalisation, electronic/steric effects and isomerism) continue to play an important role in explaining the nature and reactions of these acidic and basic functional groups in organic chemistry. The use of halogen derivatives as a starting material to prepare these compounds will also be revisited.

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1 INTRODUCTION

LO 11.1(a) part: interpret, and use the nomenclature, general formulae and displayed formulae of the following classes of compound: (iii) hydroxyl compounds (alcohols and phenols)

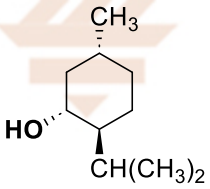
LO 11.1(b) part: interpret, and use the following terminology associated with organic reactions: (ii) degree of substitution: primary, secondary, tertiary, quaternary

Alcohols are compounds of the general formula R–**OH**, where R is any alkyl or substituted alkyl group. All alcohols contain the hydroxy (–**OH**) group, which determines the properties characteristic of this family of compounds.



ethanol

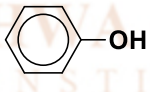
Present in alcoholic beverages and in some modern thermometers.



menthol

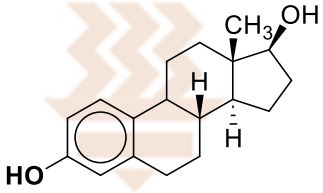
Occurs naturally in peppermint oil. It is well-known for the cooling sensation that it provokes when inhaled, eaten or applied to the skin.

Phenols are compounds in which the hydroxy (–**OH**) group is directly attached to an aromatic ring. Phenols differ markedly from alcohols in both physical and chemical properties.



phenol

An important chemical produced industrially as a precursor to many different compounds, including polycarbonates, herbicides, and pharmaceutical drugs.



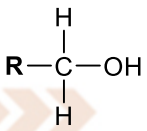
estradiol

The primary female sex hormone is an important hormone not only in reproductive and sexual functioning, and also affects other organs including the bones.

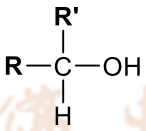
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1.1 Classification of Alcohols

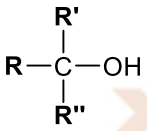
Alcohols can be subdivided into **three** different classes (similar to halogenoalkanes). An alcohol is classified as **primary (1°)**, **secondary (2°)**, or **tertiary (3°)** according to the number of carbon atoms bonded to the carbon that bears the –OH group:



primary alcohol



secondary alcohol



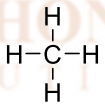
tertiary alcohol

R, R', R''
= alkyl or aryl group

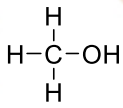
Each class of alcohol undergoes chemical reactions differently. When asked to identify the alcohol functional group in a compound, you should state whether it is a primary, secondary or tertiary alcohol explicitly and not just a generic "alcohol".

1.2 Nomenclature

Alcohols are named by replacing the terminal ***-e*** of the corresponding alkane name with ***-ol***.

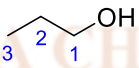


methan**e**

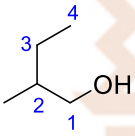


methan**ol**

The longest carbon chain containing the hydroxy group is considered the parent structure.

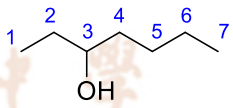


propan-1-ol



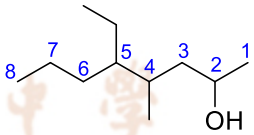
2-methylbutan-1-ol

Number the alkane chain beginning at the end nearer the hydroxy group, and use the appropriate number to indicate the position of the –OH group.



heptan-3-ol

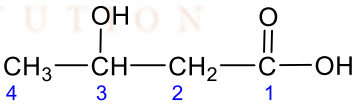
Number any substituents according to their positions on the chain, and list the substituents in alphabetical order. The priority of the functional groups can be found in Topic 8: Introduction to Organic Chemistry, subtopic 4.1.



5-ethyl-4-methyloctan-2-ol

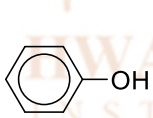
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As a substituent, the –OH group is named "hydroxy", i.e. when it appears on a structure with a higher priority functional group, i.e. ketone, aldehyde, nitrile, amide, acid halide, ester and carboxylic acid.

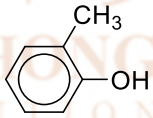


3-hydroxybutanoic acid

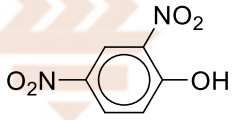
Compounds that have an –OH group directly attached to a benzene ring are called phenols.



phenol



2-methylphenol

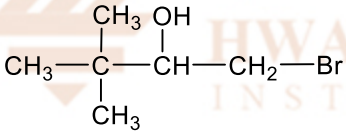


2,4-dinitrophenol

Exercise 1.1 (Worked Example)

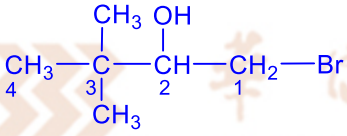
Name and classify the following alcohols or phenols.

(i)

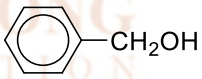


1-bromo-3,3-dimethylbutan-2-ol
(secondary alcohol)

As OH group is of higher priority than the Br group, the parent functional group is an alcohol. The longest hydrocarbon chain is 4-carbons long, hence the name of the molecule is butan-2-ol with the other substituents numbered accordingly.



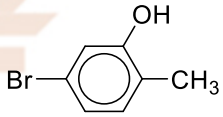
(ii)



phenylmethanol
(primary alcohol)

The highest priority group is the OH group and it is located on a 1-carbon chain, hence the parent structure is methanol. The benzene ring is a substituent and is named as 'phenyl'.

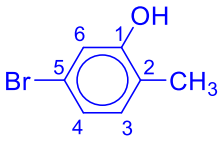
(iii)



5-bromo-2-methylphenol
(phenol)

The OH group on benzene ring will take the position '1' for a phenol.

The other substituents will be numbered to give the smaller set of locants.

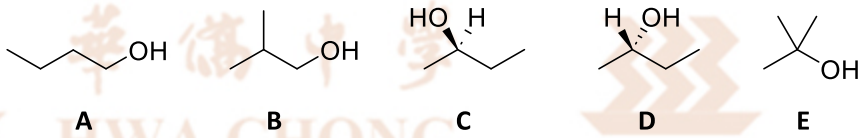


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1.3 Isomerism

Isomerism in alcohols

Alcohols can exhibit chain and positional isomerism, as well as enantiomerism. Of the five isomers with the formula C_4H_9OH, two (**A** and **B**) are primary alcohols, two (**C** and **D**) are secondary alcohols, and one (**E**) is a tertiary alcohol.



A **B** **C** **D** **E**

Isomerism of alcohols and ethers

Ethers are constitutional isomers of alcohols. Ethers do not contain the –OH group and so have none of the reactions of alcohols, and do not form intermolecular hydrogen bonds. Hence, ethers are fairly inert compounds with boiling points lower than those of the isomeric compounds. For example:



butan-1-ol, b.p. 118 °C diethyl ether, b.p. 35 °C

2 PHYSICAL PROPERTIES OF ALCOHOLS AND PHENOLS

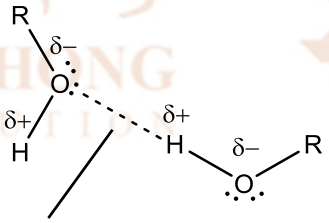
2.1 Boiling Points

Alcohols and phenols have significantly higher boiling points than those of corresponding (isoelectronic) hydrocarbons.

no. of electrons in molecule	alkane		alcohol	
	formula	b.p. / °C	formula	b.p. / °C
18	C_2H_6	−88	CH_3OH	65
26	C_3H_8	−42	C_2H_5OH	78
34	C_4H_{10}	0	C_3H_7OH	97
42	C_5H_{12}	36	C_4H_9OH	118
50	C_6H_{14}	69	$C_5H_{11}OH$	138
50	$C_6H_5CH_3$ (methylbenzene)	111	C_6H_5OH (phenol)	182

- The boiling point of an alcohol is **higher** than that of the corresponding isoelectronic alkane (same number of electrons).
    - While the strength of the dispersion forces in the alcohol and in the alkane is about the same due to the similar sizes of the electron clouds, more energy is required to overcome the intermolecular **hydrogen bonding** in alcohols which is stronger than the dispersion forces in alkanes.

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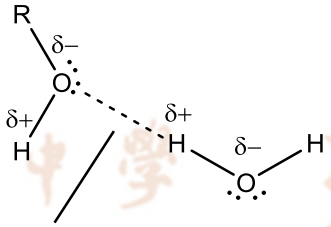
hydrogen bonding between alcohol molecules

- The boiling point of alcohols **increases** as the alkyl chain length increases.
  - While the strength of intermolecular hydrogen bonding remains largely similar for all the alcohols, the size of the electron cloud increases as the length of the alkyl chains increases. More energy is thus required to overcome the stronger **dispersion forces** between the alcohol molecules.

- Phenol and its derivatives are colourless solids. The melting point of phenol is 42 °C. The presence of hydrogen bonds makes the melting point of phenols higher than those of hydrocarbons with similar numbers of electrons.

2.2 Solubility in Water

Alcohols are more soluble in water compared to their corresponding alkanes due to their ability to form hydrogen bonds with water molecules.



hydrogen bonding between alcohol and water

The solubility of alcohols in water decreases with increasing carbon number due to the increasing length of the non-polar alkyl chain.

$$\underbrace{CH_3CH_2CH_2CH_2CH_2CH_2}_{\text{non-polar}}\underbrace{-O-H}_{\text{polar}}$$

As the length of the alkyl chain increases, the strength of the dispersion forces between alcohol molecules increases. Energy released from hydrogen bonding formed between the alcohol molecule and water is less able to overcome the increasingly stronger dispersion forces between alcohol molecules, as well as the existing hydrogen bonding in water. In addition, the hydrogen bonding with water is disrupted by the larger non-polar alkyl chain.

Phenols are only moderately soluble in water due to their large non-polar aryl group; but dissolve completely when warmed.

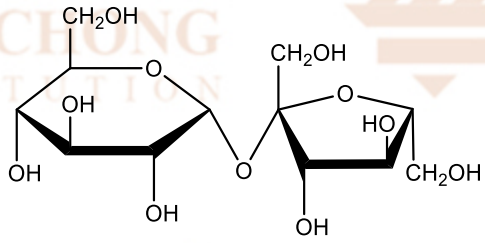
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Exercise 2.1

1. **(Worked Example)** Arrange ethanol, ethane and ethane-1,2-diol in order of increasing boiling point. Explain your answer.

2. Hexan-1-ol has a boiling point of 158 °C whereas 3,3-dimethylbutan-2-ol has a boiling point of 120 °C. Explain the difference in boiling points.

3. The structure of sucrose is shown below. Predict the physical state and solubility of the compound under standard conditions.



Answer

1. Boiling point: ethane < ethanol < ethane-1,2-diol
   Ethanol has higher boiling point than ethane as the hydrogen bonding between ethanol molecules is stronger than the dispersion forces between ethane molecules and requires more energy to overcome. Ethane-1,2-diol has 2 –OH groups while ethanol only has 1 –OH group. Hence hydrogen bonding is more extensive in ethane-1,2-diol which requires more energy to overcome.

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3 PREPARATION OF ALCOHOLS

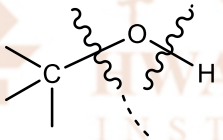
Alcohols can be prepared from:

- Electrophilic addition of water or steam to alkenes (Topic 11 Alkenes)
- Nucleophilic substitution of halogenoalkanes (Topic 15 Halogen Derivatives)
- Reduction of aldehydes and ketones (to be covered in Topic 17 Carbonyl Compounds)
  - Reduction of aldehydes yields primary alcohols
  - Reduction of ketones yields secondary alcohols
- Reduction of carboxylic acids (to be covered in Topic 18 Carboxylic Acids and Derivatives)
  - Reduction of carboxylic acids yields only primary alcohols

4 CHEMICAL PROPERTIES AND REACTIONS OF ALCOHOLS AND PHENOLS

LO 11.5(a): recall the chemistry of alcohols, exemplified by ethanol: (i) combustion, (ii) nucleophilic substitution to give halogenoalkanes, (iii) reaction with sodium, (iv) oxidation to carbonyl compounds and carboxylic acids, (v) dehydration to alkenes

The reactivity of the –OH group allows alcohols to be versatile starting materials for the preparation of a variety of organic compounds. The alcohol functional group can undergo various reactions involving the cleavage of either the C–O or O–H bonds of the –OH group.



This bond is able to break releasing H^+ ions and the alcohols are converted to alkoxides. This allows the alcohol to behave as a Brønsted acid.

This bond can be broken, for example, in elimination reactions to form alkenes, or nucleophilic substitution reactions to form halogenoalkanes.

4.1 Combustion

All alcohols burn well in air to form carbon dioxide and water, but only the combustion of ethanol has significance in everyday life:

$$CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta H_c = -1367 \text{ kJ mol}^{-1}$$

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4.2 Acid-Base Reactions of Alcohols and Phenols

LO 11.5(e): explain the relative acidities of water, phenol and ethanol in aqueous medium (interpret as Brønsted–Lowry Acids)

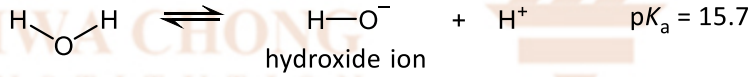
Due to the presence of the –OH group, alcohols and phenols can act as either Brønsted acids or Brønsted bases. The electron-deficient hydrogen can be removed in the presence of a sufficiently strong base, while the electron-rich oxygen can be protonated in the presence of a sufficiently strong acid.

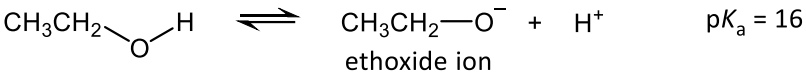
While this section mainly focuses on alcohols and phenols acting as Brønsted acids, we do see alcohols acting as Brønsted bases later in Section 4.3.

In general, the strength of an acid depends on the **stability** of the conjugate base formed after dissociation. When a more stable conjugate base is formed, it is less likely to accept a proton to re-form the acid. Hence, the extent of dissociation is greater, resulting in a stronger acid and a larger K_a (Topic 14 Acid-Base Equilibria).

4.2.1 Acidity of alcohols

In alcohols, the O−H bond can break to give H^+ and R−O^- (alkoxide ion). The extent of dissociation is lower than that of water. Therefore alcohols do not turn blue litmus red.



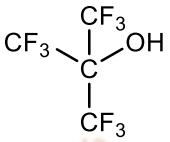


Why are alcohols weaker acids than water?

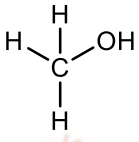
Alkyl groups are inductively electron-donating and will **intensify** the negative charge on the alkoxide ion. The alkoxide ion has a greater tendency as compared to the hydroxide ion to accept a proton to re-form the alcohol molecule. Thus the alkoxide ion is said to be **destabilised**, and deprotonation of the alcohol does not take place as easily. (Note: the length of the alkyl chain does not have a significant impact on the acidity.)

Effect of substituents on acidity of alcohols

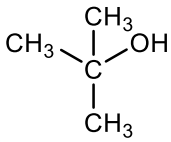
The presence of electron-withdrawing groups (e.g. $-NO_2$, –F, –Cl, –Br, –I, $-COCH_3$, $-CO_2H$, –CN, $-CO_2R$, $-NH_2$, –OH, $-OCH_3$) help to stabilise the alkoxide ion formed by dispersing the negative charge on the alkoxide ion, thus promoting the ionisation of the alcohol.
However, the presence of electron-donating groups (e.g. $-CH_3$) decreases the acidic strength of alcohols by intensifying the negative charge on the alkoxide ion, destabilising the alkoxide ion.



nonafluoro-tert-butylalcohol
pK_a = 5.4



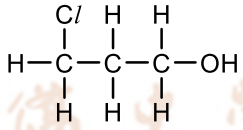
methanol
pK_a = 15.5



2-methylpropan-2-ol
pK_a = 18

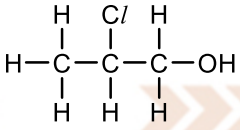
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The distance of the electron-withdrawing group from the negatively charged oxygen of the alkoxide ion also affects the degree of dispersion of the negative charge, as the inductive effect decreases with increasing distance. Thus, the nearer the electron-withdrawing group is to the negatively charged oxygen in the alkoxide ion, the greater the degree of dispersion of the negative charge and the greater the acid strength of the alcohol.



3-chloropropan-1-ol

pK_a = 15.9



2-chloropropan-1-ol

pK_a = 14.5

Exercise 4.1 (Worked Example)

Arrange the alcohols in order of increasing acid strength, giving your reasoning.

$CH_3CH_2CH_2OH$ $CH_3CHClCH_2OH$ $CH_3CH_2CH(Cl)OH$

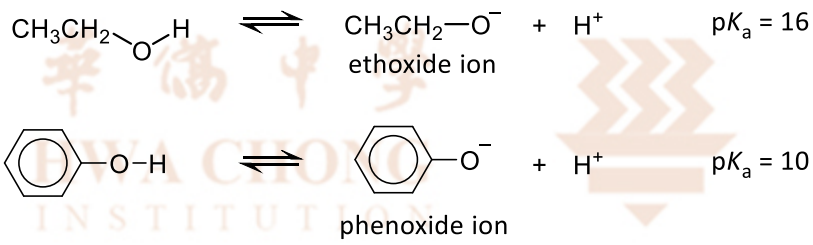
Answer: Acid strength: $CH_3CH_2CH_2OH$ < $CH_3CHClCH_2OH$ < $CH_3CH_2CH(Cl)OH$

$CH_3CHClCH_2OH$ and $CH_3CH_2CH(Cl)OH$ have an electron-withdrawing chloro group that disperses the negative charge on the alkoxide ion and stabilises the alkoxide. Hence both alcohols dissociate to a greater extent than $CH_3CH_2CH_2OH$, and are stronger acids than $CH_3CH_2CH_2OH$.

The chloro group in $CH_3CHClCH_2O^-$ is further away from the negatively charged oxygen as compared to that in $CH_3CH_2CH(Cl)O^-$, resulting in a weaker electron-withdrawing effect and dispersing the negative charge on $CH_3CHClCH_2O^-$ to a smaller extent. Thus $CH_3CHClCH_2OH$ is a weaker acid than $CH_3CH_2CH(Cl)OH$.

4.2.2 Acidity of phenols

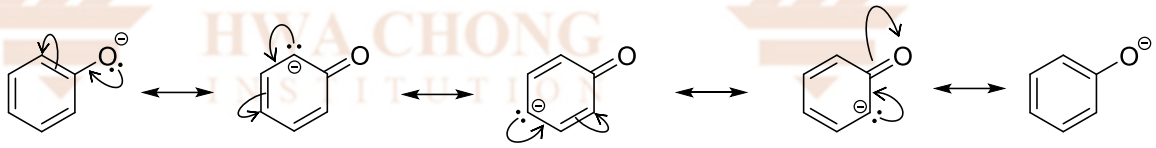
Phenols are more acidic than alcohols (and water). The pH of a 0.1 mol dm^{-3} phenol solution in water is 5.4, so a solution of phenol will turn blue litmus red.



The negative charge on the phenoxide ion can be delocalised over the benzene ring as shown in the following diagrams.



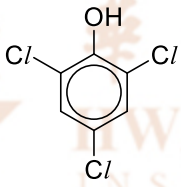
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In the phenoxide ion, a p orbital of the negatively charged oxygen is able to overlap with the π-electron cloud of the benzene ring. The negative charge is able to delocalise into the benzene ring to some extent, thus the phenoxide ion is stabilised to a larger extent than the alkoxide ion. The phenoxide anion is less likely to accept a proton to re-form phenol. This makes phenols stronger acids than both aliphatic alcohols and water.

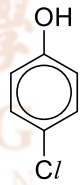
Effect of ring substituents on acidity of phenols

Similar to alcohols, the presence of electron-withdrawing groups (e.g. $-NO_2$, –F, –C*l*, –Br, –I, $-COCH_3$, $-CO_2H$, –CN, $-CO_2R$) on the benzene ring enables the ring in turn to withdraw more electron density from the negatively charged oxygen, thus stabilising the phenoxide ion further and promoting the ionisation of the phenol.



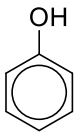
2,4,6-trichlorophenol

pK_a = 7.6



4-chlorophenol

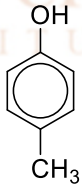
pK_a = 9.4



phenol

pK_a = 10

The presence of electron-donating groups (e.g. $-CH_3$, $-NH_2$, –OH, $-OCH_3$) on the benzene ring decreases the acid strength of phenols by reducing the delocalisation of the negative charge on the oxygen atom into the ring (or by intensifying the negative charge on the phenoxide ion), thus destabilising the phenoxide ion.



4-methylphenol

pK_a = 10.3

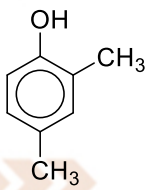


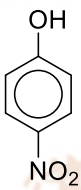
phenol

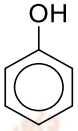
pK_a = 10

Exercise 4.2

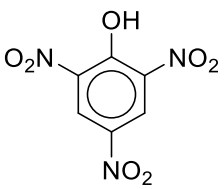
Arrange the following phenols in order of acid strength (1 for the most acidic, 5 for the least acidic).







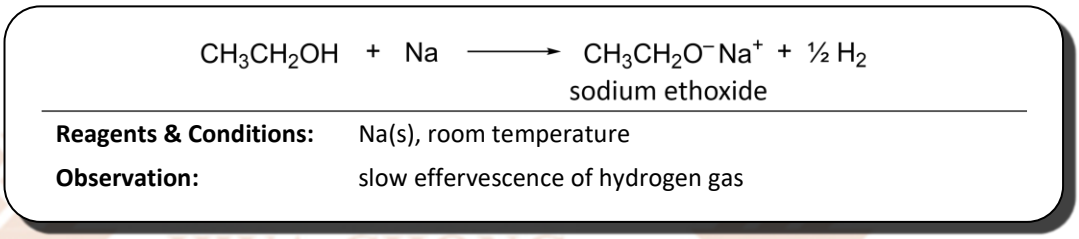




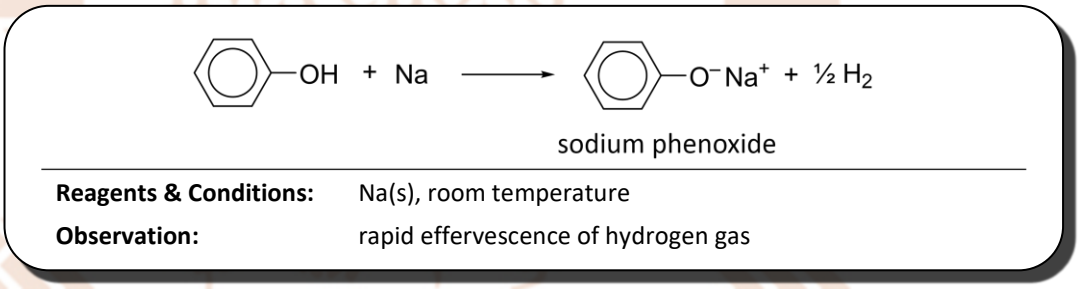
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4.2.3 Acid-metal reaction with sodium (redox)

Alcohols and phenols react with Group 1 metals such as sodium and potassium to form alkoxides or phenoxides respectively and hydrogen gas. This reaction involves the breaking of the O–H bond.



Reagents & Conditions:	Na(s), room temperature
Observation:	slow effervescence of hydrogen gas

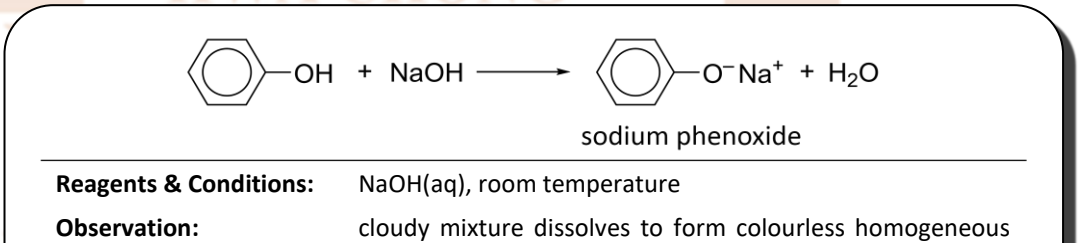


Reagents & Conditions:	Na(s), room temperature
Observation:	rapid effervescence of hydrogen gas

Alcohols and phenols both act as acids, liberating H^+, which is then reduced by sodium to H_2. Both reactions are similar to that of sodium with water. However, alcohols react more slowly as they are weaker acids than water. Phenols, being stronger acids than water, react more vigourously.

4.2.4 Acid-base reaction with sodium hydroxide

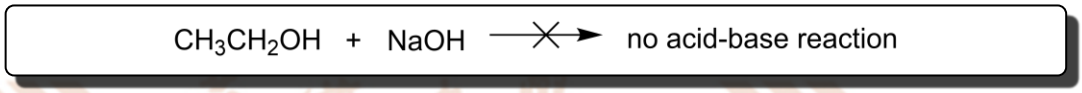
Phenols are acidic enough to react with bases like sodium hydroxide (and potassium hydroxide) to yield phenoxide salts and water. Phenol will form a cloudy mixture when mixed with water due to its poor solubility. Upon addition of aqueous NaOH, the phenol will dissolve to form a homogeneous colourless solution.



Reagents & Conditions:	NaOH(aq), room temperature
Observation:	cloudy mixture dissolves to form colourless homogeneous solution

Note that phenols are <u>not acidic enough</u> to react with carbonates to liberate CO_2 gas.

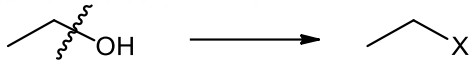
Alcohols, being weaker acids than water, are not acidic enough to react with aqueous sodium hydroxide or carbonates to form the corresponding alkoxides.



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4.3 Nucleophilic Substitution (mechanism not required)

Alcohols can be converted to halogenoalkanes by nucleophilic substitution. In this reaction, the C–O bond is broken.



We have seen in Topic 15 Halogen Derivatives that the OH^- ion can attack a halogenoalkane, e.g. R*Cl*, to form an alcohol. In this reaction, the halide ion, Cl^-, is called the **leaving group**.

Recall also from Topic 14 Acid-Base Equilibria, that Cl^- and OH^- ions are conjugate bases of acids H*Cl* and H_2O respectively.

Since H*Cl* is a stronger acid than H_2O, its conjugate base Cl^- is a weaker base than OH^-. Weaker bases are generally better leaving groups. Hence Cl^-, being a better leaving group than OH^-, is readily substituted by OH^- ions in halogenoalkanes to form alcohols in nucleophilic substitutions. This also applies to Br^- and I^-.

On the other hand, as OH^- is a poor leaving group, the conversion of alcohols to halogenoalkanes involves reagents such as acid or $SOCl_2$. These reagents first convert the –OH group into a better leaving group before the halide ion attacks, forming the halogenoalkane.

4.3.1 Nucleophilic substitution with hydrogen halides

Reaction with hydrochloric acid

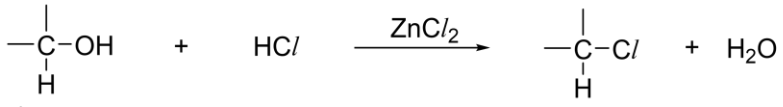
Tertiary alcohols react readily with concentrated hydrochloric acid upon shaking at room temperature to form the corresponding chloroalkane.



tertiary alcohol

Reagents & Conditions:	concentrated H*Cl*, room temperature
Observation:	solution turns cloudy

Primary and secondary alcohols also can react with concentrated hydrochloric acid, but at a slower rate. Anhydrous zinc chloride must be added as a catalyst, and the reaction mixture must be heated.



primary or secondary alcohol

Reagents & Conditions:	concentrated H*Cl*, $ZnCl_2$, heat
Observation:	solution turns cloudy

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The reaction takes place via an S_N1 mechanism, forming a carbocation intermediate. The rate of reaction depends on the stability of the carbocation formed (See Topic 15 Halogen Derivatives). Carbocations formed from tertiary alcohols have three electron-donating alkyl groups and hence are the most stable. As such, the insoluble chloroalkanes are formed fastest with tertiary alcohols, and the reaction with primary alcohols is very slow at room temperature.

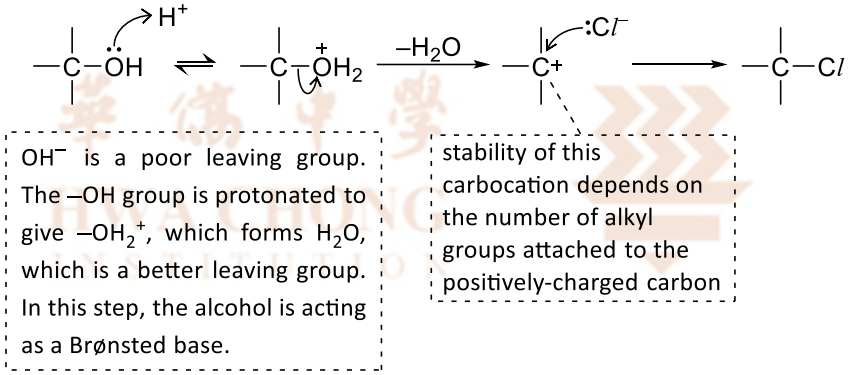


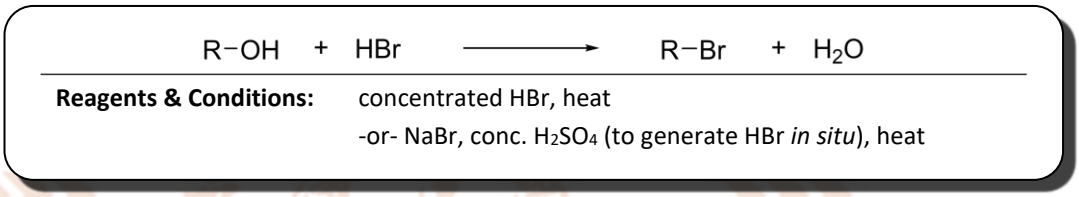
Figure 1: General mechanism of nucleophilic substitution of alcohols using HCl

These reactions form the basis of the **Lucas Test** to distinguish between primary, secondary and tertiary alcohols. The cloudiness of the solution is due to the relative insolubility of the chloroalkane.

type of alcohol	**observation on adding conc HC*l* + Zn$C*l*_2$**
R_3COH (tertiary)	immediate cloudiness appears in solution
R_2CHOH (secondary)	cloudiness appears within 5 min (at room temperature)
RCH_2OH (primary)	no cloudiness appears unless warmed

Reaction with hydrogen bromide

An alcohol can be converted to a bromoalkane by reacting it with either concentrated hydrobromic acid (HBr) or a mixture of sodium bromide with concentrated acid to generate HBr *in situ*.

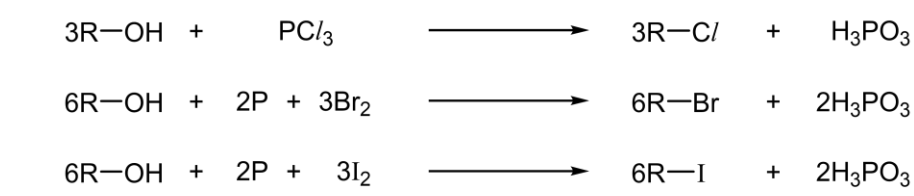


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4.3.2 Nucleophilic substitution with phosphorus halides

Reaction with phosphorus trihalides:

Alcohols react with the various phosphorus trihalides to form the corresponding halogenoalkanes and phosphoric(III) acid.



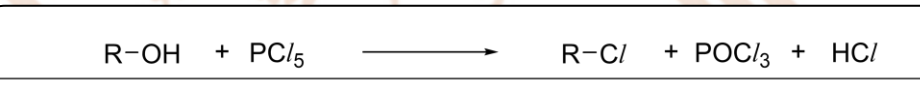
Reagents & Conditions: PCl_3, room temperature
-or- P, Br_2, heat
-or- P, I_2, heat

Comment: PBr_3 and PI_3 are prepared *in situ* by heating red phosphorus with bromine and iodine respectively.

$2P + 3X_2 \rightarrow 2PX_3$ X = Br, I

Reaction with phosphorus(V) chloride:

Phosphorus(V) chloride converts an alcohol into the corresponding chloroalkane with the evolution of hydrogen chloride. As it is highly reactive with water, the reagents must be free of water or moisture. PCl_5 is a good distinguishing test for an alcohol functional group if a carboxylic acid is absent (as PCl_5 will also react with carboxylic acids to produce HCl gas; see Topic 18 Carboxylic Acids and derivatives).



Reagents & Conditions: PCl_5, room temperature

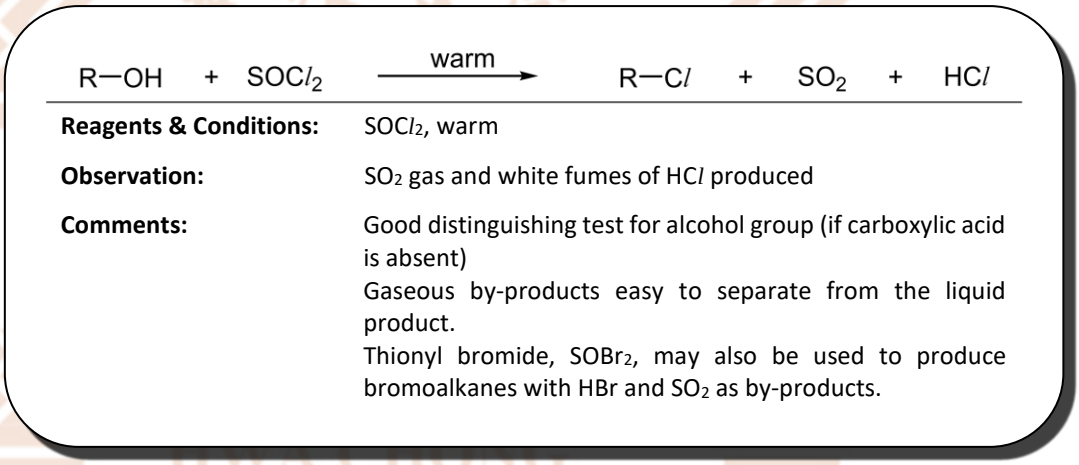
Observation: dense white fumes of HCl produced

Comment: Good distinguishing test for alcohol group (if carboxylic acid is absent)

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4.3.3 Nucleophilic substitution with thionyl chloride

Another good reagent to convert alcohols to chloroalkanes is thionyl chloride, $SOCl_2$. Thionyl chloride and PCl_5 will react with both alcohols and carboxylic acids, liberating HCl in the process. The use of thionyl chloride confers an additional advantage over the use of PCl_5 in that both by-products are acidic gases and are hence more easily separated from the chloroalkane product. Also, since both by-products are gases, the reaction is entropically driven (entropy change more positive, reaction more thermodynamically feasible).



4.3.4 Non-reactivity of phenols towards nucleophilic substitution

Phenols are very much less susceptible towards nucleophilic substitution, in which the –OH group is replaced by a halide, than alcohols. Extremely harsh conditions are required for conversion of phenols to halogenoarenes (which will not be discussed in this syllabus).

Reasons for the inertness of phenols towards nucleophilic substitution

There are several reasons for the reduced susceptibility of phenols to form halogenoarenes. These reasons are similar to those given for the reduced susceptibility of halogenoarenes to nucleophilic substitution reactions (see Topic 15 Halogen Derivatives).

1. The lone pair of electrons on the O atom in phenol delocalises into the benzene ring, resulting in partial double bond character in the C−O bond. The C−O bond strength in phenols is higher than in an alcohol, making it more difficult to break.

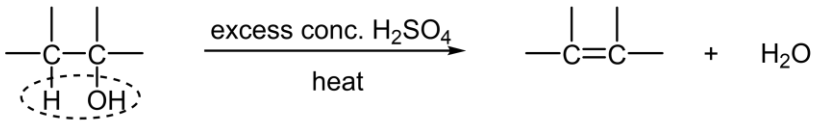
2. Sterically, the approach of a nucleophile to the rear side of the C−O bond in phenols is hindered by the benzene ring. The π-electron cloud of the benzene ring will also repel the lone pair of electrons on the approaching nucleophile.

These two factors make the attack by the nucleophile difficult.

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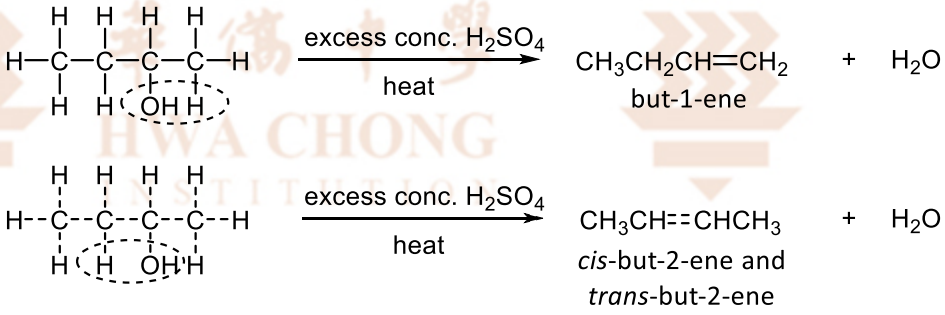
4.4 Dehydration (Elimination)

Dehydration of alcohols is carried out by heating the alcohol in the presence of a suitable catalyst. The loss of the hydroxy group together with a H atom bonded to an adjacent carbon will result in the formation of an alkene and a water molecule.



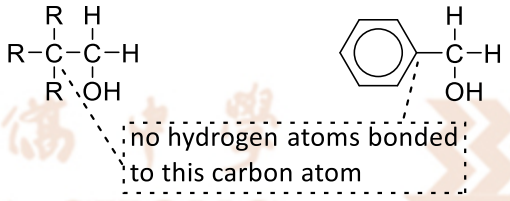
Reagents & Conditions:	excess concentrated H_2SO_4, heat -or- concentrated H_3PO_4, heat -or- Al_2O_3, heat
Comments:	Only alcohols with at least one H atom on the carbon atom adjacent to the carbon atom bearing the hydroxy group can undergo dehydration (shown in diagram above). Concentrated phosphoric(V) acid is sometimes preferred over sulfuric acid as sulfuric acid may act as an oxidising agent, producing unwanted side products. Phosphoric(V) acid is not an oxidising agent so side product formation is minimised.

Dehydration may form a mixture of alkenes, depending on the position of the hydroxy group. Consider the reaction of butan-2-ol with excess concentrated sulfuric acid:



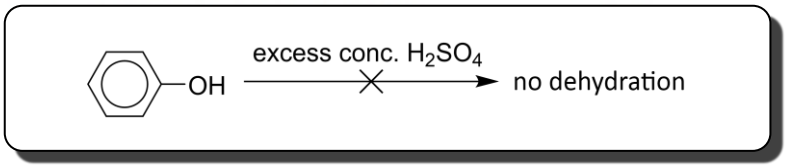
Note: There are some similarities and differences between the dehydration reaction of alcohols and elimination of halogenoalkanes. In both cases, an alkene is formed, but the differences are in the reagents used, as well as formation of H_2O and HX in the cases of alcohols and halogenoalkanes respectively. (See Topic 15 Halogen Derivatives)

If there are no hydrogen atoms bonded to the carbon atom that is adjacent to the carbon atom bearing the hydroxy group, dehydration cannot take place:

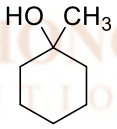


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Phenols cannot undergo dehydration. This is because the C–O bond is very strong as explained in the previous section on nucleophilic substitution.



Exercise 4.3



1-methylcyclohexanol

Give structures of all organic products formed when 1-methylcyclohexanol reacts with each of the following reagents.

(a) phosphorus pentachloride

(b) NaBr, conc H_2SO_4, heat

(c) hot concentrated sulfuric acid (excess)

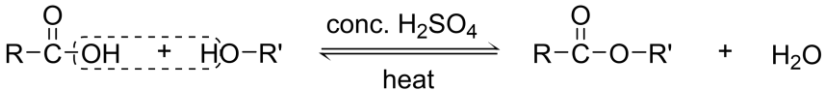
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4.5 Condensation

Alcohols and phenols possess an –OH group with two lone pairs of electrons on the oxygen atom. This allows them to act as nucleophiles (Lewis base) in their reaction with carboxylic acids and/or acyl chlorides to form esters in a condensation process.

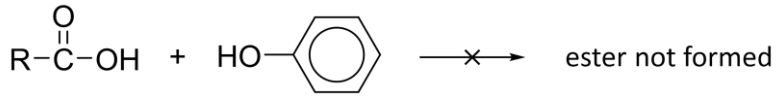
4.5.1 Condensation with carboxylic acids

Alcohols will react with carboxylic acids in a slow and reversible reaction, with a few drops of concentrated sulfuric acid as catalyst, to form the ester with the condensation of a water molecule. Note that concentrated sulfuric acid can act as a catalyst for both dehydration (to alkenes) and condensation. In this case, only a few drops of concentrated sulfuric acid are used, making the sulfuric acid less likely to act as a dehydrating agent.



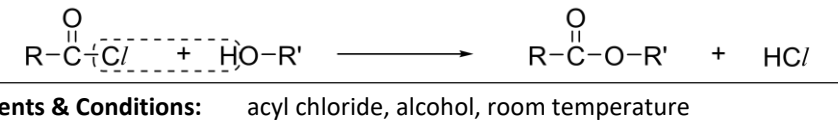
Reagents & Conditions:	alcohol, carboxylic acid, few drops of concentrated H_2SO_4, heat
Comment:	reaction slow and reversible

Unlike alcohols, phenols do **not** react with carboxylic acids in a similar condensation reaction. This is due to the delocalisation of the lone pair of electrons on the oxygen atom into the benzene ring. The lone pair of electrons is thus less available to attack the carboxyl carbon of the carboxylic acid to form the ester.



4.5.2 Condensation with acyl chlorides

Acyl chlorides react much more readily with alcohols in condensation reactions than their corresponding carboxylic acids. No heating and no catalysts are required, and the reaction goes to completion instead of establishing an equilibrium.



Reagents & Conditions:	acyl chloride, alcohol, room temperature
Observation:	white fumes of HC*l* produced
Comment:	reaction goes to completion

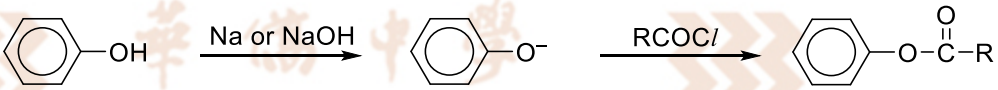
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The only method to form a phenyl ester is from the condensation reaction between a phenol and an acyl chloride. As the lone pair of electrons on the oxygen atom in phenol is delocalised into the π-electron cloud of the benzene ring, phenols are less nucleophilic than alcohols. As a result, only the acyl chloride and **not** the carboxylic acid is used for this condensation reaction.



Reagents & Conditions:	acyl chloride, phenol, room temperature
Observation:	white fumes of HC*l* produced

For a better yield, the reaction is carried out under basic conditions (by using Na or NaOH) to first generate the phenoxide ion. The negative charge of the phenoxide ion increases the electron density around the oxygen atom, making it a stronger nucleophile than phenol. Hence the phenoxide ion attacks the acyl chloride more readily.



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4.6 Oxidation

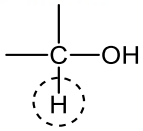
Two common sets of reagents and conditions are used for the oxidation of alcohols:

- $K_2Cr_2O_7$ / dilute H_2SO_4, heat
- $KMnO_4$ / dilute H_2SO_4, heat

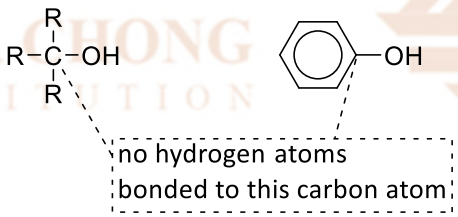
The product of oxidation is determined largely by the type of alcohol.

Note:

For the oxidation of an alcohol to occur (using the above reagents), the alcohol must have at least one hydrogen atom bonded to the carbon atom bearing the –OH group:

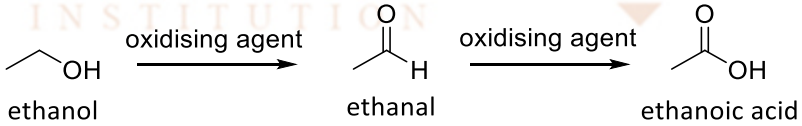


For this reason, tertiary alcohols and phenols cannot be oxidised using the above reagents:



4.6.1 Oxidation of primary alcohols

Primary alcohols are readily oxidised to aldehydes on heating. With excess oxidising agent, the reaction proceeds further, yielding carboxylic acids. The oxidation pathway for ethanol is shown below.



ethanol ethanal ethanoic acid

Oxidation to aldehydes

- Controlled oxidation of primary alcohols yields aldehydes.
- Once the aldehyde is formed in the reaction vessel, it will come into contact with more oxidant and this will lead to further oxidation, forming a carboxylic acid. This can be avoided by distilling the aldehyde away from the reaction mixture as soon as it forms. This is possible as the aldehyde lacks intermolecular hydrogen bonding and thus has a lower boiling point than the corresponding alcohol.

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- The distillation setup is shown in the diagram below.

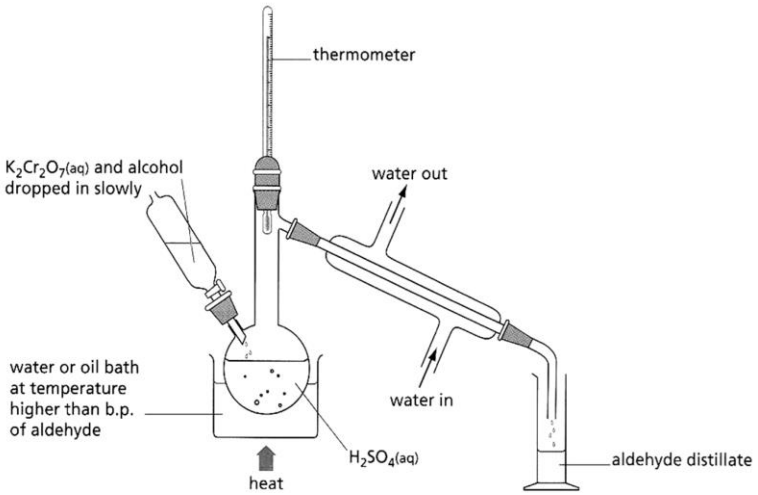
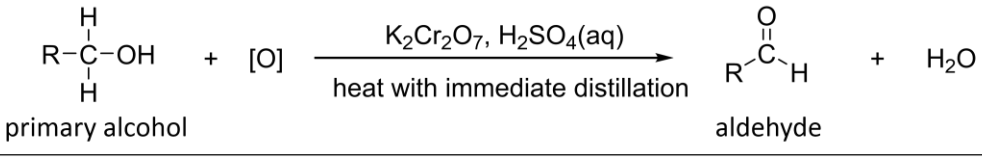


Figure 2. Experimental setup for the distillation of aldehydes by oxidising primary alcohols. (Diagram taken from Chemistry for Advanced Level by P. Cann and P. Hughes; Hodder Murray)



Reagents & Conditions:	$K_2Cr_2O_7$, H_2SO_4(aq), heat with immediate distillation
Observation:	orange solution ($Cr_2O_7^{2-}$) turns green (Cr^{3+})
Comments:	Only $K_2Cr_2O_7$ is selective enough to oxidise primary alcohols to the aldehydes. $KMnO_4$, being a stronger oxidising agent, will oxidise them directly to carboxylic acids.

Oxidation to carboxylic acids

To obtain carboxylic acids from primary alcohols, the reacting solution needs to be heated under reflux. This prevents the aldehyde formed from evaporating and allows further oxidation to the carboxylic acid. The reflux setup is shown in the diagram below.

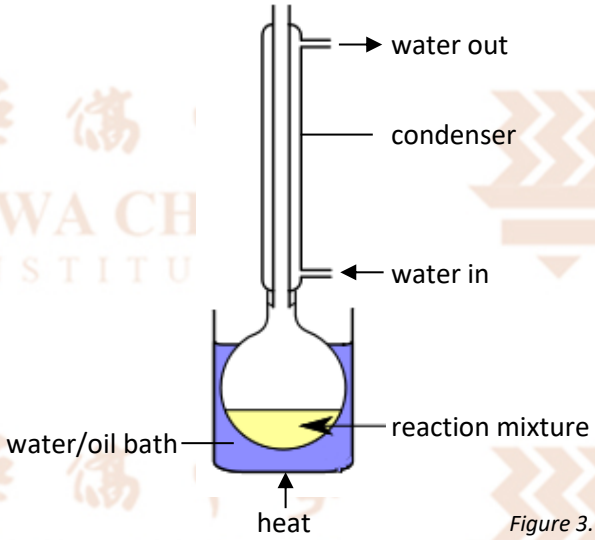
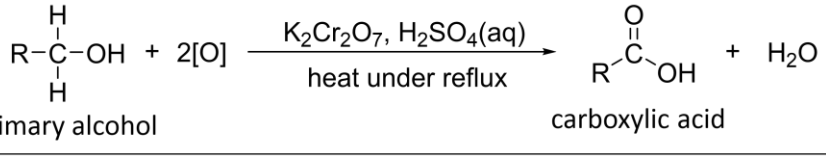


Figure 3. Example of a typical reflux setup

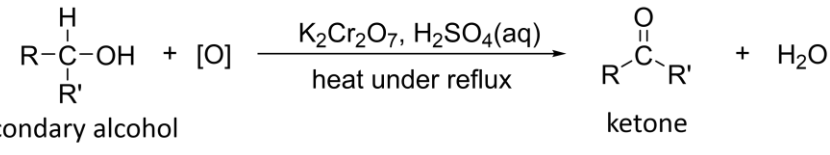
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Reagents & Conditions:	$K_2Cr_2O_7$, H_2SO_4(aq), heat under reflux -or- $KMnO_4$, H_2SO_4(aq), heat under reflux
Observation:	orange solution ($Cr_2O_7^{2-}$) turns green (Cr^{3+}) -or- purple solution (MnO_4^-) turns colourless (Mn^{2+})

4.6.2 Oxidation of secondary alcohols

Secondary alcohols are oxidised to ketones which are resistant to further oxidation.



Reagents & Conditions:	$K_2Cr_2O_7$, H_2SO_4(aq), heat under reflux -or- $KMnO_4$, H_2SO_4(aq), heat under reflux
Observation:	orange solution ($Cr_2O_7^{2-}$) turns green (Cr^{3+}) -or- purple solution (MnO_4^-) turns colourless (Mn^{2+})

Oxidation as a distinguishing test to identify primary, secondary and tertiary alcohols

LO 11.5(b): suggest characteristic distinguishing reactions for the different classes of alcohols (primary, secondary and tertiary alcohols), e.g. mild oxidation

Oxidation may be used as a method to distinguish between the various classes of alcohols (primary, secondary or tertiary), based on the products of oxidation (if any). The alcohol is first **heated under reflux** with **excess** potassium dichromate(VI) and dilute sulfuric acid. Tertiary alcohols will not be oxidised by $K_2Cr_2O_7$, so the colour of the reaction mixture remains orange.

Primary and secondary alcohols will be oxidised by $K_2Cr_2O_7$ to carboxylic acids and ketones respectively, causing the orange solution to turn green. To distinguish between these two classes of alcohols, the organic product must be **isolated** (e.g. by distillation), and distinguishing tests for the carboxylic acid or the ketone should be carried out on the product to identify the class of alcohol. (These distinguishing tests will be covered in Topic 17 Carbonyl Compounds and Topic 18 Carboxylic Acids and Derivatives.)

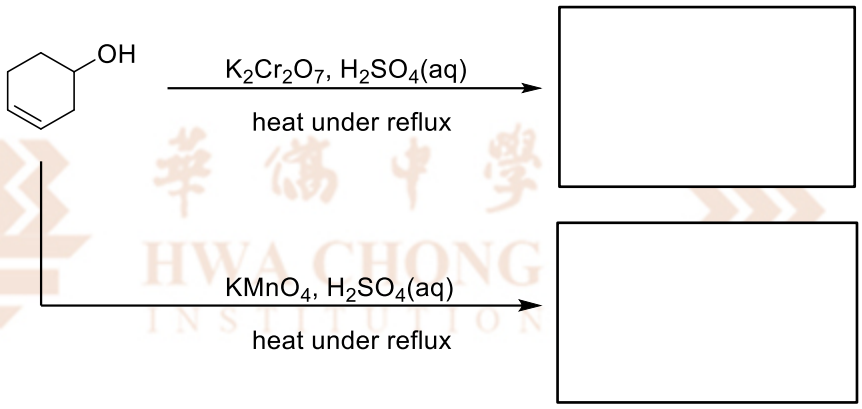
Note that in **simple** chemical tests, reflux and distillation setups are not used.

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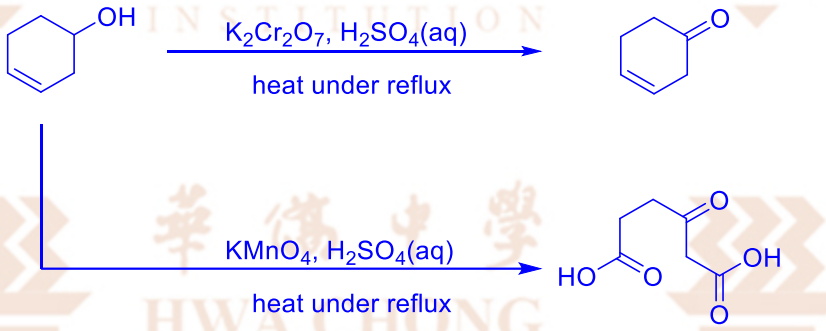
Exercise 4.4

Draw the structures of the compounds formed by oxidation of each of the following compounds.

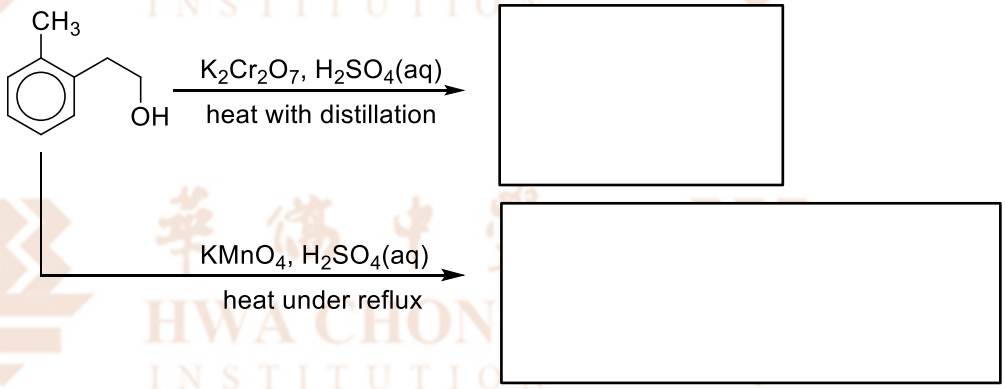
(a) (Worked Example)



Comments: There are two functional groups that can be oxidised, an alkene and a secondary alcohol. Hence when a milder oxidising agent like $K_2Cr_2O_7$ is used, only the secondary alcohol will be oxidised to a ketone. The alkene will remain unchanged. When $KMnO_4$ is used, the alkene will also undergo oxidative cleavage to form oxidation products as shown in the answer.



(b)

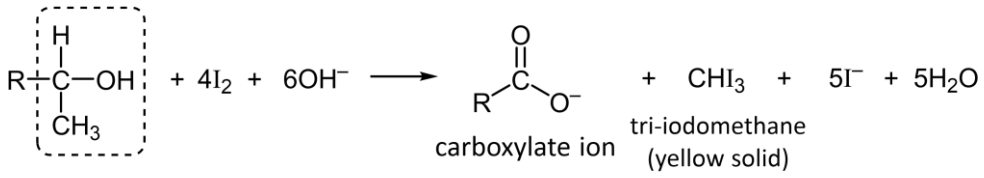


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4.7 The Tri-iodomethane (iodoform) Test

LO 11.5(c): deduce the presence of a $CH_3CH(OH)-$ group in an alcohol from its reaction with alkaline aqueous iodine to form tri-iodomethane

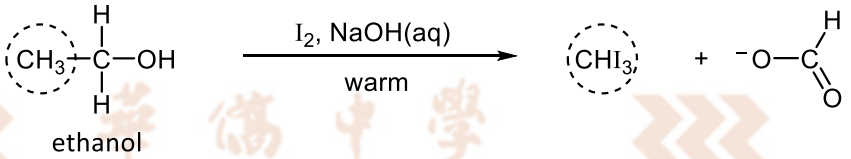
Alcohols with a $CH_3CH(OH)-$ group will react with warm alkaline aqueous iodine. In this reaction, the carbon bearing the hydroxy group is oxidised to a carboxyl carbon.

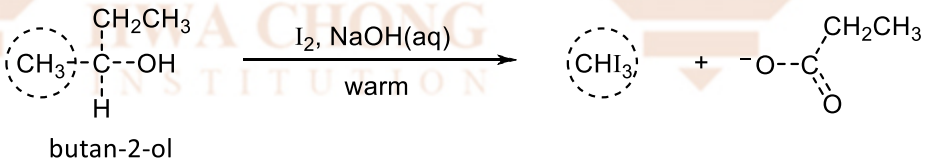


Reagents & Conditions:	I_2(aq), NaOH(aq), warm
Observation:	yellow ppt (CHI_3) formed (Note that CHI_3 is an organic compound.)
Comment:	Another name for tri-iodomethane is iodoform.

Note that this reaction involves the **breaking of a C–C bond** with the removal of the methyl ($-CH_3$) group. It is therefore a useful method to **shorten a carbon chain by a single carbon** (known as a **step-down reaction**).

Examples:





For your information:

Why do both the $CH_3CH(OH)-$ and the CH_3CO- groups give a positive iodoform test?
(Mechanism not required)

In this reaction, the $CH_3CH(OH)-$ group is first oxidised *in-situ* to the corresponding CH_3CO- group (a methyl ketone) by the iodate(I) ion. This is then followed by a series of substitutions, leading to cleavage of the $-CI_3$ group to give CHI_3.

Hence, methyl ketones also give a positive iodoform test, forming CHI_3 (to be covered in Topic 17 Carbonyl Compounds).

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Exercise 4.5

1 **(Worked Example)** Which alcohols would give a positive tri-iodomethane reaction?



1 **2** **3** **4**

Answer

Both **1** and **4** will give positive results. Both have the $CH_3CH(OH)-$ group present.

2 Chemical tests were carried out on four organic compounds are labelled **A**, **B**, **C** and **D**.

The compounds are ethanol, propan-1-ol, 2-methylpropan-2-ol and cyclohexene but not necessarily in that order.

The observations of each test are detailed in the table below.

chemical test	observations			
	A	**B**	**C**	**D**
add Na(s)	effervescence	no effervescence	effervescence	effervescence
add $K_2Cr_2O_7$ and dilute H_2SO_4, heat	orange solution remains orange	orange solution remains orange	orange solution turns green	orange solution turns green
add aqueous I_2, aqueous NaOH, heat	no yellow ppt formed	no yellow ppt formed	yellow ppt formed	no yellow ppt formed

Deduce the identity of the four compounds.

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4.8 Other Reactions of Phenols

In addition to the reactions discussed in earlier sections, phenol also undergoes some other reactions of interest.

4.8.1 Electrophilic substitution of the benzene ring

LO 11.5(d): recall the chemistry of phenol, as exemplified by the following reactions: (i) with bases, (ii) with sodium, (iii) nitration of, and bromination of, the aromatic ring

Due to the delocalisation of the lone pair of electrons of oxygen into the benzene ring, the electron density in the ring is greatly increased, making phenol much more susceptible to electrophilic attack than benzene (contrast this to the reagents and conditions required for electrophilic substitution of benzene in Topic 12 Arenes). Hence, the presence of the –OH group highly activates the benzene ring towards electrophilic substitution. Two general observations are noted:

1. Electrophilic substitution of the benzene ring in phenols takes place under milder conditions compared to benzene: **no catalyst** and **no heating** required.

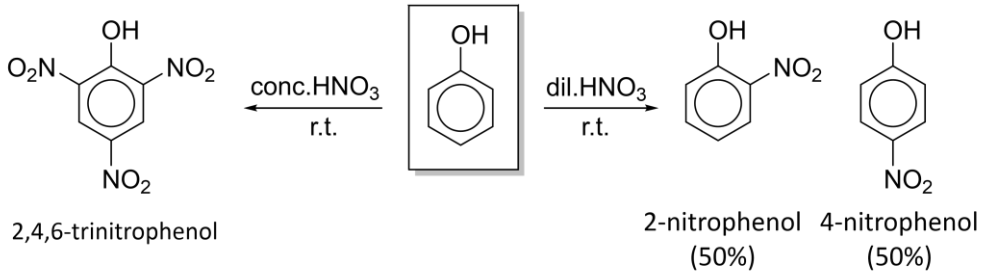
2. The –OH group is strongly activating and 2,4- directing, which may result in **multi-substituted products** at the 2-, 4-, and 6- positions easily.

Note: as the $–NH_2$ group in phenylamine is even more strongly activating than the –OH group in phenol, similar observations will be made regarding electrophilic substitution of the benzene ring in phenylamine (to be covered in Topic 19 Nitrogen Compounds).

Electrophilic substitution with nitric acid (nitration)

When phenol is treated with dilute aqueous nitric acid at room temperature, mono-substitution occurs to form a mixture of 2- and 4- nitrophenol.

If concentrated nitric acid at room temperature is used, 2,4,6-trinitrophenol is produced.

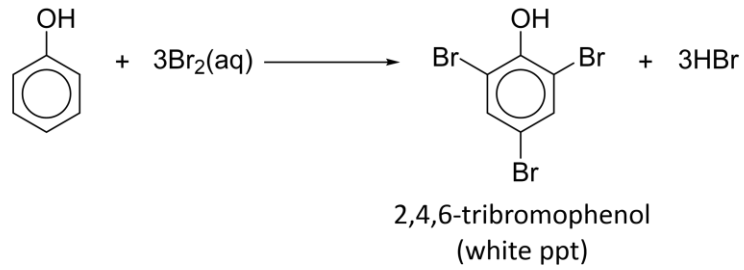


Reagents & Conditions:	dilute HNO_3, room temperature
	-or- concentrated HNO_3, room temperature
Observation:	pale yellow liquid formed

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Electrophilic substitution with bromine (bromination)

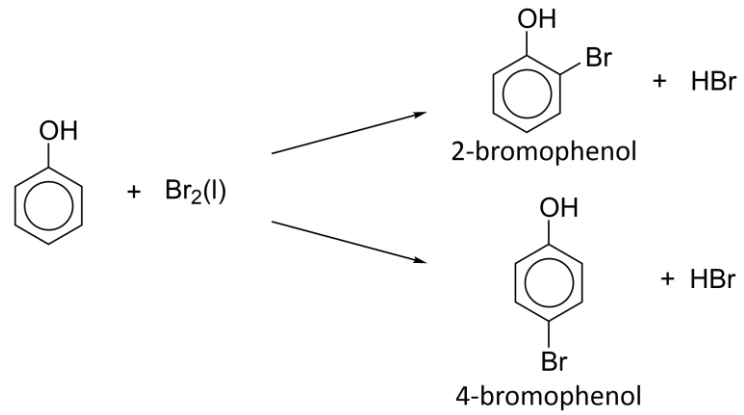
Phenol will react with **aqueous bromine** at room temperature to form a white precipitate of 2,4,6-tribromophenol. No Lewis acid catalyst is required.



2,4,6-tribromophenol
(white ppt)

Reagents & Conditions:	aqueous bromine (bromine water), room temperature
Observation:	yellow-orange solution decolourised, white ppt formed

To achieve mono-bromination of phenol, **low** temperatures must be used as the –OH group is strongly activating. Also, the reaction must be carried out using either liquid bromine or bromine dissolved in a non-polar organic solvent (such as CCl_4) with a 1:1 ratio of phenol to bromine.

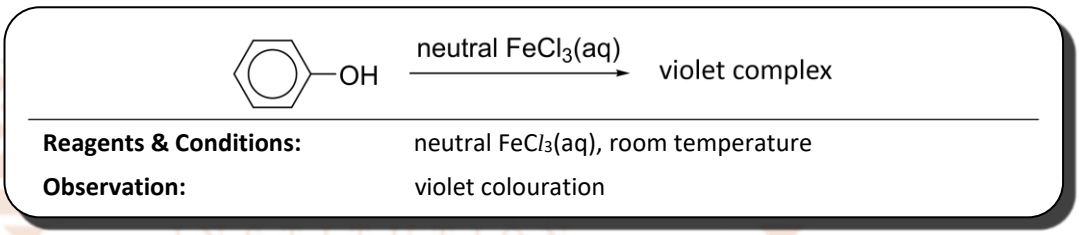


Reagents & Conditions:	$Br_2(l)$ –or- Br_2 dissolved in CCl_4
Observation:	reddish-brown liquid decolourised, white fumes of HBr evolved

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4.8.2 Complex formation with iron(III) chloride

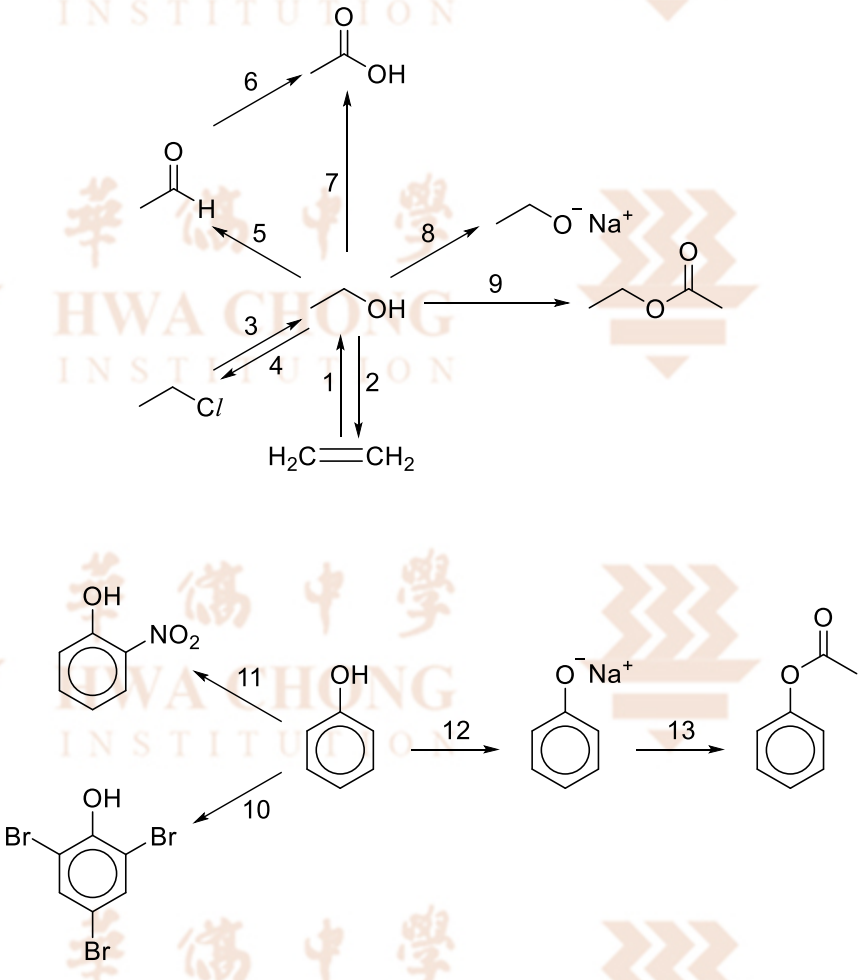
When a neutral solution of iron(III) chloride is added to a dilute solution of a phenol, a coloured complex is formed. (The reason for the complex having colour will be discussed in Topic 22 Chemistry of the Transition Elements.) The colour of the complex depends on the other substituents (if any) on the benzene ring. With phenol, a violet colour is observed.



This reaction is used as a **distinguishing test** for the presence of a phenolic group in an organic compound.

Summary of reactions for alcohols and phenols

Complete the mind map below with **(i)** reagents and conditions; **(ii)** type of reaction for steps 1 – 13.



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17 Carbonyl Compounds

GUIDING QUESTIONS

- How are carbonyl compounds synthesised?
- Which class of reagents do carbonyl compounds react with and why? What types of reactions do carbonyl compounds undergo and why?
- How do carbonyl compounds react with HCN in nucleophilic addition?

LEARNING OUTCOMES

Students should be able to:

11.6(a) describe the formation of aldehydes and ketones from, and their reduction to, primary and secondary alcohols respectively

11.6(b) describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones

11.6(c) explain the differences in reactivity between carbonyl compounds and alkenes towards nucleophilic reagents, such as lithium aluminium hydride and hydrogen cyanide.

11.6(d) describe the use of 2,4-dinitrophenylhydrazine (2,4-DNPH) to detect the presence of carbonyl compounds

11.6(e) deduce the nature (aldehyde or ketone) of an unknown carbonyl compound from the results of simple tests (i.e. Fehling's and Tollens' reagents; ease of oxidation)

11.6(f) deduce the presence of a $CH_3CO–$ group in a carbonyl compound from its reaction with alkaline aqueous iodine to form tri-iodomethane

REFERENCES

1. Peter Cann & Peter Hughes (2014). *Chemistry*, Hodder Education, Chapter 17
2. John McMurry (2012). *Organic Chemistry*. 9th Edition, Cengage Learning, Chapter 19

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1 INTRODUCTION

Carbonyl compounds are commonly found in biologically important molecules such as carbohydrates and hormones, as well as other natural and synthetic dyes, fragrances and pharmaceuticals.

Hedione (methyl hydrojasmonate) was discovered in the early 1960s and is one ingredient found in almost all fine fragrances. During a quest to identify the characteristic smell of Bulgarian rose oil, the rose ketones, damascenones, were discovered and synthesised. In general, aldehydes contribute to the floral concept in feminine perfumery and aliphatic aldehydes with 8–13 carbon atoms have a very pleasant odour, and can be detected in very low concentrations.

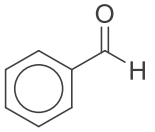
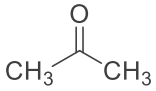
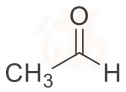
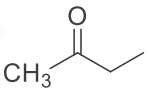
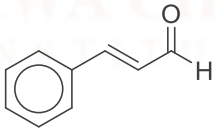
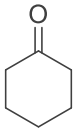
Benzaldehyde, the simplest aromatic aldehyde, has a pleasant almond-like odour, while cinnamaldehyde gives cinnamon note. Vanillin (4–hydroxyl–3–methoxybenzaldehyde) is used as vanilla note, an ubiquitous note in almost all fragrances.

A carbonyl group is composed of a carbon atom which is double bonded to an oxygen atom.



Carbonyl Group

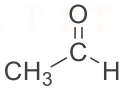
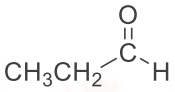
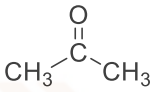
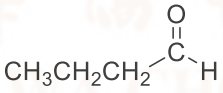
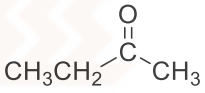
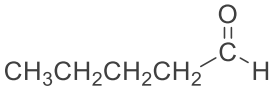
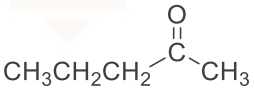
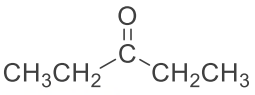
The two simplest types of carbonyl compounds are aldehydes and ketones.

Aldehydes (RCHO)	**Ketones (RCOR')**
	
R = H, alkyl or aryl *For the 1st member of the aldehydes, R = H*	R/ R' = alkyl or aryl *The 1st member of the ketones can only be propanone*
Examples of molecules containing the aldehyde group:	Examples of molecules containing the ketone group:
 Benzaldehyde	 Propanone (acetone)
 Ethanal	 Butanone (MEK)
 Cinnamaldehyde(cinnamon)	 Cyclohexanone

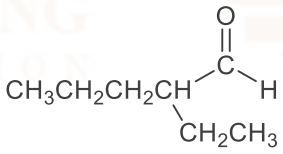
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1.1 Nomenclature

Alkanes	Aldehydes	Ketones
Name ends in **–e** e.g. propan**e**	Name ends in **–al** e.g. propan**al**	Name ends in **–one** e.g. propan**one**

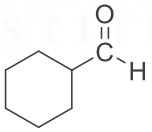
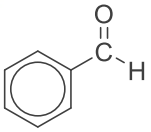
No. of C atoms	Aldehyde		Ketone	
1		methanal	-	-
2		ethanal	-	-
3		propanal		propanone
4		butanal		butanone
5		pentanal		pentan-2-one
				pentan-3-one

- For aldehydes, the longest chain carrying the –CHO group is considered the parent structure and the –CHO carbon is numbered as carbon 1.



2-ethylpentanal

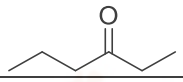
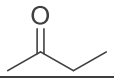
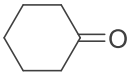
- Aldehydes in which the –CHO group is attached directly to a ring system are named by adding the suffix *-carbaldehyde*.

cyclohexanecarbaldehyde	(benzenecarbaldehyde) benzaldehyde
	

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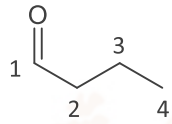
- For ketones, the parent chain is the longest one that contains the ketone group, and the numbering begins at the end nearer the carbonyl carbon.

  If the position of the carbonyl group is obvious, the number can be omitted.

hexa-3-one	butanone	cyclohexanone
		

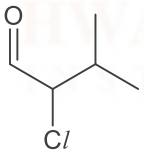
Exercise 1.1 (Worked Example)
Draw the structural formula of each of the following compounds.
(i) 2-chloro-3-methylbutanal (ii) 4-phenylpentan-2-one

'butanal' is the parent structure, aldehyde-carbon is numbered 1:

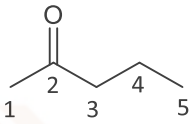


then put a *Cl* at carbon-2 and a CH_3 at carbon-3

Answer:

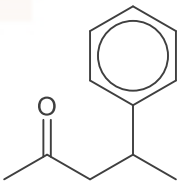


'pentan-2-one' is the parent structure, with carbon-2 bearing the ketone group:



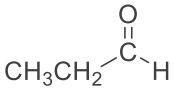
'phenyl' refers to a benzene ring, put it at carbon-4

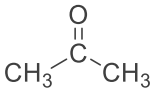
Answer:



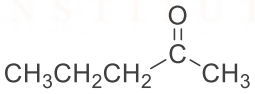
1.2 Isomerism

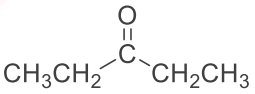
- Saturated aliphatic aldehydes and ketones have the general formula $C_nH_{2n}O$ where n equals to the number of the carbon atoms in the compound. The aliphatic aldehydes and ketones are constitutional isomers if they have the same number of carbon atoms, n, in the compound.


propanal


propanone

- For ketones, the ketone group may occur at different positions.


pentan-2-one


pentan-3-one

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2 PHYSICAL PROPERTIES OF ALDEHYDES AND KETONES

2.1 Boiling Points

Aldehydes and ketones have higher boiling points than corresponding hydrocarbons of similar number of electrons in the molecule, but have lower boiling points than their corresponding alcohols and carboxylic acids.

Compound	Structural formula	No. of electrons in the molecule	b.p. / °C	Predominant intermolecular forces
butane	$CH_3CH_2CH_2CH_3$	34	–0.5	dispersion forces
propanal	CH_3CH_2CHO	32	49	permanent dipole - permanent dipole
propanone	CH_3COCH_3	32	56	permanent dipole - permanent dipole
propan-1-ol	$CH_3CH_2CH_2OH$	34	97	hydrogen bonding
ethanoic acid	CH_3CO_2H	32	118	hydrogen bonding

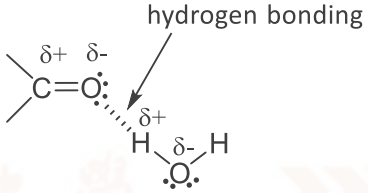
- The **carbonyl** group is **polar**, thus **permanent dipole-permanent dipole** interactions exist between molecules in aldehydes and ketones (in addition to dispersion forces) which require more energy to overcome compared to only dispersion forces present in non-polar alkanes. Hence, carbonyl compounds have **higher** boiling point than the corresponding alkanes.

- **Alcohols** and **carboxylic acids** can form **hydrogen bonds** between molecules, which are **stronger** and require more energy to overcome than **permanent dipole-permanent dipole** interactions in the corresponding aldehydes and ketones. Hence, carbonyl compounds have **lower** boiling point than the corresponding alcohols and carboxylic acids.

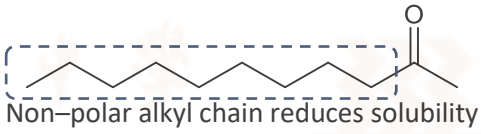
2.2 Solubility in Water

Aldehydes and ketones have both polar and non-polar regions. They can act as solvents to both polar and non-polar solutes, which gives them a wide range of uses as solvents.

The smaller aliphatic aldehydes and ketones are soluble in water due largely to their ability to form hydrogen bonds with water molecules.



Carbonyl compounds containing more than 5 carbons or aromatic rings, are virtually insoluble in water. As the number of carbon atoms in the alkyl chain increases, the strength of the dispersion forces between molecules of the carbonyl compound increases. Energy released from hydrogen bonding formed between the carbonyl group and water is less able to overcome the increasingly stronger dispersion forces, as well as the existing hydrogen bonding in water. In addition, the hydrogen bonding with water is disrupted by the larger non–polar alkyl chain.



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Exercise 2.1

The boiling points and solubility in water of some organic compounds are given below:

Compound	Structural formula	No. of electrons in the molecule	b.p. / °C	Solubility in 100g of water/g
A	$CH_3CH_2CH{=}CH_2$	32	−6	–
B	$(CH_3)_2CO$	32	56	∞
C	$CH_3CH_2CH_2OH$	34	78	∞
D	CH_3CH_2CHO	32	49	16
E	$CH_3CH_2CH_2CHO$	40	76	7

Explain each of the following.

(a) The boiling point increases in the order, **A** < **B** < **C**.

(b) The solubility of **D** is higher than that of **E**.

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3 PREPARATION OF ALDEHYDES AND KETONES

LO 11.6(a): describe the formation of aldehydes and ketones from, and their reduction to, primary and secondary alcohols respectively

Aldehydes can be prepared from:

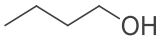
- Oxidation of primary alcohols (Topic 16 Hydroxy Compounds)

Ketones can be prepared from:

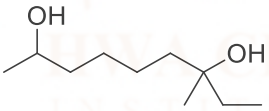
- Oxidation of secondary alcohols (Topic 16 Hydroxy Compounds)
- Oxidative cleavage of substituted alkenes (Topic 11 Alkenes)

Exercise 3.1

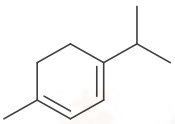
Draw the products formed from the following reactions:

(i) 

$K_2Cr_2O_7 / H^+$
heat with immediate distillation

(ii) 

$KMnO_4 / H^+$
heat

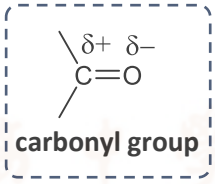
(iii) 
$KMnO_4 / H^+$
Heat

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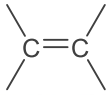
4 REACTIONS OF ALDEHYDES AND KETONES

Reactivity of aldehydes and ketones towards nucleophilic reagents and addition

LO 11.6(c): explain the differences in reactivity between carbonyl compounds and alkenes towards nucleophilic reagents, such as lithium aluminium hydride and hydrogen cyanide



carbonyl group



alkene group

- $LiAlH_4$, $NaBH_4$ and HCN are nucleophilic reagents.

($LiAlH_4$ and $NaBH_4$ can be considered as sources of the hydride anion, H^-)

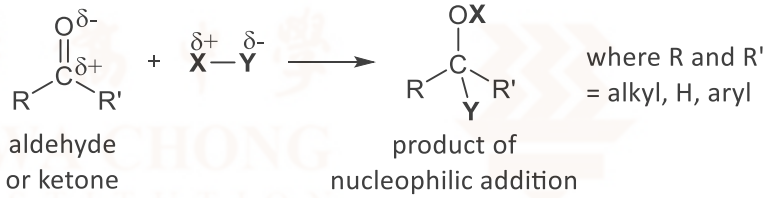
- The $^{\delta+}C{=}O^{\delta-}$ bond is polar, so the aldehyde-carbon or the ketone-carbon has δ+ charge.

δ+ carbon attracts nucleophiles. Hence, aldehydes and ketones react with the above nucleophilic reagents.

- The C=C bond (in alkenes) is non-polar and has no δ+ carbon to attract nucleophiles. In fact the electron rich C=C bond would repel nucleophiles (e.g. H^- anion, or the AlH_4^- or BH_4^- anions themselves).

4.1 Nucleophilic Addition Reaction

The overall reaction for nucleophilic addition of carbonyl compounds can be represented as:



aldehyde or ketone

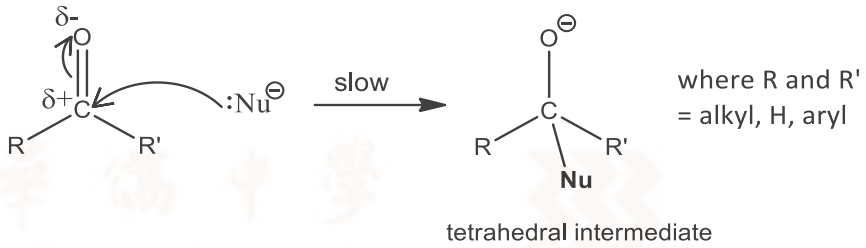
product of nucleophilic addition

Examples of nucleophiles that can react with aldehydes and ketones in a nucleophilic addition include CN^-, H_2O and ROH.

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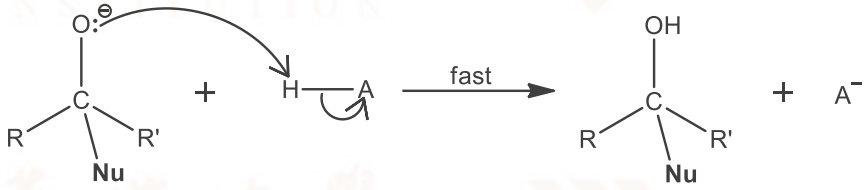
4.1.1 General mechanism of nucleophilic addition

Step 1: A nucleophile attacks the electron-deficient carbonyl carbon, breaking the π bond of the C=O group, to form an alkoxide ion.



tetrahedral intermediate

Step 2: The tetrahedral intermediate is protonated by water or acid to give an alcohol as the final product.

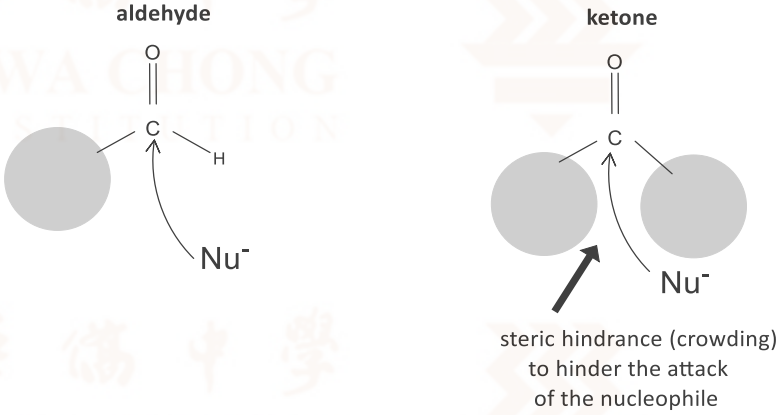


4.1.2 Relative reactivity of aldehydes and ketones in nucleophilic addition reactions

Aldehydes are generally more reactive than ketones in nucleophilic addition reactions.

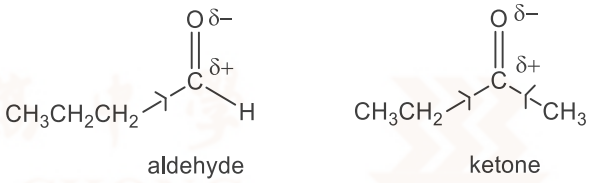
(i) Steric reason:

The presence of two relatively large substituents in ketones versus only one large substituent in aldehydes means that attacking nucleophiles are able to approach the carbonyl carbon in aldehydes with less steric hindrance than in ketones.



(ii) Electronic reason:

Aldehydes have one electron donating alkyl group while ketones have two. Hence, an aldehyde-carbon has a higher partial positive charge compared to a ketone-carbon, making the former more susceptible towards nucleophilic attack.

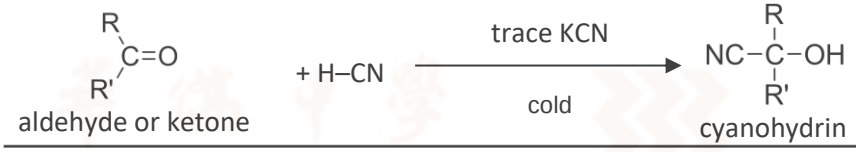


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4.1.3 Nucleophilic addition with hydrogen cyanide, HCN

LO 11.6(b): describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones

Aldehydes and ketones undergo nucleophilic addition with hydrogen cyanide, HCN, under appropriate conditions to form cyanohydrins.



Reagents and conditions:	HCN with trace KCN, cold
Comments:	KCN is used as a catalyst; CN^- ion is regenerated at the end of the reaction.

Note:

HCN is a toxic gas and has a boiling point of 25.6°C . It is usually generated *in situ* by the reaction between KCN(s) and cold dilute H_2SO_4.

$$2\ KCN + H_2SO_4 \rightarrow K_2SO_4 + 2\ HCN$$

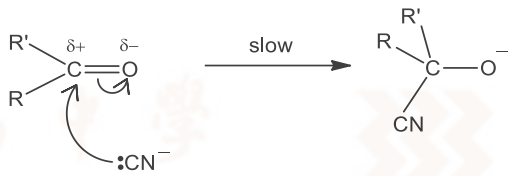
The reaction mixture is kept cold (at 10-20°C) to ensure that HCN remains as a liquid.

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Mechanism

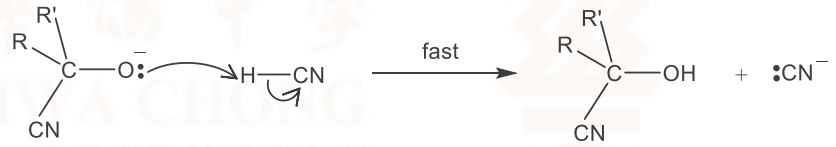
The mechanism of the nucleophilic addition with HCN involves two steps:

Step 1: The carbonyl carbon is attacked by the CN^- nucleophile

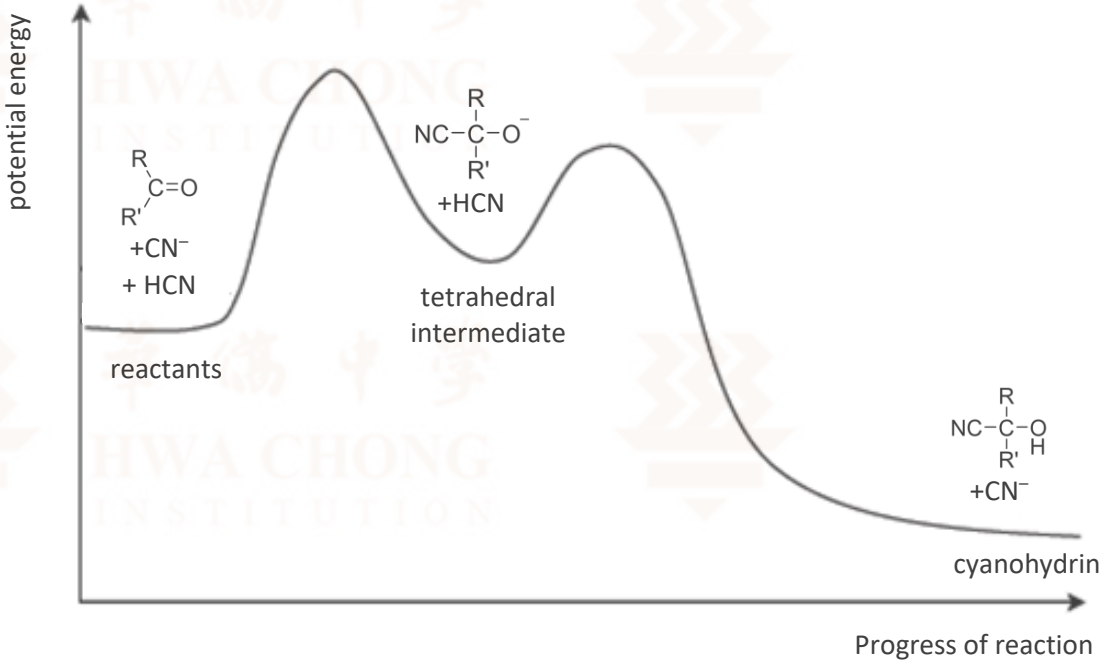


- The CN^- ion acts as nucleophile and attacks the electron-deficient carbonyl carbon breaking the π-bond of the C=O.
- This leads to the formation of a stable tetrahedral intermediate anion (an alkoxide ion).
- This is the rate-determining step.

Step 2: Protonation of the intermediate to give a cyanohydrin



- The tetrahedral alkoxide ion intermediate is protonated by attacking an undissociated HCN molecule to yield the cyanohydrin.
- The CN^- nucleophile is regenerated.



Kinetics

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This nucleophilic addition mechanism is ***bimolecular***, as it involves both the carbonyl compound and the nucleophile :CN^- in the ***rate-determining*** step. Hence, the rate equation is:

$$\text{rate} = k\,[\text{carbonyl compound}]\,[CN^-]$$

To increase the rate of reaction, the following methods are used:

1. *add a trace amount of KCN as catalyst*

- HCN is a weak acid, which only partially ionises in water to give CN^-.

$$HCN + H_2O \rightleftharpoons H_3O^+ + CN^- \qquad K_a = 6.2 \times 10^{-10}\ \text{mol dm}^{-3}$$

- The reaction takes place very slowly if only HCN is used because the solution contains a very low concentration of CN^- ions.
- The reaction can be speeded up by adding a trace amount of KCN, a salt which completely dissociates to provide free CN^- ions.

$$KCN\,(aq) \rightarrow K^+\,(aq) + CN^-\,(aq)$$

- CN^- ions used in the addition reaction are regenerated at the end of the reaction as shown in the mechanism.

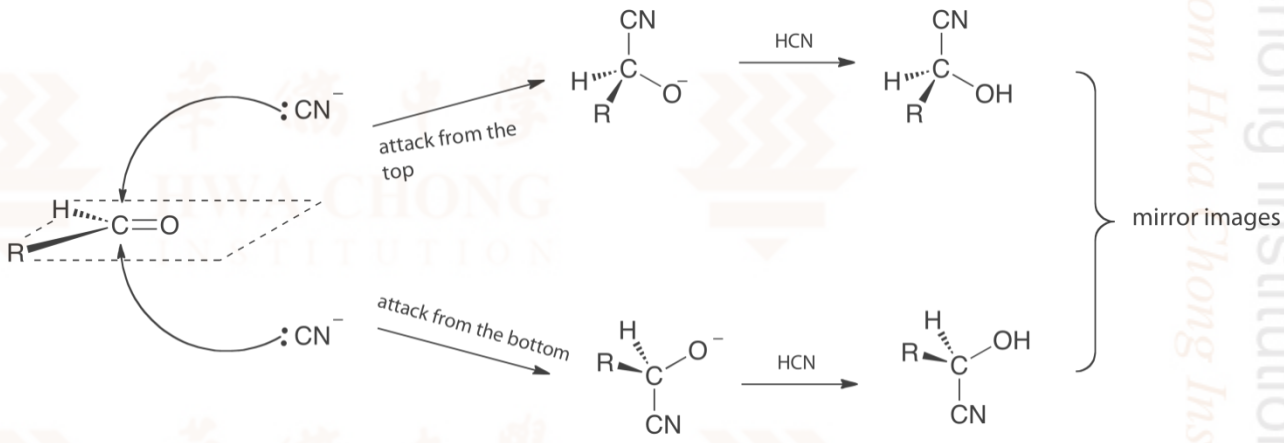
2. *add a small amount of base (e.g. NaOH)*

$$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$$

When a small amount of base is added, the H_3O^+ ions are neutralised, which by Le Chatelier's Principle, shifts the position of the above equilibrium to the right such that the concentration of the CN^- increases. Hence the rate of reaction increases.

Stereochemistry

The geometry about the carbonyl carbon atom in aldehydes and ketones is planar. Hence the nucleophile can attack the δ+ carbonyl carbon atom in equal probability from the top or bottom of the plane, producing equal amounts of both enantiomers to give a racemic mixture, <u>if the resulting sp^3 carbon is chiral</u>.

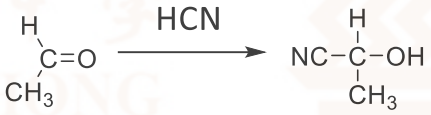


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Refer to the similar circumstances leading to the formation of racemic mixtures in Topic 11 Alkenes and Topic 15 Halogen Derivatives. In electrophilic addition and S_N1 mechanisms, the **geometry about** the *positively-charged carbon in the carbocation intermediate* is also **planar**, allowing a nucleophile to attack from either side of the plane with equal probability.

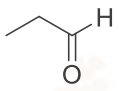
Importance of cyanohydrins in synthesis

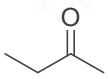
- Nucleophilic addition with CN^- ion is an important method of lengthening the carbon chain by 1 carbon (step-up reaction).



- The cyanohydrin product can be easily converted to other usable forms since the nitrile group (–CN) can be converted to other functional groups such as:
  - carboxylic acids by acid hydrolysis using mineral acids such as dilute H_2SO_4
  - carboxylate salts by alkaline hydrolysis using alkalis such as dilute NaOH
  - amines by reduction using lithium aluminium hydride (LiA/H_4) in dry ether or hydrogen with nickel catalyst

Exercise 4.1
Draw the products formed from the following reactions:

(i)  HCN, trace KCN, cold → [ ] → LiA/H_4 in dry ether → [ ]

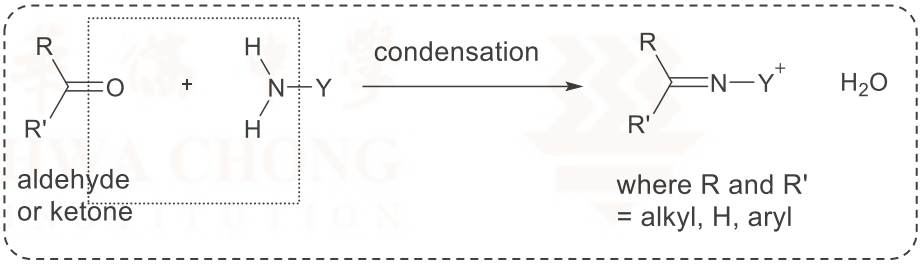
(ii)  HCN, trace KCN, cold → [ ] → dil. H_2SO_4, heat → [ ]

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4.2 Condensation Reaction (Application Example)

Nucleophiles having two H atoms on a nitrogen atom readily add onto carbonyl compounds. But usually, the initially formed addition product is not isolated because it easily loses water via elimination to give stable compounds containing a C=N bond.

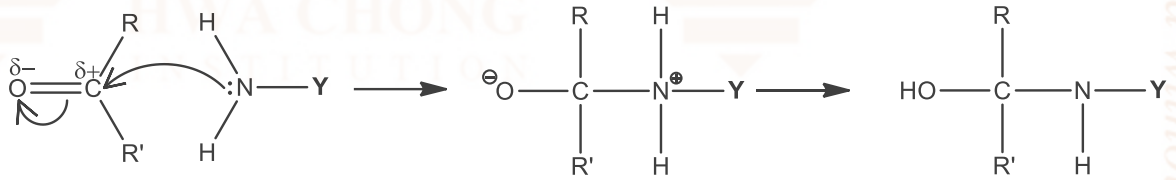
The overall reaction can be represented as:



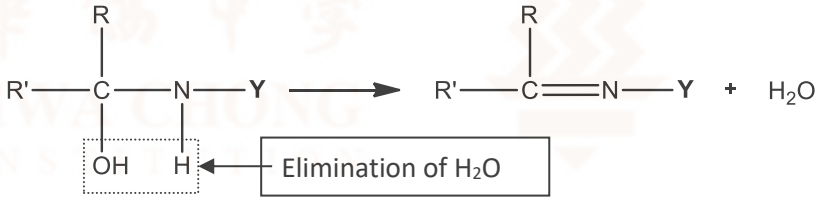
4.2.1 General mechanism (application example)

The reaction can be viewed as an addition, followed by an elimination, hence it may be referred to as an *addition-elimination* reaction.

Step 1: Addition of nucleophile to carbonyl compound



Step 2: Elimination of a water molecule

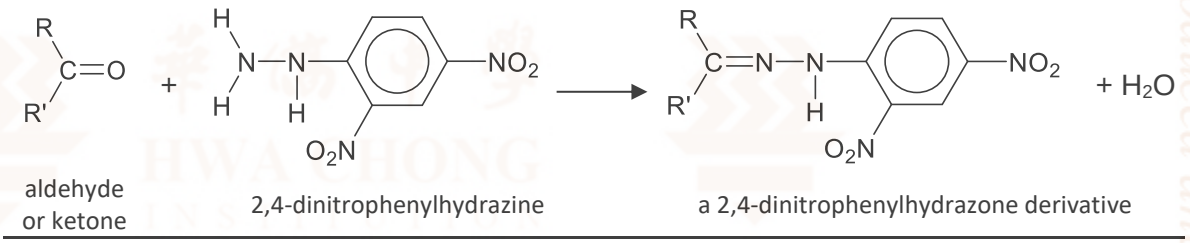


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4.2.2 Condensation reaction with 2,4-dinitrophenylhydrazine (2,4-DNPH)

LO 11.6(d): describe the use of 2,4-dinitrophenylhydrazine (2,4-DNPH) to detect the presence of carbonyl compounds

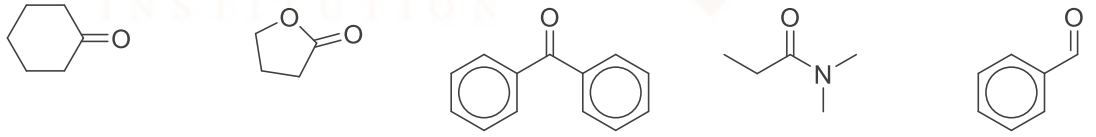
2,4-dinitrophenylhydrazine, also known as Brady's reagent, is a yellow solution. It reacts with aldehydes and ketones to form a 2,4-dinitrophenylhydrazone derivative, which is an orange precipitate. A water molecule is eliminated in the reaction. This is a characteristic test for the presence of aldehydes and ketones.



Reagents and conditions:	2,4-dinitrophenylhydrazine (2,4-DNPH), room temperature
Observations:	Orange precipitate formed

Exercise 4.2

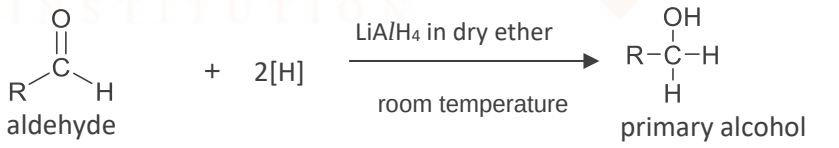
Which of the following compounds will give an orange precipitate with 2,4-dinitrophenylhydrazine?

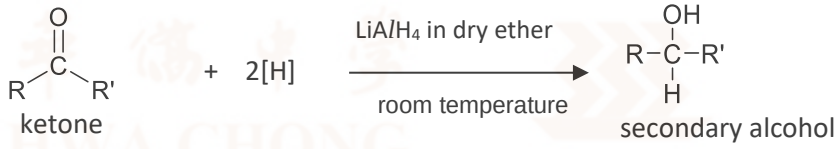


A **B** **C** **D** **E**

4.3 Reduction

Aldehydes and ketones undergo reduction to form primary and secondary alcohols respectively.

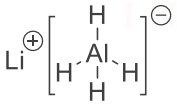




Reagents and conditions:	$LiAlH_4$ in dry ether, room temperature **Note:** When the aldehyde or ketone react with $LiAlH_4$, the alkoxide ion is form. H_2O needs to be added to protonate the alkoxide to form the alcohol.
Comments:	Other reducing agents like $NaBH_4$ in methanol or, $H_2(g)$/ Ni at high pressure may be used.

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4.3.1 Comparing reducing agents LiA/H_4 and $NaBH_4$



Lithium aluminium hydride (LiA/H_4) and sodium borohydride ($NaBH_4$) are useful hydride reagents that can reduce aldehydes and ketones in excellent yields.

- LiA/H_4 is a grayish powder that is soluble in ether. It reacts violently with water to form H_2 gas and decomposes explosively when heated above 120 °C. $NaBH_4$ is a white, crystalline solid that can be handled in the open atmosphere and used in either water or alcohol solution.

- Due to the hazardous nature of LiA/H_4 and ether (which forms highly explosive mixtures in air), the use of $NaBH_4$ is usually preferred.

- Both LiA/H_4 and $NaBH_4$ can be considered as sources of the nucleophilic hydride anion, H^-. They both have hydrogen atoms covalently bonded to aluminium and boron respectively and because hydrogen is more electronegative than aluminium and boron, the hydrogen atoms will bear the negative charge, making it a good nucleophile. As such, LiA/H_4 and $NaBH_4$ are able to react with aldehydes and ketones bearing the polar C=O group with an electron-deficient carbon.

- Aluminium is less electronegative than boron, thus more of the negative charge in the A/H_4^- ion is borne by the hydrogen atoms. Therefore, LiA/H_4 is a much stronger reducing agent, and is much less selective than $NaBH_4$.

- Both LiA/H_4 and $NaBH_4$ do not reduce the non-polar electron-rich alkene group. The alkene functional group is reduced using $H_2(g)$ over a nickel catalyst. Refer to Topic 6 Reaction Kinetics for the mechanism of this heterogeneous catalysis reaction.

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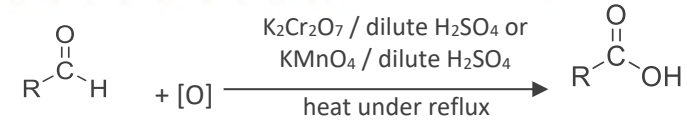
4.4 Oxidation

LO 11.6(e): deduce the nature (aldehyde or ketone) of an unknown carbonyl compound from the results of simple tests (i.e. Fehling's and Tollens' reagents; ease of oxidation)

The aldehyde group undergoes oxidation reactions with acidified potassium dichromate(VI), Tollens' reagent and Fehling's solution, while the ketone group does not. As such, these three tests are good distinguishing tests between aldehydes and ketones.

4.4.1 Oxidation with acidified potassium dichromate(VI) or acidified potassium manganate(VII)

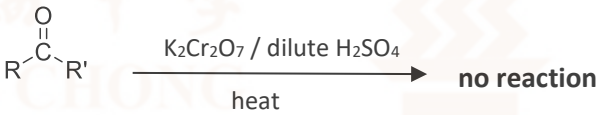
Aldehyde has a hydrogen atom attached directly to the carbonyl carbon. This enables it to be oxidised to carboxylic acids.



aldehyde carboxylic acid

Reagents and conditions:	$K_2Cr_2O_7$ / dilute H_2SO_4 or $KMnO_4$ / dilute H_2SO_4, heat under reflux
Comments:	Orange solution ($Cr_2O_7^{2-}$) turns green (Cr^{3+}) or Purple solution (MnO_4^-) turns colourless (Mn^{2+})

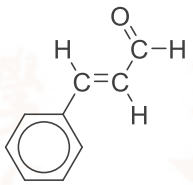
Ketones do not have a hydrogen atom attached directly to the carbonyl carbon, thus are not easily oxidised.



ketone

Exercise 4.3

How would you oxidise only the aldehyde group in cinamaldehyde to carboxylic acid?



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4.4.2 With Tollens' reagent (silver mirror test)

Tollens' reagent (ammoniacal silver nitrate) contains diamminesilver(I) ions, $[Ag(NH_3)_2]^+$.

Aldehydes reduce silver(I) in Tollens' reagent to silver metal. Under carefully controlled conditions, silver metal will deposit on the walls of the reaction vessel as a mirror.



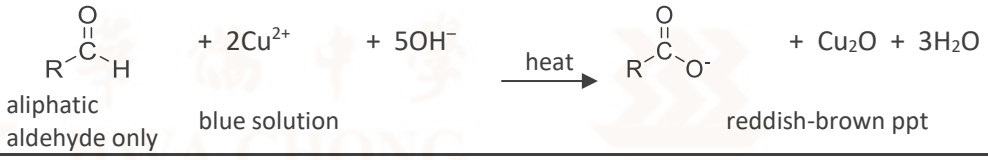
aldehyde silver mirror

Reagents and conditions:	Tollens' reagent, heat
Observations:	Silver mirror formed
Comments:	$[Ag(NH_3)_2]^+$ is unstable and should always be freshly prepared. It can be prepared as follows: 1. One drop of dilute NaOH(aq) is added to about 3 cm^3 of $AgNO_3$(aq) to produce a dark brown precipitate of Ag_2O. 2. Dilute NH_3(aq) is then added dropwise until the brown precipitate first formed just redissolves.

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4.4.3 With Fehling's reagent

Fehling's reagent is an alkaline solution of copper(II) tartrate.
Aldehydes (except benzaldehyde and its derivatives) reduce the copper(II) in Fehling's reagent to the reddish-brown copper(I) oxide, which is precipitated.

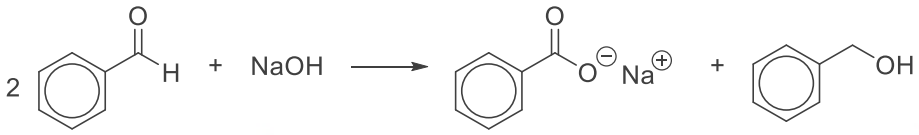


Reagents and conditions: Fehling's reagent, heat

Observations: Reddish-brown (brick-red) precipitate formed

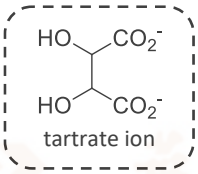
Comments: Ketones, benzaldehyde and its derivatives do not reduce Fehling's reagent.

In fact, benzaldehyde undergoes disproportionation instead due to the presence of NaOH in Fehling's reagent.



Fehling's reagent deteriorates on keeping. and is usually prepared in two parts which are added together just before the test is carried out.

It consists of:
1. Fehling's solution A ($CuSO_4$ solution) and
2. Fehling's solution B (sodium potassium tartrate + excess NaOH)

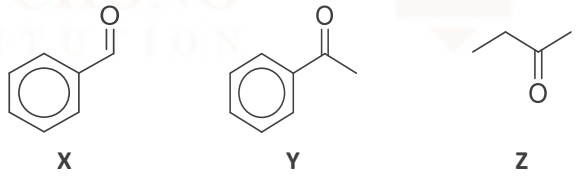


A deep blue solution is obtained on mixing the two solutions owing to the formation of copper(II) tartrate, the tartrate ions present prevent the precipitation of $Cu(OH)_2$ by complexing with the copper(II) ions.

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Exercise 4.4

Which of the following compounds will give a positive Tollens' reagent test?



X Y Z

(i) Which of the following compounds will reduce Fehling's reagent?

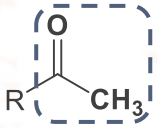


A B C D

4.5 Tri-iodomethane (iodoform) Test

LO 11.6(f): deduce the presence of a $CH_3CO–$ group in a carbonyl compound from its reaction with alkaline aqueous iodine to form tri-iodomethane

This test specifically identifies aldehydes and ketones with the structure:



"R" can be a hydrogen atom or a hydrocarbon group (alkyl or aryl).

If "R" is hydrogen, the compound is ethanal, CH_3CHO. Ethanal is the only aldehyde that gives positive tri-iodomethane test.



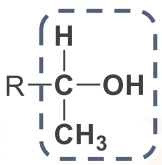
ethanal or methyl ketones carboxylate ion iodoform

Reagents and conditions:	Aqueous I_2 with NaOH(aq), warm
Observations:	Yellow crystals of CHI_3 (iodoform) formed.

Note:

This reaction breaks a C–C bond and removes a methyl ($–CH_3$) group. It is therefore a useful method of shortening a carbon chain by a single carbon atom (step-down reaction).

Recall: Alcohols with the structure below also give a positive tri-iodomethane test. Refer to the tri-iodomethane test in Topic 16 Hydroxy Compounds.



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Exercise 4.5

Suggest a structure for each of the isomers, **X**, **Y** and **Z** of the compound $C_3H_6O_2$, based on the following reactions:

X: gives tri-iodomethane with aqueous alkaline iodine and reduces Fehling's solution;

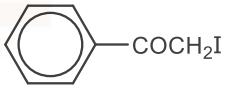
Y: gives tri-iodomethane with aqueous alkaline iodine but does not reduce Fehling's solution;

Z: does not give tri-iodomethane with aqueous alkaline iodine but does reduce Fehling's solution.

Exercise 4.6

Which compound will **not** give tri-iodomethane on warming with alkaline aqueous iodine?

A $CH_3COCHC/COCH_3$

B 

C $I_2CHCH(OH)CO_2H$

D $Cl_3CO_2CH_3$

[N2010/1]

Summary of Distinguishing Tests

Reagents & Conditions	Aldehyde	Benzaldehyde	Ketone	Comments
2,4-DNPH	+	+	+	• A characteristic test for aldehydes and ketones • All other functional groups will give negative results. • This test differentiates aldehydes and ketones from ALL other functional groups.
$K_2Cr_2O_7$ / dilute H_2SO_4 Heat	+	+	–	• Good test to differentiate aldehydes and benzaldehydes from ketones.
Tollens' reagent, Heat	+	+	–	• Another method to differentiate aldehydes from ketones. • ALL aldehydes give positive Tollens' Test.
Fehling's reagent, Heat	+	–	–	• Good test to further differentiate aldehydes from benzaldehydes.

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Exercise 4.7

Describe a simple chemical test to differentiate the following sets of compounds:

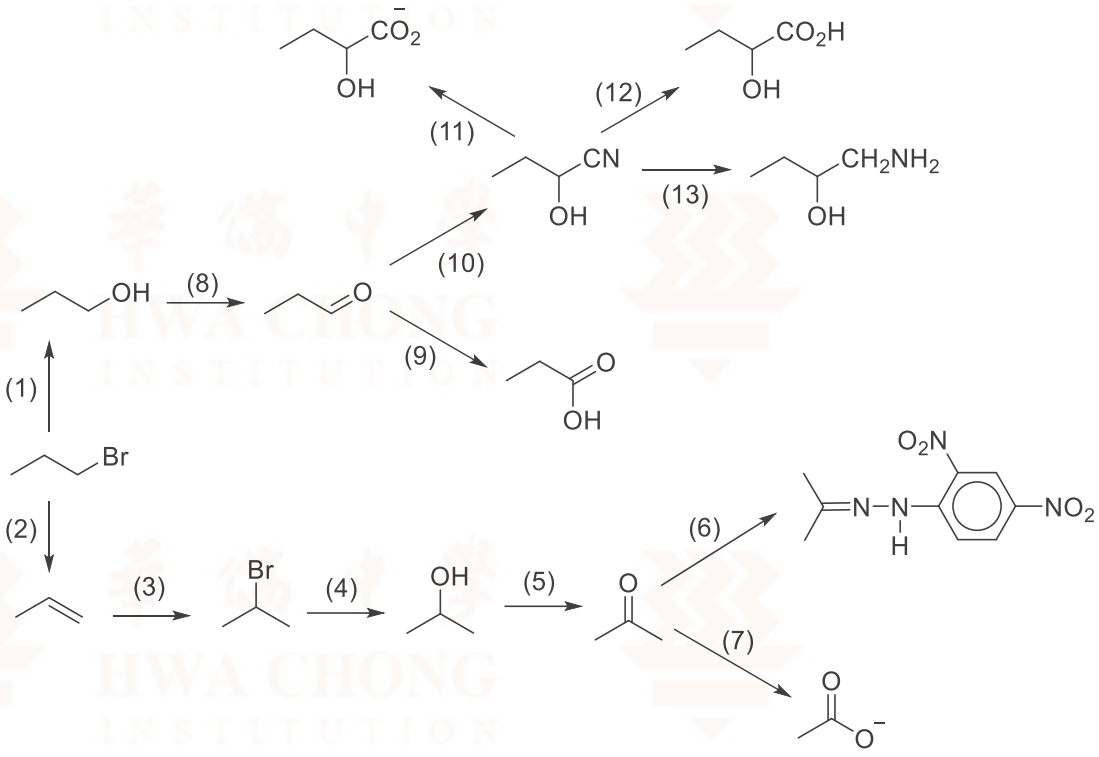
(i) butanal and butanone

(ii) propanone and propan-1-ol

(iii) propanal, propanone and benzaldehyde

Summary of reactions of aldehydes and ketones

State the reagents and conditions needed for the conversions on the arrows below:



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18 Carboxylic Acids & Derivatives

GUIDING QUESTIONS

Carboxylic Acids

- How are carboxylic acids synthesised?
- What types of reactions do carboxylic acids undergo and why?

Acid Derivatives

- How are acyl chlorides and esters synthesised?
- What types of reactions do acyl chlorides and esters undergo and why?
- How do the ease of hydrolysis of acyl chlorides compare with that of alkyl and aryl chlorides?

How do we compare the acidity of organic compounds in aqueous medium?

LEARNING OUTCOMES

Students should be able to:

11.7 (a) describe the formation of carboxylic acids from alcohols, aldehydes and nitriles

11.7 (b) describe the reactions of carboxylic acids in the formation of:
(i) salts
(ii) esters on condensation with alcohols, using ethyl ethanoate as an example
(iii) acyl chlorides, using ethanoyl chloride as an example
(iv) primary alcohols, via reduction with lithium aluminium hydride, using ethanol as an example.

11.7 (c) explain the acidity of carboxylic acids and of chlorine-substituted ethanoic acids in terms of their structures

11.7 (d) describe the hydrolysis of acyl chlorides

11.7 (e) describe the condensation reactions of acyl chlorides with alcohols, phenols and primary amines

11.7 (f) explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides

11.7 (g) describe the formation of esters from the condensation reaction of acyl chlorides, using phenyl benzoate as an example

11.7 (h) describe the acid and base hydrolysis of esters

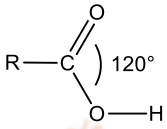
REFERENCES

1. Peter Cann & Peter Hughes, *Chemistry*, 2015, Hodder Education, Chapter 18
2. Graham C. Hill & John S. Holman, *Chemistry in Context*, Nelson, Chapter 29

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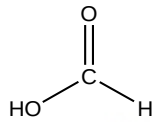
1 INTRODUCTION TO CARBOXYLIC ACIDS

All carboxylic acids contain the carboxyl group ($-CO_2H$), as shown below:



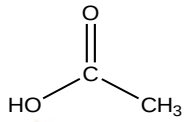
The molecule is trigonal planar about the carboxyl carbon, which is sp^2 hybridised, with bond angles approximately 120°.

Examples of carboxylic acids:



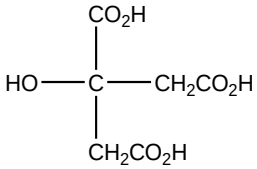
formic acid (methanoic acid)

Simplest carboxylic acid. First isolated in the 17th century by distillation of dead ants.



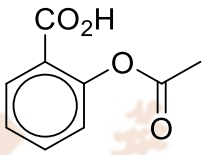
acetic acid (ethanoic acid)

Important chemical reagent and industrial chemical.



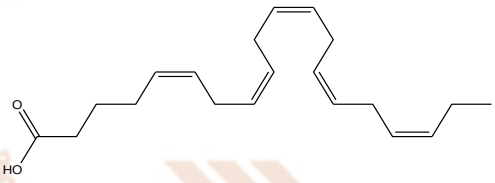
citric acid

A tribasic acid. Found in citrus fruits. Often used as a flavouring in soft drinks.



aspirin

A commonly used pain-killer, which is also an anti-inflammatory medicine.



eicosapentaenoic acid

An omega-3 fatty acid.
Found in fish such as salmon and cod.

Did you know?

Ant hills had long been known to emit acidic vapour when the English naturalist John Ray attempted his somewhat brutal distillation of ants, but it is thanks to him that the source was discovered. Methanoic acid, also known by its trivial name, formic acid, is the weapon of choice for the members of the family formicidae, along with hundreds more species of wasp, bee and termite in the invertebrate order Hymenoptera. Sprayed or stung (along with a variety of other substances) the acid is a powerful and painful deterrent for would-be aggressors, and an effective biocide. A paste of baking soda (sodium hydrogencarbonate) and very cold water can be applied to neutralise the acid and sooth the pain.



John Ray (1628-1705)

Picture source: http://www.ucmp.berkeley.edu/history/ray.html

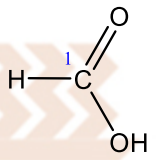


Picture source: www.CartoonStock.com

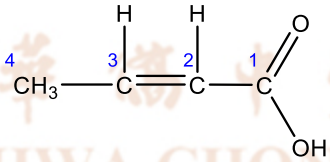
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1.1 Nomenclature

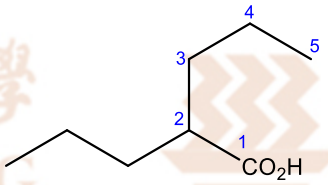
Straight chain carboxylic acids are named by replacing the terminal '-e' of the corresponding alkane with "-oic acid". For branched carboxylic acids, find the longest chain containing the $-CO_2H$ group, and change the terminal '-e' of the parent alkane to the suffix '-oic acid'. The carboxyl carbon is numbered C^1.



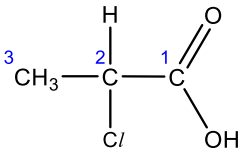
methanoic acid



cis-but-2-enoic acid



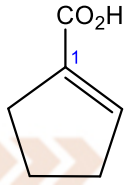
2-propylpentanoic acid



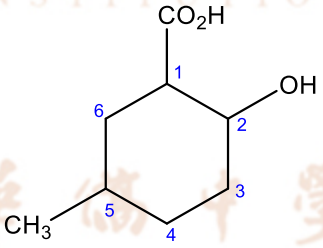
2-chloropropanoic acid

Compounds that contain the $-CO_2H$ group bonded to a ring are named using the suffix 'carboxylic acid'. If the carboxyl group is directly attached to an aromatic ring, the suffix used is 'benzoic acid'. The carbon in the ring that is attached to the $-CO_2H$ group is numbered C^1.

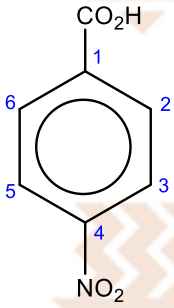
For aromatic acids which have 2 $-CO_2H$ groups attached directly to the benzene ring, it is named as dicarboxylic acids.



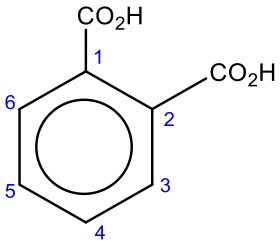
cyclopent-1-ene carboxylic acid



2-hydroxy-5-methylcyclohexane carboxylic acid



4-nitrobenzoic acid

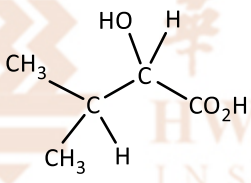


benzene-1,2-dicarboxylic acid

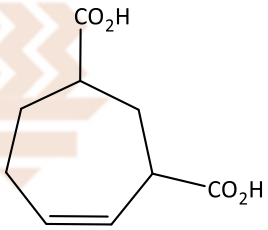
Exercise 1.1 (Worked Example)

Draw the structural formula for each of the following compounds:

1. 2-hydroxy-3-methylbutanoic acid



2. cyclohept-4-ene-1,3-dicarboxylic acid



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2 PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS

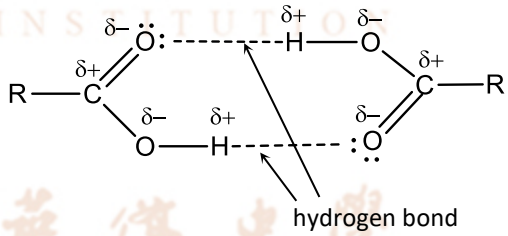
2.1 Boiling Points

Alcohol		M_r	b.p. /°C	Carboxylic acid		M_r	b.p. /°C
Ethanol	CH_3CH_2OH	46	78	Methanoic acid	HCO_2H	46	101
Propan-1-ol	$CH_3CH_2CH_2OH$	60	97	Ethanoic acid	CH_3CO_2H	60	118
Butan-1-ol	$CH_3CH_2CH_2CH_2OH$	74	118	Propanoic acid	$CH_3CH_2CO_2H$	74	141

Carboxylic acids have higher boiling points than corresponding alcohols with similar size of electron cloud (size of electron cloud may be compared based on M_r) because:

1. Hydrogen bonding between carboxylic acid molecules is stronger than that between alcohol molecules. This is due to the presence of the electron-withdrawing C=O group causing the δ+ on the H atom to be intensified and the O−H bond to be more polarised in the carboxylic acid.

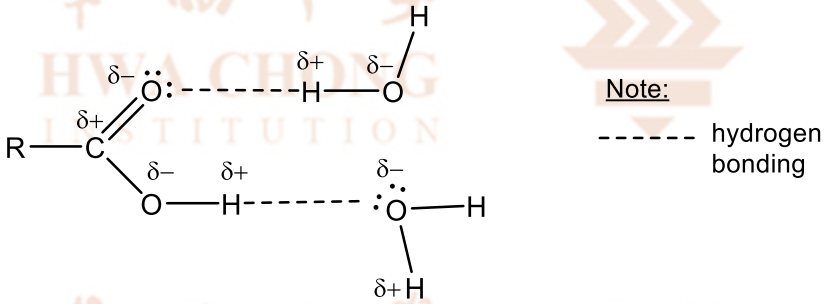
2. Carboxylic acids can dimerise (in the pure liquid) through hydrogen bonding (diagram below), effectively doubling the number of electrons (or size of electron cloud) in the dimer. This results in stronger dispersion forces between dimers.



2.2 Solubility

In non-hydrogen-bonding solvents such as benzene, carboxylic acids can form the hydrogen-bonded dimers. Carboxylic acids, especially those with longer hydrocarbon chains, are generally soluble in such non-polar solvents as dispersion forces can be formed between the solvent molecules and the hydrocarbon chain of the dimers.

In water, the carboxylic acid does not dimerise. The carboxylic acid molecules (the $–CO_2H$ group) can form hydrogen bonding with the water molecules.



For carboxylic acids with longer hydrocarbon chains, solubility in water decreases as the hydrocarbon chain gets longer. The longer the non-polar hydrocarbon chain, the stronger the dispersion forces

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between carboxylic acid molecules. Energy released from hydrogen bonding between $–CO_2H$ group and water molecules is less than the energy needed to overcome these dispersion forces, as well as the existing hydrogen bonding between water molecules.

Similarly, benzoic acid (a white crystalline solid at room temperature) is only slightly soluble in cold water but dissolves readily in hot water.

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3 PREPARATION OF CARBOXYLIC ACIDS

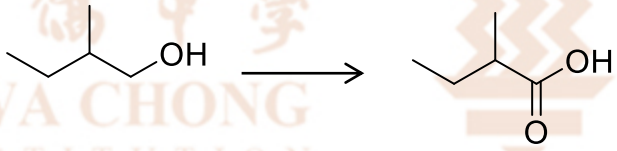
LO 11.7 (a): describe the formation of carboxylic acids from alcohols, aldehydes and nitriles

Carboxylic acids can be prepared from:

- Oxidative cleavage of alkenes (Topic 11 Alkenes)
- Side chain oxidation of alkylbenzenes (Topic 12 Arenes)
- Acid and alkaline hydrolysis of nitriles (Topic 15 Halogen Derivatives)
- Oxidation of primary alcohols (Topic 16 Hydroxy Compounds)
- Oxidation of aldehydes (Topic 17 Carbonyl Compounds)
- Hydrolysis of acyl chlorides (covered later in Section 6.2.1)
- Acid and alkaline hydrolysis of esters/amides (esters covered later in Section 7.4, amides in Topic 19 Nitrogen Compounds)

Exercise 3.1 (Worked Example)

1. Suggest the product formed from the oxidation of 2-methyl-1-butanol, using hot acidified potassium manganate(VII).



The primary alcohol is oxidised to a carboxylic acid.

2. Give the synthetic routes to show the conversion of the halogenoalkane to propanoic acid:

(i) CH_3CH_2Br

$CH_3CH_2Br \rightarrow CH_3CH_2CN \rightarrow CH_3CH_2CO_2H$

Step 1: ethanolic KCN, heat (bimolecular nucleophilic substitution S_N2)

Step 2: dilute H_2SO_4 (aq), heat (acid hydrolysis)

(ii) $CH_3CH_2CH_2Br$

$CH_3CH_2CH_2Br \rightarrow CH_3CH_2CH_2OH \rightarrow CH_3CH_2CO_2H$

Step 1: NaOH(aq), heat (bimolecular nucleophilic substitution S_N2)

Step 2: $KMnO_4$, dilute H_2SO_4, heat (oxidation)

(iii) $CH_3CH_2CHBrCH_2CH_2CH_3$

$CH_3CH_2CHBrCH_2CH_2CH_3 \rightarrow CH_3CH_2CH{=}CHCH_2CH_3 \rightarrow CH_3CH_2CO_2H$

Step 1: ethanolic NaOH, heat (elimination)

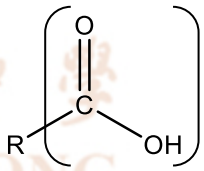
Step 2: $KMnO_4$, dilute H_2SO_4, heat (oxidative cleavage)

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4 REACTIONS OF CARBOXYLIC ACIDS

LO 11.7 (b): describe the reactions of carboxylic acids in the formation of:
(i) salts
(ii) esters on condensation with alcohols, using ethyl ethanoate as an example
(iii) acyl chlorides, using ethanoyl chloride as an example
(iv) primary alcohols, via reduction with lithium aluminium hydride, using ethanol as an example.

The characteristic chemical behaviour of carboxylic acids is determined by the carboxyl group.



There are 3 main kinds of reactions that carboxylic acids undergo:

(i) **Acid-metal/Acid-base reactions** (O–H bond is broken to form salts)
(ii) **Nucleophilic (acyl) substitution** (replacement of the –OH group)
(iii) **Reduction** of the CO_2H group

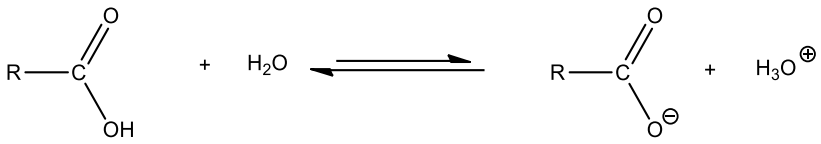
The C=O and O–H bonds are so close in proximity that carboxylic acids do not behave exactly like alcohols, aldehydes or ketones. For example,

(i) carboxylic acids are stronger acids than alcohols (discussed further in Section 4.1.1)
(ii) carboxylic acids do not undergo nucleophilic addition like aldehydes and ketones and do not give a positive test with 2,4-dinitrophenylhydrazine and aqueous alkaline iodine. This is because the delocalisation of electrons from the O–H group into the C=O group makes the carboxyl carbon less electron deficient and less readily attacked by nucleophiles.

4.1 Acidity of Carboxylic Acids

LO 11.7 (c): explain the acidity of carboxylic acids and of chlorine-substituted ethanoic acids in terms of their structures

Carboxylic acids are weak Bronsted acids. The O–H bond breaks to give H^+ and the conjugate base, RCO_2^- (carboxylate ion).



carboxylic acid carboxylate ion

As seen in Topic 16 Hydroxy Compounds, the strength of acids depends on the stability of the conjugate base formed.

The conjugate base is negatively charged. The more dispersed the negative charge, the less likely the conjugate base will accept a proton (to re-form the acid), the more stable it is.

The more stable the conjugate base, the greater the extent of acid dissociation, the larger the K_a (the smaller the pK_a) and the stronger the acid.

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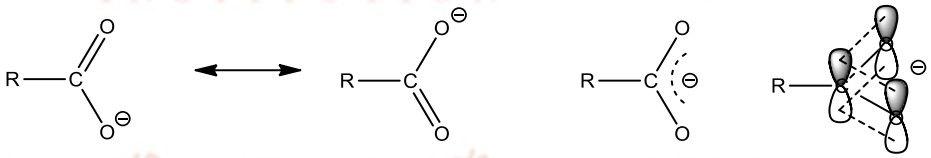
4.1.1 Relative acidities of carboxylic acids, phenols and aliphatic alcohols

	Ethanol CH_3CH_2OH	Water H_2O	Phenol C_6H_5OH	Ethanoic acid CH_3CO_2H
pK_a	15.9	15.7	9.95	4.75

Table 1. pK_a values to compare the acidities of ethanol, water, phenol and ethanoic acid.

From the pK_a values above, carboxylic acids are stronger acids than phenols or aliphatic alcohols.

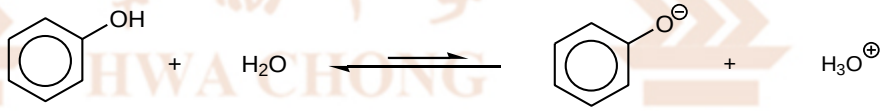
The negative charge on the carboxylate ion is <u>delocalised **equally over two highly electronegative oxygen atoms**</u>. The negative charge is **dispersed** and the carboxylate anion is greatly **stabilised**.



two equivalent resonance forms

resonance stabilised carboxylate ion

Recall that the negative charge on the phenoxide ion is also delocalised i.e. over the benzene ring which explains why phenol is more acidic than alcohols and water. However, the delocalisation in the phenoxide ion is less than that in the carboxylate ion, as the carbon atoms in the benzene ring do not bear the negative charge as well as the two electronegative O atoms in the carboxylate ion. Hence the carboxylate ions are more stabilised than the phenoxide ion and phenols are weaker acids than carboxylic acids.



phenol phenoxide ion

The <u>electron-donating alkyl group</u> (–R) **intensifies** the negative charge on the alkoxide anion and the alkoxide anion is **destabilised.**



alcohol alkoxide ion

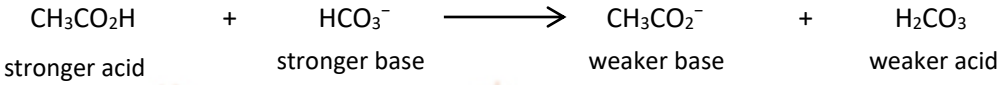
The difference in acidity of carboxylic acids, phenols and alcohols affects their behaviour with sodium metal, sodium hydroxide and sodium carbonate (or sodium hydrogencarbonate):

	Na	NaOH(aq) a strong base	Na_2CO_3(aq) / $NaHCO_3$(aq) weak bases
Aliphatic alcohols (ROH)	√	x	x
Phenols	√	√	x
Carboxylic acids (RCO_2H)	√	√	√

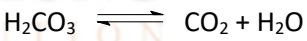
(√: react x: does not react)

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Recall from Topic 14 Acid-Base Equilibria that **the stronger acid is able to protonate the conjugate base of the weaker acid**. Carboxylic acids (e.g. ethanoic acid, pK_a = 4.75) are stronger acids than carbonic acid, H_2CO_3, (pK_a = 6.4) so they can donate a proton to the carbonate or hydrogencarbonate ion.



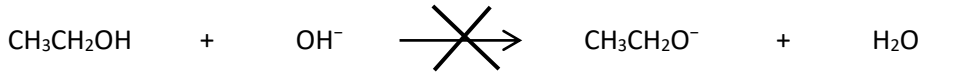
Hence whenever we add carbonate or hydrogencarbonate to carboxylic acid, an acid-base reaction occurs. Effervescence of CO_2 is observed as the H_2CO_3 produced decomposes readily into CO_2 and H_2O.



Phenol (pK_a = 9.95) is a weaker acid than carbonic acid, hence phenol is unable to donate a proton to the carbonate or hydrogencarbonate ion.



Similarly, alcohols (e.g. ethanol, pK_a = 15.9) do not react with sodium hydroxide, as being weaker acids than water (pK_a = 15.7), they are unable to donate a proton to the hydroxide ion.



Exercise 4.1 (Worked Example)

(a) Arrange the following molecules in order of decreasing acid strength (as Bronsted acid).

C_6H_5OH, H_2CO_3, CH_3CO_2H, HC*l*, CH_3CH_2OH

- Recall: HC*l* is a strong acid that dissociates completely in water
- Refer to the p*K*a values given in Section 4.1.1

HCl, CH_3CO_2H, H_2CO_3, C_6H_5OH, CH_3CH_2OH

(b) State if each of the following reactions will occur. If yes, complete the equation.

(i) $C_6H_5O^- + H_2CO_3$

Yes, carbonic acid has lower pK_a and hence is a stronger acid than phenol. It will be able to protonate a phenoxide ion. $C_6H_5O^- + H_2CO_3 \rightarrow C_6H_5OH + HCO_3^-$

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(ii) $CH_3CO_2^- + H_2CO_3$

No reaction. Because H_2CO_3 has higher pK_a and hence is a weaker acid than CH_3CO_2H. It will not be able to protonate an ethanoate ion.

(iii) $CH_3CO_2^- + HCl$

Yes HC*l* is a strong acid while ethanoic acid is a weak acid. HC*l* will be able to protonate ethanoate ion. $CH_3CO_2^- + HCl \rightarrow CH_3CO_2H + Cl^-$

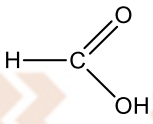
(iv) $CH_3CH_2O^- + CH_3CO_2H$

Yes ethanoic acid is a stronger acid than ethanol. Ethanoic acid will be able to protonate the ethoxide ion. $CH_3CH_2O^- + CH_3CO_2H \rightarrow CH_3CH_2OH + CH_3CO_2^-$

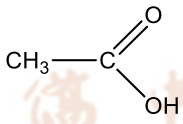
4.1.2 Effect of substituents on acidity of carboxylic acids

Electron-donating groups

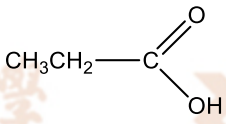
Electron-donating groups (e.g. alkyl groups) intensify the negative charge on the carboxylate anion, destabilise the anion and decrease the acidity of the carboxylic acid.



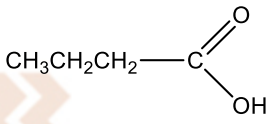
pK_a = 3.77



pK_a = 4.75



pK_a = 4.88

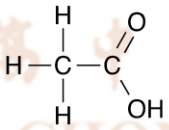


pK_a = 4.82

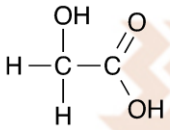
(The similar pK_a values of ethanoic acid, propanoic acid and butanoic acid suggest that the length of the alkyl chain does not have a significant impact on acidity.)

Electron-withdrawing groups

Electron-withdrawing groups (e.g. halogens, NO_2, OH, NH_2) disperse the negative charge on the carboxylate anion, stabilise the anion and increase the acidity of the carboxylic acid.



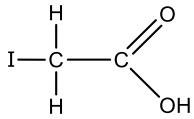
pK_a = 4.75



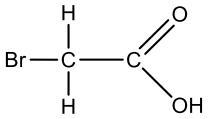
pK_a = 3.83

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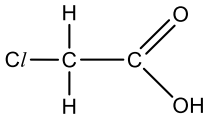
The halogen (e.g. C*l*), –OH or $–NH_2$ group exert an electron-withdrawing inductive effect (O and N are electronegative atoms). The more electronegative the halogen atom, the greater the electron-withdrawing effect, the stronger the acid.



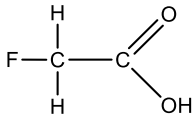
pK_a = 3.15



pK_a = 2.89



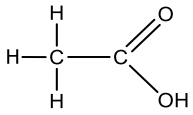
pK_a = 2.87



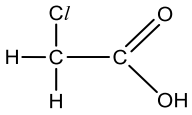
pK_a = 2.60

Number of electron-withdrawing groups

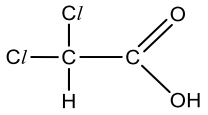
Increasing the number of electron-withdrawing groups increases acidity.



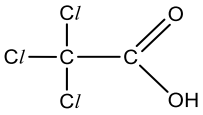
pK_a = 4.75



pK_a = 2.87



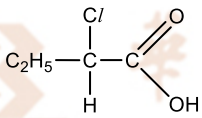
pK_a = 1.48



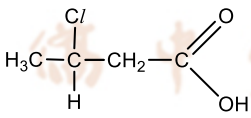
pK_a = 0.64

Proximity of electron-withdrawing groups to the $–CO_2H$ group

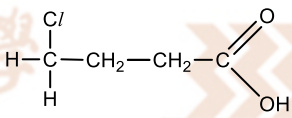
The nearer the electron-withdrawing group is to the carboxyl group, the greater the inductive effect, and the stronger the acid. As inductive effect decreases with increasing distance, it becomes insignificant when the electron-withdrawing effect is acting through more than 4 atoms.



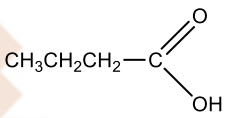
pK_a = 2.86



pK_a = 4.05

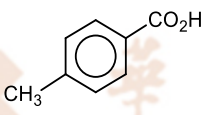


pK_a = 4.52

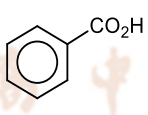


pK_a = 4.82

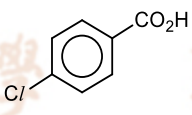
The effects of electron-donating and electron-withdrawing groups are also observed for substituted benzoic acids.



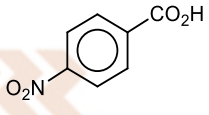
pK_a = 4.34



pK_a = 4.19



pK_a = 4.00



pK_a = 3.41

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Exercise 4.2 (Worked Example)

Arrange these compounds in order of increasing pK_a values.

ethanoic acid, chloroethanoic acid, ethanol, phenol, water

pK_a: chloroethanoic acid < ethanoic acid < phenol < water < ethanol

The higher the pK_a value, the weaker the acid. The strength of the acid depends on the stability of its anion. The more stabilised the anion, the stronger the acid.

Ethanol is less acidic than water. The electron donating alkyl group (R) intensifies the negative charge on the alkoxide anion, destabilising it.

Phenol is more acidic than ethanol and water. The negative charge on the phenoxide anion is delocalised over the benzene ring. The negative charge is dispersed and phenoxide anion is stabilised.

Ethanoic acid is more acidic than phenol. The negative charge on the ethanoate anion is delocalised equally over two highly electronegative oxygen atoms. The delocalisation in the ethanoate anion is greater than that in the phenoxide ion so the ethanoate anion is more stabilised than the phenoxide ion.

Chloroethanoic acid is more acidic than ethanoic acid. The electron-withdrawing chlorine atom in chloroethanoic acid disperses the negative charge on the carboxylate anion causing it to be more stabilised.

4.1.3 Acid-metal (redox)/acid-base reactions

Like inorganic acids, carboxylic acids react with metals, bases, carbonates and hydrogencarbonate to form salts.

With metals	$CH_3CO_2H + Na \longrightarrow CH_3CO_2^-Na^+ + ½\ H_2$
With bases	$CH_3CO_2H + NaOH \longrightarrow CH_3CO_2^-Na^+ + H_2O$
With carbonates	$2\ CH_3CO_2H + Na_2CO_3 \longrightarrow 2\ CH_3CO_2^-Na^+ + CO_2 + H_2O$
With hydrogencarbonate	$CH_3CO_2H + NaHCO_3 \longrightarrow CH_3CO_2^-Na^+ + CO_2 + H_2O$

The effervescence of CO_2 with carbonates or hydrogencarbonates can be used as a *distinguishing test* for the presence of carboxylic acids. CO_2 forms a white ppt when bubbled through limewater.

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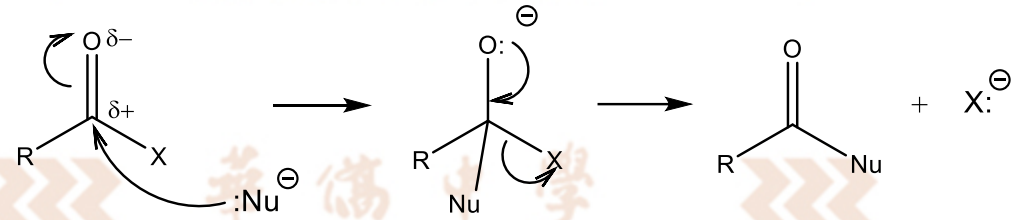
4.2 Nucleophilic (acyl) Substitution

Carboxylic acid and its derivatives can undergo nucleophilic (acyl) substitution reactions at the C=O carbon. This type of reaction occurs because:

- the C=O carbon has a partial positive charge due to the electronegative O
- the C=O carbon has a planar geometry and is relatively unhindered, which makes it susceptible towards nucleophilic attack.

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Nucleophilic (acyl) substitution reactions of carboxylic acids, esters, amides and acyl chlorides involves first the nucleophilic addition of nucleophile across the C=O, to form a tetrahedral intermediate, followed by elimination of a small molecule of H_2O, ROH, NH_3 or HC*l* respectively:



R= alkyl, aryl, H
X = OH, OR, NH_2, C*l*, etc

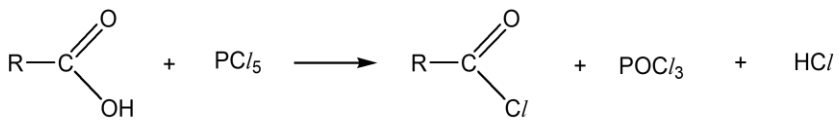
4.2.1 Condensation to form esters

Carboxylic acids can react with alcohols, but not phenols, in a condensation reaction to form esters, when heated in the presence of concentrated sulfuric acid (refer to Topic 16 Hydroxy Compounds).

In this reaction, the C–O bond of the $–CO_2H$ group is broken, as evidenced by isotopic labelling (recall this technique under Reaction Mechanisms in Topic 6 Reaction Kinetics).

4.2.2 Formation of acyl chlorides

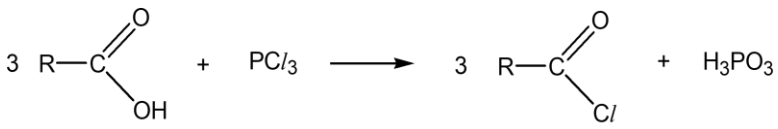
Like alcohols, the –OH group in carboxylic acids can be replaced with a –C*l* group to form acyl chlorides, using the same chlorinating reagents: PCl_5, PCl_3 and $SOCl_2$.



Reagents and conditions: PCl_5, room temperature

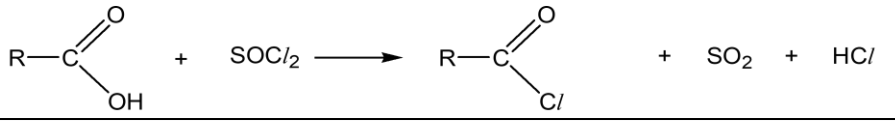
Observations: White fumes of HC*l* produced.

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Reagents and conditions: PCl_3, room temperature

Comments: PBr_3 or P/I_2 heat may be used to obtain respective acyl halides.



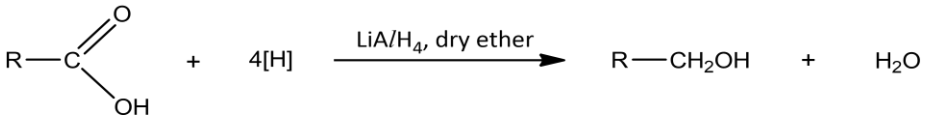
Reagents and conditions: $SOCl_2$, warm

Comments: Most convenient industrial method as by-products are gases and easily removed. Unreacted $SOCl_2$ is also easily distilled off (b.p. 79°C).

Carboxylic acids are often converted into acyl chlorides, which are highly reactive and could in turn be easily converted to other compounds.

4.3 Reduction to Primary Alcohols

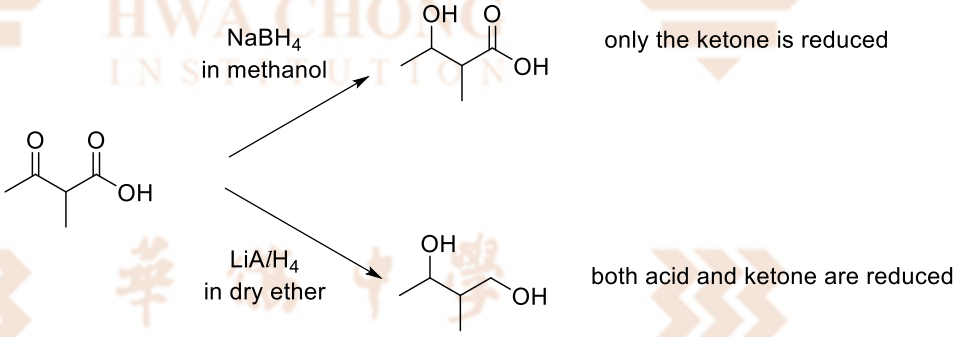
Carboxylic acids are reduced to primary alcohols using lithium aluminium hydride.



Reagents and conditions: $LiAlH_4$, dry ether, room temperature

The $LiAlH_4$ must be used in anhydrous conditions! Note that carboxylic acids can only be reduced back to primary alcohols and not aldehydes.

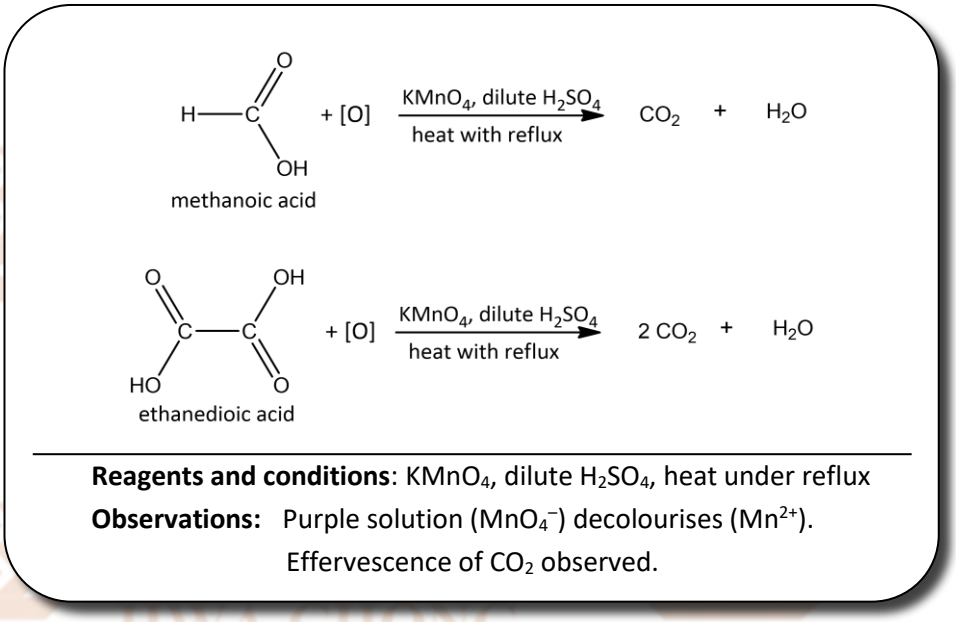
Weaker reducing agents, such as $NaBH_4$ or H_2 with catalyst, will **not** work. Refer to Topic 17 Carbonyl Compounds for the comparison between the different reducing agents. With careful consideration of the reducing agents to be used, selective reduction can be done. For example,



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4.4 Special Case: Oxidation of Methanoic Acid and Ethanedioic Acid

Only **TWO** carboxylic acids undergo further oxidation – **methanoic acid** and **ethanedioic acid**.
All other acids cannot be oxidised by $KMnO_4$.



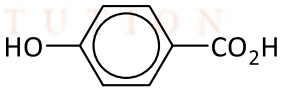
Reagents and conditions: $KMnO_4$, dilute H_2SO_4, heat under reflux
Observations: Purple solution (MnO_4^-) decolourises (Mn^{2+}).
Effervescence of CO_2 observed.

Exercise 4.3 (Worked Example)

Substance **P** is now commonly used in antiseptic creams. **P** could be synthesised in the lab from compound **Q** by a method which involves an intermediate **R**.



(i) Draw the structure of the intermediate **R**.



The $-CH_3$ group undergoes side-chain oxidation to become $-CO_2H$

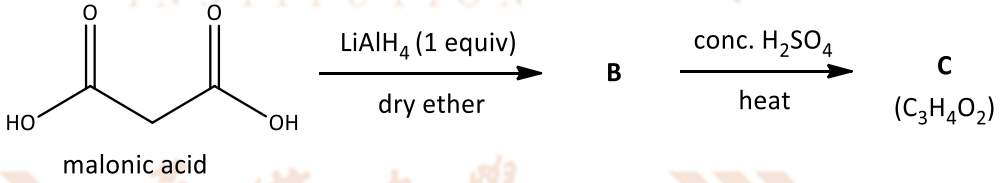
(ii) Suggest reagents and conditions for Steps 1 and 2.

Step 1: $KMnO_4$, dilute H_2SO_4, heat under reflux (side-chain oxidation)
Step 2: CH_3OH, conc. H_2SO_4, heat under reflux (nucleophilic substitution/condensation)

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Exercise 4.4 (Worked Example)

The reaction scheme below shows how compound **C** can be made from malonic acid. **C** is made from **B** via intra-molecular esterification.



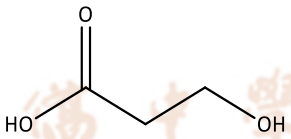
malonic acid

Suggest the structures for compound **B** and **C**.

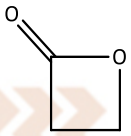
In step 1, only one of the $-CO_2H$ groups is reduced to a primary alcohol.

In step 2, B undergoes intramolecular esterification (condensation reaction) to form C.

B



C

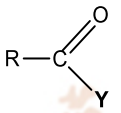


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5 CARBOXYLIC ACID DERIVATIVES

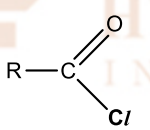
5.1 Introduction

Carboxylic acid derivatives are compounds in which the –OH group in the acid is replaced by –**Y**.

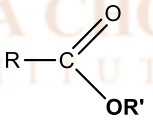


where **Y** = –X (F, C*l*, Br, I), –OR', –NH_2

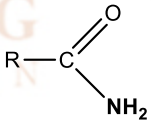
Some examples of acid derivatives are as follows:



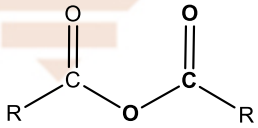
acyl chloride
(acid chloride)



ester



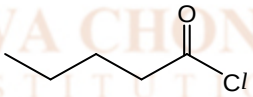
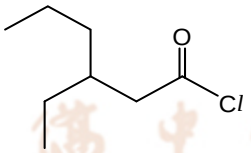
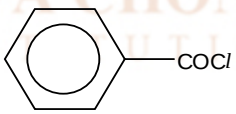
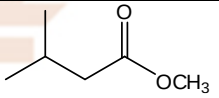
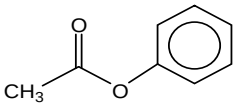
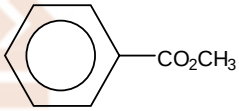
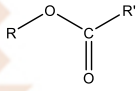
amide



acid anhydride
(not in H2 syllabus)

In the following sections, we will focus on acyl chlorides and esters.
Amides will be covered in Topic 19 Nitrogen Compounds.

5.2 Nomenclature

Functional Group	Acyl chloride (RCOC*l*)	Ester (RCO_2R')
Nomenclature	Replace the *'-oic acid'* of the parent carboxylic acid with *'-oyl chloride'*.	First, name the R group attached to the oxygen, followed by the parent carboxylic acid, replacing the *'-oic acid'* with *'oate'*.
Examples	 pentanoyl chloride  3-ethylhexanoyl chloride  benzoyl chloride	 methyl 3-methylbutanoate  phenyl ethanoate  methyl benzoate Note that condensed structural formula of esters can also be written as R–OCO–R' which just refers to: 

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5.3 Physical Properties of Carboxylic Acid Derivatives

5.3.1 Boiling points

Name	Formula	M_r	Boiling point/ °C
ethanoic acid	CH_3CO_2H	60	118
ethanoyl chloride	CH_3COCl	78.5	51
methyl ethanoate	$CH_3CO_2CH_3$	74	58

Esters and acyl chlorides have lower boiling points than their corresponding carboxylic acids. Their intermolecular **permanent dipole-permanent dipole attractions** are weaker than the hydrogen bonding for carboxylic acids, and require less energy to break. (Esters and acyl chlorides are unable to form intermolecular hydrogen bonding as they lack a hydrogen atom *directly* attached to a highly electronegative oxygen atom.)

5.3.2 Solubility

Esters are much less soluble in water compared to carboxylic acids and alcohols. Many esters are immiscible with water. Acyl chlorides, on the other hand, hydrolyse in water:



5.3.3 Odour

Acyl chlorides are colourless liquids with a sharp, irritating odour (partly due to the rapid hydrolysis to HCl and carboxylic acids).
Esters are colourless liquids with a pleasant and sweet or fruity smell. Esters are often used in the preparation of perfumes and artificial flavourings.

Exercise 5.1 (Worked Example)
Suggest a reason why the boiling point of ethanoyl chloride is higher than that of 2-chloropropane.

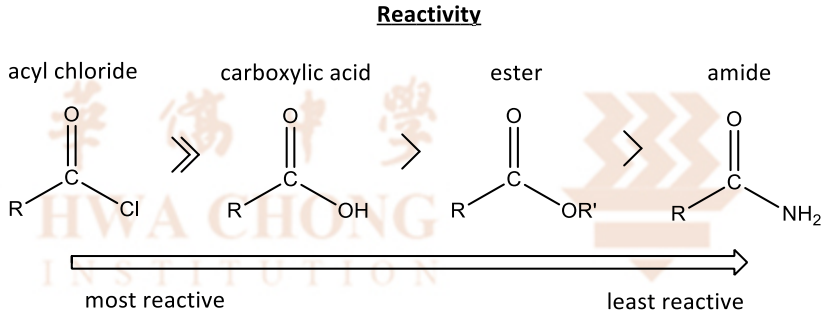
In the ethanoyl chloride, the C=O group provides a stronger electron-withdrawing effect which results in a larger permanent dipole compared to 2-chloropropane. Hence more energy is required to overcome the stronger permanent-dipole-permanent dipole interactions between ethanoyl chloride compared to 2-chloropropane.

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5.4 Chemical Reactivity of Carboxylic Acid Derivatives

Relative reactivity of carboxylic acids and their derivatives

Carboxylic acids and their derivatives differ greatly in reactivity towards nucleophilic substitution.



Reasons for the above trend:

1. Electronic Effects

- A halogen substituent withdraws electrons through inductive effect from the C=O group, thus increases the partial positive charge on the carbon atom. This makes acyl halides more readily attacked by nucleophiles.
- An amino group (—NH_2) or alkoxy group (—OR') donates electrons to the carbonyl carbon through resonance effect. This decreases the partial positive charge on C=O carbon atom. Hence, amides and esters are less readily attacked by nucleophiles.

2. Leaving Group

- In general, the weaker the base, the better the leaving group. Halide anions are better leaving groups compared to the hydroxide ion as halides are weaker bases while the hydroxide ion is a stronger base (refer to discussion of leaving groups under nucleophilic substitution of alcohols in Topic 16 Hydroxy Compounds).

Because of these reactivity differences, it is usually possible to convert a more reactive acid derivative into a less reactive one.

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6 ACYL CHLORIDES

6.1 Preparation of Acyl Chlorides

Acyl chlorides can be prepared from the following:

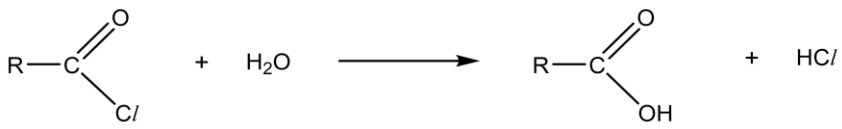
- Nucleophilic substitution of carboxylic acids (Section 4.2.2)

6.2 Reactions of Acyl Chlorides

6.2.1 Hydrolysis to form carboxylic acids (nucleophilic (acyl) substitution with water)

LO 11.7 (d): describe the hydrolysis of acyl chlorides

Acyl chlorides react with water violently at room temperature to give a carboxylic acid and white fumes of HCl. In fact, aliphatic acyl chlorides usually fume in moist air due to the formation of hydrogen chloride.



Reagents and conditions: water, room temperature

Comments: Rapid reaction forming white fumes of HCl

Exercise 6.1 (Worked Example)

Suggest a simple chemical test to distinguish CH_3CO_2H from CH_3COCl.

Add a few drops of water – dense white fumes of HCl will be observed for acyl chloride, no white fumes for carboxylic acid.

OR

Add a few drops of aqueous silver nitrate – white ppt of AgCl observed for acyl chloride, no white ppt for carboxylic acid.

6.2.2 Condensation to form esters (nucleophilic (acyl) substitution with alcohols/phenols)

LO 11.7 (e)part: describe the condensation reactions of acyl chlorides with alcohols, phenols

LO 11.7 (g)part: describe the formation of esters from the condensation reaction of acyl chlorides

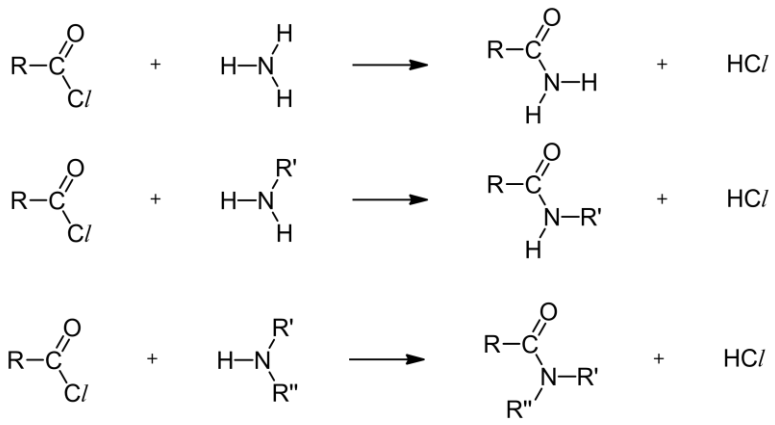
Acyl chlorides react with both alcohols and phenols to form esters via a condensation reaction. Refer to Topic 16 Hydroxy Compounds for the details of the reaction.

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6.2.3 Condensation to form amides (nucleophilic (acyl) substitution with ammonia/amines)

LO 11.7 (e)part: describe the condensation reactions of acyl chlorides with primary amines

Acyl chlorides react readily with ammonia to form amides, and with primary and secondary amines to form N-substituted amides. Tertiary amines do not form amides as they do not contain a replaceable H atom on the N.



Reagents and conditions: ammonia or primary amines or secondary amines (in excess), room temperature

Ammonia or amines are added in **excess** to ensure complete reaction as some ammonia or amines reacts with the acidic HC*l* to form an ammonium salt via acid-base reaction, i.e., $NH_3 + HCl \rightarrow NH_4Cl$

Carboxylic acids **cannot** be used in place of the acyl chlorides. This is because they react with amines/ammonia in an acid-base reaction instead. E.g. $CH_3CO_2H + NH_3 \rightarrow CH_3CO_2^-NH_4^+$

Exercise 6.2 (Worked Example)

Which of these compounds **cannot** be made in one step from ethanoyl chloride?

A $CH_3COC_2H_5$ **C** CH_3CONH_2

B $CH_3CONHC_6H_5$ **D** CH_3CO_2H

[N1997/III/28]

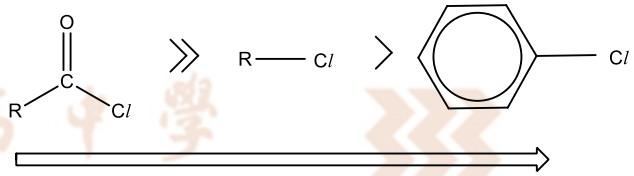
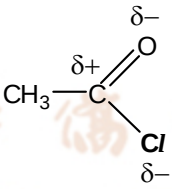
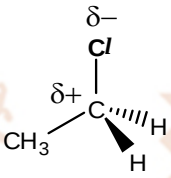
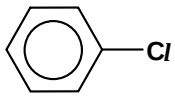
Answer: A

$CH_3COC_2H_5$ is a ketone and it cannot be synthesised in one step from an acyl chloride.

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6.3 Relative Rate of Hydrolysis of Acyl Chlorides, Alkyl Chlorides and Aryl Chlorides

LO 11.7 (f): explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides

<table>
<tr><th colspan="2">Type of chlorides</th><th>Acyl chlorides</th><th>Alkyl chlorides</th><th>Aryl chlorides</th></tr>
<tr><td colspan="2">Rate of hydrolysis</td><td colspan="3">acyl chloride » alkyl chloride > aryl chloride
 
fastest → slowest (no reaction)
Note: The relative reactivity of alkyl chlorides and aryl chlorides was covered in Halogen Derivatives.</td></tr>
<tr><td colspan="2">Example</td><td>ethanoyl chloride
  </td><td>chloroethane
  </td><td>Chlorobenzene
  </td></tr>
<tr><td colspan="2">Hydrolysis conditions</td><td>H_2O
room temperature</td><td>aqueous NaOH/ KOH
heat under reflux</td><td>Not possible under ordinary lab conditions (only possible under very high temperature and pressure with aq. alkali)</td></tr>
<tr><td rowspan="2">Reasons</td><td>Electronic factor</td><td>C–Cl cleaves easily without heating

Highly electron deficient carbon on C–Cl due to 2 electronegative atoms Cl and O

Attracts nucleophile more strongly</td><td>C–Cl cleaves only with heating

Less electron deficient carbon on C–Cl due to polarisation by one electronegative Cl atom only

Attracts nucleophile less strongly</td><td>C–Cl does not cleave easily

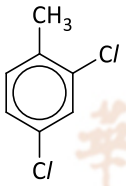
Least electron deficient carbon on C–Cl due to the delocalisation of the lone pair of electrons on Cl into the benzene ring imparting partial double bond character to the C– Cl bond in aryl chlorides, strengthening the bond.

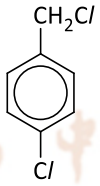
Attracts nucleophile minimally</td></tr>
<tr><td>Steric factor</td><td>Planar acyl carbon makes it less hindered for the nucleophile to attack.</td><td>Tetrahedral geometry around chloro-substituted carbon is relatively more hindered.</td><td>Bulky aromatic ring hinders nucleophilic attack. Electron-rich benzene ring repels nucleophile.</td></tr>
<tr><td colspan="2">Reaction with aq $AgNO_3$</td><td>White ppt of AgCl observed immediately.</td><td>No ppt formed in the cold. To obtain AgCl ppt, aqueous NaOH and heating are required (refer to Topic 15 Halogen Derivatives)</td><td>No ppt observed even after prolonged boiling with aqueous NaOH.</td></tr>
</table>

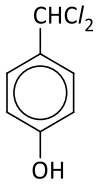
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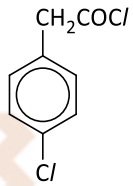
Exercise 6.3 (Worked Example)

Liquid **L** gives a white precipitate immediately when shaken with aqueous silver nitrate. Which of the following structure(s) could be **L**?

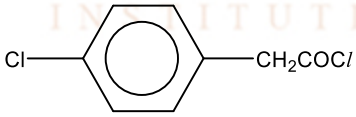








Answer:



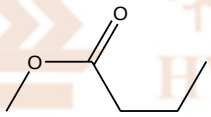
Only could be **L** because it is the only acyl chloride in the list (which gives white ppt *immediately* with $AgNO_3$.

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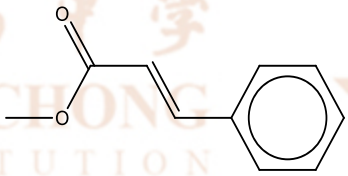
7 ESTERS

7.1 Introduction

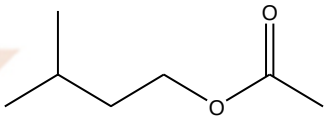
Esters are generally sweet-smelling compounds and are widely used as flavourings and perfumes. Ester linkages also occur naturally in fats and lipids. Small esters, together with other volatile organic compounds, often give off fragrances that are characteristic of fruits.



methyl butanoate
(apples)



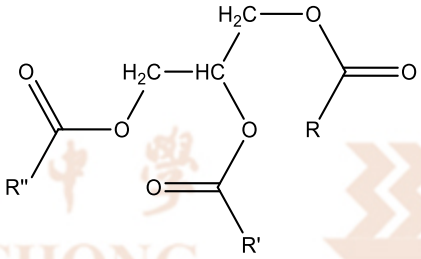
methyl trans-cinnamate
(strawberry)



isoamyl acetate
(banana)

Some esters are pheromones (chemicals that will influence the behavior of animals of the same species). For instance, isoamyl acetate is a pheromone that attracts other bees and is released by a honey bee's sting. This serves as a trigger for other bees to congregate and attack!

Fats are made up of triglycerides which are esters of fatty acids, as shown below (the R groups represent long hydrocarbon chains). Saponification is used in making soap from fats.



A trigylceride

Saponification involves base (such as NaOH) hydrolysis of triglycerides to form the sodium salt of a carboxylate, which has a long chain hydrocarbon non-polar "tail" and a polar negatively charged "head". These carboxylate salts are effectively soap. Your hands feel slippery when they come into contact with alkalis because of the saponification of fats and oils on your hands. The esters in the oil (triglycerides) undergo saponification in the presence of hydroxide ions and soap is effectively produced!

Esters are prepared industrially mainly for use as essence, perfumes and artificial flavourings, e.g.:

(i) ethyl methanoate – rum flavouring
(ii) methyl butanoate – apple flavour
(iii) propyl pentanoate – pineapple flavour

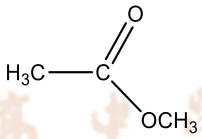
Esters are also widely used as organic solvents, e.g.:

(i) ethyl ethanoate – paints and varnishes
(ii) butyl ethanoate – extraction of penicillin
(iii) pentyl ethanoate – nitrocellulose

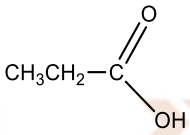
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7.2 Isomerism

Saturated esters and carboxylic acids have the general formula $C_nH_{2n}O_2$ where n equals to the number of carbon atoms in the compound. Esters and carboxylic acids are constitutional isomers if they have the same number of carbon atoms in the compound.

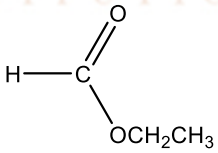


methyl ethanoate

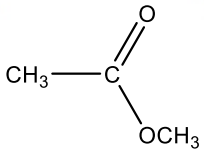


propanoic acid

For esters only, the carboxyl group may occur at different positions along the alkyl chain.



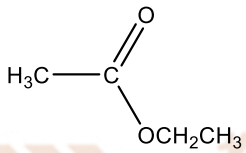
ethyl methanoate



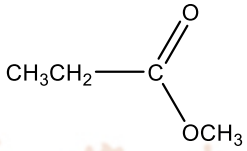
methyl ethanoate

Exercise 7.1 (Worked Example)

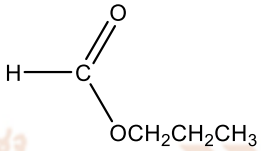
Draw the structures of four isomeric esters with the formula $C_4H_8O_2$, and name them.



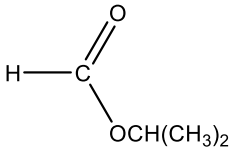
ethyl ethanoate



methyl propanoate



1-propyl methanoate



2-propyl methanoate

7.3 Preparation of Esters

LO 11.7 (g)part: describe the formation of esters from the condensation reaction of acyl chlorides

Esters can be prepared from:

- condensation reaction between carboxylic acid and an alcohol (Topic 16 Hydroxy Compounds)
- condensation reaction between acyl chloride and an alcohol (Section 6.2.2)

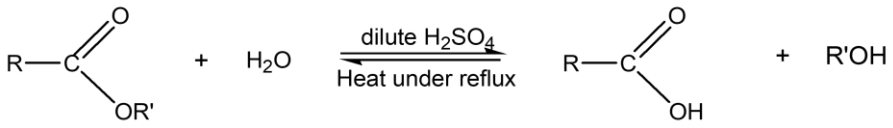
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7.4 Reactions of Esters

LO 11.7 (h): describe the acid and base hydrolysis of esters

Esters can undergo acid or base hydrolysis to yield the alcohols and carboxylic acids. These reactions occur via the general nucleophilic (acyl) substitution mechanism shown in Section 4.2.

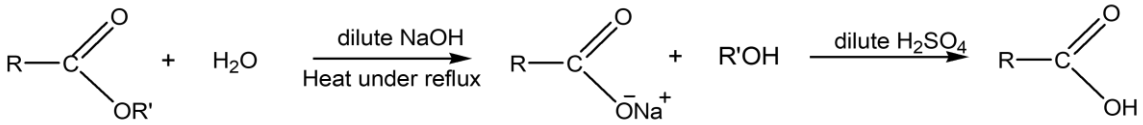
7.4.1 Acid hydrolysis



Reagents and conditions: dilute H_2SO_4, heat under reflux

The acid hydrolysis reaction is reversible. A large excess of water (dilute acid) is used to ensure equilibrium lies to the right. Notice that this is the reverse of the condensation reaction of alcohols and carboxylic acids to form esters.

7.4.2 Base hydrolysis (saponification)



Reagents and conditions: dilute NaOH, heat under reflux
followed by acidification with dilute H_2SO_4 at room temperature and pressure

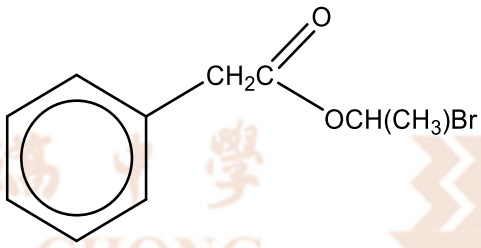
The base hydrolysis reaction is rapid and irreversible. The RCO_2^- ion formed has little tendency to undergo nucleophilic attack again by the alcohol, thus the reaction goes to completion.

To obtain the carboxylic acid from its salt, aqueous acid is added to the mixture at the end of the reaction to protonate the carboxylate anion.

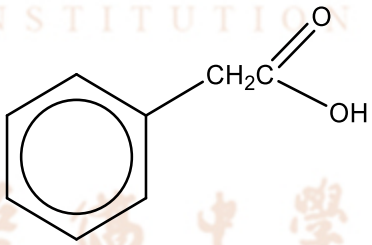
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Exercise 7.2 (Worked Example)

Draw the structures of the products formed when the following ester is subjected to

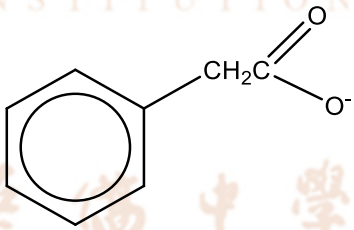


(i) acid hydrolysis,



HOCH(CH$_3$)Br

(ii) base hydrolysis.



HOCH(CH$_3$)OH

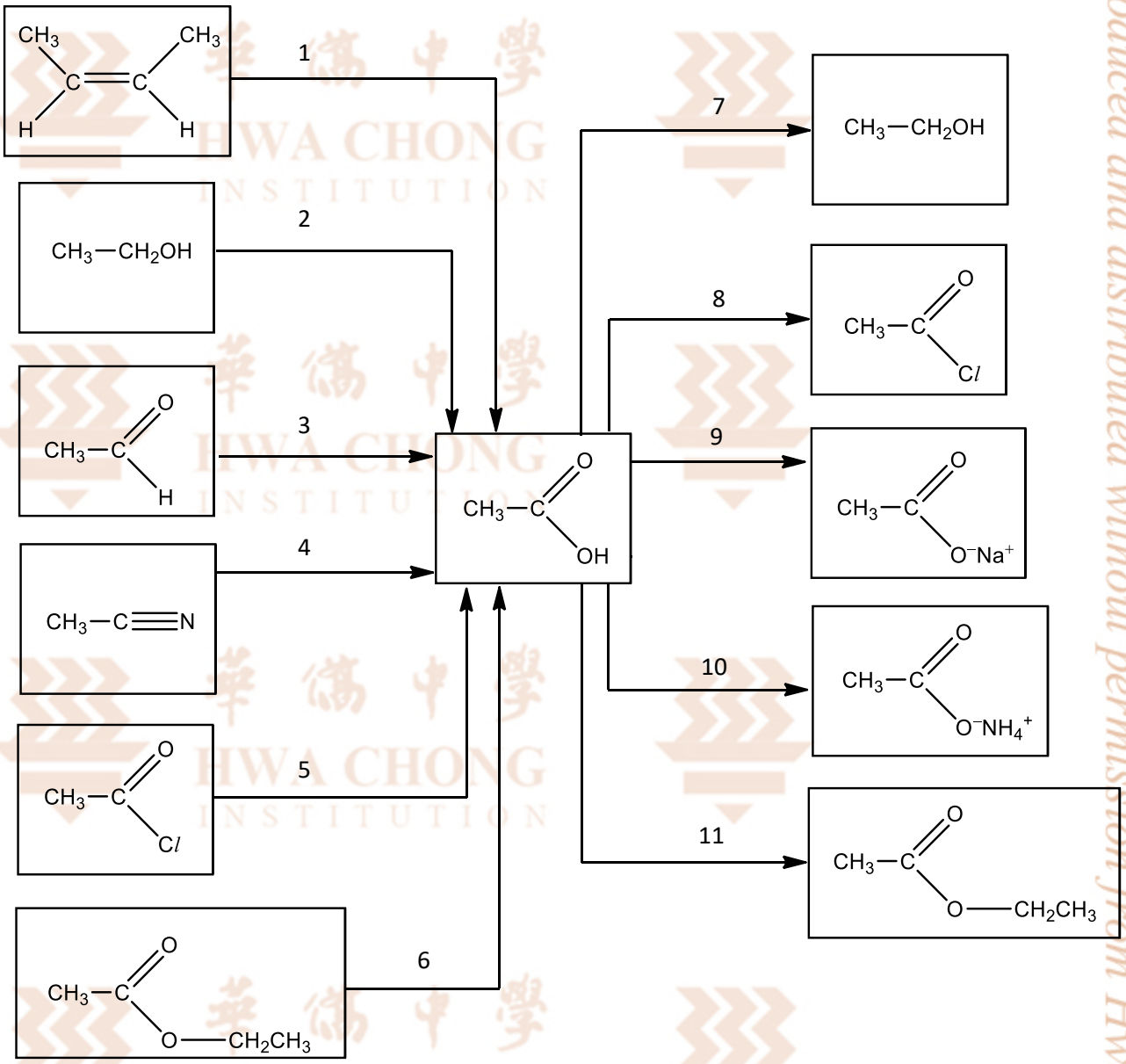
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Summary of reactions of carboxylic acids and derivatives

Summary Exercise

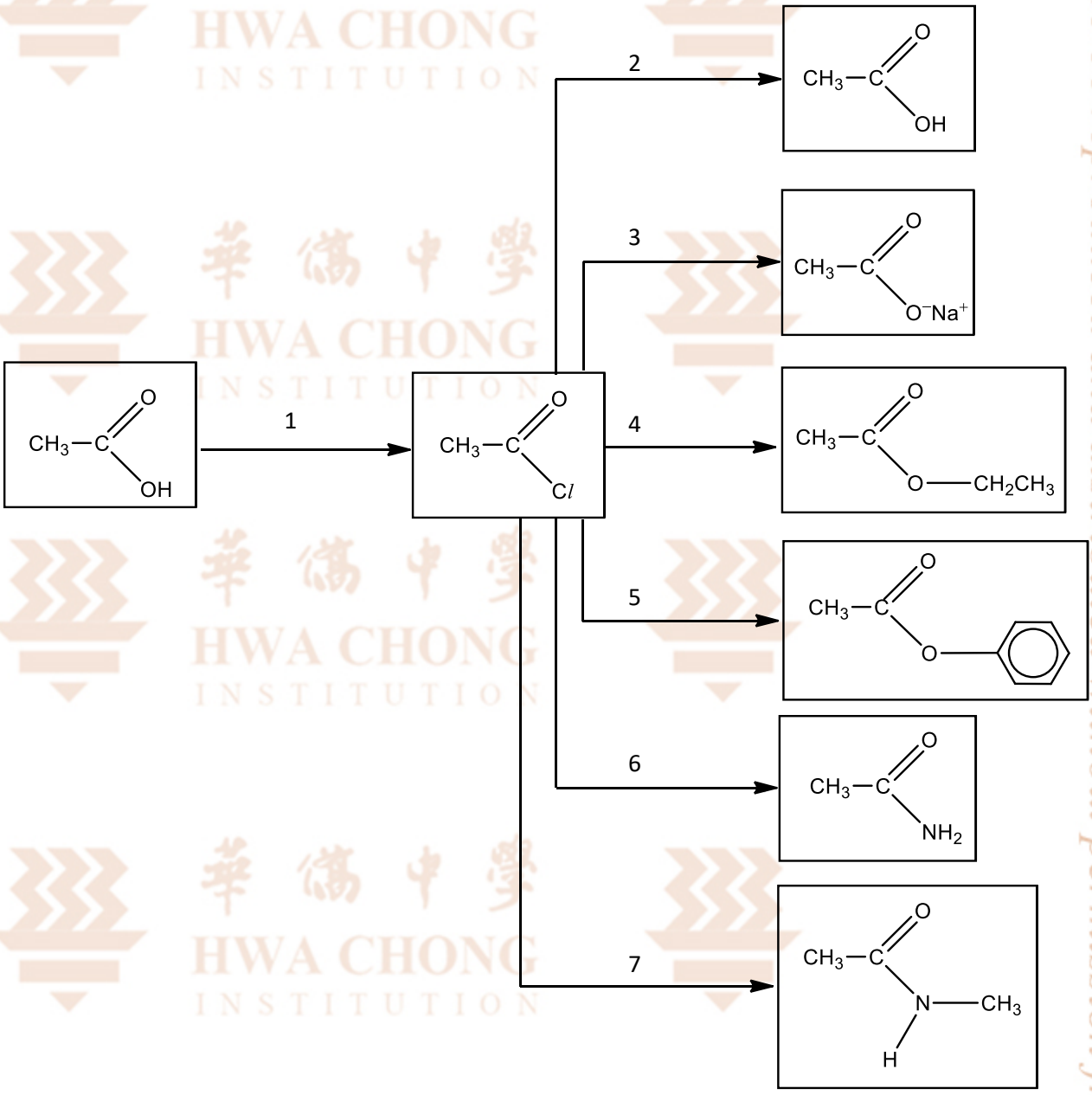
State the reagents and conditions needed for the conversions on the arrows below:

Carboxylic acids



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Acyl chlorides



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19 Nitrogen Compounds

GUIDING QUESTIONS

Amines

- How are amines synthesised?
- What types of reactions do amines undergo and why?

Phenylamines

- How are phenylamines synthesised?
- What types of reactions do phenylamines undergo and why?
- What are the effects of the delocalisation of the lone pair of electrons on nitrogen of phenylamine into the benzene ring?

Amides

- How are amides synthesised?
- Why are amides neutral?
- What types of reactions do amides undergo and why?

Amino Acids

- What are the properties of amino acids?
- What types of reactions do amino acids undergo and why?

How do we compare the basicity of organic nitrogen compounds?

LEARNING OUTCOMES

Students should be able to:

19(a) describe the formation of amines as exemplified by ethylamine (through amide and nitrile reduction; refer to Topic 15 Halogen Derivatives) and by phenylamine (through the reduction of nitrobenzene)

19(b) describe the reaction of amines in the formation of salts

19(c) describe and explain the basicity of primary, secondary and tertiary amines in the gaseous phase (interpret as Lewis bases)

19(d) explain the relative basicities of ammonia, ethylamine and phenylamine, in aqueous medium, in terms of their structures

19(e) describe the reaction of phenylamine with aqueous bromine

19(f) describe the formation of amides from the condensation reaction between RNH_2 and R'COC*l*

19(g) explain why amide is neutral in terms of delocalisation of the lone pair of electrons on nitrogen

19(h) describe the chemistry of amides, exemplified by the following reactions:

(i) hydrolysis on treatment with aqueous alkali or acid

(ii) reduction to amines with lithium aluminium hydride

19(i) describe the acid/base properties of amino acids and the formation of zwitterions (knowledge of isoelectric points is **not** required)

19(j) describe the formation of peptide (amide) bonds between α-amino acids and, hence explain protein formation

19(k) describe the hydrolysis of proteins

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REFERENCES

1. Peter Cann & Peter Hughes (2014). *Chemistry*, Hodder Education, Chapter 27
2. John McMurry (2012). *Organic Chemistry*. 9th Edition, Cengage Learning, Chapter 24

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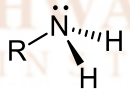
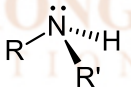
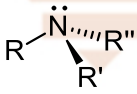
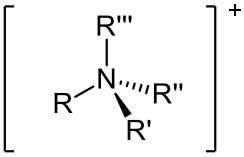
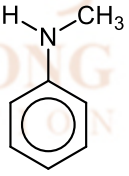
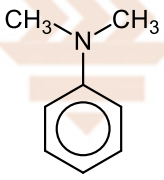
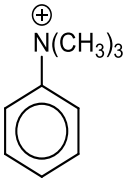
1 INTRODUCTION

Nitrogen Compounds

Amines

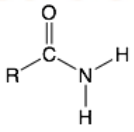
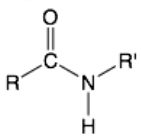
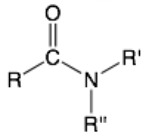
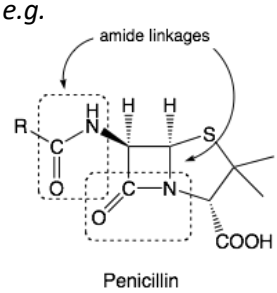
Amines are derivatives of ammonia, NH_3, in which one or more hydrogen atoms are replaced by alkyl or aryl groups.

Amines are classified as **primary**, **secondary** and **tertiary** according to the number of carbon atoms directly attached to the N atom.

	Primary (1°) amines	**Secondary (2°) amines**	**Tertiary (3°) amines**	**Quaternary ammonium ions**
				
Aliphatic	*e.g.* $CH_3CH_2NH_2$ ethylamine	*e.g.* $CH_3CH_2NHCH_3$ N-methyl ethylamine	*e.g.* $(CH_3)_3N$ trimethylamine	*e.g.* $(CH_3)_4N^+$ Tetramethyl-ammonium ion
Aromatic	 *e.g.* phenylamine	 *e.g.* *N*-methylphenyl amine	 *e.g.* *N*,*N*-dimethyl phenylamine	 *e.g.* *N*,*N*,*N*-trimethyl phenyl-ammonium ion
	For aromatic amine, the nitrogen atom is directly attached to the benzene ring			

Amides

Amides are derivatives of carboxylic acids.

Primary amides	**Substituted amides**		*e.g.*
			 Penicillin

Amino Acids

Amino acids contain both an acidic carboxyl group ($-CO_2H$) and a basic amino group ($-NH_2$) on the same molecule.

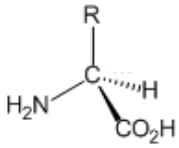


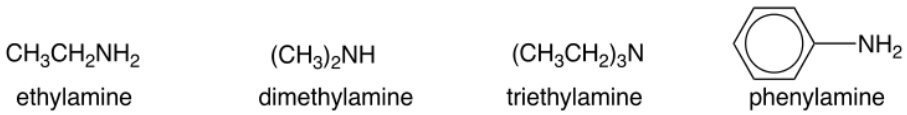
Table 1. Various functional groups of nitrogen compounds

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1.1 Nomenclature

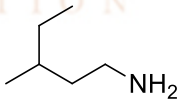
1.1.1 Amines

Simple amines are named by adding the suffix *–amine* to the name of the longest alkyl group that is attached to the nitrogen atom.



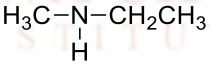
The longest carbon chain containing the amine group is considered the parent structure. Number the alkane chain beginning at the end nearer the amine group.

Note: An alternative way of naming amines is to replace the final *–e* in the name of the parent compound with the suffix *–amine*.

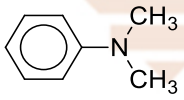


3-methylpentan-1-amine

In secondary and tertiary amines, the capital N denotes the location of the substituents directly attached to the nitrogen atom.

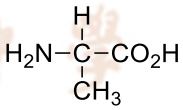


N-methylethylamine



N,*N*-dimethylphenylamine

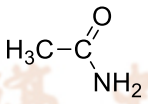
If there is a functional group of higher priority, the $–NH_2$ group can be considered as an *amino* substituent in the prefix.



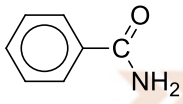
2-aminopropanoic acid

1.1.2 Amides

Primary amides with an unsubstituted $–NH_2$ group are named by replacing the *–oic acid* of the parent carboxylic acid with *–amide*.

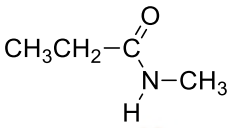


ethanamide

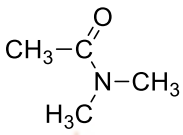


benzamide

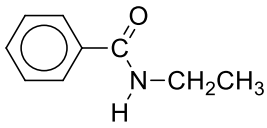
If the nitrogen atom is further substituted, the location of the substituent group is denoted by a capital N.



N-methylpropanamide



N,*N*-dimethylethanamide



N-ethylbenzamide

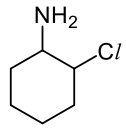
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Exercise 1.1

Name the following compounds and indicate whether it is a primary, secondary or tertiary amine:

(Worked Example)

1.



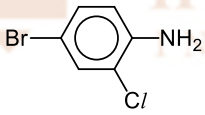
2-chlorocyclohexylamine
(primary amine)

(Worked Example)

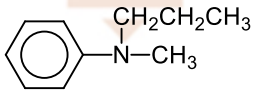
2. $CH_3CH_2NHCH_2CH_2CH_3$

N-ethylpropylamine
(secondary amine)

3.



4.



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2 PHYSICAL PROPERTIES OF AMINES AND AMIDES

2.1 Odour

The aliphatic amines of lower molecular weight have a characteristic pungent smell whereas the higher members have strong "fishy" odours. Sometimes even "foul smelling" is an understatement, and two of the amines produced in decaying flesh are named cadaverine and putresine.

2.2 Boiling points

Name	Structural formula	Number of electrons in the molecules	b.p. / °C	Predominant Intermolecular forces
Methylamine	CH_3NH_2	18	−6	hydrogen bonding
Ethylamine	$CH_3CH_2NH_2$	26	17	hydrogen bonding
Propylamine	$CH_3CH_2CH_2NH_2$	34	50	hydrogen bonding
N-methylethanamine	$CH_3CH_2NHCH_3$	34	34	hydrogen bonding
N,N-dimethylmethanamine	$(CH_3)_3N$	34	3	permanent dipole-permanent dipole interactions

Table 2. Boiling points of some amines

- Comparing methylamine, ethylamine and propylamine, as the number of carbon atoms and electrons increases, more energy is required to overcome the increasing strength of dispersion forces between the molecules. Thus, boiling point increases with increasing number of carbon atoms.
- Primary and secondary amines have higher boiling points than tertiary amines. Since tertiary amines have no N—H bond, they are unable to form hydrogen bonds. Their molecules are held together by weaker permanent dipole – permanent dipole interaction which requires less energy to overcome as compared to stronger hydrogen bonds between molecules of primary and secondary amines.

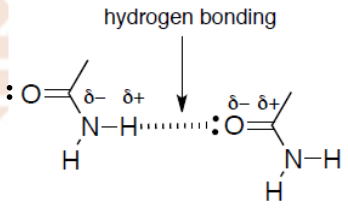
Name	Structural formula	Number of electrons in the molecules	b.p. / °C	Predominant Intermolecular forces
Methylamine	CH_3NH_2	18	−6	hydrogen bonding
Ethane	CH_3CH_3	18	−89	dispersion forces
Methanol	CH_3OH	18	65	hydrogen bonding

Table 3. Boiling points of corresponding alkane, alcohol and amine (similar no. of electrons in the molecules)

- Methylamine, CH_3NH_2, has a considerably higher boiling point compared to its corresponding alkane (ethane) due to the presence of stronger intermolecular hydrogen-bonding compared to only weaker dispersion forces in the alkane.
- However, boiling point of CH_3NH_2 is lower than that of the corresponding alcohol (methanol), since the N-H bond is less polar than the O-H bond. Hence, the intermolecular hydrogen-bonds in alcohols are stronger than those between amine molecules and require more energy to overcome.

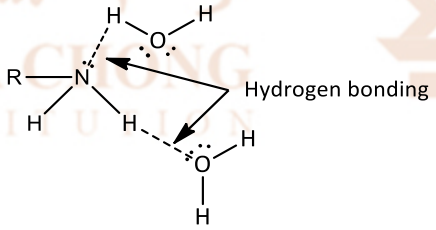
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Amides are white crystalline solids at room temperature, apart from methanamide, which is a liquid. Amides can form extensive intermolecular hydrogen bonds as a result of the polar nature of the N–H bond, and these hydrogen bonds result in relatively high melting and boiling points.



2.3 Solubility in water

Aliphatic amines with four carbon atoms or fewer are readily soluble in water due to their ability to form strong hydrogen bonds with water molecules.



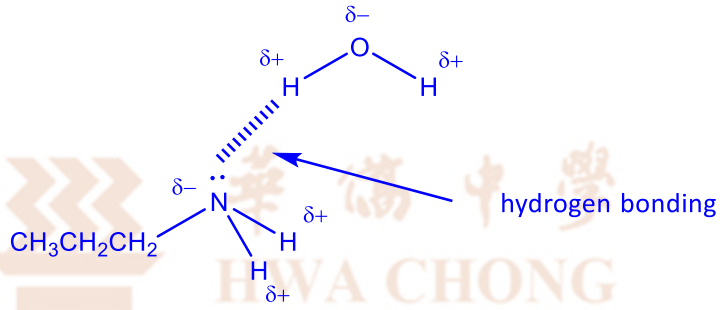
Phenylamines and amines with increasing length of hydrocarbon chain are virtually insoluble in water because the energy released from hydrogen bonding formed between these amines with water is less able to overcome the energy required to overcome the increasing strength of dispersion forces between larger hydrocarbon chains, as well as the existing hydrogen bonding in water. In addition, the non-polar large hydrocarbon skeletons also disrupt the hydrogen bonding with water molecules. These compounds do dissolve, though, in organic solvents, e.g. benzene.

For amides, their ability to form extensive hydrogen bonds with water also means that simple amides are very soluble in water.

Exercise 2.1

(a) (Worked Example)

Propylamine is highly soluble in water. Draw a diagram to illustrate how a molecule of propylamine interacts with a molecule of water.



(b) Explain why $H_2NCH_2CH_2NH_2$ has a boiling point of 116°C while propylamine has a boiling point of 50°C.

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3 BASICITY OF NITROGEN COMPOUNDS

LO 19(c): describe and explain the basicity of primary, secondary and tertiary amines in the gaseous phase (interpret as Lewis bases)
LO 19(d): explain the relative basicities of ammonia, ethylamine and phenylamine, in aqueous medium, in terms of their structures

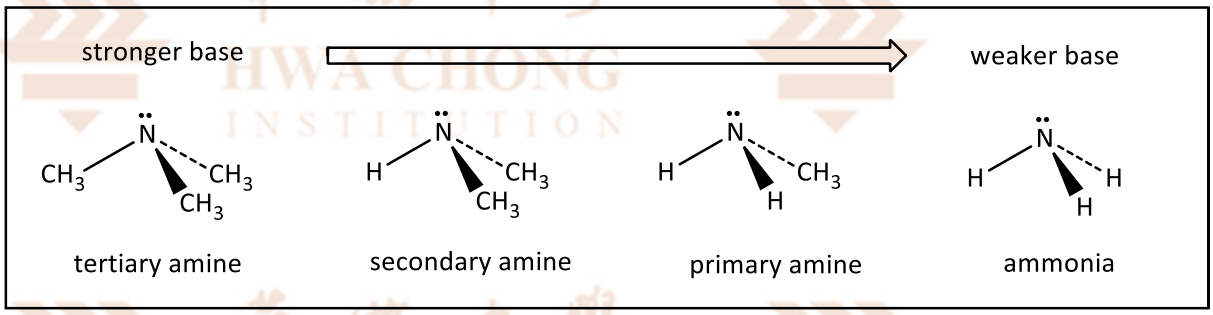
3.1 Amines

Like ammonia, amines contain a lone pair of electrons on the nitrogen atom that can form a co-ordinate (dative covalent) bond with a proton. Hence, amines can act as proton-acceptors or Bronsted-Lowry bases. Amines can also act as Lewis bases by donating this electron pair to an acid. (Refer to Topic 4 Reactions and Stoichiometry for the theories of acids and bases.) The basicity of amines depends on the availability of the lone pair of electrons on nitrogen for protonation (or donation to an acid).

3.1.1 Basicity of amines in the gaseous phase (Lewis bases)

In the gaseous phase, aliphatic amines are more basic than ammonia because alkyl groups are electron-donating; they increase the electron density on nitrogen atom, making the lone pair of electrons more available to form a dative bond with an acid.

Therefore,



3.1.2 Basicity of amines in the aqueous medium

When amines are dissolved in water, an equilibrium is established in which the water donates a hydrogen ion to the amine. The extent of this reaction is a measure of the amine's basicity.

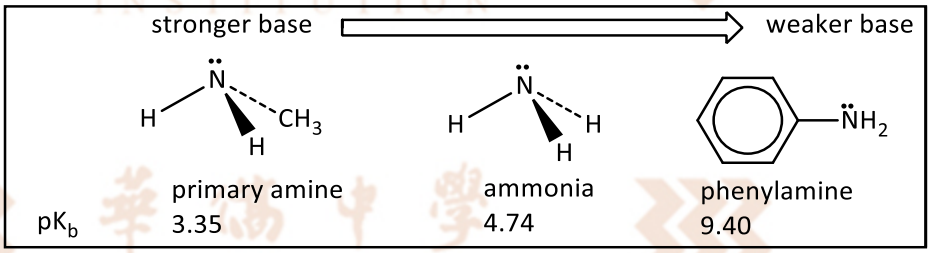
$$\underset{\text{Base}}{RNH_2} + H_2O \rightleftharpoons \underset{\text{Conjugate acid}}{RNH_3^+} + OH^- \qquad K_b = \frac{[RNH_3^+][OH^-]}{[RNH_2]} \text{ and } pK_b = -\lg K_b$$

The larger the K_b values, the greater its basicity; the smaller the pK_b, the stronger the base.

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3.2 Phenylamines

The pK_a values below show phenylamines are considerably less basic than ammonia.



This is because in phenylamine, the lone pair of electron on nitrogen is delocalised into the benzene ring. This decreases the electron density on the nitrogen atom, making the lone pair of electrons less available to form a dative bond with a proton.

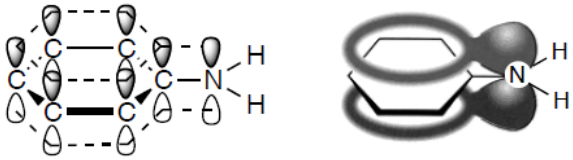


Figure 1. Extended delocalised π- electron cloud is present in phenylamines

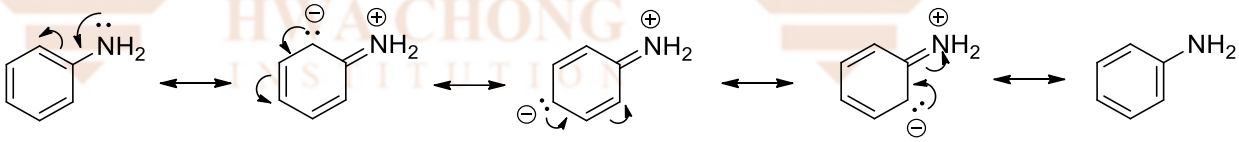
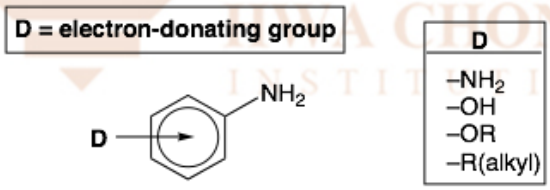


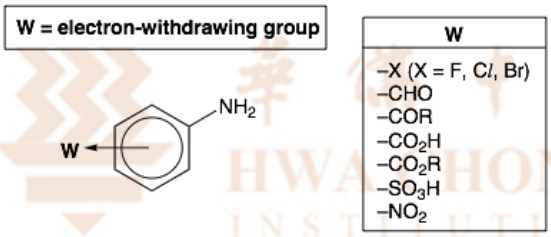
Figure 1. Resonance structure of phenylamines

3.2.1 Substituted Phenylamines

Their relative basicity depends on the nature of the substituent attached to the benzene ring.

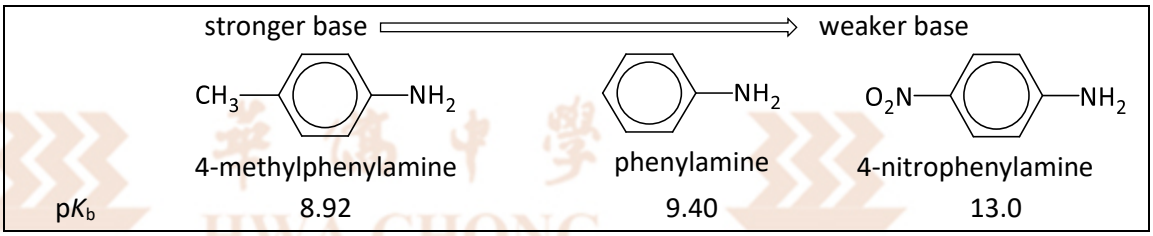


Electron-donating groups increase electron density on the benzene ring, making the lone pair of electrons on nitrogen atom more available for donation to an acid. Hence these substituted phenylamines are more basic than phenylamine.



Electron-withdrawing groups decrease electron density on the benzene ring, making the lone pair of electrons on nitrogen atom less available for donation to an acid. Hence, these substituted phenylamines are less basic than phenylamine.

Therefore,

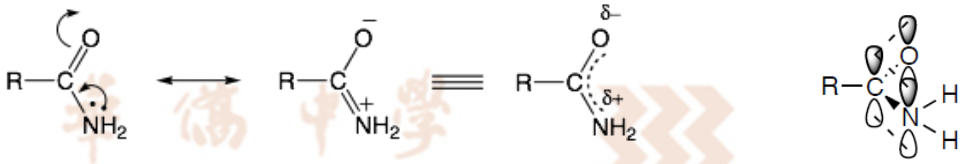


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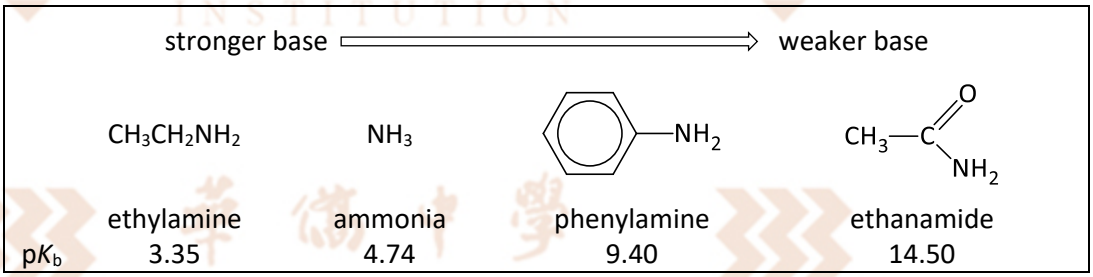
3.3 Amides

LO 19(g): explain why amide is neutral in terms of delocalisation of the lone pair of electrons on nitrogen

Amides give neutral solutions in water (not basic). The delocalisation of the lone pair of electrons on the nitrogen atom over the C=O bond reduces the electron density on the nitrogen atom such that the lone pair of electrons on the nitrogen atom is not available for protonation.

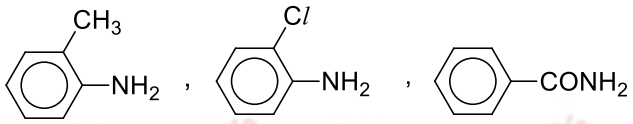


Therefore, the relative basicity of ammonia, ethylamine, phenylamine and amide are as follows:



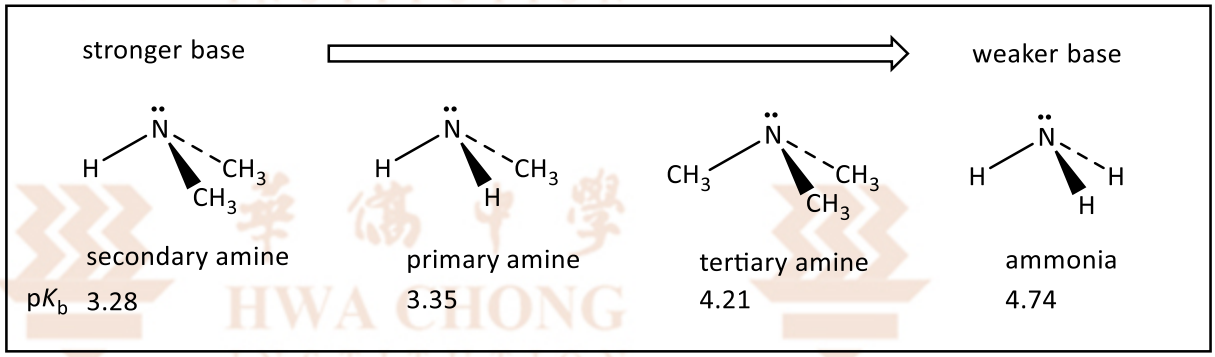
Exercise 3.1

Arrange the following compounds in order of increasing basicity, giving your reasoning.



A **B** **C**

Basicity of amines in the aqueous phase (Background info)



In the aqueous medium, tertiary amines are less basic than expected because the resulting conjugate acids are not as effectively solvated through hydrogen bonding by the surrounding water molecules (absent in gaseous phase) as compared to conjugate acids of primary and secondary amines. Thus, the conjugate acids are less stable, resulting in tertiary amines to ionise in water to a smaller extent.

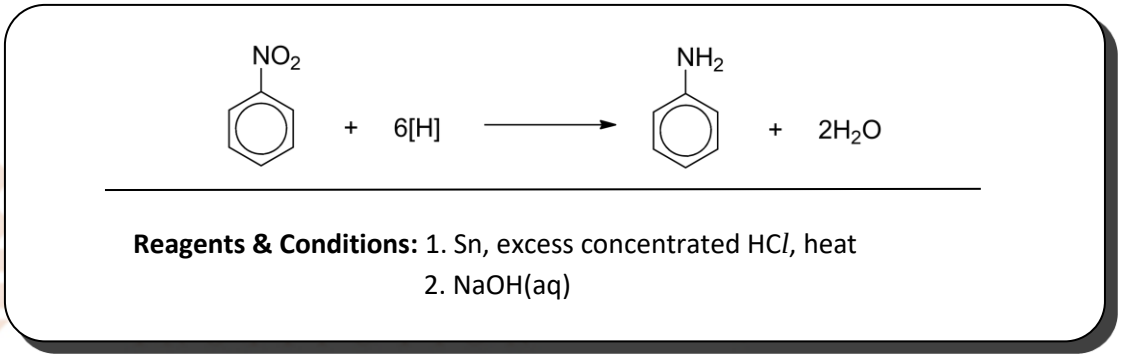
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4 PREPARATION OF AMINES AND AMIDES

LO 19(a): describe the formation of amines as exemplified by ethylamine and by phenylamine
LO 19(f): describe the formation of amides from the condensation reaction between RNH_2 and R'COCl

Amines can be prepared from:

- Nucleophilic substitution of halogenoalkanes (Topic 15: Halogen Derivatives)
- Reduction of nitriles (Topic 15: Halogen Derivatives) and amides (to be covered later in this topic)
- Reduction of nitrobenzene
  Phenylamine can be prepared by reduction of aromatic nitro-compounds using tin and excess concentrated hydrochloric acid. The product first forms as a salt, $C_6H_5NH_3^+Cl^-$ and excess NaOH(aq) is then added to liberate the free phenylamine. Aliphatic nitro-compounds are not reduced using the same reagent.



LiA*l*H_4 and $NaBH_4$ are **not** used in this above reaction because $NaBH_4$ does not reduce nitro groups at all, while $LiAlH_4$ will reduce nitrobenzene to azo compounds instead, giving $C_6H_5–N=N–C_6H_5$.

Amides can be prepared from:

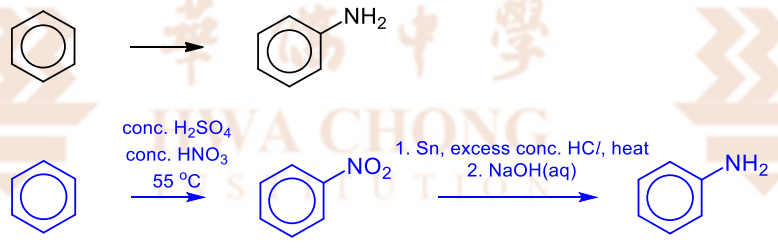
- Condensation of acyl chlorides (Topic 18: Carboxylic Acids & Derivatives)

Note: Carboxylic acids cannot be used in the preparation of amides. This is because they react with amines/ammonia in an acid-base reaction instead. E.g. $CH_3CO_2H + NH_3 \rightarrow CH_3CO_2^-NH_4^+$.

Exercise 4.1

Give the reagents and conditions that you would use in the following conversions:

(a) (Worked Example)



(b)



(c) $CH_2{=}CH_2 \longrightarrow CH_3CH_2CH_2NH_2$

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5 REACTIONS OF AMINES AND AMIDES

5.1 Amines

The chemistry of amines is dominated by the lone pair of electrons on nitrogen atom. They can behave:

- as bases (donating the lone pair to a H^+ ion or an acid)
- as good nucleophiles (being able to attack at the partial positive end of a polarized bond)
- as excellent ligands (with transition metals) – refer to Topic 22: Chemistry of the Transition Elements

5.1.1 Reaction with acids

LO 19(b): describe the reaction of amines in the formation of salts

Amines (both aliphatic and phenylamines) can act as a base to react with acids (mineral or carboxylic acids) to form salts.

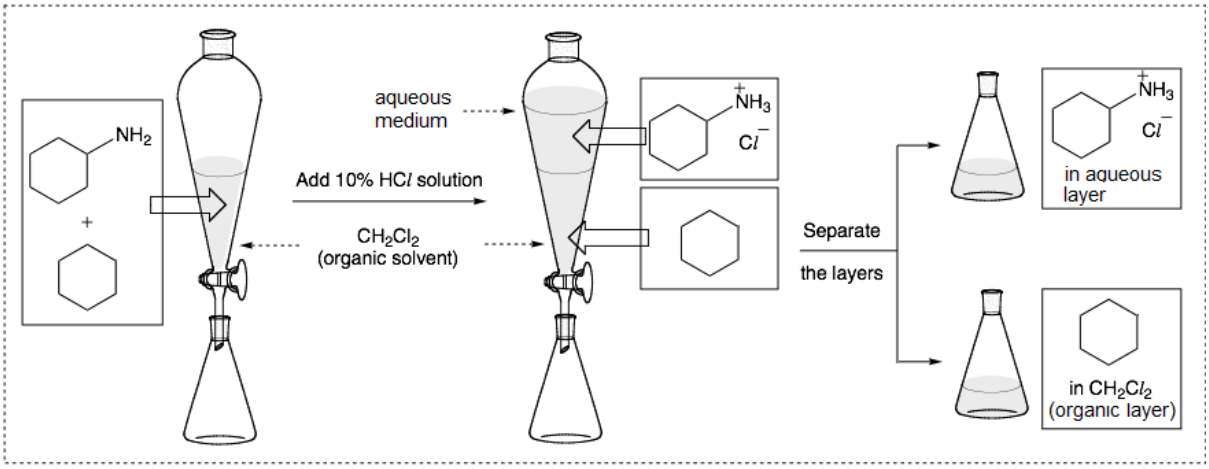
$$RNH_2 + HCl \longrightarrow RNH_3^+ Cl^-$$

Reagents & conditions: Mineral acids or carboxylic acids, room temperature

Comment: The salts are soluble in aqueous solution. On evaporating this solution, the salts can be obtained as white crystalline solids.

Amines with bulky R-groups are insoluble in water (forming two immiscible layer when mixed) due to the presence of non-polar hydrocarbon skeleton which hinder the formation of hydrogen bonds with water molecules.

However, soluble ionic salts are formed through acid-base reaction when acids are added. The ionic salts are soluble in water (forming a homogeneous solution as they can form favourable ion-dipole interaction with water molecules) but insoluble in organic solvents. Thus an amine can be separated from other organic compounds by converting it to a water-soluble ammonium salt. You may refer to Topic 8: Introduction to Organic Chemistry on the details of the extraction procedure.



The amines can be regenerated from their corresponding salts by using strong bases, such as NaOH(aq).

$$RNH_3^+ + OH^- \longrightarrow RNH_2 + H_2O$$

Stronger acid **Stronger base** **Weaker base** **Weaker acid**

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5.1.2 Nucleophilic substitution

Primary, secondary and tertiary amines can act as a nucleophile to react with halogenoalkanes and form secondary amines, tertiary amines and quaternary ammonium salts respectively (refer to Topic 15: Halogen Derivatives).

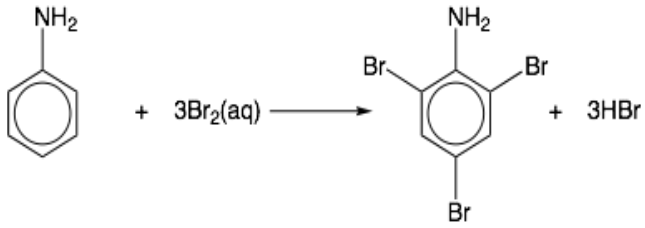
5.1.3 Condensation

Primary and secondary amines (both aliphatic and phenylamines) can act as a nucleophile to react with acid chlorides to form amides (refer to Topic 18: Carboxylic Acids & Derivatives).

5.1.4 Electrophilic substitution of phenylamine

LO 19(e): describe the reaction of phenylamine with aqueous bromine

Phenylamine reacts very quickly with aqueous bromine via an electrophilic substitution mechanism to form a white precipitate. This is similar to the reaction of phenol with bromine (refer to Topic 16: Hydroxy Compounds). Aliphatic amines do not react with bromine.



Reagents & Conditions: Aqueous bromine, room temperature

Observations: Yellow-orange solution decolourise; white ppt formed
(White fumes of HBr may not be observed as HBr dissolved in aqueous solution.)

Comments: 2,4,6-tribromophenylamine is formed because the $-NH_2$ group is 2,4-directing. No Lewis acid catalyst (halogen carrier) is required for this reaction, unlike bromination of benzene (which requires $AlCl_3$ or $FeCl_3$).

Explanation: Like phenol, the lone pair of electrons on the nitrogen atom is delocalised into the benzene ring, the electron density in the ring is greatly increased, making it much more susceptible to electrophilic attack than benzene. Hence, the presence of the $-NH_2$ group highly activates the benzene ring towards electrophilic substitution and no catalyst is required.

5.2 Amides

LO 19(h): describe the chemistry of amides, exemplified by the following reactions:
(i) hydrolysis on treatment with aqueous alkali or acid
(ii) reduction to amines with lithium aluminium hydride

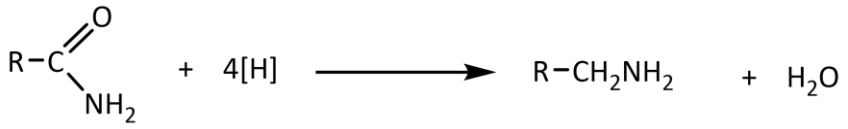
In amides, the lone pair of electrons on the nitrogen atom is delocalised into the adjacent C=O bond. Thus, the electron density on the nitrogen atom is reduced, making it unable to act as a nucleophile, unlike amines.

The delocalisation also gives good stability to amides and makes them the least reactive of the carboxylic acid derivatives.

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5.2.1 Reduction of amides

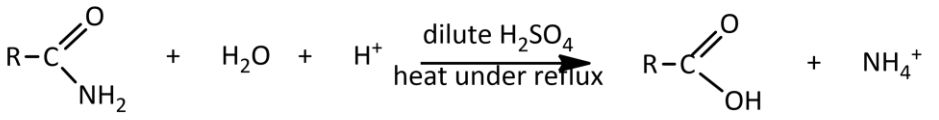
Amides can be reduced to amines by lithium aluminium hydride.



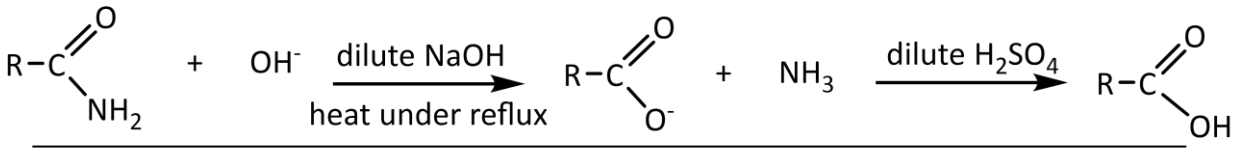
Reagents & Conditions: $LiAlH_4$ in dry ether

5.2.2 Hydrolysis of amides

Amides can be hydrolysed by aqueous acids (e.g. dil H_2SO_4) or alkalis (e.g. dil NaOH) when heated under reflux to yield the carboxylic acid or salt respectively. Although the exact same bond is cleaved in both acidic and alkaline hydrolysis, the products of hydrolysis depend on the pH of the environment.



Reagents and conditions: dilute H_2SO_4, heat under reflux



Reagents and conditions: dilute NaOH, heat under reflux, followed by acidification with dilute H_2SO_4 to yield the carboxylic acid

Comments: Ammonia will be produced if the primary amides undergo alkaline hydrolysis (a distinguishing test). For substituted amides, amines are formed instead.

Exercise 5.1

Predict the products of the following reactions:

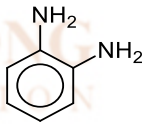
a) (Worked Example)

N,N-dimethylamine, $(CH_3)_2NH$, and ethanoic acid at room temperature

$(CH_3)_2NH_2^+ \ CH_3CO_2^-$

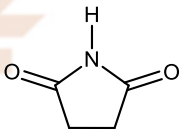
Acid-base reaction to produce a salt.

b)



and Br_2 (aq)

c)

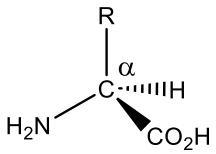


and NaOH(aq) heat

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6 AMINO ACIDS

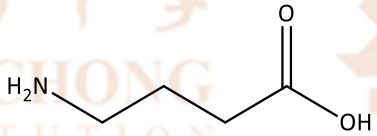
α-Amino acids are the building blocks for all the proteins in the human body. Naturally occurring amino acids are **α-amino acids** where the amino and carboxyl groups are bonded directly to the same α-carbon. The general formula of an α-amino acid is as follows:



There are 20 naturally occurring α-amino acids (as shown in the next two pages), differing only in the identity of the R group bonded to the α-carbon. The R group is called the side chain of the amino acid. The simplest amino acid, called glycine, has R = H. Except for glycine, all other α-amino acids are chiral and exist in optically active forms (enantiomers).

For your information

There are some non-α-amino acids in nature apart from the 20 common α-amino acids. One notable example is γ-aminobutanoic acid (GABA), which is the chief inhibitory neurotransmitter in the mammalian central nervous system. Note that the amino and carboxyl groups are attached to different carbons.

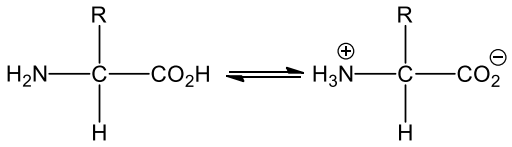


γ-aminobutanoic acid

6.1 Formation of zwitterion

*LO 19(i): describe the acid/base properties of amino acids and the formation of zwitterions (knowledge of isoelectric points is **not** required)*

Amino acids can undergo an intramolecular acid-base reaction, and exist as dipolar ions with no overall electrical charge called **zwitterions**.



un-ionised form zwitterion

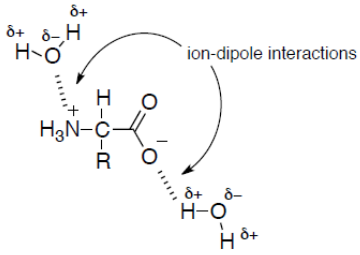
Amino acids exist as zwitterions in aqueous solutions and in the solid state. Therefore, many physical properties of amino acids resemble that of ionic compounds.

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6.2 Physical properties of amino acids

The formation of zwitterions gives amino acids some unusual properties:

- Amino acids are crystalline solids with **high melting points**, *e.g.* glycine has a melting point of 262°C. This is due to strong electrostatic forces of attraction between the dipolar zwitterions in the solid lattice structure. Large amount of energy is required to overcome the **strong ionic bonds between oppositely charged ions**.

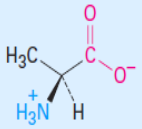
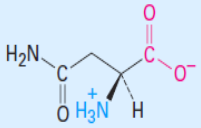
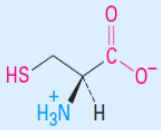
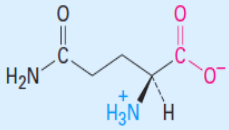
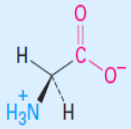
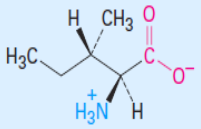
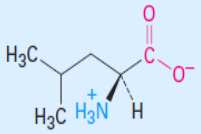
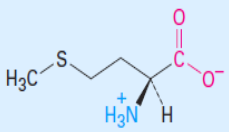
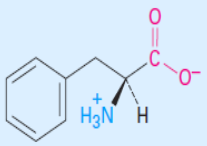
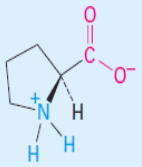


- Amino acids are **more soluble in water than in organic solvents**. This is due to the **strong ion-dipole interaction between the zwitterions and water molecules**.

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For your information

Here are 20 naturally occurring α-amino acids and their names can be represented by either a one-letter or a three-letter abbreviation as shown in the table.

Name	Abbreviations		MW	Structure at pH = 7.3	pK_a α-CO_2H	pK_a α-NH_3^+	pK_a side chain	p*I*
Neutral Amino Acids								
Alanine	Ala	A	89		2.34	9.69	—	6.01
Asparagine	Asn	N	132		2.02	8.80	—	5.41
Cysteine	Cys	C	121		1.96	10.28	8.18	5.07
Glutamine	Gln	Q	146		2.17	9.13	—	5.65
Glycine	Gly	G	75		2.34	9.60	—	5.97
Isoleucine	Ile	I	131		2.36	9.60	—	6.02
Leucine	Leu	L	131		2.36	9.60	—	5.98
Methionine	Met	M	149		2.28	9.21	—	5.74
Phenylalanine	Phe	F	165		1.83	9.13	—	5.48
Proline	Pro	P	115		1.99	10.60	—	6.30

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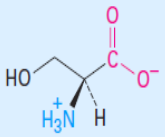
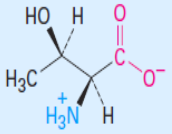
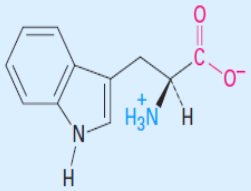
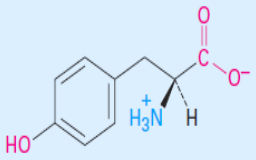
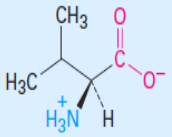
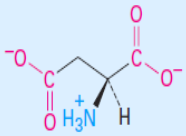
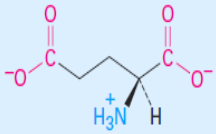
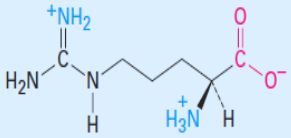
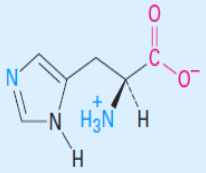
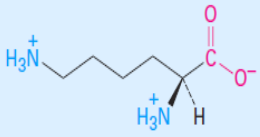
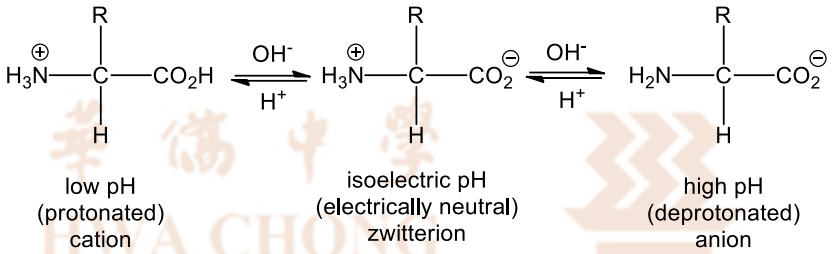
Neutral Amino Acids *(continued)*								
Serine	Ser	S	105		2.21	9.15	—	5.68
Threonine	Thr	T	119		2.09	9.10	—	5.60
Tryptophan	Trp	W	204		2.83	9.39	—	5.89
Tyrosine	Tyr	Y	181		2.20	9.11	10.07	5.66
Valine	Val	V	117		2.32	9.62	—	5.96
Acidic Amino Acids								
Aspartic acid	Asp	D	133		1.88	9.60	3.65	2.77
Glutamic acid	Glu	E	147		2.19	9.67	4.25	3.22
Basic Amino Acids								
Arginine	Arg	R	174		2.17	9.04	12.48	10.76
Histidine	His	H	155		1.82	9.17	6.00	7.59
Lysine	Lys	K	146		2.18	8.95	10.53	9.74

Table 4. 20 naturally occurring amino acids (at pH = 7.3). Extracted from McMurry J., Organic Chemistry. *8th ed. USA: Brooks/Cole*

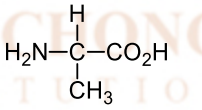
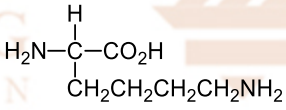
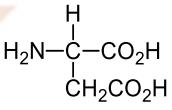
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6.3 Acid-Base behaviour (Application Example)

Having both the acidic and basic groups, amino acids are amphoteric, reacting with both acids and bases to form ionic salts.



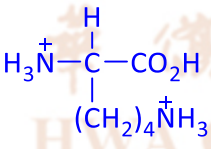
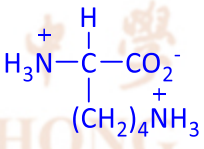
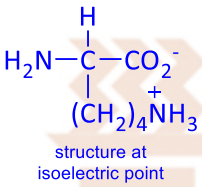
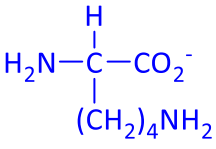
Isoelectric point (pI) of an amino acid (or protein) is the pH at which the overall net charge on the amino acid is zero and it exists primarily as the neutral zwitterion. This isoelectric pH depends on the nature of the side chain, R.

Amino acid	Alanine	Lysine	Aspartic acid
Structure			
Nature of side-chain	neutral	basic	acidic
Isoelectric point	6.01	9.74	2.77

At a pH below isoelectric point (pH << pI), the amino acid exists predominantly as cations. However, when pH >> pI, the amino acid exists predominantly as anions.

Exercise 6.1 (Worked Example)

Draw the structures of the major species of lysine that can exist in aqueous solution of various pH. Start with the species in a solution of very low pH and consider the change in structure as pH increases. Hence identify the major species that exists at isoelectric point.

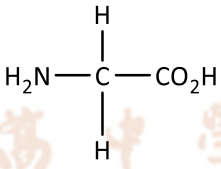
Structure			 structure at isoelectric point	
pH	Very low pH	*Increasing pH* →		Very high pH

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6.4 Titration curves of amino acids (Application Example)

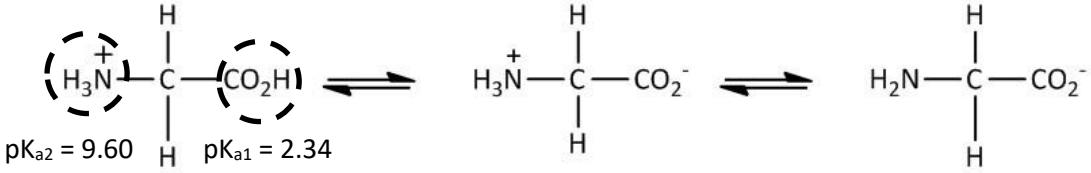
Titration of amino acids are very similar to the titration of polyprotic acids. Refer to Topic 14 Acid-Base Equilibria for titration curves and polyprotic acids.

Using glycine as an example,



Glycine

pK_{a1}= 2.34
pK_{a2}= 9.60



pK_{a2} = 9.60 pK_{a1} = 2.34

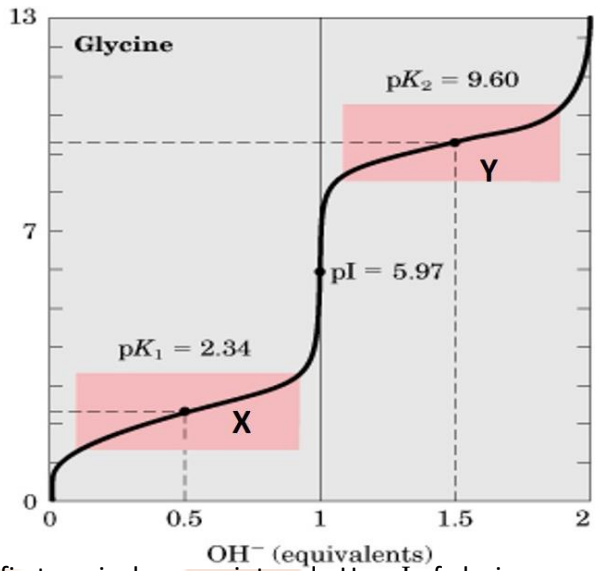
pH < 2.34 2.34 < pH < 9.60 9.60 < pH

At pH < 2.34, all possible sites of glycine are protonated. Since $–CO_2H$ group is a stronger acid than $–NH_3^+$ group, the stronger acidic $–CO_2H$ group will be neutralised first by the addition of base, $OH^–$, followed by the $–NH_3^+$ group. The reaction is as follows:



In the titration curve, the protonated (cationic) form of glycine was titrated against NaOH of same concentration. The cationic form predominates at low pH before $OH^–$ is added. When some $OH^–$ is added, a portion of the cationic form undergoes neutralisation to form zwitterion, resulting in buffer region **X** (mixture of cationic form and zwitterion).

Note that when 0.5 equivalent of $OH^–$ is added, amount of cationic form unreacted = amount of zwitterion formed. This is the maximum buffering capacity where pH=pK_{a1}.



The solution only contains zwitterion when at the first equivalence point and pH = pI of glycine.

As more $OH^–$ is added, the $–NH_3^+$ group is neutralised to form the anionic form, leading to a new buffer mixture containing zwitterion and the anionic form in region **Y**. Note that when 1.5 equivalent of $OH^–$ is added, amount of zwitterion unreacted = amount of anionic form produced. This is the maximum buffering capacity where pH=pK_{a2}.

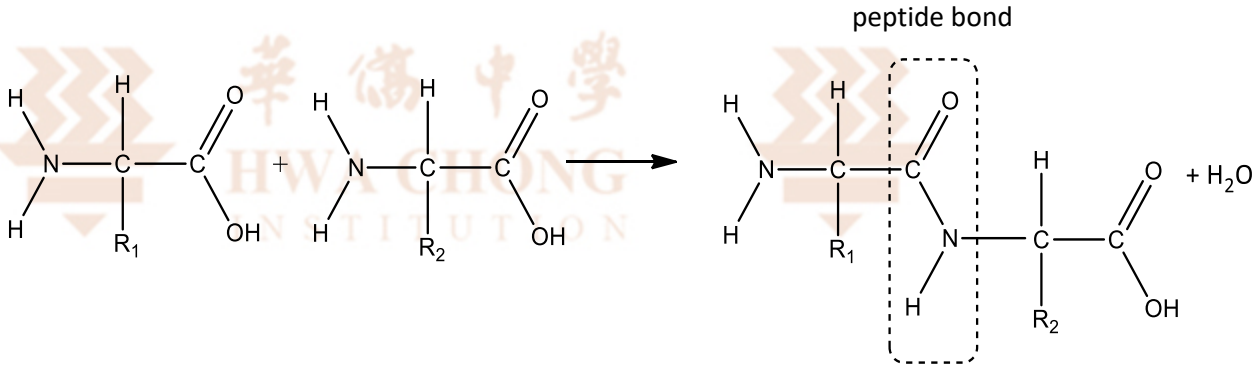
At the second equivalence point and beyond, all sites are de-protonated and the solution only contains the anionic form of glycine.

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6.5 Peptide bond formation to form polypeptides and proteins

LO 19(j): describe the formation of peptide (amide) bonds between α-amino acids and, hence, explain protein formation

Amino acids are the basic units of polypeptides and proteins. An amide bond between amino acids is also called a peptide bond. Peptide bonds are formed from the condensation reaction between the $–CO_2H$ and the $–NH_2$ groups on two amino acids through the elimination of a water molecule. In this manner, any number of amino acids can be bonded in a continuous chain.



A **dipeptide** is the result of 2 amino acid molecules condensing together to form a peptide bond with the elimination of a water molecule while a **tripeptide** results from 3 amino acids molecules doing so with the formation of two peptide bonds and the elimination of two water molecules, and so on.

Exercise 6.2 (**N2009/I/30**) **(Worked Example)**

A small peptide **X** is hydrolysed according to the following reaction.

$$\mathbf{X} \xrightarrow{\text{hydrolysis}} 2NH_2CH_2CO_2H + NH_2CH(CH_3)CO_2H + 2NH_2CH(CH_2OH)CO_2H$$

$M_r = 75$ $M_r = 89$ $M_r = 105$

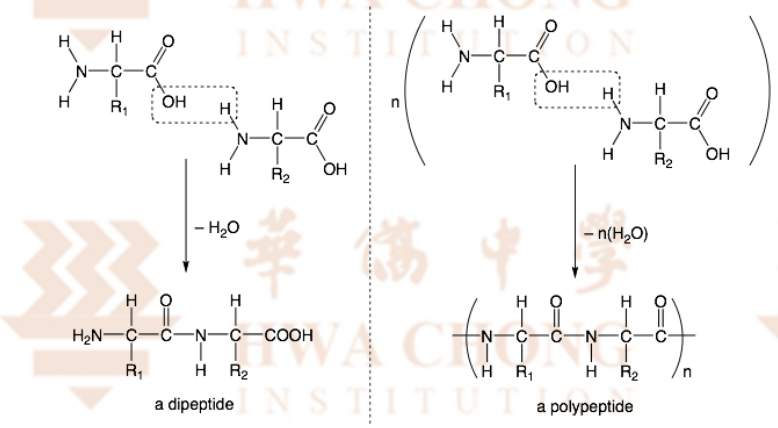
What is the M_r of **X**?

$M_r = 75 \times 2 + 89 + 105 \times 2 – 4(18) = 377$

Since there are five amino acids obtained as products, peptide **X** must be a pentapeptide with four peptide bonds broken during hydrolysis.

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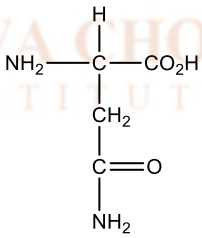
Peptides made from the condensation of up to about 50 amino acid molecules are called **polypeptides (or polyamides)**. Anything larger is classified as a **protein molecule**.



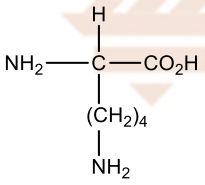
Note: In the lab, the reaction between a carboxylic acid and an amine would result in salt formation, but living organisms employ *enzymes* to form peptide bonds.

Exercise 6.3

Draw the structural formula of a dipeptide with the sequence asn-lys, showing the ionic form which it would exist at pH 3.



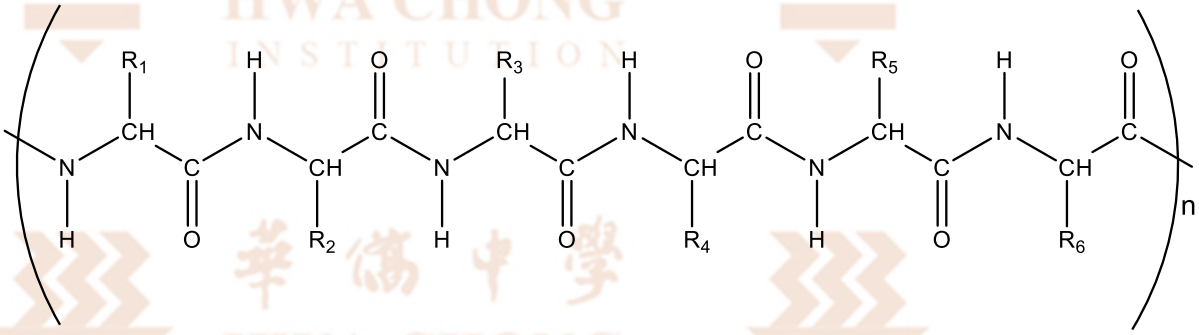
Asparagine (asn)



Lysine (lys)

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7 PROTEINS



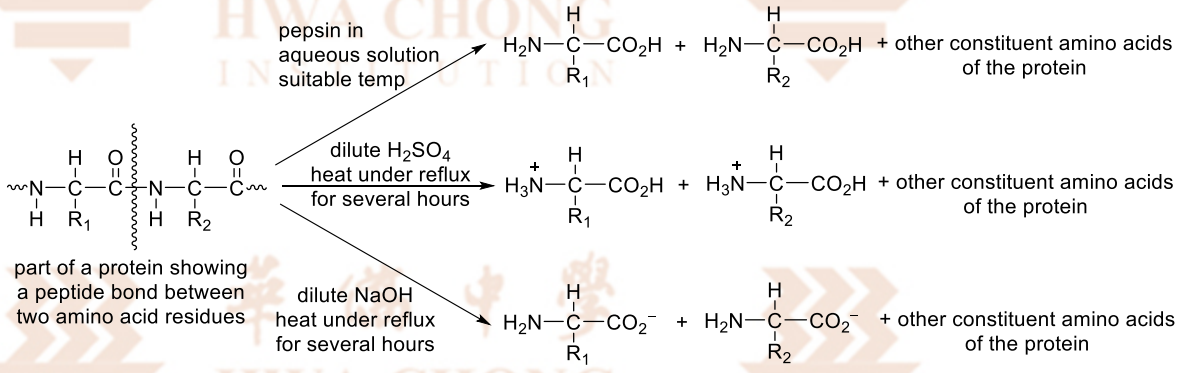
Proteins are naturally occurring polypeptides of molecular weight > 5000 and are formed when over 10^5 amino acids condense together, all linked by peptide bonds. They are essential for life in all living organisms and have many biological functions in the body, for example:

Type of Protein	Function	Examples
Structural proteins	Provide the framework which defines the size and shape of cells	Keratin is the protein of hair, nails, horns and feathers. Collagen and elastin provide a fibrous framework in animal connective tissues
Catalytic proteins (enzymes)	Accelerate metabolic processes to produce energy, build new cell structures and destroy old ones	Pepsin, trypsin and chymotrypsin which hydrolyses proteins in our diets so that subunits can be absorbed for use by our cells.

7.1 Hydrolysis of Proteins

LO 19(k): describe the hydrolysis of proteins

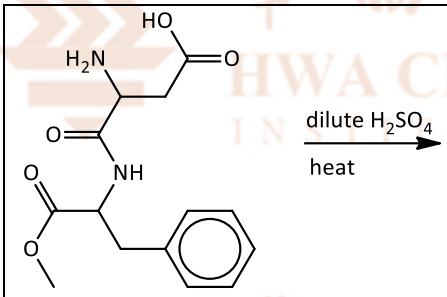
Proteins can by hydrolysed into their constituent amino acids either by an appropriate enzyme or heating under reflux in the presence of aqueous acid or alkali for several hours in the laboratory.



Exercise 7.1

Aspartame is the name for an artificial sweetener used as a sugar substitute in many foods and beverages. Draw the structural formulae of all the organic products obtained when aspartame is heated with dilute H_2SO_4.

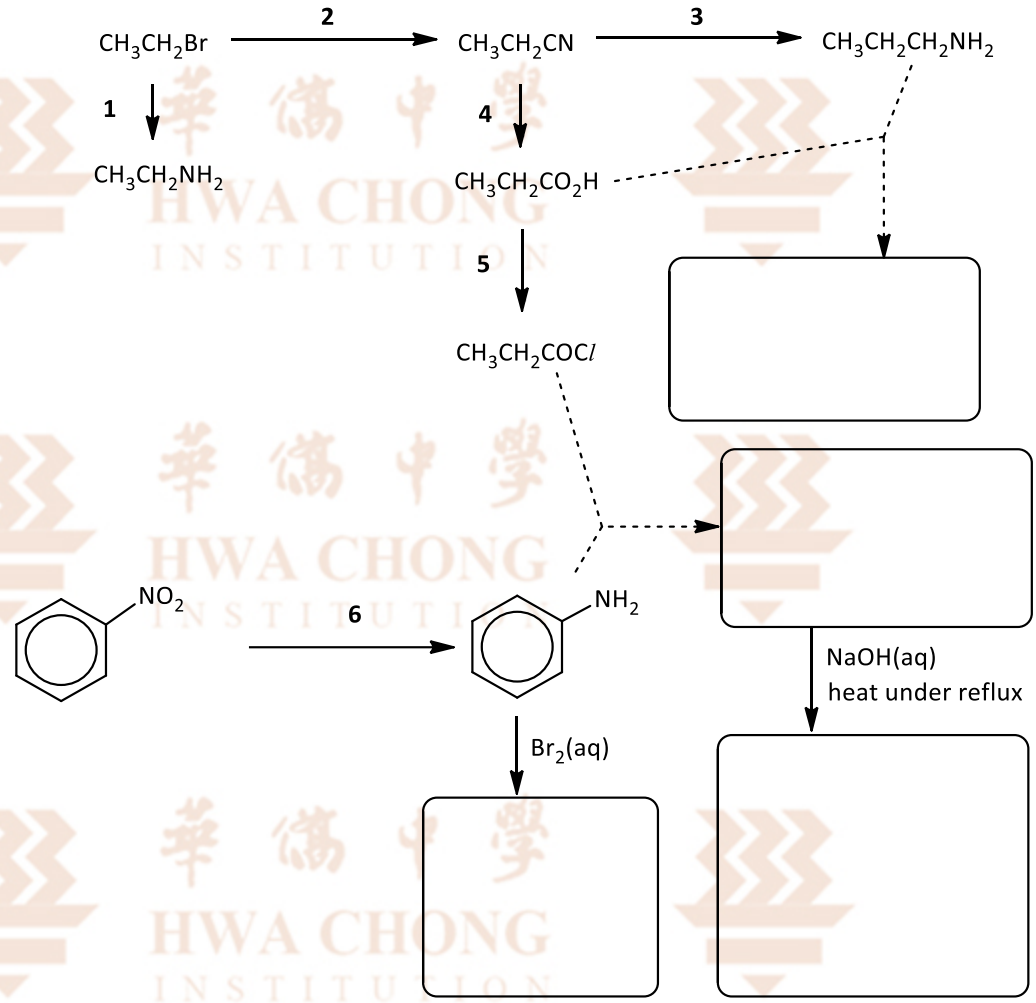
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aspartame

Summary of reactions of amines and amides

State the reagents and conditions needed for the conversions on the arrows below. Draw the structure of the organic products formed in the boxes.



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Summary of oxidising and reducing agents

Functional groups	Ability to be oxidised by			Ability to be reduced by		
	$KMnO_4$, dilute NaOH, cold	$KMnO_4$, dilute H_2SO_4, heat	$K_2Cr_2O_7$, dilute H_2SO_4, heat	H_2 / Ni high P	$LiAlH_4$ in dry ether	$NaBH_4$ in methanol
alkenes	√	√	X	√	X	X
alkylbenzenes		√	X			
nitriles (-CN)				√	√	X
1° & 2° alcohol		√	√			
aldehydes		√	√	√	√	√
ketones		X	X	√	√	√
carboxylic acids		X	X	X	√	X
esters		X	X			
amides		X	X		√	X

Note that nitrobenzene may be reduced to phenylamine using Sn, conc HC*l*, heat followed by dilute NaOH.

LOOKING AHEAD

In our study of the extension topic on organic chemistry, we have learnt the general concepts in organic chemistry (Topic 8 Introduction and Topic 9 Isomerism) and the nature & reactions of specific functional groups, which exemplify these general concepts as well as earlier concepts of structure and bonding, thermodynamics and kinetics. As we move on to the next topic of Electrochemistry and Transition Elements, bear in mind that organic compounds can undergo redox reactions and act as fuels in electrochemical cells (e.g. methane and ethanol). Organic molecules are also common ligands in transition metal complexes as many contain electron-rich centers e.g. alcohols, phenols, carboxylic acids, amines, alkenes and arenes.

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20 Electrochemistry

GUIDING QUESTIONS

Electrochemical Cell

- What happens in a redox reaction?
- How can the tendency of a substance to be reduced or oxidised be measured?
- What are the factors affecting electrode potential?
- How can the direction and feasibility of a redox reaction be predicted, and what are the limitations?

Electrolytic Cell

- What are the factors affecting the discharge of a substance during electrolysis?
- How to calculate the amount of substance liberated during electrolysis?
- What are some industrial applications of electrolysis?

What are the differences between an electrochemical cell and an electrolytic cell?

LEARNING OUTCOMES

Students should be able to:

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

12(b) define the terms:
- (i) *standard electrode (redox) potential*
- (ii) *standard cell potential*

12(c) describe the standard hydrogen electrode

12(d) describe methods used to measure the standard electrode potentials of:
- (i) metals or non-metals in contact with their ions in aqueous solution
- (ii) ions of the same element in different oxidation states

12(e) calculate a standard cell potential by combining two standard electrode potentials

12(f) use standard cell potentials to:
- (i) explain/deduce the direction of electron flow from a simple cell
- (ii) predict the spontaneity of a reaction

12(g) understand the limitations in the use of standard cell potentials to predict the spontaneity of a reaction

12(h) construct redox equations using the relevant half-equations (Refer to Topic 4 Reactions & Stoichiometry)

12(i) state and apply the relationship $\Delta G = -nFE^{\ominus}$ to electrochemical cells, including the calculation of $E^{\ominus}$ for combined half reactions

12(j) predict qualitatively how the value of an electrode potential varies with the concentration of the aqueous ion

12(k) state the possible advantages of developing other types of cell, e.g. the H_2/O_2 fuel cell and improved batteries (as in electric vehicles) in terms of smaller size, lower mass and higher voltage

12(l) state the relationship, $F = Le$, between the Faraday constant, the Avogadro constant and the charge on the electron

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12(m) predict the identity of the substance liberated during electrolysis from the state of electrolyte (molten or aqueous), position in the redox series (electrode potential) and concentration

12(n) calculate:

(i) the quantity of charge passed during electrolysis

(ii) the mass and/or volume of substance liberated during electrolysis

12(o) explain, in terms of the electrode reactions, the industrial processes of:

(i) the anodising of aluminium

(ii) the electrolytic purification of copper

[technical details are **not** required]

REFERENCES

1. Peter Cann & Peter Hughes (2015). *Chemistry*. Hodder Education.
2. Martin S. Silberberg (2006). *Chemistry – The Molecular Nature of Matter & Change*, 4th Edition. McGraw Hill. Section 21.7.

LOOKING BACK

This topic is closely linked to redox chemistry covered in Topic 4, where we learnt how to construct an equation for a redox reaction by combining two half-equations. In this topic, we will study how electricity can be harnessed from redox reactions, and how we can predict whether a redox reaction is spontaneous by using standard electrode potentials, $E^{\ominus}$. Since we are dealing with spontaneity here, we will see how $E^{\ominus}$ is related to Gibbs' free energy change, G, from Topic 5. We will also look at electrolysis, in which electricity (produced by spontaneous redox reactions) is used to drive many reactions that are otherwise not spontaneous to produce useful chemicals.

1 INTRODUCTION

Electrochemistry is the study of the **inter-conversion of chemical and electrical energy**. The study is typically done using cells in which **redox reactions** either produce or consume electrical energy.

There are **two** types of cells.

- **Electrochemical cell** (also known as galvanic cell or voltaic cell)
  The redox reaction is **spontaneous**. Chemical energy from the reaction is converted to electrical energy.
  Examples: batteries, fuel cells

- **Electrolytic cell**
  The redox reaction is **non-spontaneous**. Electrical energy is used to cause the reaction to occur.
  Examples: electrolysis of water, purification of copper, extraction of aluminium metal from molten aluminium oxide, electroplating

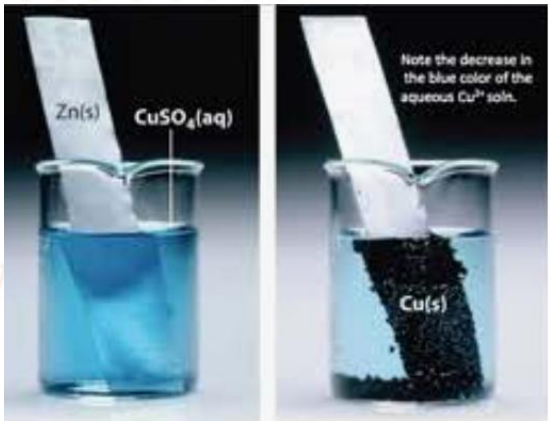
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1.1 REDOX REACTIONS

LO12(a): describe and explain redox processes in terms of electron transfer and/or of changes in oxidation number (oxidation state)
LO12(h): construct redox equations using the relevant half-equations

Whether the redox reaction occurs in an electrochemical cell or electrolytic cell, it always involves the transfer of electrons. The number of **electrons lost** by the reducing agent must be **equal** to the number of **electrons gained** by the oxidising agent.

Consider the reaction between Zn metal and Cu^{2+} ions. If a strip of Zn metal is placed in a solution of Cu^{2+} ions, the blue solution turns pale blue (eventually colourless) and red Cu solid forms on the Zn strip (Figure 1).



(a) start of experiment *(b) after some time*

Figure 1. Reaction between Zn and Cu^{2+}

In the reaction, Zn is the reducing agent and reduces Cu^{2+} to Cu metal. Cu^{2+} is the oxidising agent as it oxidises Zn metal to Zn^{2+} ions. The overall reaction consists of two **half-reactions**:

Reduction half-reaction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
Oxidation half-reaction: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
Overall redox reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Electrons are transferred from Zn metal (reducing agent) to Cu^{2+} ion (oxidising agent). Each Zn atom loses 2 electrons while each Cu^{2+} ion gains 2 electrons. Hence, one Zn atom reacts with one Cu^{2+} ion in the overall reaction. This is because the number of electrons lost must equal to the number of electrons gained when combining two **half-equations** to give the overall equation.

Table 1 summarises the terminology used to describe redox reactions.

reducing agent	**oxidising agent**
undergoes **oxidation**	undergoes **reduction**
loses electrons	**gains** electrons
oxidation number **increases**	oxidation number **decreases**

Table 1. Summary of redox terminology

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In the above set-up (Figure 1), Zn and Cu^{2+} ions are in the same beaker so the electrons are transferred **directly** from Zn to Cu^{2+} hence no electrical energy can be generated. If, however, the half-reactions are physically separated in an **electrochemical cell** (Figure 2), we can harness the electrical energy from the spontaneous reaction. Each half-reaction occurs in a **half-cell**. The electrons are now 'forced' to move through an external circuit, resulting in an electric current. The electrical energy produced can be used to operate electrical devices such as a light bulb. Hence, an electrochemical cell is essentially a battery.

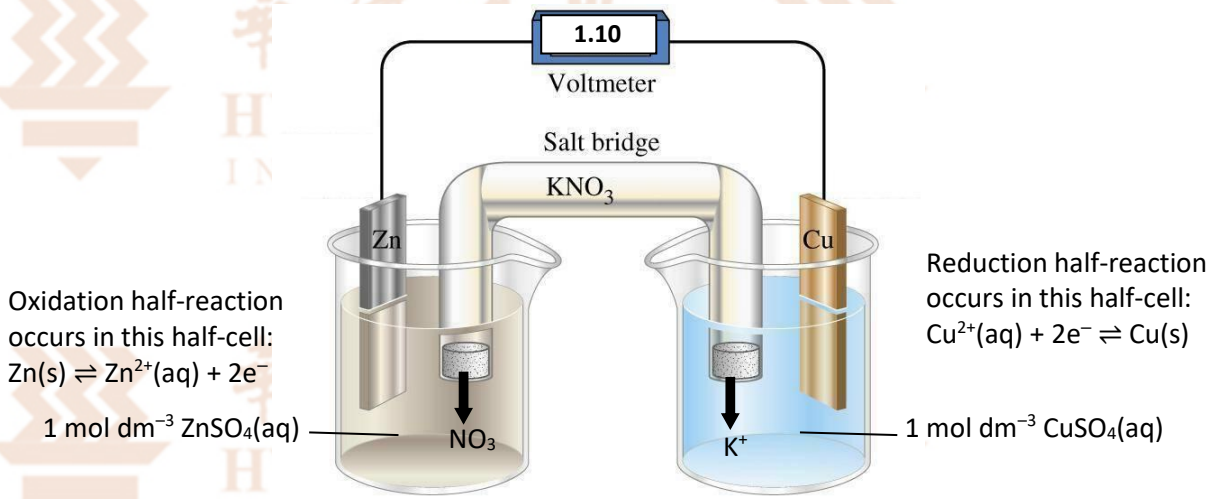


Figure 2. An electrochemical cell consisting of a Zn^{2+}/Zn half-cell and a Cu^{2+}/Cu half-cell

We will discuss more about half-cells and electrochemical cells in Section 2 and Section 3 respectively.

2 HALF-CELL AND ELECTRODE POTENTIAL

2.1 HALF-CELL

In every half-reaction, there is an oxidised form and a reduced form. An oxidised form in equilibrium with the reduced form makes a **half-cell**.

$$\text{oxidised form} + ne^- \rightleftharpoons \text{reduced form}$$

For a half-cell containing a metal placed in a solution containing its ions, M^{n+} is the oxidised form while M is the reduced form.

$$M^{n+}(aq) + ne^- \rightleftharpoons M(s)$$

At equilibrium, the rate of M dissolving into the solution as M^{n+} is equal to the rate of M^{n+} reforming M. The position of equilibrium depends on the reactivity of the metal. The more reactive the metal, the more the position of equilibrium lies on the left.

Consider a reactive metal such as Zn. As Zn tends to dissolve into the solution to form Zn^{2+} ions, there is a build-up of electrons on the Zn rod. This results in a negative charge on the Zn rod which is surrounded by a layer of positive ions (Figure 3). A potential difference develops between the metal and its solution. This is the **electrode potential** of the metal (symbol: ***E*(M^{n+}/M)**).

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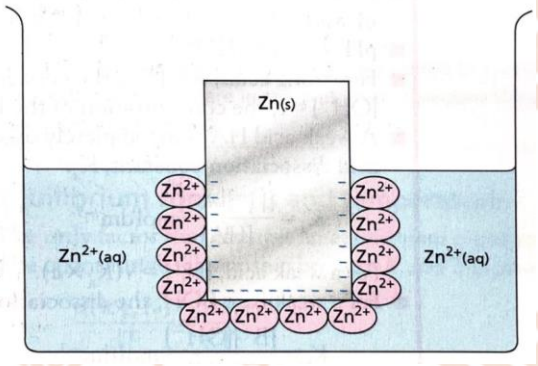


Figure 3. Zn^{2+}/Zn half-cell

Nickel is a less reactive metal than zinc. The position of equilibrium for Ni lies less on the left. The build-up of electrons on the Ni rod is smaller so the potential difference between Ni metal and its solution is smaller.

We cannot measure the absolute electrode potential of a half-cell. In practice, the electrode potential of a half-cell has to be measured by connecting it to a reference half-cell (Section 2.1.1).

Besides the metal-metal ion half-cell, a half-cell can also consist of a non-metal in contact with its aqueous ions (Figure 4) or ions of the same element in different oxidation states (Figure 5).

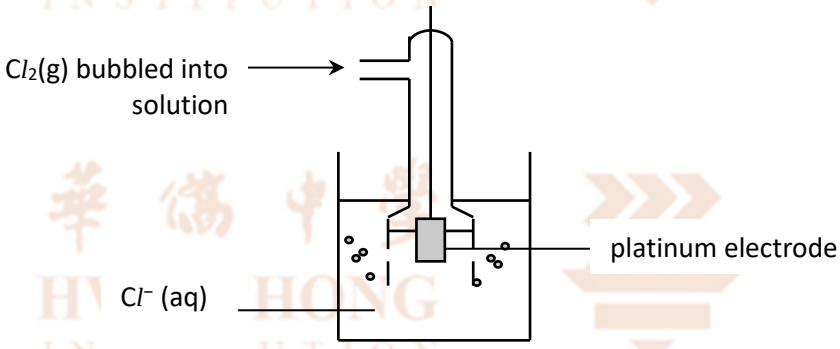


Figure 4. Cl_2/ Cl^- half-cell

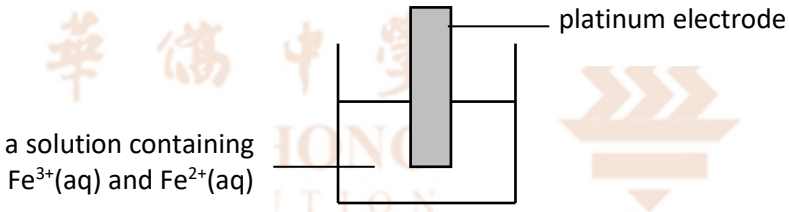


Figure 5. Fe^{3+}/ Fe^{2+} half-cell

In half-cells that consist of a metal and its ions (e.g. Zn^{2+}/Zn), the metal acts as the **electrode** which is used to transfer electrons in the electrochemical cell. In half-cells that do not include a metal, platinum (Pt) is usually used as the **inert electrode**. It transfers electrons without taking part in the reaction.

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2.1.1 STANDARD HYDROGEN ELECTRODE

LO12(c): describe the standard hydrogen electrode

The **standard hydrogen electrode** (Figure 6) is a commonly used reference half-cell or reference electrode against which the electrode potential of all other half-cells are measured. Its electrode potential is assigned a value of **0.00 V**.

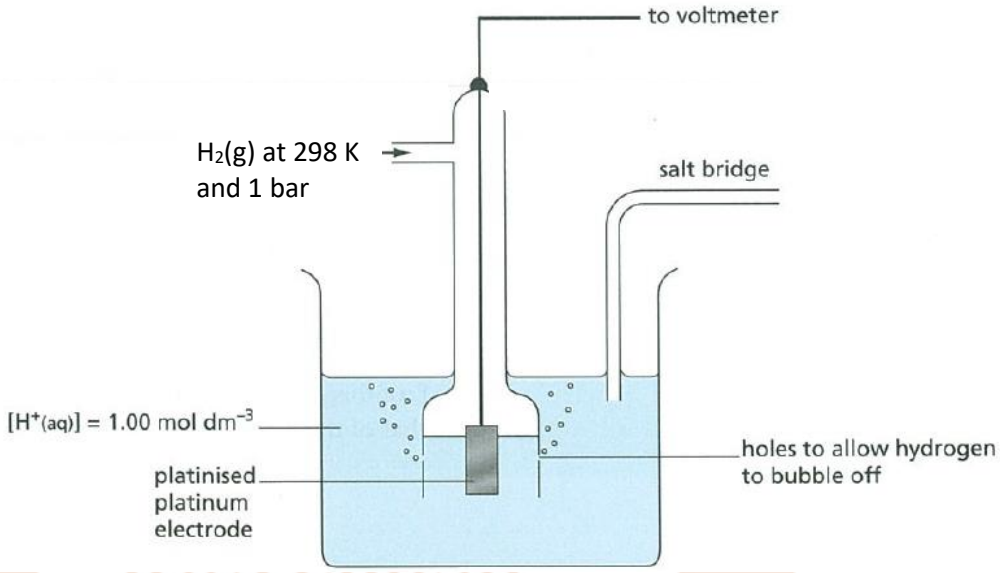


Figure 6. The standard hydrogen electrode

The standard hydrogen electrode comprises:

- a platinum wire and a piece of platinum foil covered with finely divided platinum (**platinised platinum**) that serves as an inert surface for redox reaction to take place,
- a solution of **1 mol dm^{-3} H^+(aq)** ions, in which the platinum electrode, encased in a glass tube, is immersed,
- **hydrogen gas at a pressure of 1 bar and 298 K** bubbling over the electrode.

On the surface of the platinum, equilibrium is established between hydrogen gas and hydrogen ions.

$$H^+(aq) + e^- \rightleftharpoons \tfrac{1}{2} H_2(g) \quad E^{\ominus}(H^+/H_2) = 0.00\ V$$

2.2 MEASURING STANDARD ELECTRODE (REDOX) POTENTIAL, $E^{\ominus}$

LO12(b)(i): define the term standard electrode (redox) potential

Electrode potential, *E*, depends on the position of equilibrium so its value depends on conditions such as temperature, pressure and concentration (to be discussed in Section 3.4.1). As such, electrode potentials are measured under a set of standard conditions.

Standard conditions for measuring electrode potential are:

- temperature of **298 K**
- pressure of **1 bar** for any gas
- concentration of **1 mol dm^{-3}** for any aqueous ions / species

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The **standard electrode potential** of a half-cell is the **potential difference** between the **half-cell** and a **standard hydrogen electrode** at **standard conditions** (298 K, 1 bar for gases, 1 mol dm^{-3} for solutions).

LO12(d): describe methods used to measure the standard electrode potentials of:
(i) metals or non-metals in contact with their ions in aqueous solution
(ii) ions of the same element in different oxidation states

To measure the standard electrode potential of a half-cell, we connect the half-cell to a standard hydrogen electrode and measure the potential difference with a **high resistance voltmeter**. A high resistance voltmeter takes very little current to operate so the potential difference measured is the highest possible value. This is known as the **electromotive force** (e.m.f.).

Since the standard hydrogen electrode is assigned an electrode potential of 0.00 V, the potential difference measured by the voltmeter gives the standard electrode potential of the respective half-cell.

(1) To measure $E^{\ominus}$ of **a metal in contact with its ions in aqueous solution**
Example: $Zn^{2+}(aq)$ / Zn(s) half-cell

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \quad E^{\ominus} = ?$$

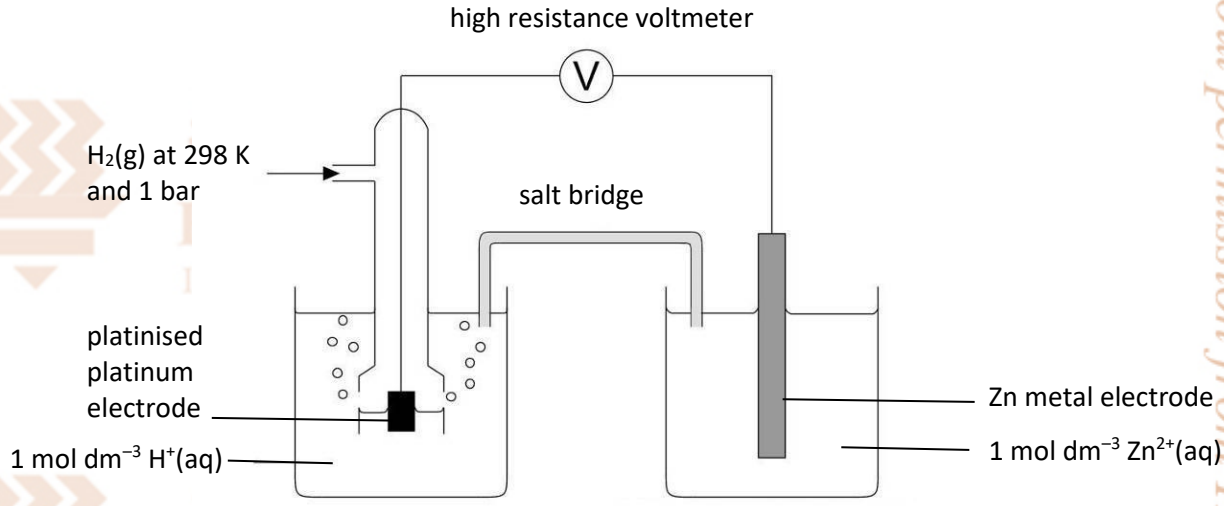


Figure 7. Measuring the standard electrode potential of $Zn^{2+}(aq)$ / Zn(s) half-cell

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(2) To measure $E^{\ominus}$ of a **non-metal in contact with its ions in aqueous solution**
Example: $Cl_2(g)$ / Cl^- (aq) half-cell

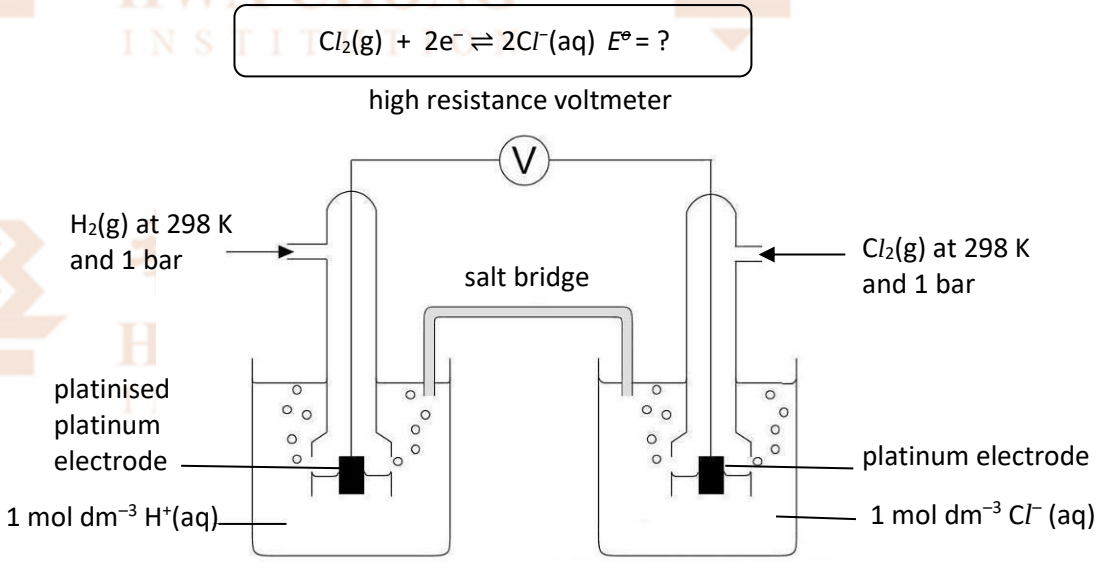


Figure 8. Measuring the standard electrode potential of $Cl_2(g)$ / Cl^- (aq) half-cell

(3) To measure $E^{\ominus}$ involving **ions of the same element in different oxidation states**
Example: $Fe^{3+}(aq)$ / $Fe^{2+}(aq)$ half-cell

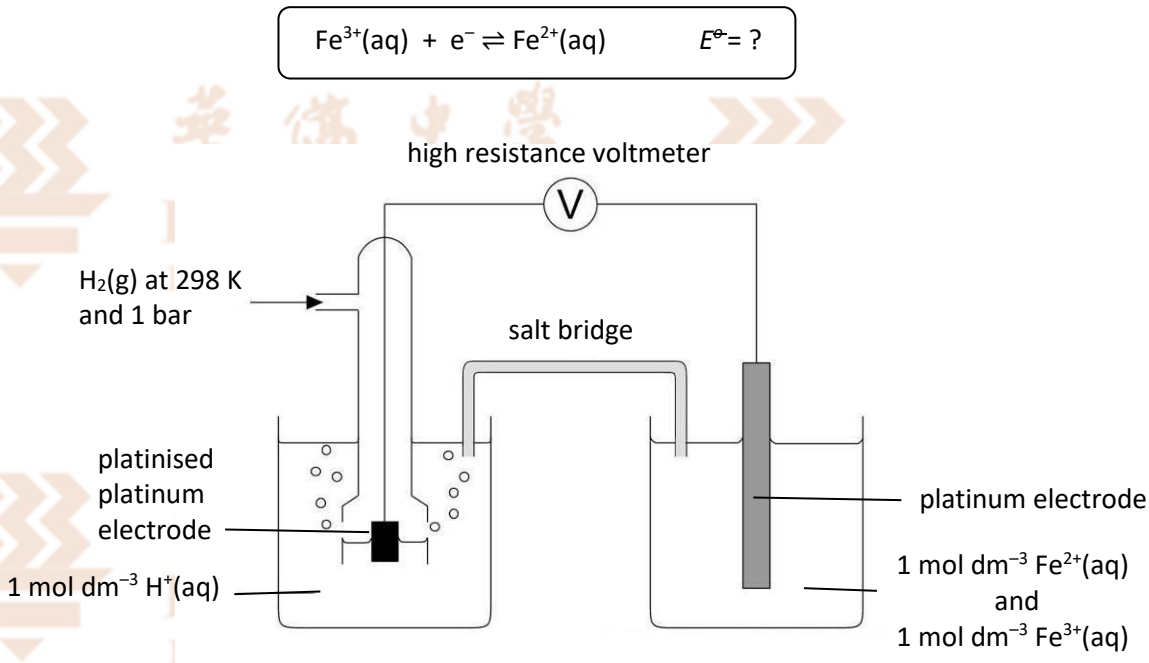


Figure 9. Measuring the standard electrode potential of $Fe^{3+}(aq)$ / $Fe^{2+}(aq)$ half-cell

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2.3 Understanding Standard Electrode Potential, $E^{\ominus}$

- Standard electrode potentials, $E^{\ominus}$ values, can be obtained from the *Data Booklet*. By convention, the half-reactions are written as **reductions** (i.e. electrons are written on the left). Hence $E^{\ominus}$ value is also called **standard reduction potential** or **standard redox potential**.

  For example, in the *Data Booklet*, we see:

  $$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O \qquad +1.33\ V$$

  This means that the "standard reduction potential of $Cr_2O_7^{2-}$ (to be reduced to Cr^{3+})" is +1.33 V. We can also write "$E^{\ominus}_{Cr_2O_7^{2-}/Cr^{3+}}$" = +1.33 V.

- When the half-reaction is reversed, the $E^{\ominus}$ of the reversed half-reaction will have the **same magnitude** but **opposite sign**.

  Using the same example as above:

  $$2Cr^{3+} + 7H_2O \rightleftharpoons Cr_2O_7^{2-} + 14H^+ + 6e^- \qquad -1.33\ V$$

  The value –1.33 V is the standard oxidation potential of Cr^{3+} (to be oxidised to $Cr_2O_7^{2-}$) and is less commonly used.

- The standard electrode potential (or standard reduction potential) is a measure of how favourable the forward reduction process is.

  The **more positive** the $E^{\ominus}$ value, the **more favourable** the forward **reduction** half-reaction.
  The **more negative** the $E^{\ominus}$ value, the **more favourable** the backward **oxidation** half-reaction.

- Multiplying a half-equation by a factor will **not** change the $E^{\ominus}$ value (as it is an intensive property.

  Example: $Ag^+(aq) + e^- \rightleftharpoons Ag(s)$ $E^{\ominus} = +0.80\ V$
  $2Ag^+(aq) + 2e^- \rightleftharpoons 2Ag(s)$ $E^{\ominus} = +0.80\ V$

Intensive Property and Extensive Property (Background Info)

Intensive property is a physical property that does not depend on the amount of substance present.
Examples: density, concentration

Extensive property is a physical property that depends on the amount of substance present.
Examples: volume, mass

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2.4 Using $E^{\ominus}$ to compare relative strengths of oxidising and reducing agents

As mentioned in Section 2.3, by convention, the half-reactions are written as reductions. Hence, the chemical species on the left is the oxidising agent (accepts electrons and undergoes reduction) while the chemical species on the right is the reducing agent (donates electrons and undergoes oxidation).

oxidised form + ne^- ⇌ reduced form

oxidising agent **reducing agent**

Table 2 shows the electrochemical series arranged in order of increasing standard electrode potential.



Oxidising agent accepts electron

increasing ease of reduction & increasing oxidising strength

Reducing agent donates electron

increasing ease of oxidation & increasing reducing strength



half-reaction			$E^{\ominus}$ / V
$Li^+ + e^-$	⇌	Li	−3.04
$K^+ + e^-$	⇌	K	−2.92
$Ba^{2+} + 2e^-$	⇌	Ba	−2.90
$Ca^{2+} + 2e^-$	⇌	Ca	−2.87
$Na^+ + e^-$	⇌	Na	−2.71
$Mg^{2+} + 2e^-$	⇌	Mg	−2.38
$Al^{3+} + 3e^-$	⇌	Al	−1.66
$Cr^{2+} + 2e^-$	⇌	Cr	−0.91
$2H_2O + 2e^-$	⇌	$H_2 + 2OH^-$	−0.83
$Zn^{2+} + 2e^-$	⇌	Zn	−0.76
$Fe^{2+} + 2e^-$	⇌	Fe	−0.44
$Cr^{3+} + e^-$	⇌	Cr^{2+}	−0.41
$Co^{2+} + 2e^-$	⇌	Co	−0.28
$Ni^{2+} + 2e^-$	⇌	Ni	−0.25
$Sn^{2+} + 2e^-$	⇌	Sn	−0.14
$Pb^{2+} + 2e^-$	⇌	Pb	−0.13
$2H^+ + 2e^-$	⇌	H_2	0.00
$Cu^{2+} + 2e^-$	⇌	Cu	+0.34
$O_2 + 2H_2O + 4e^-$	⇌	$4OH^-$	+0.40
$I_2 + 2e^-$	⇌	$2I^-$	+0.54
$O_2 + 2H^+ + 2e^-$	⇌	H_2O_2	+0.68
$Ag^+ + e^-$	⇌	Ag	+0.80
$Br_2 + 2e^-$	⇌	$2Br^-$	+1.07
$O_2 + 4H^+ + 4e^-$	⇌	$2H_2O$	+1.23
$Cr_2O_7^{2-} + 14H^+ + 6e$	⇌	$2Cr^{3+} + 7H_2O$	+1.33
$Cl_2 + 2e^-$	⇌	$2Cl^-$	+1.36
$MnO_4^- + 8H^+ + 5e^-$	⇌	$Mn^{2+} + 4H_2O$	+1.52
$H_2O_2 + 2H^+ + 2e^-$	⇌	$2H_2O$	+1.77
$F_2 + 2e^-$	⇌	$2F^-$	+2.87

Table 2. The Electrochemical Series

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- The **more positive** the $E^{\ominus}$ value, the **more easily** the oxidised form is **reduced**
  ⇒ the oxidised form is a **stronger oxidising agent**

  Example: $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E^{\ominus} = +1.36$ V
  $Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$ $E^{\ominus} = +1.07$ V

  Cl_2 is more easily reduced than Br_2. Hence, Cl_2 is a <u>stronger oxidising agent</u> than Br_2 (which also means Cl^- is a weaker reducing agent than Br^-).

- The **more negative** the $E^{\ominus}$ value, the **more easily** the reduced form is **oxidised**
  ⇒ the reduced species is a **stronger reducing agent**

  Example : $Ca^{2+}(aq) + 2e \rightleftharpoons Ca(s)$ $E^{\ominus} = -2.87$ V
  $Mg^{2+}(aq) + 2e \rightleftharpoons Mg(s)$ $E^{\ominus} = -2.38$ V

  Ca is more easily oxidised than Mg. Hence, Ca is a <u>stronger reducing agent</u> than Mg (which also means Ca^{2+} is a weaker oxidising agent than Mg^{2+}).

Exercise 2.1

(a) Decide if each of the following statements is true or false.

- Br_2 is more easily reduced than I_2.
- Ba is more readily oxidised than Cu.
- Br_2 is a stronger oxidising agent than Fe^{2+}.
- A*l* is a weaker reducing agent than Cr.
- It is easier to reduce Cr^{2+} than to oxidise it.
- Reducing power is in the order Cl^- > Pb > A*l*

(b) Among the species given in *Table 2 on the previous page*,

- Which is the strongest oxidising agent?
- Which has the strongest reducing power?
- Which species can act as both oxidising and reducing agents?

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3 THE ELECTROCHEMICAL CELL AND CELL POTENTIAL

3.1 THE ELECTROCHEMICAL CELL

An **electrochemical cell** consists of two half-cells. In one half-cell, oxidation takes place. In the other, reduction takes place. The redox reaction is **spontaneous** and **chemical energy is converted to electrical energy**. Figure 2 in Section 1 and Figures 7 to 9 in Section 2.2 are examples of electrochemical cells. We can connect any two half-cells together to make an electrochemical cell.

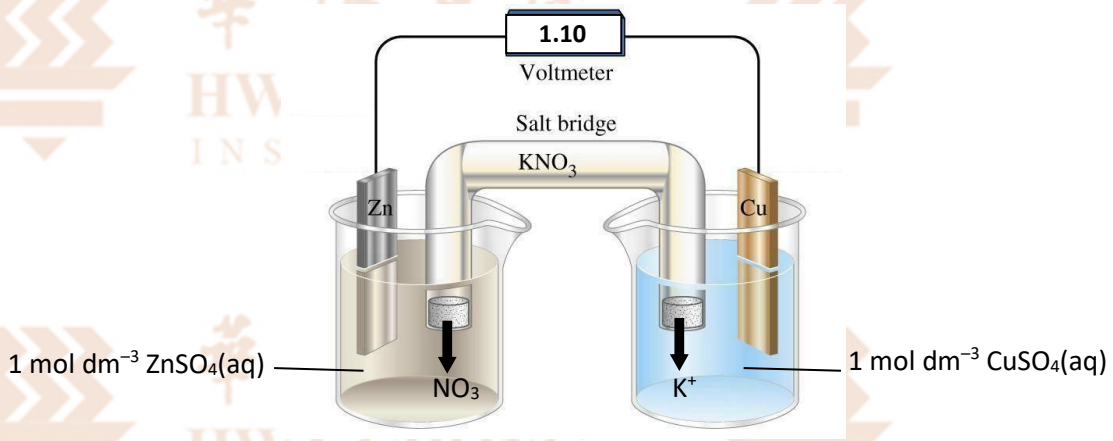


Figure 2 (from Section 1). An electrochemical cell consisting of a Zn^{2+}/Zn half-cell and a Cu^{2+}/Cu half-cell

We use the following to connect the two half-cells and to complete the circuit:

- wires to connect the two metal electrodes
- salt bridge which also serves to maintain charge neutrality

The **salt bridge** is an inverted U-tube containing a solution of **non-reacting ions**, in this case, K^+ and NO_3^-, in a gel. Each end of the tube is dipped into a half-cell. It has porous plugs on the ends that allow ions to flow through while minimising the mixing of the electrolytes by diffusion. Other non-reacting ions such as Na^+ and SO_4^{2-} can also be used in a salt bridge.

To measure the potential difference between the two half-cells, a high resistance voltmeter is added in the path of the wires connecting the electrodes.

When the above electrochemical cell is set-up, we observe a voltmeter reading of +1.10 V. This reading is the **cell potential**. It is the potential difference between the two half-cells, which (in this case) arises due to the difference in reactivity of the two metals, Cu and Zn.

Zn is a more reactive metal than Cu. This means that Zn has a higher tendency to lose electrons and be oxidised to Zn^{2+} compared to Cu. Hence, **oxidation occurs** in the Zn^{2+}/Zn half-cell while **reduction occurs** in the Cu^{2+}/Cu half-cell.

Oxidation half-reaction: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Reduction half-reaction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Overall redox reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

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An electrode is identified as either anode or cathode depending on the half-reaction that takes place there. The **oxidation** half-reaction occurs at the **anode** while the **reduction** half-reaction occurs at the **cathode**.

Electrons are produced by the oxidation half-reaction hence the anode has an excess of electrons and a **negative polarity relative to the cathode**. Electrons are consumed at the cathode by the reduction half-reaction. Hence **electrons flow from** the **oxidation** half-cell **to** the **reduction** half-cell, i.e. from the **anode to the cathode**. In the above electrochemical cell, the electrons produced at the Zn anode (negative electrode) will flow to the Cu cathode (positive electrode) via the electrical wire (in the external circuit).

Table 3 summarises the differences between the electrodes in an electrochemical cell.

Electrode	Anode	**C**athode
Polarity	Negative	**P**ositive
Half-reaction	Oxidation	**R**eduction

Table 3. Differences between the electrodes in an electrochemical cell

How does the salt bridge work? (Background Info)

We mentioned that the salt bridge **completes the circuit** and also allows ions to flow through. The flow of ions occurs to **maintain neutrality in the solutions** in the half-cells. At the start, both half-cells contain a neutral solution ($ZnSO_4$ and $CuSO_4$) where the number of positive charges equals to the number of negative charges. As the reaction occurs, Zn^{2+} enters the solution in the anode so the solution develops a net positive charge. In the cathode, Cu^{2+} leaves the solution to form Cu so the solution develops a net negative charge.

This charge imbalance would stop the reaction as excess charges in the solutions will prevent more ions from being formed.

To maintain neutral charge in the solutions, NO_3^- ions move from the salt bridge into the solution at the anode (and some Zn^{2+} ions can also enter the salt bridge). At the cathode, K^+ ions move from the salt bridge into the solution (and some SO_4^{2-} ions can also enter the salt bridge).

Cell notation (Background Info)

A **cell notation** can be written to represent an electrochemical cell. For example, the cell notation for the electrochemical cell in Figure 2 (Section 3.1) is:

$$Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$$

- The half-cell where **oxidation** takes place is placed on the **left** while the half-cell where **reduction** takes place is placed on the **right**.
- The electrode of each half-cell is placed at the ends.
- The solid vertical line | indicate a phase boundary, with the reduced form on the outside.
- The double lines || represent the salt bridge.
- The concentration of an aqueous ion may be written next to the ion if not at 1 mol dm^{-3}.

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3.2 STANDARD CELL POTENTIAL, $E^{\ominus}_{cell}$

LO12(b)(ii): define the term standard cell potential

If the two half-cells that make the electrochemical cell are at standard conditions, the cell potential is the standard cell potential, $E^{\ominus}_{cell}$.

The **standard cell potential** is the **potential difference between two half-cells** measured at **standard conditions** (298 K, 1 bar for gases, 1 mol dm^{-3} for solutions).

LO12(e): calculate a standard cell potential by combining two standard electrode potentials

- The standard cell potential, $E^{\ominus}_{cell}$, can be calculated by combining two standard electrode potentials.

  Consider the electrochemical cell in Figure 2 (Section 3.1). The standard electrode potentials of the two half-cells are:

  $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $\quad E^{\ominus} = +0.34$ V
  $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $\quad E^{\ominus} = -0.76$ V

  The voltmeter shows a reading of +1.10 V which is equal to the standard cell potential. Notice that this value is the numerical <u>difference</u> between the $E^{\ominus}$ values of the two half-cells.

  (Reduction) +0.34V
  (Oxidation) –0.76V
  $E_{cell} = +0.34 - (-0.76) = +1.10$ V

  Recall from Section 3.1 that reduction occurs in the Cu^{2+}/Cu half-cell and Cu is the cathode while oxidation occurs in the Zn^{2+}/Zn half-cell and Zn is the anode.

  Hence,

  $$E^{\ominus}_{cell} = E^{\ominus}_{reduction} - E^{\ominus}_{oxidation}$$
  $$= E^{\ominus}_{cathode} - E^{\ominus}_{anode}$$

  Remember to include the sign (+) or (–) as well as the units (V) for $E^{\ominus}_{cell}$.

  In general, to calculate $E^{\ominus}_{cell}$ of an **electrochemical cell**, we
  - select the two standard electrode potentials from the *Data Booklet*
  - decide which half-cell undergoes reduction and which half-cell undergoes oxidation

  In an **electrochemical cell**, **reduction** occurs in the half-cell with the **more positive $E^{\ominus}$ value**. **Oxidation** occurs in the half-cell with a **less positive $E^{\ominus}$ value**. The electrode in the reduction half-cell is the **cathode** while the electrode in the oxidation half-cell is the **anode**.
  In the above example, since $E^{\ominus}$ (Cu^{2+}/Cu) is <u>more positive</u> than $E^{\ominus}$ (Zn^{2+}/Zn), <u>reduction</u> occurs in the Cu^{2+}/Cu half-cell and Cu is the cathode while oxidation occurs in the Zn^{2+}/Zn half-cell and Zn is the anode.

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LO12(f)(i): use standard cell potentials to explain/deduce the direction of electron flow from a simple cell

- We can use standard cell potentials to deduce the direction of electron flow in the external circuit of an electrochemical cell.

  Electrons are produced at the anode (by the oxidation half-reaction) and consumed at the cathode (by the reduction half-reaction). Hence, **electrons flow from the oxidation half-cell to the reduction half-cell**, i.e. from the **anode to the cathode**.

  In the electrochemical cell in Figure 2 (Section 3.1), Zn is the anode (less positive $E^{\ominus}$ value) and Cu is the cathode (more positive $E^{\ominus}$ value). Electrons flow from the Zn electrode to the Cu electrode in the external circuit.

LO12(h): construct redox equations using the relevant half-equations

- We can use half-equations to construct redox equations. The half-equations in the *Data Booklet* are shown with an equilibrium arrow (⇌) because each can occur as a reduction or oxidation, depending on the other half-reaction. A redox reaction must consist of a reduction half-reaction and an oxidation half-reaction.

  For example,

  $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \quad E^{\ominus} = +0.34\ V$
  $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \quad E^{\ominus} = -0.76\ V$

  In the electrochemical cell in Figure 2 (Section 3.1), Zn is oxidised to Zn^{2+} so we need to reverse the zinc half-equation. In addition, we must use the **single forward arrow** (→) for both half-equations to represent the **reactions that <u>actually occur</u>**.

  Oxidation half-reaction: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
  Reduction half-reaction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

  Electron **lost** must **equal** to electron **gained** when combining two half-equations to give the overall redox equation. Each Zn atom loses 2 electrons while each Cu^{2+} ion gains 2 electrons. Hence, one Zn atom reacts with one Cu^{2+} ion in the overall reaction.

  Overall redox reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

  To represent redox reactions that <u>actually occur</u>, the <u>single forward arrow</u> must be used.

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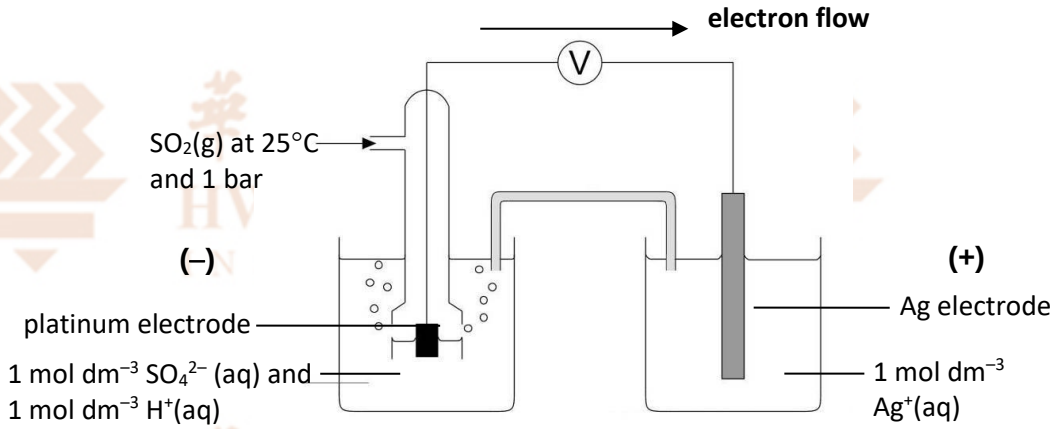
Exercise 3.1 (Worked Example)

The voltaic cell below consists of a SO_4^{2-}/SO_2 half-cell connected to a Ag^+/Ag half-cell.

(a) Calculate the $E^{\ominus}_{cell}$.

(b) Indicate on the diagram the polarity of the electrodes and the direction of electron flow.

(c) Write half-equations for the reactions that occur at the cathode and the anode respectively.



(a) $SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O$ $\quad E^{\ominus} = +0.17$ V [O]

$Ag^+ + e^- \rightleftharpoons Ag$ $\quad E^{\ominus} = +0.80$ V [R]

$\therefore E^{\ominus}_{cell} = E^{\ominus}_{red} - E^{\ominus}_{ox} = +0.80 - (+0.17) = +0.63$ V

(b) *Electrons are produced at the anode (by the SO_4^{2-}/SO_2 oxidation half-reaction) and consumed at the cathode (by the Ag^+/Ag reduction half-reaction). Hence, electrons flow from the Pt electrode to the Ag electrode.*

(c) **cathode:** $Ag^+ + e^- \rightarrow Ag$

anode: $SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$

3.3 Standard Cell Potential and Gibbs' Free Energy

LO12(i)part: state and apply the relationship $\Delta G = -nFE^{\ominus}$ to electrochemical cells

In Topic 5, we discussed the change in Gibbs free energy, ΔG, that accompanies chemical reactions. The change in Gibbs free energy of a redox reaction can be converted into electrical energy in an electrochemical cell.

The following equation shows the relationship between Gibbs' free energy change and cell potential:

$$\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$$

where $\Delta G^{\ominus}$ is the standard Gibbs free energy change in joules per mole (J mol^{-1}),
n is the number of moles of electrons transferred per mole of the cell reaction and
F is the Faraday's constant (96500 C mol^{-1}).

Hence, a **spontaneous** redox reaction ($\Delta G < 0$) would imply that $E_{cell} > 0$.

We will use $\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$ in calculations in Section 3.5.

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3.4 Predict Spontaneity of a Redox Reaction

LO12(f)(ii): use standard cell potentials to predict the spontaneity of a reaction

We can use standard cell potentials to predict whether a redox reaction will occur between two given reactants.

- If $E^{\ominus}_{cell}$ **is positive**, reaction is expected to be **spontaneous** under standard conditions.
- If $E^{\ominus}_{cell}$ **is negative**, reaction is expected to be **non-spontaneous** under standard conditions.
- If $E^{\ominus}_{cell}$ **= 0**, the reaction is at **equilibrium**, and there is no net reaction in either direction.

To calculate $E^{\ominus}_{cell}$, we use $E^{\ominus}_{cell} = E^{\ominus}_{reduction} - E^{\ominus}_{oxidation}$. We need to decide which reactant undergoes reduction and which reactant undergoes oxidation. **This depends on the reactants given to you**.

Look for the relevant half-equations in the *Data Booklet* that contains the given reactants. It is useful to circle the given reactants in the half-equations.

- If *both reactants are on the same side of the half-equations*, then either both are oxidising agents or both are reducing agents. The redox reaction cannot occur. In this case, we cannot calculate the $E^{\ominus}_{cell}$ value.
- If the *two reactants are on opposite sides of the half-equations*, the redox reaction may occur. Calculate the $E^{\ominus}_{cell}$ value to predict the spontaneity of the reaction.
  If more than one redox pair or reaction are possible, the **reaction with the most positive $E^{\ominus}_{cell}$** will be the **most spontaneous**.

For example, if Zn metal is placed in a solution containing Cu^{2+} ions, a spontaneous reaction occurs.

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \qquad E^{\ominus}_{cell} = +0.34 - (-0.76) = +1.10\ V > 0$$

What happens if Cu metal is placed in a solution containing Zn^{2+} ions? Will the following reaction occur?

$$Zn^{2+}(aq) + Cu(s) \rightarrow Zn(s) + Cu^{2+}(aq) \qquad E^{\ominus}_{cell} = ?$$

The relevant half-equations are:

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E^{\ominus} = +0.34\ V$$

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad E^{\ominus} = -0.76\ V$$

In this case, Zn^{2+} needs to undergo reduction and Cu needs to undergo oxidation.

$E^{\ominus}_{cell} = E^{\ominus}_{reduction} - E^{\ominus}_{oxidation} = (-0.76) - (+0.34) = -1.10\ V < 0$. Hence, no reaction will occur between Zn^{2+} and Cu.

Note that the reaction between Zn and Cu^{2+} is spontaneous ($E^{\ominus}_{cell} > 0$), hence we would expect the reverse reaction to be non-spontaneous ($E^{\ominus}_{cell} < 0$).

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Exercise 3.2 (Worked Example)

Predict whether the following pairs of reagents are likely to react when mixed in acidified aqueous solution. Calculate the $E^{\ominus}_{cell}$ and write a balanced equation for each reaction you predict will occur.

(a) $I_2(aq)$ and $Cr^{3+}(aq)$

(b) $H_2O_2(aq)$ and $MnO_4^-(aq)$

(a)

[R]	$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54 V
	$Cr^{3+} + 3e^- \rightleftharpoons Cr$	–0.74 V
	$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	–0.41 V
[O]	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33 V

Note: I_2 can only undergo reduction as there is only one half-equation involving I_2 whereby I_2 is on the left side of the half-equation. However, there are 3 half-equations involding Cr^{3+}. Thus, for Cr^{3+}, you need to choose the half-equation which shows Cr^{3+} undergoing oxidation (i.e. Cr^{3+} on the right side of half-equation).

$E^{\ominus}_{cell}$ = +0.54 – (+1.33) = –0.79 V < 0

∴ Reaction is not spontaneous => No reaction occurs

(b)

	$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.77 V
[O]	$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	+0.68 V
[R]	$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52 V

Note: There are 3 half-equations which can represent the reduction of MnO_4^-. However, you have learnt under "Redox Reactions" in Topic 04 Reactions and Stoichiometry that MnO_4^- is reduced to Mn^{2+} in acidic medium (MnO_4^- is reduced to MnO_2 instead in alkaline medium).

$E^{\ominus}_{cell}$ = +1.52 – (+0.68) = +0.84 V > 0

∴ Reaction is spontaneous => Reaction occurs

MnO_4^- oxidises H_2O_2 to O_2 gas, causing effervescence.

MnO_4^- is reduced to Mn^{2+}. The purple solution turns colourless.

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

Exercise 3.3

Predict whether the following pairs of reagents are likely to react when mixed in acidified aqueous solution. Calculate the $E^{\ominus}_{cell}$ and write a balanced equation for each reaction you predict will occur.

(a) $V^{3+}(aq)$ and $Cu^{2+}(aq)$

(b) $F_2(g)$ and $Cr_2O_7^{2-}(aq)$

(a) 0V (b) no value

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3.4.1 Non-Standard Conditions

LO12(j): predict qualitatively how the value of an electrode potential varies with the concentration of the aqueous ion

Changes in concentration, pressure and temperature may affect the values of electrode potentials. We can predict the effect of these changes on the electrode potential using Le Chatelier's Principle.

(i) Effect of concentration of aqueous ions on electrode potential

Consider: $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$
At 298 K and 1.00 mol dm^{-3} of $Cu^{2+}(aq)$, $E^{\ominus}$ = +0.34 V
At 298 K and 0.10 mol dm^{-3} of $Cu^{2+}(aq)$, E = +0.31 V

Explanation: If the concentration of the $Cu^{2+}(aq)$ ions is decreased, the position of the equilibrium will shift to the left. Hence the tendency for Cu^{2+} to be reduced is decreased, and reduction potential becomes **less positive** (or more negative).

(ii) Effect of pressure of gaseous species on electrode potential

Consider: $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E^{\ominus}$ = +1.36 V

When the pressure of chlorine gas is increased from say 1 bar to 1.5 bar, the equilibrium position shifts to the right to favour the forward reduction reaction. Hence the reduction potential becomes **more positive** (or less negative).

(iii) Effect of temperature

Consider: $Na^+(aq) + e^- \rightleftharpoons Na(s)$
At 298K and 0.1 mol dm^{-3} of $Na^+(aq)$, E = – 2.77 V
At 398K and 0.1 mol dm^{-3} of $Na^+(aq)$, E = – 2.79 V

The above data shows that at a higher temperature, the position of equilibrium shifts to the left and the reduction potential becomes more negative (or less positive) for Na^+.

Nernst Equation (Background Info)

Electrode potentials under <u>non-standard conditions</u> may be determined using the Nernst equation.

For a reaction: aA + bB ⇌ cC + dD, let $Q = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

Nernst equation can be written as: $E_{cell} = E^{\ominus}_{cell} - \dfrac{RT}{nF} \ln Q$

where R is the gas constant,
T is the temperature in K,
n is the number of moles of selectrons transferred (per mole of the redox reaction) when the oxidised species changes into the reduced species and
F is the Faraday's constant, 96 500 C mol^{-1}.

At 298K, the Nernst equation can be rewritten in the log form: $E_{cell} = E^{\ominus}_{cell} - \dfrac{0.0591}{n} \lg Q$

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3.4.2 Limitations of Using Standard Cell Potentials

LO12(g): understand the limitations in the use of standard cell potentials to predict the spontaneity of a reaction

Using $E^{\ominus}_{cell}$ to predict the spontaneity of a reaction may not be correct for two reasons:

- **Non-standard conditions**
  $E^{\ominus}_{cell}$ values apply only to standard conditions (298 K, 1 bar, 1 mol dm^{-3}). Since changes in concentration, pressure and temperature may affect the values of electrode potentials, they will also affect the cell potential calculated and hence the prediction.

- **High activation energy** (energetic vs kinetic feasibility)

Similar to ΔG, $E^{\ominus}$ values **cannot predict the rate of a redox reaction**. It only tells us whether a reaction is **thermodynamically feasible i.e. spontaneous**. No information is given about the kinetic feasibility, which is related to activation energy.

For example, $E^{\ominus}$ values predict that $Cu^{2+}(aq)$ should oxidise $H_2(g)$ to $H^+(aq)$.

$$Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^+(aq) \qquad E^{\ominus}_{cell} = +0.34\ V$$

However, in practice, no reaction occurs when hydrogen is bubbled into copper(II) sulfate solution at r.t.p. because the reaction rate is effectively zero due to a very high activation barrier.

3.5 Calculation of $E^{\ominus}$ for combined half reactions

LO12(i)part: apply $\Delta G = -nFE^{\ominus}$ to electrochemical cells, including the calculation of $E^{\ominus}$ for combined half reactions

$E^{\ominus}$ values cannot be combined directly to evaluate the $E^{\ominus}$ for another half-reaction.

Consider the following three redox half-equations:

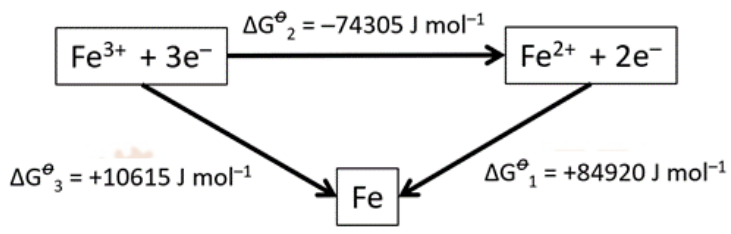
(1)	$Fe^{2+} + 2e^-$	⇌	Fe	$E^{\ominus}_1 = -0.44$ V
(2)	$Fe^{3+} + e^-$	⇌	Fe^{2+}	$E^{\ominus}_2 = +0.77$ V
(3)	$Fe^{3+} + 3e^-$	⇌	Fe	$E^{\ominus}_3 = -0.04$ V

The sum of half-equations (1) and (2) gives half-equation (3), but $E^{\ominus}_3$ is **not** +0.33 V (sum of $E^{\ominus}_1$ and $E^{\ominus}_2$). The number of electrons transferred in each half-reaction must be taken into account. To find the $E^{\ominus}$ value of combined half reactions, we use the relationship $\Delta G^{\ominus} = -nFE^{\ominus}$.

Using the above example, we shall first convert the relevant $E^{\ominus}$ values to ΔG:

(1) $Fe^{2+} + 2e^- \rightleftharpoons Fe$ $\quad E^{\ominus}_1 = -0.44$ V $\quad \Rightarrow \Delta G^{\ominus}_1 = -(2)(96500)(-0.44) = +84920$ J mol^{-1}

(2) $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $\quad E^{\ominus}_2 = +0.77$ V $\quad \Rightarrow \Delta G^{\ominus}_2 = -(1)(96500)(+0.77) = -74305$ J mol^{-1}



Using Hess' Law, $\Delta G^{\ominus}_3 = \Delta G^{\ominus}_1 + \Delta G^{\ominus}_2 = +84920 + (-74305) = +10615$ J mol^{-1}

Since n = 3 for half-equation (3), $E^{\ominus}_3 = -\Delta G^{\ominus}_3 / nF = -10615/(3 \times 96500) = -0.04$ V

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Exercise 3.4 (RIJC 2011/ 3/ 1b *modified*) (Worked Example)

The standard electrode potentials, $E^{\ominus}$, and standard Gibbs free energy changes, $\Delta G^{\ominus}$, of different chlorine-containing species are tabulated below.

	Half-equation	$E^{\ominus}$ **/ V**	$\Delta G^{\ominus}$ **/ kJ mol^{-1}**
1	$2ClO_3^-(aq) + 12H^+(aq) + 10e^- \rightleftharpoons Cl_2(aq) + 6H_2O(l)$	+1.47	**?**
2	$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36	−262

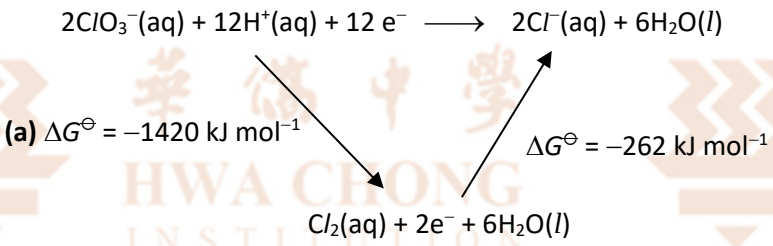
(a) Calculate $\Delta G^{\ominus}$ for half-reaction 1.

(b) The standard electrode potential of converting ClO_3^- to Cl^- is **not** the summation of +1.47 V and +1.36 V. This is because the number of electrons transferred in each step must be taken into account.

By writing a half-equation for the conversion of ClO_3^- to Cl^- and using your knowledge of Hess' Law for $\Delta G^{\ominus}$ and your answers to **(a)**, show with the aid of an energy cycle that the $E^{\ominus}$ for the conversion of ClO_3^- to Cl^- is +1.45 V.

(a) $\Delta G^{\ominus} = -nFE^{\ominus} = -(10)(96500)(+1.47) =$ **$\underline{-1420\ kJ\ mol^{-1}}$**

(b) $2ClO_3^-(aq) + 12H^+(aq) + 12\ e^- \longrightarrow 2Cl^-(aq) + 6H_2O(l)$



Applying Hess' Law,

$\Delta G^{\ominus} = -1420 + (-262) =$ **$\underline{-1682\ kJ\ mol^{-1}}$**

$E^{\ominus} = -[-1682 \times 10^3 / (12 \times 96500)] =$ **$\underline{+1.45\ V}$** (shown)

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4 PRACTICAL APPLICATIONS OF ELECTROCHEMICAL CELLS

LO12(k): state the possible advantages of developing other types of cell, e.g. the H_2/O_2 fuel cell and improved batteries (as in electric vehicles) in terms of smaller size, lower mass and higher voltage

Fuel cells (Section 4.1) and batteries (Section 4.2) are two common examples of electrochemical cells that provide a portable and convenient way of obtaining energy from chemical reactions.

Hydrogen-oxygen fuel cells have been used for years to provide electricity and pure water during space flights. Similar ones are being used to supply electric power for transportation (e.g. electric vehicles), residential and commercial needs.

Advantages of fuel cells

- No pollution
- High efficiency and good energy-to-mass ratio
  They convert about 75% of the chemical energy of the fuel into useable power as compared to 40% for a coal-fired power plant and 20-25% for a gasoline-powered car engine.



Figure 10. Mercedes-Benz F600 with hydrogen fuel cell

Disadvantages of fuel cells

- Expensive
- High temperature to operate
  The electrode reactions are slow, even when the electrodes are made of platinum which acts as a catalyst.
- The alkali may absorb CO_2 from air to form carbonates that clog up the porous electrodes.
- Bulky storage of fuel
  For cars, the hydrogen must be transported either in cylinders (heavy) or at very low temperatures as a liquid. Efforts are made to carry the hydrogen in the form of transition metal hydrides but these are costly and can absorb only a limited amount of hydrogen. As an alternative to transporting hydrogen to fuel cars, methanol is a fuel that is easy to carry and can be broken down to produce carbon dioxide and hydrogen (which is then used as the fuel in the H_2/O_2 fuel cell). However, there is the danger that some poisonous carbon monoxide may be produced in addition to the carbon dioxide.

Despite steady progress, the focus of current fuel cell research remains on lowering costs by improving membrane conductivity and developing more efficient catalysts.

Although the operation of a battery is similar in principle to that of the electrochemical cells described in Section 3.1, a battery has the advantage of being completely self-contained and required no auxiliary components such as salt bridges.

The trend in developing improved batteries is to look for batteries with

- smaller size
- lower mass
- higher voltage
- longer shelf-life
- lower production cost

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4.1 Fuel Cells (Background Info and Application Example)

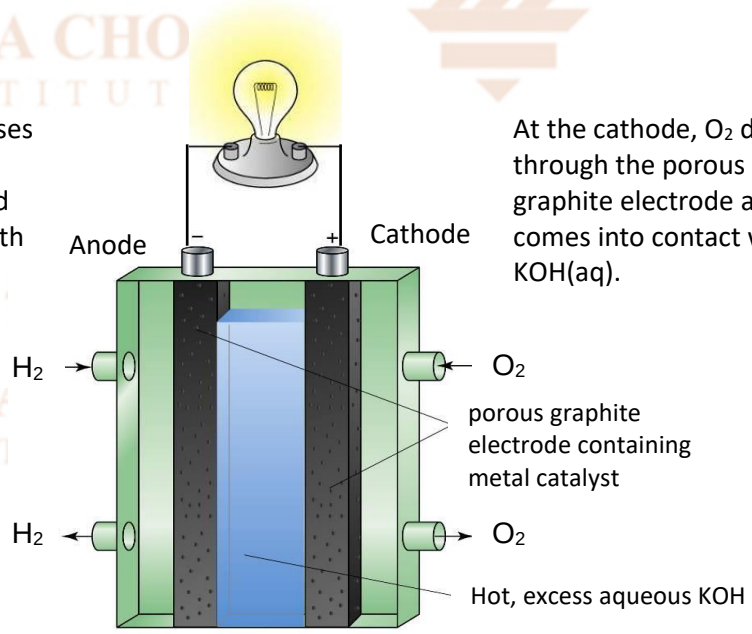
When a fuel is burnt in a power station, the heat is usually used to produce steam to drive a piston or to turn the blades of a turbine. The overall efficiency is always low no matter how well the plant is designed.

In order to achieve higher efficiencies, efforts have been made to convert the chemical energy of a fuel *directly* into electrical energy by means of a **fuel cell**. In contrast to batteries, the reactants in a fuel cell are supplied *continuously* and the cell is able to operate without theoretical limit as long as the supply of reactants is maintained.

The fuel (e.g. hydrogen, a hydrocarbon or an alcohol) and an oxidant (usually oxygen) enter the fuel cell, and the products leave, generating electricity through the controlled oxidation of the fuel. The fuel *does not burn* because, as in other batteries, the half-reactions are separated and the electrons are transferred through an external circuit.

The most common fuel cell is the **hydrogen-oxygen fuel cell**:

At the anode, H_2 diffuses through the porous graphite electrode and comes into contact with KOH(aq).



At the cathode, O_2 diffuses through the porous graphite electrode and comes into contact with KOH(aq).

Figure 11. Hydrogen-oxygen fuel cell

Anode (*oxidation*): $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$

Cathode (*reduction*): $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

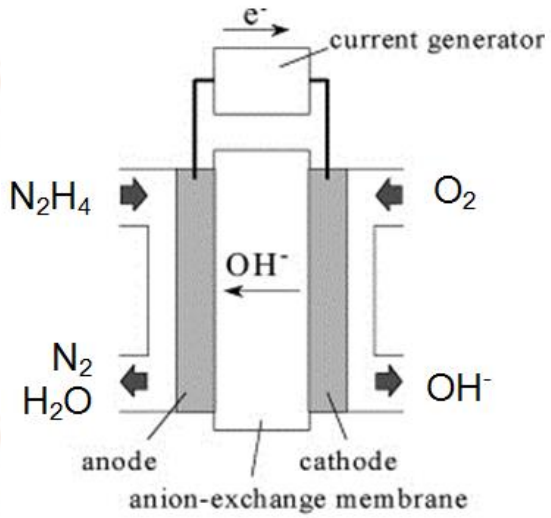
Overall cell reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ $\quad E^\ominus_{cell} = +1.23$ V

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Exercise 4.1 (Worked Example)

The Italian catalyst manufacturer *Acta* proposed using hydrazine as an alternative to hydrogen in fuel cells. The chief benefit of using hydrazine is that it can produce more energy than a similar hydrogen-oxygen cell.

The following diagram shows a typical hydrazine-oxygen fuel cell system incorporated with an anion exchange membrane between the electrodes.



(i) Write the two ion-electron half equations for the reactions that take place at each electrode. Hence, write an overall equation for the cell reaction.

(ii) Given that $E^{\ominus}(N_2/N_2H_4)$ is −1.16 V, calculate the cell e.m.f. if the process takes place under standard conditions.

(iii) Based on the physical properties of hydrazine, suggest an advantage of the hydrazine-oxygen fuel cell over the hydrogen-oxygen fuel cell.

PJC 2013/ 3/ 3b modified

(i) Anode: $N_2H_4(l) + 4OH^-(aq) \rightarrow N_2(g) + 4H_2O(l) + 4e^-$

Cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

Overall: $N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(l)$

(ii) $E^{\ominus}_{cell} = E^{\ominus}(red) - E^{\ominus}(ox)$

$= +0.40\ V - (-1.16)$

$= \underline{+1.56\ V}$

(iii) Hydrazine is a liquid at room temperature and can be handled and stored more easily than hydrogen gas.

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4.2 Batteries (Application Examples)

(Diagrams of batteries are not required in exams)

(i) Non-rechargeable alkaline battery used in portable radios, toys and flashlights

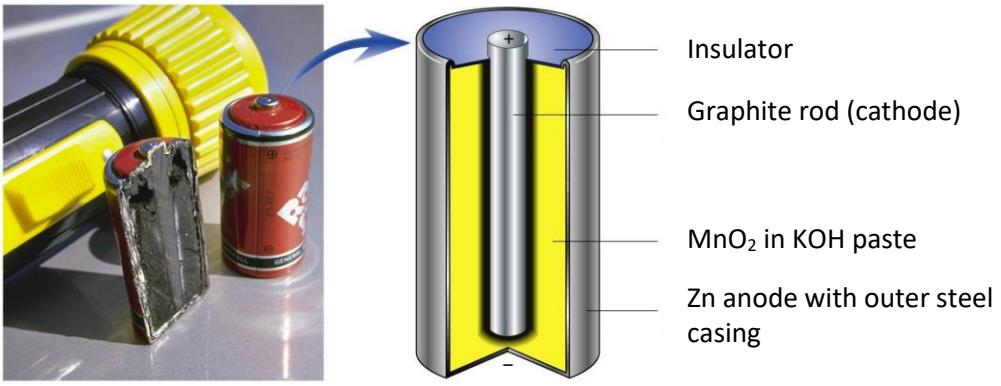


Figure 12. Alkaline battery

Anode (*oxidation*): $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$

Cathode (*reduction*): $MnO_2(s) + 2H_2O(l) + 2e^- \rightarrow Mn(OH)_2(s) + 2OH^-(aq)$

Overall cell reaction: $Zn(s) + MnO_2(s) + H_2O(l) \rightarrow ZnO(s) + Mn(OH)_2(s)$ $E_{cell} = +1.5$ V

(ii) Non-rechargeable silver button battery used in watches, cameras, heart pacemakers and hearing aids

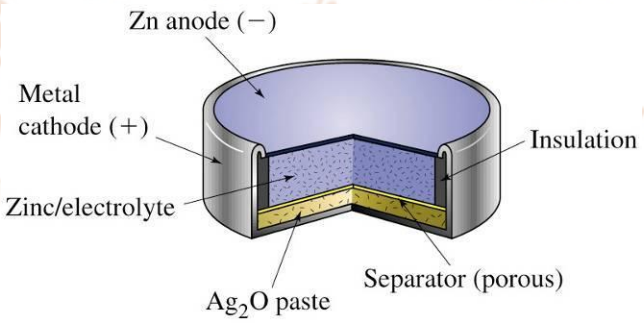


Figure 13. Silver button battery

Anode (*oxidation*): $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$

Cathode (*reduction*): $Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq)$

Overall cell reaction: $Zn(s) + Ag_2O(s) \rightarrow ZnO(s) + 2Ag(s)$ $E_{cell} = +1.6$ V

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(iii) Rechargeable lead-acid battery used to power the starter motor in a car

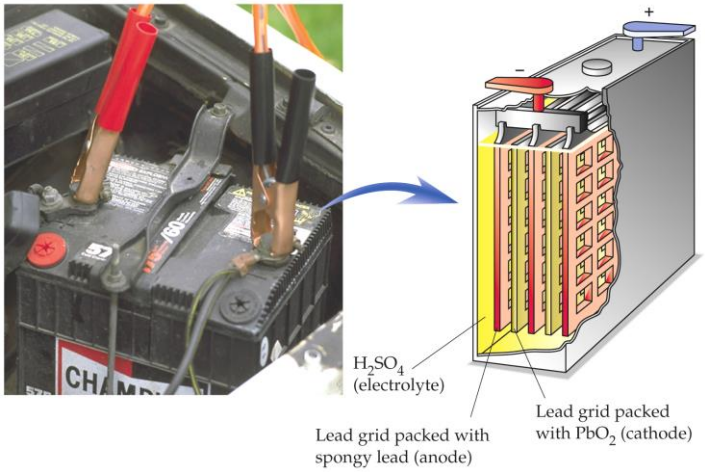


Figure 14. Lead-acid battery

Anode (*oxidation*): $Pb(s) + H_2SO_4(aq) \rightarrow PbSO_4(s) + 2H^+(aq) + 2e^-$

Cathode (*reduction*): $PbO_2(s) + H_2SO_4(aq) + 2H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

Overall cell reaction (*during discharge*):

$$PbO_2(s) + Pb(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l) \qquad E_{cell} = +2.1\ V$$

When the cell is ***recharged***, it uses electrical energy as an electrolytic cell (electrolysis) and the half-reactions and overall reaction are reversed.

Overall cell reaction (*during recharge*):

$$2PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + Pb(s) + 2H_2SO_4(aq)$$

(iv) Rechargeable lithium-ion battery used in cell phones, digital cameras and laptops

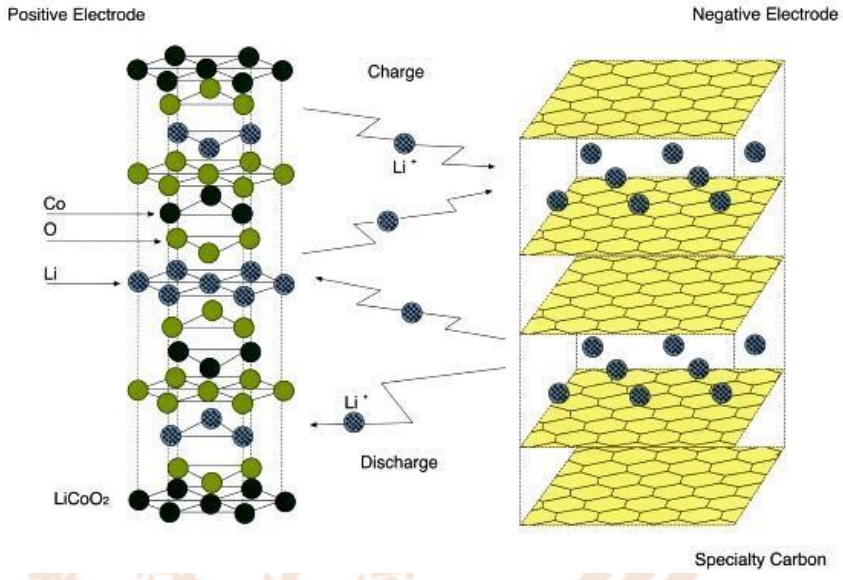


Figure 15. Lithium-ion battery

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Anode (*oxidation*): $Li(s) \rightarrow Li^+ + e^-$

Cathode (*reduction*): $Li^+ + CoO_2(s) + e^- \rightarrow LiCoO_2(s)$

Overall cell reaction (*during discharge*):

$Li(s) + CoO_2(s) \rightarrow LiCoO_2(s)$ $E_{cell} = +3.4$ V

During recharging, the half-reactions and overall reaction are reversed.

The anode (negative electrode) is made of a carbon material (usually graphite) with tiny spaces in its structure to hold both Li atoms and Li^+ ions. The cathode (positive electrode) is made of a transition metal oxide such as CoO_2, which can also hold Li^+ ions. Because of the high reactivity of lithium metal, a non-aqueous electrolyte (organic solvent) must be used. The advantage of the battery is that lithium has the most negative $E^{\ominus}$ and is the lightest metal. A lithium-ion battery can be recharged literally hundreds of times without deterioration.

4.3 Rusting (Application Example)

Paint protects iron and steel from corrosion as it prevents them from contacting directly with air. However, in many instances, part of the paint could be removed due to various reasons and it led to the bare metal being exposed. This result in the metal directly below the paint to rust as illustrated in the diagram below.

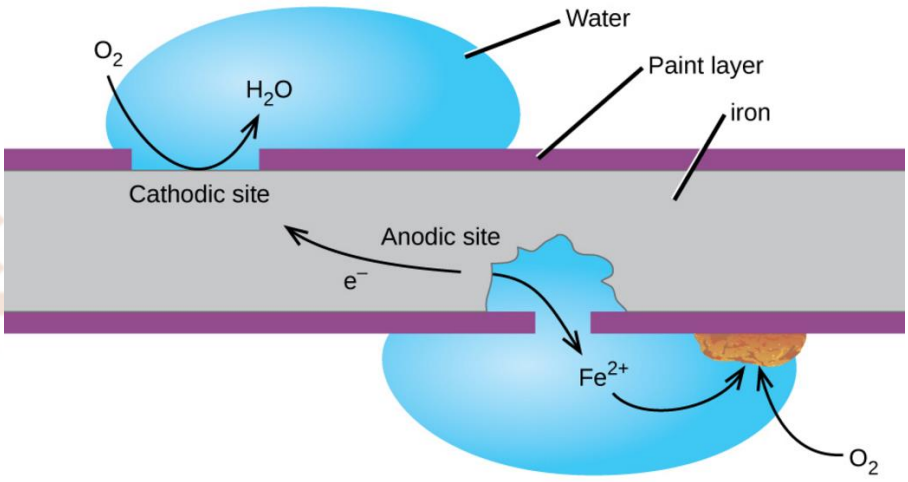


Figure 16. The corrosion of iron

The relevant equations involved in the cathodic and anodic sites are shown below:

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $E^{\ominus} = +1.23$ V

$Fe^{2+} + 2e^- \rightleftharpoons Fe$ $E^{\ominus} = -0.44$ V

The resultant E_{cell} is greater than 0 V, indicating a spontaneous reaction. The Fe^{2+} produced will be further oxidised by oxygen to produce Fe_2O_3, a form of rust.

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5 THE ELECTROLYTIC CELL

Electrolysis is a process that involves the splitting (or lysing) of a substance, often to its component elements, by supplying electrical energy. The cell in which electrolysis occurs is called the electrolytic cell.

The principle of an electrolytic cell (Figure 17) is the opposite of an electrochemical cell: the redox reaction is **non-spontaneous** and electrical energy (from an external source) is used to cause the reaction to occur, i.e. the cell **converts electrical energy to chemical energy**.

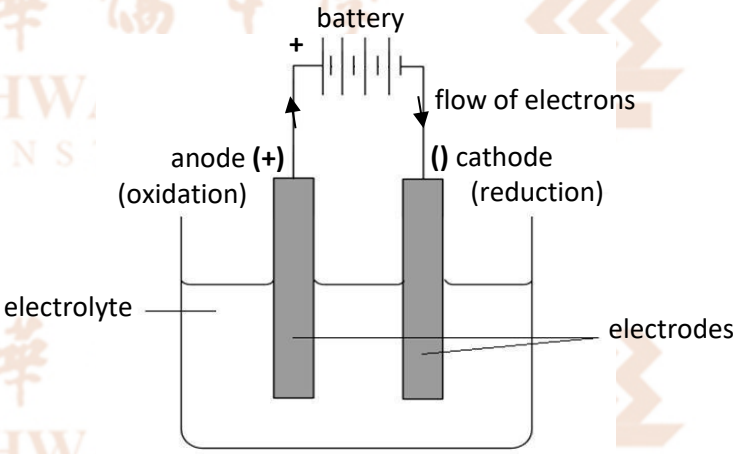


Figure 17. General set-up of an electrolytic cell

The **electrolyte** in the electrolytic cell is a liquid or an aqueous solution that can conduct electricity (due to presence of mobile ions). Examples: molten $PbBr_2$ or aqueous $CuSO_4$

Table 4 compares some features of an electrochemical cell and an electrolytic cell.

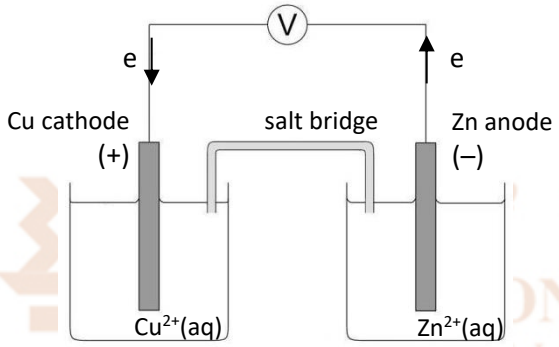
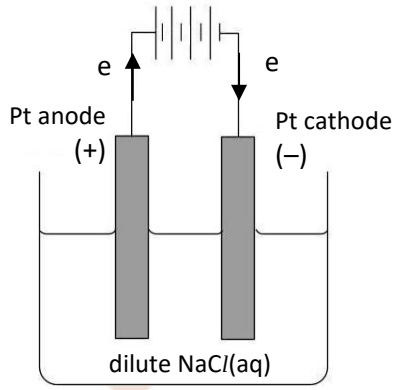
Electrochemical Cell chemical energy → electricity energy reaction is spontaneous	**Electrolytic cell** electricity energy → chemical energy reaction is non-spontaneous
Example: 	
Polarity of electrodes depends on the half-reaction: **C**a(**t**)hode: **P**ositive (**R**eduction) Anode: negative (oxidation)	Polarity of electrodes depends on the battery terminal: **C**athode: negative (reduction) **A**node: positive (oxidation)
Half-reactions: **A**node - oxid**A**tion, **C**athode - redu**C**tion	
Direction of electron flow in the external circuit: Anode to Cathode	

Table 4. Comparison of electrochemical cell and electrolytic cell

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In both cells, oxidation takes place at the anode and reduction takes place at the cathode. However, the **polarities of the electrodes are reversed**. To understand this, keep in mind the following:

- In an electrochemical cell, electrons are generated at the anode, so the anode is negative (having excess electrons), and electrons are consumed at the cathode, so the cathode is positive (lack of electrons).

- In an electrolytic cell, the electrons come from an external power source e.g. a battery, which *supplies electrons to* the **cathode**, so the cathode is **negative** (excess electrons), and *removes electrons from* the **anode**, so the anode is **positive** (lack of electrons).

6 PREDICTING THE PRODUCTS OF ELECTROLYSIS

LO12(m)part: predict the identity of the substance liberated during electrolysis from the state of electrolyte (molten or aqueous), position in the redox series (electrode potential) and concentration

In an electrolytic cell the cathode is negative so **cations** are attracted to the **cathode** and are **reduced**. On the other hand, the anode is positive so **anions** are attracted to the **anode** and are **oxidised**.

When there is more than one species that can be oxidised or reduced, the substance that is liberated at each electrode is the one that requires the least energy. This is called **selective discharge** which depends on:

- electrode potential, *E* values
  - At the **cathode**, the **reduction** of the species with the **more positive** (or less negative) electrode potential occurs.
  - At the **anode**, the **oxidation** of the species with the **more negative** (or less positive) electrode potential occurs.
- concentration of the ion (which affects the electrode potential (recall Section 3.4.1)
- nature of the electrode

6.1 Electrolysis of pure molten salts

Predicting the product at each electrode is simple if the salt contains one cation and one anion.

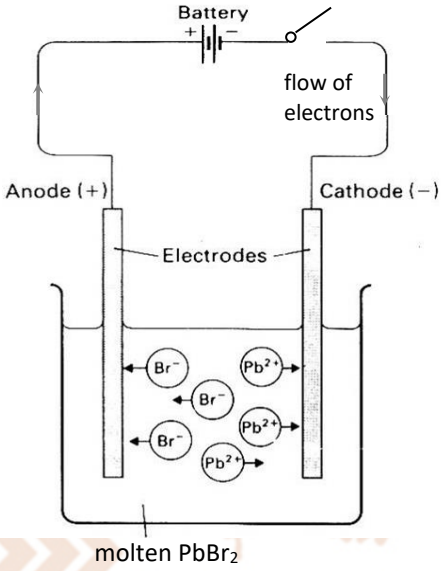


Figure 18. Electrolysis of molten $PbBr_2$

Consider the electrolysis of molten lead(II) bromide using inert platinum electrodes (Figure 18). The two species present are Pb^{2+} and Br^- ions.

The reactions that occur at the electrodes are:

Cathode (reduction): $Pb^{2+}(l) + 2e^- \rightarrow Pb(l)$

Anode (oxidation): $2Br^-(l) \rightarrow Br_2(g) + 2e^-$

Overall: $Pb^{2+}(l) + 2Br^-(l) \rightarrow Pb(l) + Br_2(g)$

At the cathode, beads of molten Pb will be deposited. At the anode, brown fumes of Br_2 gas will be seen.

FYI: m.p. of $PbBr_2$ = 373 °C, m.p. of Pb = 327 °C, b.p. of Br_2 = 58.8 °C

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Exercise 6.1

Predict the product formed at the anode, and at the cathode, when $MgCl_2(l)$ is electrolysed using inert electrodes. Explain your reasoning and write equations, including state symbols, for the electrode reactions.

Given: melting point of $MgCl_2$ = 714 °C, Mg = 650 °C

6.2 Electrolysis of dilute aqueous solutions

Aqueous salt solutions are mixtures of ions and water, so we have to compare the electrode potentials of the ions and water to predict the products at each electrode.

Water is a polar molecule so it can also be attracted to the electrodes and be discharged. In aqueous salt solutions, water is the solvent and present in large excess while the concentrations of H^+ and OH^- ions are very low (in pure water at 25 °C, $[H^+]$ and $[OH^-]$ are 10^{-7} mol dm^{-3} each). Hence, we consider the **reduction of H_2O** (not H^+) at the cathode and the **oxidation of H_2O** (not OH^-) at the anode. H^+ and OH^- ions are discharged only when the electrolyte contains aqueous acid or alkali respectively.

Consider the electrolysis of aqueous NaCl solution using platinum electrodes.

- At the **cathode** (negative electrode), the possible reduction and their electrode potentials are:

		$E^\ominus$/V
$Na^+ + e^- \rightleftharpoons$	Na	–2.71
$2H_2O + 2e^- \rightleftharpoons$	$H_2 + 2OH^-$	–0.83

  Since $E^\ominus$ (H_2O/H_2) is **more positive** than $E^\ominus$ (Na^+/Na), H_2O has a higher tendency to be reduced than Na^+ so H_2O is **preferentially reduced**.

  Reaction at cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

  Note: Cations of highly reactive metals e.g. Na^+ are not reduced in aqueous solution. H_2O is always reduced in preference.

- At the **anode** (positive electrode), the possible oxidation and their electrode potentials are:

	$E^\ominus$/V
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23

  Since $E^\ominus$ (O_2/H_2O) is **less positive** (or more negative) than $E^\ominus$ (Cl_2/Cl^-), H_2O has a higher tendency to be oxidised than Cl^- so H_2O is **preferentially oxidised**.

  Reaction at anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

  Overall reaction: $2H_2O(l) \rightarrow O_2(g) + 2H_2(g)$

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The above is effectively the electrolysis of water. Pure water is not used because very few ions are present to conduct the current ($[H^+] = [OH^-] = 10^{-7}$ mol dm^{-3}). The electrolyte used is often an aqueous solution like aqueous sodium chloride.

Exercise 6.2 (N2006/3/1a modified)

Predict the products formed at the anode, and at the cathode, when the following liquids are electrolysed using inert electrodes.

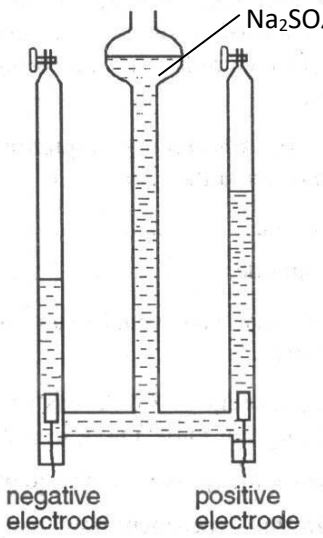
i) NaBr(aq)

ii) CuF_2(aq)

In each case explain your reasoning, using data from the *Data Booklet*. Write equations, including state symbols, for the electrode reactions.

Exercise 6.3 (J97/2/3a)

The electrolysis of aqueous sodium sulfate containing litmus indicator was carried out in the apparatus illustrated. Inert electrodes were used. After some time, the volumes of gas liberated were as shown in the diagram. The litmus in both electrode compartments had changed colour.



a) Write the appropriate ion-electron half-equations, with state symbols, for the changes which take place in each electrode compartment. Indicate whether oxidation or reduction has occurred.

The negative electrode:

The positive electrode:

b) Hence explain why the gas volumes are in the ratio 2:1.

c) State and explain the colour of the litmus around each electrode.

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6.3 Electrolysis of concentrated aqueous solutions

Ions which are present in high concentrations may be preferentially discharged even though its standard electrode potential suggests otherwise. This is because changes in concentration may affect the value of the electrode potential.

Consider the electrolysis of concentrated NaCl solution (brine) using platinum electrodes.

- At the **anode** (positive electrode), the possible oxidation and their electrode potentials are:

	$E^\ominus$ /V	
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36	------ (I)
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23	

The high Cl^- concentration in brine causes the position of equilibrium (I) to shift to the left. ***E*(Cl_2/Cl^-) decreases and becomes less positive than *E*$^\ominus$(O_2/H_2O)**. Thus, **Cl^- is preferentially oxidised** at the anode.

∴ Reaction at anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

Recall from Section 6.2 that when aqueous NaCl solution is electrolysed, H_2O is preferentially oxidised at the anode instead to give O_2.

- At the **cathode** (negative electrode), the possible reduction and their electrode potentials are:

	$E^\ominus$ /V
$Na^+ + e^- \rightleftharpoons Na$	–2.71
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	–0.83

Since *E*$^\ominus$(H_2O/H_2) is **more positive** (or less negative) than *E*$^\ominus$(Na^+/Na), H_2O is **preferentially reduced**.

∴ Reaction at cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

In this case, the difference between *E*$^\ominus$(Na^+/Na) and *E*$^\ominus$(H_2O/H_2) is too large, hence the effects of concentration is not enough to cause Na^+ to be reduced.

Overall reaction: $2Cl^-(aq) + 2H_2O(l) \rightarrow Cl_2(g) + H_2(g) + 2OH^-(aq)$

The electrolysis of brine is used in the industrial production of chlorine. In addition to chlorine, sodium hydroxide is also obtained as a useful by-product.

Overvoltage (Background Info)

The production of H_2 and O_2 by electrolysis often requires a greater voltage than is predicted by the standard electrode potentials. We say that H_2 and O_2 need an **overvoltage** before they are discharged. This overvoltage is required to overcome the high activation energy. Hence, in the electrolysis of brine, the overvoltage to form O_2 and the high $[Cl^-]$ makes it easier to form Cl_2.

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6.4 Electrolysis using active electrodes

Platinum and graphite (carbon) are **chemically inert**. They do not usually take part in the electrode reactions. However, there are electrodes which can undergo oxidation themselves if used as the **anode**. These are known as **reactive** or **active electrodes**.

(Note: Although graphite is inert, it may react with O_2 gas produced at the anode to form CO_2 and CO gases at high temperatures.)

Consider the electrolysis of $CuSO_4(aq)$ using **copper anode**.

- At the **anode** (positive electrode), the possible oxidation and their electrode potentials are:

	$E^\ominus$ /V
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2.01

Since $E^\ominus(Cu^{2+}/Cu)$ is the **least positive** among the three, Cu is **preferentially oxidised**. The copper anode dissolves and Cu^{2+} ions enter the solution.

∴ Reaction at anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

On the other hand, if the electrolysis of $CuSO_4(aq)$ is done using Pt electrodes, H_2O would be preferentially oxidised at the anode instead.

Exercise 6.4

a) Predict the reaction that occurs at each electrode when the following aqueous solutions are electrolysed using platinum electrodes.

electrolyte	equation for cathode reaction **(reduction)**	equation for anode reaction **(oxidation)**
i) dilute NaOH		
ii) dilute H_2SO_4		
iii) $AgNO_3(aq)$		
iv) a solution of $CaCl_2$ in dilute HNO_3		

b) Predict the reaction that occurs at each electrode when dilute H_2SO_4 is electrolysed using a platinum cathode and a brass (Cu/Zn alloy) anode.

equation for cathode reaction:

equation for anode reaction:

Remarks: $E^\ominus(Zn^{2+}/Zn)$ –0.76V is less positive than $E^\ominus(Cu^{2+}/Cu)$ +0.34V and $E^\ominus(O_2/H_2O/H_2)$ +0.40V

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7 CALCULATIONS IN ELECTROLYSIS

LO12(n): calculate: (i) the quantity of charge passed during electrolysis; (ii) the mass and/or volume of substance liberated during electrolysis

The amount of substance produced during electrolysis is directly proportional to the amount of electrons that is passed through the cell.

For example, if 2 moles of electrons are passed through a cell containing molten $PbBr_2$ (see Section 6.1), 1 mole of Pb and 1 mole of Br_2 will be formed at the cathode and anode respectively.

Cathode (reduction): $Pb^{2+}(l) + 2e^- \rightarrow Pb(l)$
Anode (oxidation): $2Br^-(l) \rightarrow Br_2(g) + 2e^-$

1 mole of electrons carries a charge equals to the **Faraday constant**, ***F***. Hence, the quantity of charge, Q, carried by n moles of electrons is equal to:

$$\mathbf{Q = n\,F}$$

where Q is the quantity of charge in coulombs (C)
n is the number of moles of electrons (mol)
F is the Faraday constant = **96 500 C mol^{-1}**

From the above, the **amount of substance** produced at each electrode during electrolysis is **directly proportional** to the **quantity of charge** that is passed through the cell. This is Faraday's law of electrolysis.

The quantity of charge passed through the cell depends on the magnitude of the current and the time the current flows:

$$\mathbf{Q = I\,t}$$

where Q is the quantity of charge in coulombs (C)
I is the current in amperes (A)
t is the time in seconds (s)

Hence, we can determine n (the number of moles of electrons passed through the cell) using I, t and F, and then use n and the half-equation to determine the mass or volume of substance produced at each electrode during electrolysis.

The mass or volume of substance produced **only depends on the magnitude of current (I) and the duration the current is passed (t)**. The mass or volume of substance produced does **not** depend on the concentration of the ions.

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Exercise 7.1 (Worked Example)

Calculate the quantity of charge (in coulombs) required to liberate 44.8 dm^3 of chlorine at s.t.p. in the electrolysis of molten sodium chloride using inert electrodes.

$2Cl^- \rightarrow Cl_2 + 2e^-$

$n(e^-)$ passed = $2 \times n(Cl_2)$ liberated = $2 \times \frac{44.8}{22.7} = 3.95$ mol

$Q = 3.95 \times 96500 =$ **$\underline{3.81 \times 10^5\ C}$**

Exercise 7.2

A technician needs to plate a bathroom fixture with 0.86 g of chromium from an electrolytic bath containing aqueous $Cr_2(SO_4)_3$. If he is expected to complete the job in 10 min, what would be the minimum current needed? (Assume the electroplating process is 100% efficient.)

[7.98A]

Exercise 7.3

A current of 0.025 A is passed through a solution of sulfuric acid for 4 hours using inert electrodes. Write equations for the electrode reactions and calculate the volume of gas formed at each electrode at r.t.p.

[0.0448 dm^3 H_2, 0.0224 dm^3 O_2]

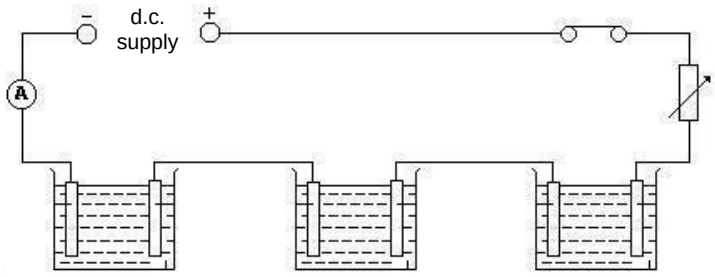
Exercise 7.4

An electric current is passed through solutions of copper(II) sulfate, silver nitrate and dilute sulfuric acid, connected in series for 20 min. Platinum electrodes are used. If 0.21 g of copper is deposited in the first cell, calculate the

a) mass of silver deposited in the second cell,

b) volume of hydrogen liberated, at r.t.p., in the third cell,

c) current passed.



	Cell 1	Cell 2	Cell 3
electrolyte	$CuSO_4(aq)$	$AgNO_3(aq)$	$H_2SO_4(aq)$
product at cathode	Cu(s)	Ag(s)	$H_2(g)$
product at anode	$O_2(g)$	$O_2(g)$	$O_2(g)$

[0.714g, 0.0794 dm^3, 0.532A]

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LO12(l): state the relationship, F = Le, between the Faraday constant, the Avogadro constant and the charge on the electron

The relationship between the Faraday constant, the Avogadro constant and the charge on an electron is:

$$F = Le$$

where L is Avogadro constant = 6.02×10^{23} = no. of electrons in 1 mol
e is the charge on one electron = 1.60×10^{-19} C

The above relationship allows us to determine a value for L or e by conducting an experiment to find a value for the Faraday constant.

Exercise 7.5

A current of 0.50 A was passed for 1 hour and 40 seconds, into an electrolytic cell containing aqueous silver nitrate as the electrolyte and silver as the electrodes. 2.0 g of silver was deposited on one of the electrodes. (A_r of Ag = 108; electronic charge, $e = -1.60 \times 10^{-19}$ C)

a) At which electrode was the silver deposited? What is the polarity of this electrode?

b) i) Calculate the quantity of charge passed (in coulombs).

ii) Using only the data provided and your answer in **b(i)**, calculate a value for the Avogadro number.

[1820 C, 6.14×10^{23}]

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Quantitative electrolysis and Generic Procedure for an Electrolysis experiment

Scenario:

To construct an electrolytic cell and determine a value for Avogadro constant, L, or Faraday constant, F.

Approach:

Set up the electrolytic cell using an external power source (usually a 6 V d.c. battery) and an ammeter. Measure the amount of substance discharged (by gas collection or by titration), or the change in mass of an electrode. Make sure the **polarities** of the electrodes are correct!

Below shows a generic procedure for an electrolysis experiment where the change in mass of electrode is measured.

Figure 19. Set up for the electrolysis of $CuSO_4$ (aq)

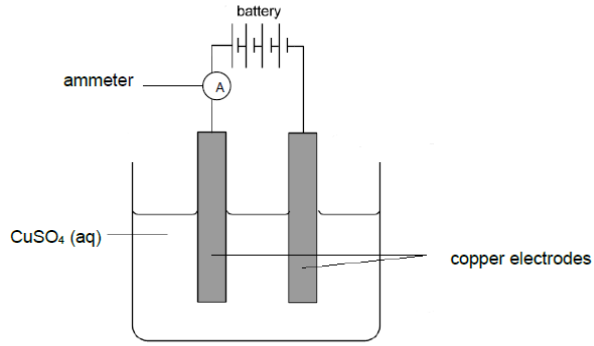
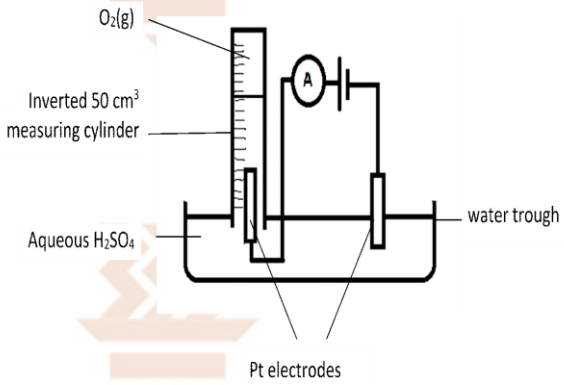


Figure 20. Set up for the electrolysis of water (acidified with sulfuric acid)



Generic procedure for an electrolysis experiment

1. Clean the _(metal)_ electrode(s) with sand paper to remove the oxide layer.
2. Wash the **anode** with water and then with ethanol, dry it and weigh it accurately. Record its initial mass, m_i. (The cathode is usually not used because some of the discharged metal may fall off from its surface).
3. Set up the electrolytic cell as shown in the diagram in Figure 2 (the electrodes must not come into contact with each other).
4. Close the circuit and start a stopwatch at the same time.
5. Record the initial current, I_i, shown on the ammeter.
6. At the end of _(30 min)_, record the final current reading, I_f, and break the circuit.
7. Remove the anode, wash it with water and then ethanol, dry it and reweigh it. Record its final mass, m_f.

- From the loss in mass of the anode, the mass and moles of metal lost can be deduced.
- From the average current and time, the charge which flowed through the circuit can be calculated using Q (in coulombs) = I (in A) x t (in s).
- From Q, the no of moles of electrons can be calculated, and this is linked to the Faraday constant by $Q = n(e^-) \times F$; and the Avogadro constant by $F = L \times e$ (the electronic charge).
- The amount of substance produced can also be measured by gas collection if a gas is produced (see Figure 3), or by titration of the electrolyte if the product enters the electrolyte. In the case of the latter, the electrolyte should be stirred thoroughly if a sample is to be withdrawn for titration.
- Sources of errors should be identified (e.g. high measurement error due to small changes in mass, or fluctuation in current) and suggestions made to limit / eradicate them. (e.g. use a longer time to get more mass loss to lower the percentage error, or use a variable resistor to fix the current throughout the duration of the experiment)

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8 APPLICATIONS OF ELECTROLYSIS

8.1 Electrolytic purification of copper

LO12(o)(ii): explain, in terms of the electrode reactions, the industrial process of: (ii) the electrolytic purification of copper

Copper is a good conductor of electricity, and is used extensively to make electrical wiring and components. The extraction of copper from copper ore is done by reduction with carbon. However, the copper produced is not pure enough for use as a conductor, so it is purified using electrolysis.

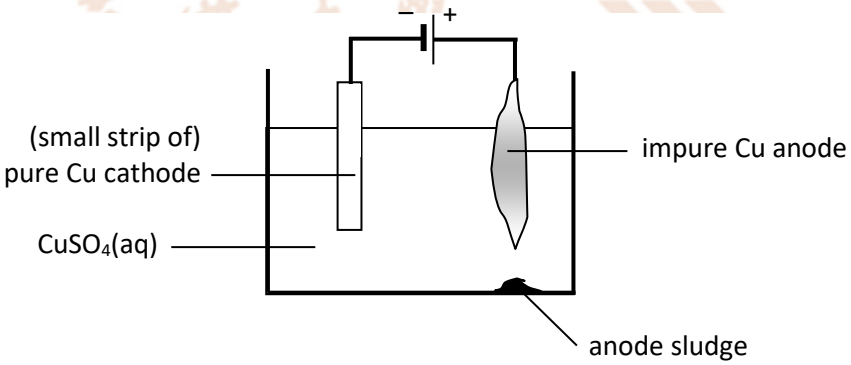


Figure 21. Set up for the electrolytic purification of copper

Electrolyte: $CuSO_4(aq)$
Anode: impure copper
Cathode: pure copper

During electrolysis, the voltage used is such that copper at the anode will be oxidised into Cu^{2+} ions.

Reaction at anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

- Metal impurities that have $E^\ominus$ values **less positive** than $E^\ominus(Cu^{2+}/Cu)$ are **more readily oxidised** than Cu. They will also be oxidised and enter the electrolyte as the **metal ions**.
- Metal impurities that have $E^\ominus$ values **more positive** than $E^\ominus(Cu^{2+}/Cu)$ will **not be oxidised** at the anode. These metals will stay as solid metal and eventually drop off as **anode sludge**.

At the cathode, the Cu^{2+} ions in the electrolyte are **preferentially reduced**. Hence more copper deposits onto the pure copper cathode.

Reaction at cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

- The metal ions that came from the metal impurities which dissolved at the anode have $E^\ominus$ values that are **less positive** than $E^\ominus(Cu^{2+}/Cu)$. These ions are **less easily reduced** than Cu^{2+} ions. They are not reduced and remain in the electrolyte.

Overall, there is a net transfer of copper from the impure copper anode to the cathode. The anode decreases in mass and the cathode increases in mass. Metal impurities that are above copper in the electrochemical series (e.g. Zn, Fe) will remain in the electrolyte as ions while those below copper in the series (e.g. Ag, Au) will form the anode sludge.

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Exercise 8.1: Electrolytic purification of copper

The conductivity of copper increases tenfold when it is more than 99.9% pure. Copper minerals often contain copper sulfide mixed with the sulfides of silver and zinc. After roasting in air to produce the oxides and reduction to the crude metals with carbon, the solid impure copper is purified by electrolysis.

With reference to $E^{\ominus}$ data, explain in detail the electrode reactions that take place during this electrolysis and how each of the two impurity metals (zinc and silver) is removed from the copper.

8.2 Anodising of Al

LO12(o)(i): explain, in terms of the electrode reactions, the industrial process of: (i) the anodizing of aluminium

Aluminium is a reactive metal that oxidises easily. However, aluminium objects are usually resistant to corrosion because when exposed to air, aluminium forms a layer of Al_2O_3 (about 10^{-6} cm thickness) on its surface. This oxide layer is resistant to corrosion and it acts as a protective layer which seals off the aluminium beneath it from further reaction.

Anodising of aluminium is a surface treatment to **increase the thickness of the corrosion resistant Al_2O_3(s) layer** on the surface of an aluminium object by **electrolysis**.

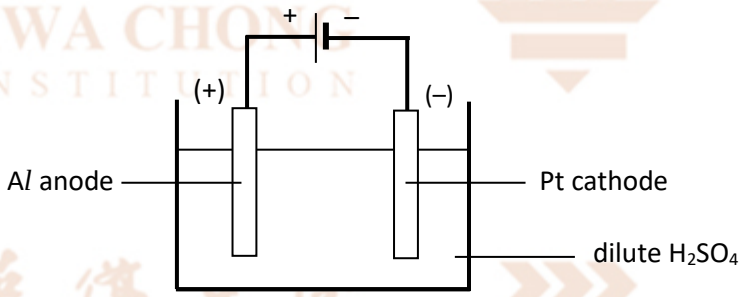


Figure 22. Anodising of aluminium

Electrolyte: dilute H_2SO_4
Anode: aluminium object to be anodised
Cathode: Pt or graphite

The reactions occurring at each electrode are:

Reactions at anode : $2Al(s) + 3H_2O(l) \rightarrow Al_2O_3(s) + 6H^+(aq) + 6e^-$

Reaction at cathode : $2H^+(aq) + 2e^- \rightarrow H_2(g)$

The Al_2O_3 layer formed this way is porous. The pores are then sealed by dipping the aluminium object in hot water. Because of the way it is formed, the oxide coating is porous enough to accept and hold dyes that would not otherwise stick to aluminium. Since the thickness of the deposit of aluminium oxide increases with electrolysis time, the amount of dye deposited and the intensity of colour developed also increase with electrolysis time. Anodised objects can therefore be decorative. Anodised aluminium can be used to make window frames, drink cans and iPad cases.

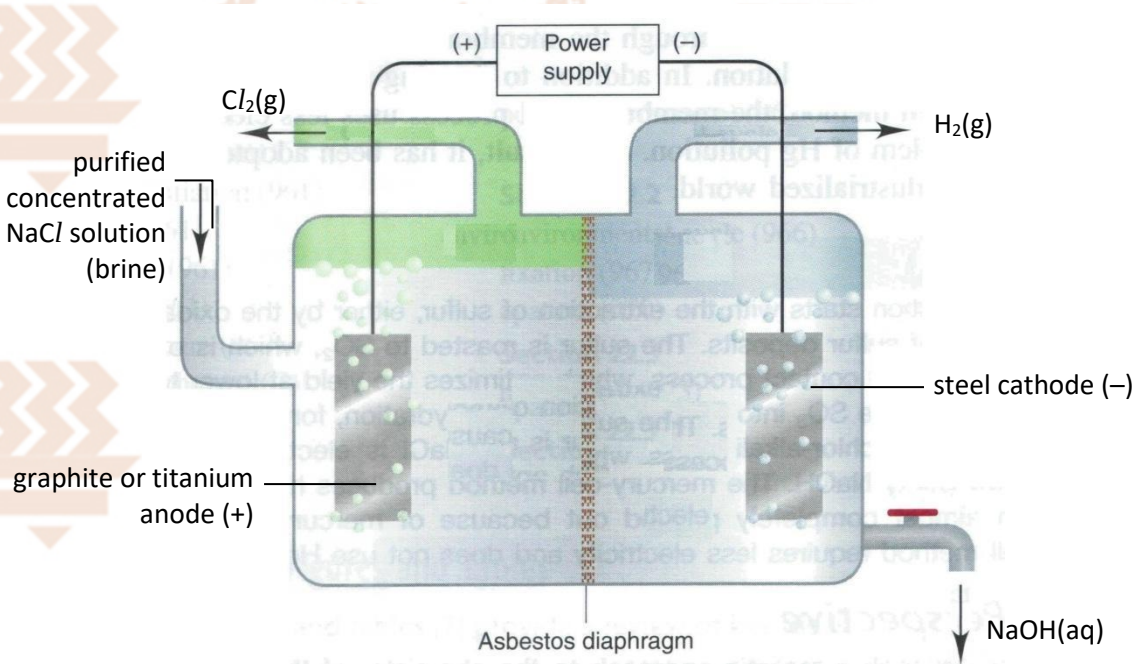


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Exercise 8.2: Manufacture of NaOH and NaClO by electrolysis of brine [modified from N05/2/2]

The diagram below shows the diaphragm cell used for the electrolysis of concentrated sodium chloride solution (brine). This is a commercially important industrial process used to manufacture chlorine gas, hydrogen gas and aqueous sodium hydroxide. The overall process is represented by the equation:

$$2NaCl(\text{concentrated}) + 2H_2O(l) \xrightarrow{\text{electrolysis}} 2NaOH(aq) + Cl_2(g) + H_2(g)$$



a) With reference to $E^{\ominus}$ data, explain why the electrolysis of dilute NaCl produces mainly oxygen gas at the anode, whereas the electrolysis of concentrated NaCl solution produces mainly chlorine gas.

b) The sodium hydroxide made in the diaphragm cell is formed in aqueous solution. Suggest with the aid of an appropriate half-equation, how sodium hydroxide is obtained in the process.

c) In the diaphragm cell, the anode is made of titanium and the cathode is made of steel. Suggest why steel is never used for the anode.

d) The Asbestos diaphragm prevents a negative ion produced in the cathode compartment from moving into the anode compartment, because that negative ion may be oxidised in preference over Cl^- at the anode.

(i) Using the *Data Booklet*, write an equation that shows how this negative ion may be oxidised.

(ii) Explain why this negative ion may be more readily oxidised than Cl^-.

e) Suggest one large-scale use for each of the following products.

f) The Asbestos diaphragm is removed and the contents of the cell are stirred so that Cl_2 reacts with NaOH to form NaCl and NaClO (bleach). The cell is kept cold. Construct a balanced equation for this disproportionation reaction.

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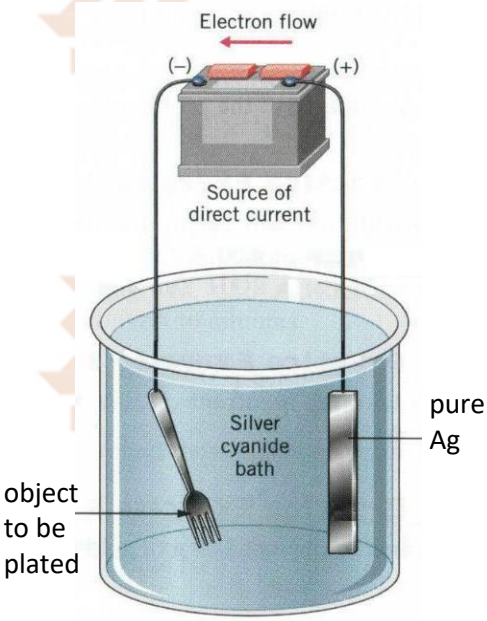
Exercise 8.3: Electroplating

a) In silver plating, an aqueous solution containing $[Ag(CN)_2]^-$ ions is used. This is a stable complex and produces a very low concentration of $Ag^+(aq)$ ions.

$$[Ag(CN)_2]^-(aq) \rightleftharpoons Ag^+(aq) + 2CN^-(aq)$$

i) Write an equation, including state symbols, for the cathode reaction.

ii) Suggest why a very low concentration of Ag^+ is used.



b) (J99/1/3c) In order to replace the worn silver coating on a trophy, it is estimated that 0.50 g of silver needs to be electroplated onto it. Calculate the length of time that a current of 0.20 A has to be passed through the electrolysis bath in order to achieve this.

[2240s (3 sf)]

LOOKING AHEAD

In this topic, you learnt how the standard electrode potential, $E^\ominus$, is a measure of the ease of reduction of an atom or ion. The difference between two electrode potentials gives rise to a cell potential, $E^\ominus_{cell}$, the magnitude and sign of which indicates the spontaneity of a reaction. In electrolysis, we can control the products obtained by choosing appropriate conditions such as concentration and electrodes used. In the next few topics such as Group 2 and Group 17, we will use $E^\ominus$ values to explain the relative reactivity of Group 2 elements as reducing agents and Group 17 elements as oxidising agents. In the topic of Transition Elements, we will use the position of the ion or substance in the electrochemical series to select a suitable homogeneous catalyst. We will also use $E^\ominus$ values to explain redox processes in QA experiments.

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21 Periodicity

GUIDING QUESTIONS

- What are the trends and variations in physical and chemical properties in elements and compounds?
- How can the trends and variations in atomic / physical / chemical properties be explained?
- How can we predict the properties of elements and their compounds?

LEARNING OUTCOMES

Students should be able to:

5(a) recognise variation in the electronic configurations across a Period and down a Group. (Refer to Topic 1 Atomic Structure & Physical Periodicity)

5(b) describe and explain qualitatively the trends and variations in atomic radius, ionic radius, first ionisation energy and electronegativity,

i. across a Period in terms of shielding and nuclear charge,

ii. down a Group in terms of increasing number of electronic shells and nuclear charge

(Refer to Topic 1 Atomic Structure & Physical Periodicity)

5(c) interpret the variation in melting point and in electrical conductivity across a Period in terms of structure and bonding in the elements (metallic, giant molecular, or simple molecular) (Refer to Topic 2 Chemical Bonding)

5(d) describe and explain the trend in volatility of the group 17 elements in terms of instantaneous dipole-induced dipole attraction (Refer to Topic 2 Chemical Bonding)

5(e) for elements across the third period:

(i) state and explain the variation in the highest oxidation number of the elements in oxides (for Na_2O; MgO; Al_2O_3; SiO_2; P_4O_{10}; SO_3) and chlorides (for NaCl; $MgCl_2$; $AlCl_3$; $SiCl_4$; PCl_5)

(ii) state and explain the variation in bonding in oxides and chlorides in terms of electronegativity (with the exception of $AlCl_3$)

(iii) describe the reactions of the oxides with water (for Na_2O; MgO; Al_2O_3; SiO_2; P_4O_{10}; SO_3)

(iv) describe and explain the acid/base behaviour of oxides (for Na_2O; MgO; Al_2O_3; SiO_2; P_4O_{10}; SO_3) and hydroxides (for NaOH; $Mg(OH)_2$; $Al(OH)_3$), including, where relevant, amphoteric behaviour in reaction with sodium hydroxide (only) and acids

(v) describe and explain the reactions of the chlorides with water (for NaCl; $MgCl_2$; $AlCl_3$; $SiCl_4$; PCl_5)

(vi) suggest the types of structure and bonding present in the oxides and chlorides from observations of their chemical and physical properties

5(f) describe and deduce from $E^{\ominus}$ values the relative reactivity of elements of:

(i) Group 2 as reducing agents;

(ii) Group 17 as oxidising agents

5(g) describe and explain the trend in thermal stability of:

(i) Group 2 carbonates in terms of the charge density of the cation and the polarisability of the large anion

(ii) Group 17 hydrides in terms of bond energies

5(h) predict the characteristic properties of an element in a given Group by using knowledge of chemical periodicity

5(i) deduce the nature, possible position in the Periodic Table, and identity of unknown elements from given information of physical and chemical properties

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REFERENCES

1. Peter Cann & Peter Hughes (2015), *Chemistry*, Hodder Education, Chapters 10 and 11.
2. Martin S. Silberberg, *Chemistry – The Molecular Nature of Matter and Change*, 6th Edition, McGraw-Hill, Chapter 8

LOOKING BACK

In this topic, we will study the trends in chemical properties of elements and their compounds. It is essential to recall knowledge from earlier topics on Atomic Structure & Physical Periodicity and Chemical Bonding: ionisation energy trends and electronegativity have an impact on the types of the bonding found in compounds, and this will in turn affect their physical properties. To explain chemical properties and trends, concepts on redox reactions, electrode potential and acid-base behaviour are also relevant.

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1 INTRODUCTION

LO 5(a): Recognise variation in the electronic configurations across a Period and down a Group.

Periodicity is the study of repeating patterns in the physical and chemical properties of the elements in the periodic table.

The arrangement in the periodic table is closely related to the electronic configuration of the elements.

- In the periodic table, elements are arranged in order of <u>increasing proton number</u>.

Prior to 1913, Mendeleev's Periodic Table, which arranged elements according to *atomic mass*, was widely accepted by chemists though there were inconsistencies. Then in 1913, Henry Moseley, using new technology (X-ray electron gun) at that time, showed the link between *atomic number* and element's position in the table, which addressed the inconsistencies and led to the Periodic Table we use today.



Figure 1. Dalton's original table of elements

Table 1. Some trends in Period 3 elements

Element	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
	metal	metal	metal	metalloid	non-metal	non-metal	non-metal	non-metal
Electronic structure	[Ne] $3s^1$	[Ne] $3s^2$	[Ne] $3s^2\,3p^1$	[Ne] $3s^2\,3p^2$	[Ne] $3s^2\,3p^3$	[Ne] $3s^2\,3p^4$	[Ne] $3s^2 3p^5$	[Ne] $3s^2\,3p^6$
No. of valence electrons	1	2	3	4	5	6	7	8
Group	1	2	13	14	15	16	17	18
Period	3	3	3	3	3	3	3	3
Electrical conductivity	good conductors			semi-conductor	non-conductors			

- Elements in the <u>same group</u> resemble one another in their chemical properties due to their <u>similar outer electronic configuration</u>. The group number of groups 1 and 2 is the same as the number of <u>valence electrons</u>. The group number of groups to the right of the *d*-block elements can be remembered by adding 10 to the number of valence electrons in each group.

- The <u>period</u> number is the same as the <u>number of quantum shells</u>. Elements in the same period show a periodic change in their chemical and physical properties across the period.

Thus, knowledge of periodicity is useful in understanding and predicting the physical and chemical behaviour of elements.

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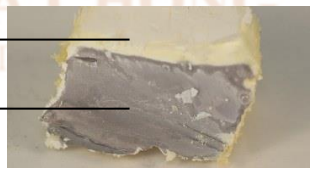
2 CHEMICAL PROPERTIES OF THE ELEMENTS (Background Info)

The following table describes the chemical properties of Period 3 elements and their common uses:

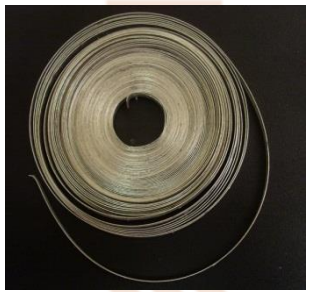


Sodium stored in oil

Na
Sodium
Soft silvery metal
Must be stored in oil to prevent oxidation by air



In air, sodium quickly forms a layer of oxide



Roll of magnesium ribbon

Mg
Magnesium
Often cut into magnesium ribbon strips (left)

Tarnishes (forms oxide) in air, but much less readily than sodium

Magnesium burns with a bright white light, and hence is often used to make fireworks.



Magnesium fireworks



Aluminium foil

Al
Aluminium
The metal instantly protects itself in air by forming a thin, but tough, layer of aluminium oxide, Al_2O_3, which is harder than the metal itself.

The toughness of the oxide layer, and the relatively low density of the metal combine to give it an unbeatable strength to weight ratio.



Lightweight sunglasses frame made from aluminium





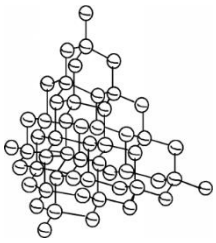
Aluminium is tough and lightweight, making it perfect for use in the transport and packaging industries.



Crystalline silicon has a shiny reflective surface

Si
Silicon
Shiny black metalloid solid

Does not react with air at room temperature.



Structure of silicon



The silicon chip revolutionised electronics

Because silicon is a semiconductor, one of its most important uses is in electronics.

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P

Phosphorus

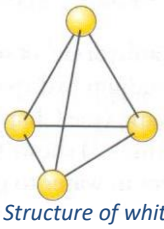
Phosphorus exists as several allotropes. The most common are white and red phosphorus.

White phosphorus with a corner sliced off



White phosphorus stored under water

White Phosphorus, P_4, is a very reactive waxy solid which generally must be stored under water.



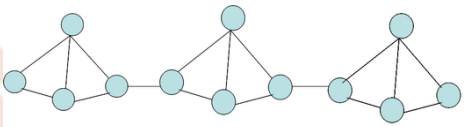
Structure of white phosphorus, P_4

Due to bond angle strain (as the P-P-P bond angle is more acute), it catches fire spontaneously in air.



Red Phosphorus, P, is polymeric and appears as a red powder.

Because of the network of linked P atoms, it is much more stable than white phosphorus.





However, it still reacts with air when given enough energy (heating or striking). A common use of red phosphorus is in matches!

Note: In this chapter, we will concentrate on the reactions of white phosphorus P_4.

S

Sulfur

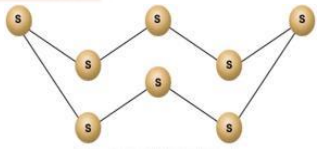
Bright yellow crystalline solid

Pure sulfur is an odourless non-metal.



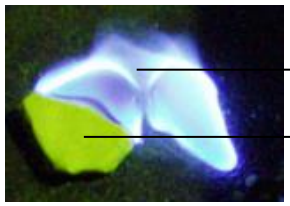
The characteristic smell associated with sulfur is due to its compounds rather than pure sulfur itself.

Elemental sulfur has many different allotropes, but cyclic S_8, is the most common.

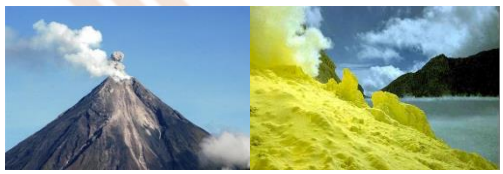


Structure of S_8

Sulfur burns with a blue flame, to form sulfur dioxide



Sulfur combusting



Elemental sulfur can be found near hot springs and volcanoes.



Cl

Chlorine

Chlorine is a yellow-green toxic gas with a distinctive "bleach" smell.

It exists as diatomic Cl_2 molecules.

Chlorine is a strong oxidising agent that reacts with almost every element to form chlorides. However, it does not react directly with oxygen.



Plasma globe with a pure argon atmosphere

Ar

Argon

Argon is a colourless inert gas. It appears violet when placed in a high voltage electric field (as in the plasma globe to the left).

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Exercise 2.1

1 Which of the following statements about the properties associated with ionic and covalent compounds is correct?

A The only covalent compounds with high melting points are those in which hydrogen bonding occurs.

B Any compound that contains both hydrogen and oxygen atoms in its molecule can form hydrogen bonds.

C Ionic bonds and covalent bonds cannot both occur in the same compound.

D Ionic compounds differ from metals in that ionic compounds do not conduct electricity in the solid state.

[PromoHCl09/P1/Q5]

2 The bond in the compound **XY** is likely to be ionic rather than covalent if

1 **X** is a large cation

2 **Y** is a small anion

3 **X** has a large positive charge

[PromoTJC12/P1/Q17]

3 ***W***, ***X***, ***Y*** and ***Z*** are elements in Period 3.

W has greater electrical conductivity than ***Y*** but lower first ionisation energy than ***X***. ***Y*** has higher melting point than ***W***, and ***Z*** has a greater atomic radius than ***W***.

Based on this information, which of the following is a possible arrangement of these elements in increasing proton number?

A ***W, X, Y, Z***

B ***X, Y, W, Z***

C ***Y, X, Z, W***

D ***Z, W, Y, X***

[PrelimDHS12/P1/Q14]

4 State and explain the trend in the electrical conductivity across Period 3 elements, from Na to Al.

5 State and explain the trend in the melting point across Period 3 elements, from P to Ar.

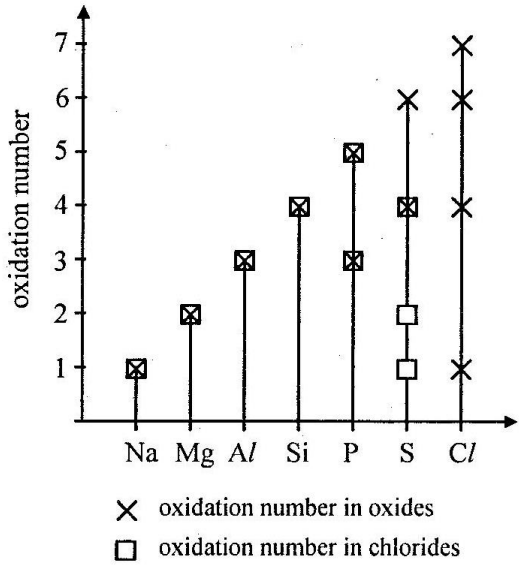
melting [illegible] ed by P_4,

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3 VARIATION IN OXIDATION NUMBER OF PERIOD 3 OXIDES AND CHLORIDES

LO 5(e)(i): for elements across the third period: state and explain the variation in the highest oxidation number of the elements in oxides (for Na_2O; MgO; Al_2O_3; SiO_2; P_4O_{10}; SO_3) and chlorides (for NaCl; $MgCl_2$; $AlCl_3$; $SiCl_4$; PCl_5)

The following diagram and table summarise the oxidation numbers that are found in the oxides and chlorides of Period 3 elements.



Period 3 element	**Na**	**Mg**	**Al**	**Si**	**P**		**S**	
Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_6	P_4O_{10}	SO_2	SO_3
O.N. in oxides	+1	+2	+3	+4	+3	+5	+4	+6
Chloride	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	PCl_5		
O.N. in in chlorides	+1	+2	+3	+4	+3	+5		

Note: Sulfur chlorides and chlorine oxides are not in the syllabus.

A few trends can be observed across the period:

- Oxidation numbers of the elements in their oxides are always positive (except for fluorine, where O.N. of F is −1 in F_2O) as oxygen is the most electronegative element other than fluorine.
- From Na to Cl, there is a regular increase in the number of O and Cl atoms that can combine with an atom of the element.
- The maximum positive oxidation number shown by an element often corresponds to the number of valence electrons in an atom of the element.
    - e.g. phosphorus has 5 valence electrons and thus has a maximum oxidation number of +5
- From left to right, the elements show **increasing variation** in possible oxidation numbers: e.g.
    - In their oxides and chlorides, the metals Na, Mg and Al display **only one** possible oxidation number each, corresponding to the loss of all their valence electrons.
    - P, S and Cl exhibit a wider range of oxidation numbers because they can **expand their octets** (by utilising their vacant *d*-orbitals, which are close enough in energy to their valence electrons to be used for chemical bonding as well). The oxidation number thus depends on the number of electrons used for bonding.

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4 PROPERTIES OF THE OXIDES

4.1 Structure and bonding of the oxides

LO 5(e)(ii): state and explain the variation in bonding in oxides in terms of electronegativity

The trends in physical properties of the oxides can be explained by the gradual change in their structures and bonding.

Formula of oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3
Structure	giant ionic lattice structure (with increasing covalent character from left to right)			giant molecular lattice structure	simple, discrete covalent molecules	
Bonding	strong electrostatic forces of attraction between oppositely-charged ions			strong covalent bonds between atoms	weak intermolecular forces between molecules	

As we move across the period, the bonding of the oxides changes from ionic to covalent.

- This is because the difference in electronegativity between each element and oxygen decreases across the period, hence bonding becomes increasingly covalent. Recall from Topic 2 Chemical Bonding that covalent bonds usually form between atoms of similar electronegativity while atoms with a great difference in electronegativity tend to form ionic bonds. The difference in electronegativity can help us predict if the compound is predominantly ionic or covalent.

4.2 Trend in melting points of the oxides

The trend in melting points of the oxides across the period can be explained by the structure and bonding involved in each oxide.

Formula of oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3
Physical state at 25 °C	solid	solid	solid	solid	solid	liquid
Melting point (°C)	1130	2850	2070	1700	sublimes at 360	17

- Na_2O, MgO and Al_2O_3 are all ionic oxides:
  - (Structure) giant ionic lattice with
  - (Bonding) strong electrostatic forces of attraction between oppositely charged ions
  - A large amount of energy is required to overcome the strong ionic bonds ⇒ high m.p.

Recall in Topic 2 Chemical Bonding that lattice energy gives an indication of the strength of the ionic bonding – the larger the magnitude of L.E., the stronger the ionic bonding. For ionic compounds, this means a higher m.p.

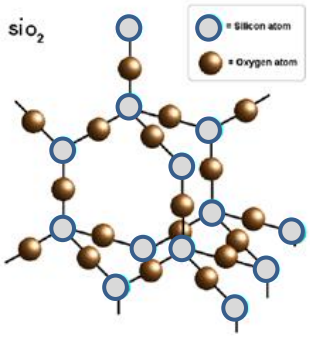
$$\text{Lattice energy } \alpha \frac{q_+ \times q_-}{r_+ + r_-}$$

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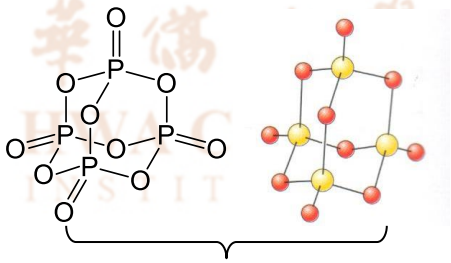
- Melting point of MgO is higher than that of Na_2O:
  - Mg^{2+} has smaller ionic radius and higher charge than Na^+
  - Thus, lattice energy of MgO is much greater in magnitude than that of Na_2O.
  - More energy is required to overcome the electrostatic forces of attraction between Mg^{2+} and O^{2-} than in the Na_2O lattice.

- Melting point of Al_2O_3:
  - Although the lattice energy expression predicts the L.E. of Al_2O_3 to be larger in magnitude than that of MgO, m.p. of Al_2O_3 is actually lower than that of MgO.
  - Possible reason for Al_2O_3 having lower m.p. than MgO:
    - Al^{3+} has very high charge density which can polarise the O^{2-} ion (even though O^{2-} is small and normally not easily polarized) $\Rightarrow$ this confers covalent character to Al_2O_3, which causes magnitude of L.E. to differ from expected.

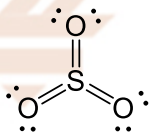
- Melting point of silicon dioxide (also called silicon(IV) oxide), SiO_2:
  - (Structure) giant molecular structure (resembling that of diamond) with
  - (Bonding) strong covalent bonds between Si and O atoms. Each Si atom is bonded to four O atoms, and each O atom is bonded to two Si atoms.
  - A large amount of energy is required to break the strong covalent bonds $\Rightarrow$ high m.p.



- Oxides of phosphorus and sulfur:
  - (Structure) simple discrete covalent molecules with
  - (Bonding) relatively weak intermolecular dispersion forces between molecules
  - Comparatively less energy is required to overcome these weaker dispersion forces $\Rightarrow$ lower m.p.



Structure of P_4O_{10}



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4.3 Acid-base behaviour of the oxides and hydroxides

LO 5(e)(iii): describe the reactions of the oxides with water
(iv): describe and explain the acid/base behaviour of oxides, including, where relevant, amphoteric behaviour in reaction with sodium hydroxide (only) and acids
(vi): suggest the types of structure and bonding present in the oxides from observations of their chemical and physical properties
LO 5(h): predict the characteristic properties of an element in a given Group by using knowledge of chemical periodicity
LO 5(i): deduce the nature, possible position in the Periodic Table, and identity of unknown elements from given information of physical and chemical properties

From their structure and bonding, the oxides of Period 3 elements can be classified into ionic oxides and covalent oxides. Ionic oxides tend to act as bases whereas covalent oxides act as acids. Oxides of elements that are near the ionic/covalent boundary tend to form amphoteric oxides - i.e. oxides that can act as acids or bases depending on the conditions.

This section will also cover the acid-base behaviour of the three metal hydroxides, NaOH, $Mg(OH)_2$ and $Al(OH)_3$.

- **Ionic oxides** contain the O^{2-} ions in their ionic lattice. The O^{2-} ions readily hydrolyse in water to form OH^- ions. Hence, ionic oxides tend to be **basic** in nature:

$$O^{2-}(aq) + H_2O(l) \rightarrow 2OH^-(aq)$$

- **Covalent oxides** are usually classified as **acidic** oxides because they form acidic solutions when reacted with water, producing H_3O^+ and an oxo-anion (i.e. a negatively charged ion containing the element covalently bonded to a number of oxygen atoms, e.g. SO_4^{2-} and PO_4^{3-}). [Refer to section 4.3.5 on the acidic oxides]

- Aluminium oxide is the only **amphoteric** oxide in Period 3. [Refer to section 4.3.3 for definition of 'amphoteric']

Table 2. Summary list of Period 3 oxides, their bonding and their acid-base nature

	Na	Mg	Al	Si	P	S
Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10} *P_4O_6	SO_3 *SO_2
Bonding	ionic			covalent		
Nature	basic		amphoteric	acidic		

*Note: The behaviour and reactions of P_4O_6 and SO_2 are not in the syllabus.

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4.3.1 The basic oxides

Sodium oxide and magnesium oxide both react with water and acids, as shown in the table below.

Oxide	Reaction with water	Reaction with acids
Na_2O	**Observation** • appears to dissolve completely in water • vigorous and exothermic reaction, even in cold water • forms a strongly alkaline colourless solution around **pH 13** (depending on concentration) **Equation** $Na_2O_{(s)} + H_2O_{(l)} \rightarrow 2Na^+_{(aq)} + 2OH^-_{(aq)}$	**Observation** • dissolves in acids • reaction is exothermic • reaction produces a salt solution **Equation** $Na_2O_{(s)} + 2H^+_{(aq)} \rightarrow 2Na^+_{(aq)} + H_2O_{(l)}$
MgO	**Observation** • very slow reaction and limited solubility in water, may appear as though nothing is happening • some magnesium hydroxide is formed but it is only sparingly soluble, so not all hydroxide ions formed are released into the solution ⇒ pH is lower than for Na_2O, around **pH 9** **Equations** $MgO_{(s)} + H_2O_{(l)} \rightarrow Mg(OH)_{2(s)}$ $Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2OH^-_{(aq)}$	**Observation** • dissolves in acids • reaction produces a salt solution **Equation** $MgO_{(s)} + 2H^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_2O_{(l)}$

4.3.2 The basic hydroxides

Both sodium and magnesium hydroxides contain the hydroxide ion, OH^-, which is a strong base. Thus, they are basic hydroxides, and can react with acids to form salt solutions in a classic neutralisation reaction.

		Reaction with acids (e.g. dil. hydrochloric acid)	
Hydroxide	**Appearance**	**Observation**	**Equation for the neutralisation**
NaOH	White pellets when solid	Solid dissolves exothermically to give a colourless solution	$NaOH_{(s)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$
	Colourless solution when dissolved in water	No visible change, but resultant mixture becomes warmer (exothermic reaction)	$NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$
$Mg(OH)_2$	White solid/ppt only sparingly soluble in water	Solid/ppt dissolves in acids to give a colourless solution	$Mg(OH)_{2(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + 2H_2O_{(l)}$

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4.3.3 The amphoteric oxide – Aluminium oxide

Aluminium oxide is an ionic oxide containing Al^{3+} and O^{2-} ions. However, the high charge density of the Al^{3+} ion gives it great polarizing power, allowing the O^{2-} ion to be slightly polarized, despite its small size. This confers some covalent character to the oxide.

This mixture of ionic and covalent character allows Al_2O_3 to display both basic and acidic properties - i.e. it is amphoteric.

Oxide	Reaction with water	Reaction with acids	Reaction with strong bases (sodium hydroxide)
Al_2O_3	**Observation** No reaction in water (insoluble)	**Observation** • dissolves in acids to form a salt solution, with Al^{3+} as the cation **Equation** when reacting as a basic oxide: $Al_2O_{3\,(s)} + 6H^+_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3H_2O_{(l)}$	**Observation** • dissolves in **excess** base to form a salt solution with the Al being part of the anion, the colourless aluminate complex ion, $[Al(OH)_4]^-$. **Equation** when reacting as an acidic oxide: $Al_2O_{3\,(s)} + 2OH^-_{(aq)} + 3H_2O_{(l)} \rightarrow 2[Al(OH)_4]^-_{(aq)}$ aluminate ion

4.3.4 The amphoteric hydroxide – Aluminium hydroxide

Just like aluminium oxide, aluminium hydroxide is also amphoteric.

- With acids, it reacts just like sodium and magnesium hydroxides, dissolving to form a colourless salt solution of the metal cation, Al^{3+}.
- With strong bases like sodium hydroxide, the hydroxide shows its acidic nature and reacts to form the aluminate anion.

Hydroxide	Appearance	Reaction with acids	Reaction with strong bases (sodium hydroxide)
$Al(OH)_3$	White solid/ppt insoluble in water	**Observation** • dissolves readily in acids to form a colourless salt solution, with Al^{3+} as the cation **Equation** $Al(OH)_{3\,(s)} + 3HCl_{(aq)} \rightarrow AlCl_{3(aq)} + 3H_2O_{(l)}$ salt solution	**Observation** • dissolves in **excess** strong base to form the colourless aluminate complex ion, $[Al(OH)_4]^-$. **Equation** $Al(OH)_{3\,(s)} + NaOH_{(aq)} \rightarrow Na[Al(OH)_4]_{(aq)}$ salt solution

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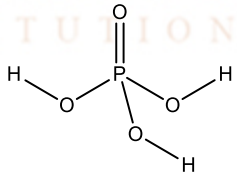
4.3.5 The acidic oxides

As we move across the period, the electronegativity difference between each element and oxygen becomes too small for ionic bonds to form. The remainder of the oxides in Period 3 are thus all covalent in nature.

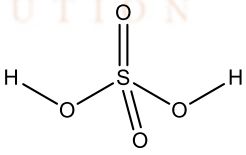
- Silicon dioxide, SiO_2, is a macromolecular (i.e. giant covalent) oxide that does not contain the O^{2-} ion and hence shows no basic properties at all. It is, however, weakly acidic in nature, and may react with strong bases, usually requiring more vigorous conditions (e.g. higher concentrations, temperatures, or pressures) to help in breaking up the macromolecular lattice.

Oxide	Reaction with water	Reaction with strong bases
SiO_2	**Observation** • does not dissolve in/react with water	**Observation** • no reaction with hot aqueous bases (e.g. NaOH) under laboratory conditions • usually requires hot and concentrated strong bases before reaction proceeds • a solution of the silicate salt, SiO_3^{2-}, is formed **Equation** $SiO_{2\,(s)} + 2\,OH^-_{(conc)} \xrightarrow{\Delta} SiO_3^{2-}{}_{(aq)} + H_2O_{(l)}$ silicate ion (colourless)

- The oxides of phosphorus and sulfur (and even those of chlorine, though not in the syllabus), are all simple covalent oxides which readily react with water to form acidic solutions.

Oxide	Reaction with water	Reaction with strong bases
P_4O_{10}	phosphorus(V) oxide **Observation** • reacts violently with water to give an acidic solution of H_3PO_4 • forms a fairly strongly acidic solution around **pH 2** (depending on concentration) Phosphoric(V) acid, H_3PO_4, is a triprotic acid, slightly weaker than H_2SO_4. Structure of an undissociated molecule of H_3PO_4:  **Equation** $P_4O_{10\,(s)} + 6\,H_2O_{(l)} \rightarrow 4\,H_3PO_{4\,(aq)}$	**Observation** • dissolves in strong bases to form a salt solution **Equation** if excess OH^- is added: $P_4O_{10\,(s)} + 12\,OH^-_{(aq)} \rightarrow 4\,PO_4^{3-}{}_{(aq)} + 6\,H_2O_{(l)}$

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Oxide	Reaction with water	Reaction with strong bases
SO_3	Sulfur trioxide **Observation** • <u>violent</u> and <u>very exothermic</u> reaction in water, producing a very acidic mist of H_2SO_4 droplets • forms a <u>strongly acidic</u> solution around **<u>pH 1</u>** (depending on concentration) The sulfuric acid formed, also known as sulfuric(VI) acid, is a strong dibasic acid, which ionises completely in water. Structure of an undissociated molecule of H_2SO_4:  **Equation** $SO_{3\,(l)} + H_2O_{(l)} \rightarrow H_2SO_{4\,(aq)}$ strongly acidic solution	**Observation** • reacts directly with bases to form salt solutions **Equation** $SO_{3\,(l)} + 2\ OH^-_{(aq)} \rightarrow SO_4^{2-}{}_{(aq)} + H_2O_{(l)}$

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4.4 Summary of the properties of oxides across Period 3

The following table summarises the trends in the Period 3 oxides (in their highest oxidation states):

Formula of oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3
Oxidation number	+1	+2	+3	+4	+5	+6
Physical state at 25 °C	solid	solid	solid	solid	solid	liquid
Melting point (°C)	1130	2850	2070	1700	sublimes at 360	17
Bonding & structure	giant ionic lattice structure with strong electrostatic forces of attraction between oppositely-charged ions (with increasing covalent character from left to right)			giant molecular structure, covalent bonding	simple, discrete covalent molecules with relatively weak dispersion forces between molecules	
Acidic/basic nature	basic		ampho-teric	acidic		
Reaction with water	soluble reacts to form strongly basic NaOH	sparingly soluble reacts to form weakly basic $Mg(OH)_2$	Insoluble in water large amount of energy required to break lattice structures		soluble reacts to form fairly acidic H_3PO_4	soluble reacts to form strongly acidic H_2SO_4
Approx. pH of aqueous solution	13	9	7	7	2	1

Exercise 4.1 (Worked Example)

1 Describe how the bonding in the oxides of the elements changes across Period 3. Explain the change in terms of the electronegativities of the element.

The bonding changes from ionic to ionic with covalent character to covalent across period 3. Across period 3, the electronegativity of the element increases. A large difference in electronegativity between the element and oxygen results in an ionic oxide while a small difference in electronegativity results in a covalent oxide.

2 Describe how the acid-base behaviour of the oxides changes across period 3. Explain the trend in terms of structure and bonding.

Across period 3, the oxide behaviour changes from basic to amphoteric to acidic.
The basic oxides, Na_2O and MgO have giant ionic structures while the covalent oxides, P_4O_{10} and SO_3, have simple molecular structure. Al_2O_3 is an amphoteric oxide (has both acidic and basic properties) as it has giant ionic structure with covalent character.

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Exercise 4.2

1 Based on your knowledge of periodicity and Period 3 elements, predict the nature of Cl_2O_7, an oxide of chlorine.

A Basic **B** Acidic **C** Amphoteric **D** Neutral

2 A mixture of the oxides of two elements of the third period is dissolved in water. The solution remained approximately neutral.

What could be the constituents of the mixture?

A Al_2O_3 and MgO
B Na_2O and MgO
C Na_2O and P_4O_{10}
D SO_3 and P_4O_{10}

[J03/P1/Q13]

3 Consider the sequence of oxides Na_2O, SiO_2, P_4O_{10}. Which of the following factors decreases from Na_2O to SiO_2 and also from SiO_2 to P_4O_{10}?

A melting point
B covalent character
C pH when mixed with water
D solubility in aqueous alkali

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5 PROPERTIES OF THE CHLORIDES

LO 5(e)(ii): state and explain the variation in bonding in chlorides in terms of electronegativity (except for $AlCl_3$)
(v): describe and explain the reactions of the chlorides with water (for NaCl; $MgCl_2$; $AlCl_3$; $SiCl_4$; PCl_5)
(vi): suggest the types of structure and bonding present in the chlorides from observations of their chemical and physical properties
LO 5(h): predict the characteristic properties of an element in a given Group by using knowledge of chemical periodicity
LO 5(i): deduce the nature, possible position in the Periodic Table, and identity of unknown elements from given information of physical and chemical properties

5.1 Structure and bonding of the chlorides

The trends in physical properties of the chlorides can also be explained by the gradual change in their structure and bonding. Like the oxides, the bonding of the chlorides changes from ionic to covalent across the period.

Formula of chloride	**NaCl**	**$MgCl_2$**	**$AlCl_3$**	**$SiCl_4$**	**PCl_5**
Structure	giant ionic lattice structure		simple discrete covalent molecules *(in vapour phase)*	simple discrete covalent molecules	simple discrete covalent molecules *(in vapour phase)*
Bonding	strong electrostatic forces of attraction between oppositely-charged ions		weak dispersion forces between molecules		

Again, this is because the <u>electronegativity difference</u> between each element and chlorine <u>decreases</u> across the period, hence bonding becomes increasingly covalent.

5.2 Trend in melting points of the chlorides

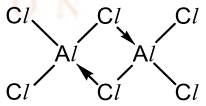
As for the oxides, the trend in melting points of the chlorides across the period can be explained by their <u>structure and bonding</u>.

Formula of chloride	**NaCl**	**$MgCl_2$**	**$AlCl_3$**	**$SiCl_4$**	**PCl_5**
Physical appearance at 25 °C	solid	solid	solid	liquid	solid
Melting point (°C)	801	714	sublimes at ~180	–70	sublimes at ~160

- NaCl and $MgCl_2$:
  - white crystalline solids at room temperature
  - (Structure) giant ionic lattice with
  - (Bonding) strong electrostatic forces of attraction between oppositely charged ions
  - A large amount of energy is required to overcome the strong ionic bonds ⇒ high m.p.

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- Aluminium chloride:
  - very pale yellow powder at room temperature
  - In the vapour phase, aluminium chloride is simple molecular in structure, forming gaseous Al_2Cl_6 dimers (which involve dative bonding):



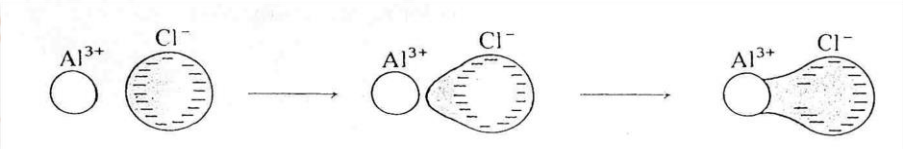
Al_2Cl_6 dimer

  - In the vapour phase, there exists an equilibrium between Al_2Cl_6 dimers and $AlCl_3$ monomers. As the temperature increases, the position of the equilibrium shifts more to the right, favouring the monomers.

$$Al_2Cl_{6\,(g)} \rightleftharpoons 2AlCl_{3\,(g)}$$

Is aluminium chloride really a simple covalent compound? (Background Info)

In the solid state, $AlCl_3$ actually has an ionic lattice structure with a large amount of covalency. This covalency is due to the very high charge density of the Al^{3+} ion (small ionic radius and high charge) which is able to polarise the large electron cloud of nearby Cl^- ions.



Just below 180 °C, the solid expands and $AlCl_3$ loses all ionic character, converting to discrete Al_2Cl_6 gas molecules with comparatively weaker dispersion forces between them, causing the solid to suddenly vaporise (i.e. it sublimes).

Aluminium chloride is said to have a borderline type of bonding, somewhere in between that of purely ionic and purely molecular compounds.

- Silicon tetrachloride, $SiCl_4$:
  - It is a colourless fuming liquid at room temperature
  - (Structure) simple discrete covalent molecules with
  - (Bonding) relatively weak intermolecular forces between molecules
  - Comparatively less energy is required to overcome these weaker forces ⇒ lower m.p.

- phosphorus(V) chloride, PCl_5:
  - off-white to pale yellow powder at room temperature
  - PCl_5 is considered to have a simple molecular structure and can largely be treated as such in the context of A-level chemistry.

Why is PCl_5 a solid at room temperature? (Background Info)

At room temperature, when in the solid state, PCl_5 self-ionises, causing it not to melt as expected due to stronger ionic interactions:

$$PCl_5 + PCl_5 \rightarrow PCl_4^+ + PCl_6^-$$

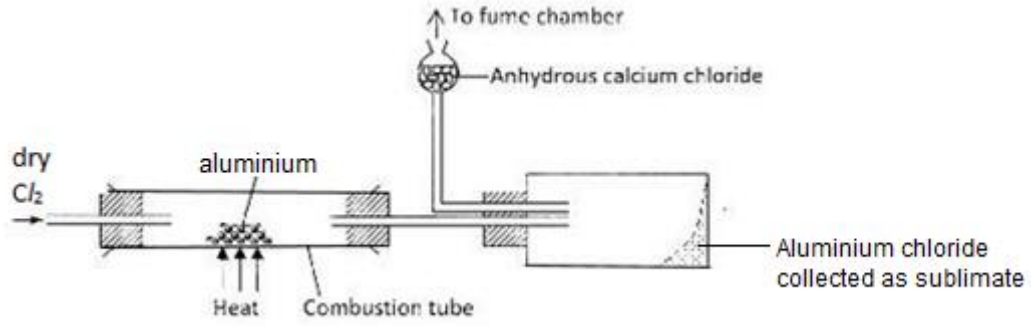
At around 160 °C, the ions convert back to simple molecular PCl_5 with relatively weaker intermolecular dispersion forces. Because these attractions are easier to overcome, PCl_5 then sublimes.

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Inorganic Synthesis – Preparation of Inorganic Compounds: e.g. Aluminium chloride

You may be required to plan experiments to prepare and purify inorganic substances. The separation and purification techniques used in Organic Chemistry are also applicable for inorganic compounds: filtration, extraction, distillation, recrystallization, and melting point determination.

Using aluminium chloride as an example, here is a fully labelled diagram of a laboratory set up used to produce, purify and collect an inorganic compound. Of course, the physical state and properties of the desired compound should be considered when designing the experiment.



Ensuring a moisture-free environment

Drying the chlorine gas before feeding it through the system, and adding a calcium chloride guard tube at the exit point help to ensure that the environment in which the aluminium chloride is prepared is free from water. This is particularly important because aluminium chloride reacts very readily with water.

Anhydrous calcium chloride is very hygroscopic (i.e. easily absorbs moisture from air), hence very useful as a desiccant (i.e. a drying agent). Placing some in a guard tube allows for absorption of any moisture from the air, particularly when the set-up cools (which causes some air to enter the set up via contraction).

How are gases like chlorine 'dried'?

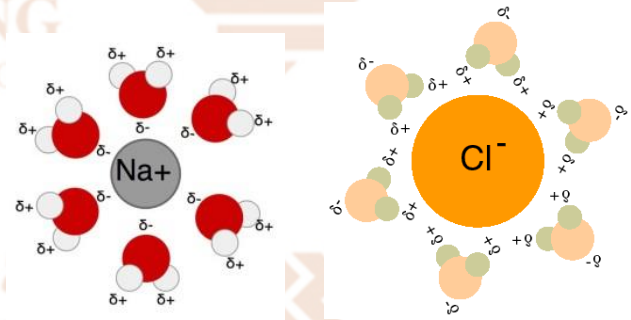
It is possible to dry chlorine gas by bubbling the supply of chlorine through concentrated sulfuric acid, which readily absorbs any moisture in the gas supply.

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5.3 Reactions of the chlorides with water

On the whole, all chlorides of Period 3 elements appear to dissolve in water.

- In the case of the ionic chlorides, their ions get solvated, and form favourable ion-dipole interactions with the polar water molecules. We refer to the solvated ions as hydrated ions.
- Recall that the chloride ion, being the conjugate base of the strong acid HC*l*, is a very poor base which does not react with water. Hence, it will not be responsible for any deviations from neutral pH.
- Depending on their charge density, the hydrated metal cations formed may undergo **partial hydrolysis** in water.

Chloride	Reaction with water
NaC*l*	**Observation with equation** • dissolves in water to form a colourless solution of neutral pH $NaCl_{(s)} + aq \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$ **Explanation** • Na^+ has low charge density, and hence does not react with water molecules (no hydrolysis). The solution thus remains neutral at **pH 7**. $Na^+ Cl^-_{(s)} \xrightarrow{\text{water}}$ 
$MgCl_2$	**Observation with equation** • dissolves in water to form a colourless solution of slightly acidic pH $MgCl_{2(s)} + 6\ H_2O_{(l)} \rightarrow [Mg(H_2O)_6]^{2+}_{(aq)} + 2\ Cl^-_{(aq)}$ $[Mg(H_2O)_6]^{2+}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Mg(H_2O)_5OH]^+_{(aq)} + H_3O^+_{(aq)}$ **Explanation** • Due to the higher charge density of Mg^{2+} compared to Na^+, the hydrated magnesium ion undergoes slight hydrolysis to form a very weakly acidic solution of around **pH 6.5**. • The above equilibrium lies very much to the left. Nonetheless, enough H_3O^+ is produced to lower the pH away from neutral.

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Chloride	Reaction with water
$AlCl_3$	**Observation with equations** **1. Reaction in a limited amount of water** When a few drops of water are added to solid $AlCl_3$, steamy white fumes of HCl are evolved and a white solid remains, which is insoluble in water. $AlCl_{3\,(s)} + 3\,H_2O_{(l)} \rightarrow Al(OH)_{3(s)} + 3\,HCl_{(g)}$ white solid steamy white fumes **2. Reaction in a large amount of water** In an excess of water, $AlCl_3$ dissolves to form a colourless solution of acidic pH. Al^{3+} forms a complex ion with 6 water molecules, as shown below. $AlCl_{3(s)} + 6\,H_2O_{(l)} \rightarrow [Al(H_2O)_6]^{3+}_{(aq)} + 3\,Cl^-_{(aq)}$ $[Al(H_2O)_6]^{3+}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Al(H_2O)_5OH]^{2+}_{(aq)} + H_3O^+_{(aq)}$ Due to the very high charge density of Al^{3+}, the O−H bonds in the H_2O ligands are sufficiently polarised, weakened and break readily to donate a proton. The hydrated aluminium complex can undergo hydrolysis to a further extent than for $Mg^{2+}(aq)$, resulting in a distinctly acidic solution around **pH 3.** **3. Acidic behaviour of $Al^{3+}(aq)$** • Adding a controlled amount of OH^- ions to an aqueous solution of Al^{3+} can further deprotonate the water ligands, until a white ppt of aluminium hydroxide is formed: $[Al(H_2O)_5OH]^{2+}_{(aq)} + OH^-_{(aq)} \rightleftharpoons [Al(H_2O)_4(OH)_2]^+_{(aq)} + H_2O_{(l)}$ $[Al(H_2O)_4(OH)_2]^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons [Al(H_2O)_3(OH)_3]_{(s)} + H_2O_{(l)}$ white ppt • If an excess of OH^- ions is added, the white ppt dissolves to form a colourless solution with the formation of the aluminate ion: $[Al(H_2O)_3(OH)_3]_{(s)} + OH^-_{(aq)} \rightleftharpoons [Al(OH)_4]^-_{(aq)} + 3\,H_2O_{(l)}$ aluminate N.B. The aluminate complex is sometimes written as $[Al(H_2O)_2(OH)_4]^-$, the octahedral complex. However, this is rather unstable, quickly forcing out the 2 water molecules and converting to the tetrahedral $[Al(OH)_4]^-$. • A solution of Al^{3+} is usually acidic enough to react with sodium carbonate and produce effervescence of CO_2 gas and the white ppt of aluminium hydroxide. $2\,[Al(H_2O)_6]^{3+}_{(aq)} + 3\,CO_3^{2-}{}_{(aq)} \rightarrow 2\,[Al(H_2O)_3(OH)_3]_{(s)} + 3\,H_2O_{(l)} + 3\,CO_{2(g)}$ white ppt effervescence Refer to Section 3.5 in Topic 14 Acid-Base Equilibria for more details on hydrolysis caused by metal ions with high charge density.

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- The remainder of the chlorides undergo **complete hydrolysis** in water to form **strongly acidic** solutions due to the **HCl** formed.

Chloride	Reaction with water
$SiCl_4$ / PCl_5	**Observation** • violent reaction with water producing fumes of HCl gas Note that even if left exposed to moist air, fumes of HCl will be observed. ∴ these chlorides must be kept in air-tight containers • If water is added in large excess, the HCl fumes may not be observed as they mostly dissolve in the water, forming a strongly acidic solution (**pH 1**) containing hydrochloric acid. **Equations** Complete hydrolysis occurs in each case, i.e. these chlorides react with water irreversibly. $SiCl_{4(l)} + 4\ H_2O_{(l)} \rightarrow SiO_2.2H_2O_{(s)} + 4\ HCl_{(aq)}$ hydrated silicon dioxide* $PCl_{5(s)} + 4\ H_2O_{(l)} \rightarrow H_3PO_{4(aq)} + 5\ HCl_{(aq)}$ phosphoric(V) acid • Upon dropwise addition of water (or when exposed to moist air), phosphorus(V) chloride tends to produce phosphorus oxychloride, $POCl_3$, instead: $PCl_{5(s)} + H_2O_{(l)} \rightarrow POCl_{3(l)} + 2\ HCl_{(g)}$ **Recall**: This is similar to the reaction when PCl_5 is used as a test for the −OH group in organic chemistry! $PCl_{5(s)} + ROH_{(l)} \rightarrow POCl_{3(l)} + HCl_{(g)} + RCl_{(l)}$

*Note: Hydrated silicon dioxide is sometimes written as $Si(OH)_4$, a misleading notation that leads some to believe it is basic (it's not!), or as H_4SiO_4, in which it looks more like the molecular formula of an acid, which is more accurate here (*orthosilicic acid*, H_4SiO_4, has pK_{a1}=9.84, pK_{a2}=13.2 at 25 °C *from Wikipedia*). However, silicic acids such as H_4SiO_4 readily lose water to form randomly polymeric silica gel, a form of silicon dioxide, hence the use of the formula $SiO_2.2H_2O$.

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5.4 Summary of the properties of chlorides across Period 3

The following table summarises the trends in the Period 3 chlorides (in their highest oxidation states):

Formula of chloride	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_5
Oxidation number	+1	+2	+3	+4	+5
Physical appearance at 25 °C	solid	solid	solid	liquid	solid
Melting point (°C)	801	714	sublimes at ~180	–70	sublimes at ~160
Boiling point (°C)	1413	1412	-	58	-
Bonding & structure	giant ionic lattice structure with relatively strong electrostatic forces of attraction between oppositely-charged ions		simple discrete covalent molecules with relatively weak dispersion forces between molecules		
Effect of adding chloride to water	soluble does not hydrolyse	soluble hydrolyses slightly	soluble hydrolyses in water to form acidic solutions; HCl fumes may be observed		
Approx. pH of resulting solution	7	6.5	3	1	1

Exercise 5.1 (Worked Example)

1 Describe how the bonding in the chlorides of the elements changes across Period 3. Explain the change in terms of the electronegativities of the element.

The bonding in the chlorides changes from ionic to covalent across period 3. Across period 3, the electronegativity of the element increases. A large difference in electronegativity between the element and chlorine results in an ionic chloride while a small difference in electronegativity results in a covalent chloride.

2 Describe briefly how the reaction of the chlorides with water changes across period 3. Explain the trend in terms of structure and bonding.

In general, the chlorides with giant ionic structure dissolve in water to give ions while the chlorides with simple covalent structure hydrolyse to give acidic solutions.
As the bonding changes from ionic to covalent, the tendency to hydrolyse increases.

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Exercise 5.2

For the following questions, you may select **more than one** correct option.

1 Which of the following pairs of compounds contains one that is giant ionic and one that is simple molecular?

1 Al_2O_3 and Al_2Cl_6

2 SiO_2 and $SiCl_4$

3 P_4O_{10} and PCl_5

2 Why is a solution of aluminium chloride acidic?

1 Chloride ions react with water to form hydrochloric acid.

2 Aluminium ions have a large charge to surface area ratio.

3 The H−O bonds are weaker in $[Al(H_2O)_6]^{3+}$ than in H_2O.

3 Which of the following are correct descriptions of the properties of anhydrous aluminium chloride?

1 It dissolves in benzene to give a solution which conducts electricity.

2 It fumes in moist air due to the formation of hydrogen chloride.

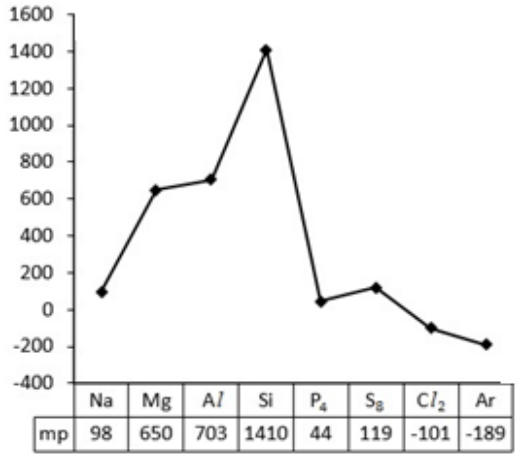
3 In the vapour phase, it has a covalent molecular structure.

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6 SUMMARY OF PERIOD 3 TRENDS

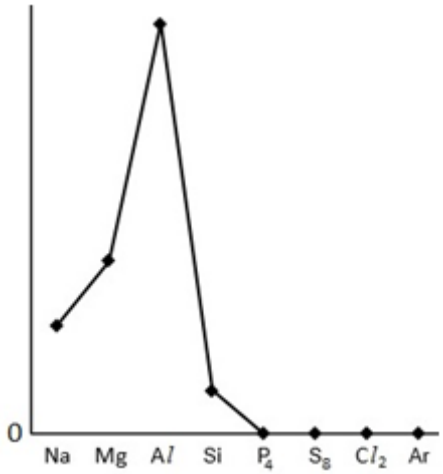
- **Variations in physical properties of the Period 3 elements**

melting point (in °C)



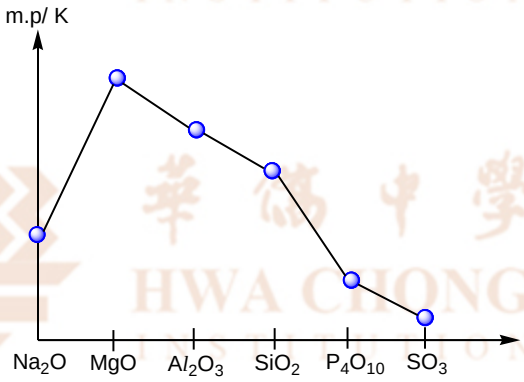
	Na	Mg	Al	Si	P_4	S_8	Cl_2	Ar
mp	98	650	703	1410	44	119	-101	-189

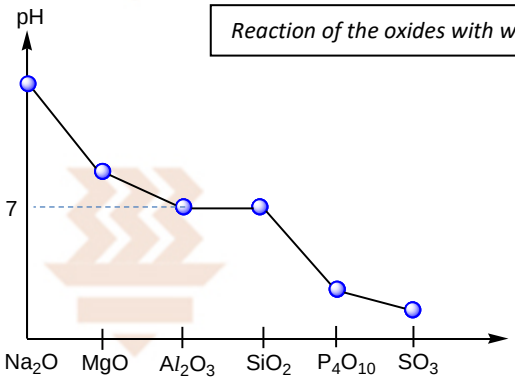
electrical conductivity



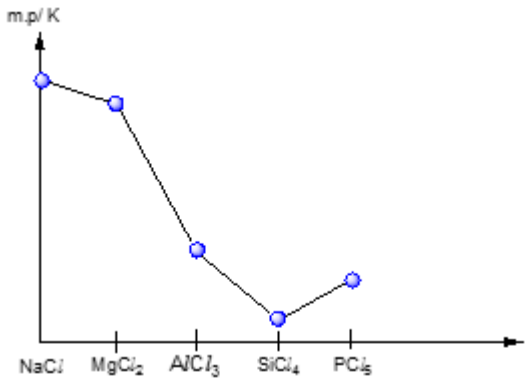
Refer to Topic 2 Chemical Bonding for the explanations of melting point and electrical conductivity variation using concepts of structure and bonding.

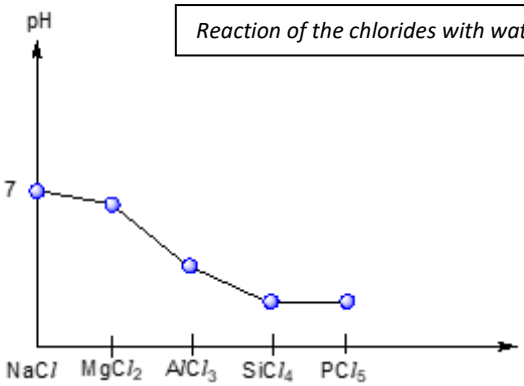
- **Variations in properties of the Period 3 oxides**





- **Variations in properties of the Period 3 chlorides**





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7 GROUP 2

LO 5(f)(i): describe and deduce from $E^{\ominus}$ values the relative reactivity of elements of Group 2 as reducing agents
LO 5(g)(i): describe and explain the trend in thermal stability of Group 2 carbonates in terms of the charge density of the cation and the polarisability of the large anion

7.1 Relative strength of Group 2 metals as reducing agents

Reactivity of the Group 2 metals **increases** down the group. As atomic radii increase, the metal atoms lose their electrons more readily (1st and 2nd ionisation energies decrease) going down the group. So, they form M^{2+} cations more easily.

Therefore, **reducing power** of the group 2 metals **increases** (tendency to be oxidised increases) down the group.

This is illustrated in the **increasingly negative** $E^{\ominus}$ values down the group.

Table 3. Standard electrode potential values of Group 2 metals

Element	Standard electrode potential, $E^{\ominus}$ / V
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.38
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \rightleftharpoons Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \rightleftharpoons Ba(s)$	−2.90

7.2 Thermal stability of Group 2 carbonates

Group 2 carbonates are **unstable** towards heat. Thermal decomposition gives stable oxides.

$$MCO_3(s) \rightarrow MO(s) + CO_2(g)$$

Table 4. Decomposition temperatures of Group 2 carbonates

Element	Decomposition Temperature of carbonate / °C
Mg	400
Ca	900
Sr	1280
Ba	1360

Group 2 carbonates become **more thermally stable** down the group. The ones lower in the group need to be heated more strongly before they will decompose, i.e. the ease of decomposition decreases down the group, hence they will have a **higher decomposition temperature**.

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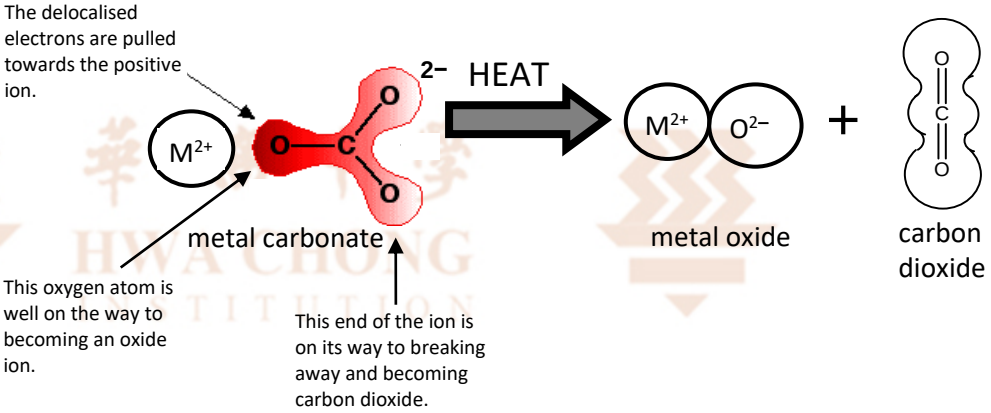
7.2.1 Factors affecting thermal stability of Group 2 carbonates

The thermal stability of the Group 2 carbonates is affected by the polarising power of the cation and the polarisability of the large anion.

- **Polarising power of the cation**

  Polarising power refers to the ability of a cation to distort the electron cloud of another ion, atom or molecule. In general, the higher the **charge density of the cation**, the greater the polarising power of the cation and the lower the thermal stability of the compound.

  The small and highly charged M^{2+} cation in these Group 2 compounds polarises the anion's larger electron cloud, weakening the covalent bonds within the anion. Hence these compounds decompose on heating as the weakened covalent bonds within the anion are easily broken.



For Group 2 carbonates,

- **Cationic radius increases** down the group while charge remains the same
- Therefore **charge density of cation decreases** down the group
- **Polarising power of the cation decreases** down the group and is **less able to distort the electron cloud of the carbonate**, weakening the C–O bonds within the carbonate anion to a smaller extent
- **Covalent bonds** within the carbonate anion are **less likely to be broken** down the group
- The **ease of decomposition decreases** (or thermal stability increases) down the group so **higher temperature** is required to decompose the compound

- **Polarisability of large anion**

  Polarisability refers to the ease with which an anion, atom or molecule's electron cloud can be distorted by another. The greater the polarisability of the anion, the lower the thermal stability of the compound.

  - **Larger anions** are more susceptible to polarisation of their electron cloud.
  - Only **polyatomic anions** are susceptible to decomposition as monoatomic anions (e.g. O^{2-}, Cl^-) cannot be broken down further.

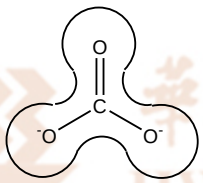
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Decomposition of other Group 2 Compounds (Application Example)

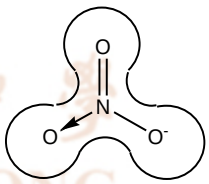
Other group 2 compounds that are susceptible to decomposition include nitrates and hydroxides, as these also have polarisable polyatomic anions and are thus also **unstable** towards heat.

Nitrates : $M(NO_3)_2(s) \rightarrow MO(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$

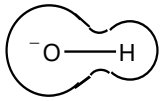
Hydroxides : $M(OH)_2(s) \rightarrow MO(s) + H_2O(g)$



carbonates

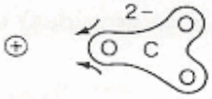
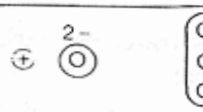
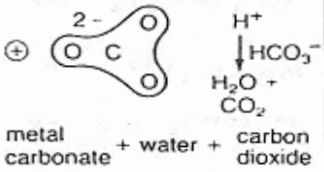
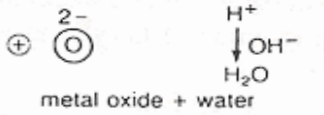
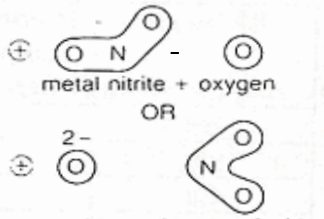


nitrates



hydroxides

The following table shows the products of decomposition of other polyatomic anions.

Anion	slight polarisation	further polarisation
 carbonate		 metal oxide + carbon dioxide
 hydrogencarbonate		 metal carbonate + water + carbon dioxide
 hydroxide		 metal oxide + water
 nitrate		 metal nitrite + oxygen OR metal oxide + nitrogen dioxide

There are also other factors that may contribute to ease of decomposition of these compounds. One factor is the way the ions are packed in the lattice structure, as well as the ratio of cations to anions in the solid structure.

Comparison with thermal stability of Group 1 carbonates (Application Example)

The Group 1 carbonates are <u>resistant to decomposition</u> except for Li_2CO_3. The charge density of Li^+ is high enough to distort the carbonate's electron cloud so that the compound decomposes on heating.

$$Li_2CO_3(s) \rightarrow Li_2O(s) + CO_2(g)$$

The other Group 1 metal cations have low charge density due to their larger radii and so are unable to sufficiently distort the carbonate's electron cloud. Therefore the carbonates after lithium do not decompose on heating.

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8 GROUP 17

8.1 Trend in volatility of Group 17 elements

LO 5(d): describe and explain the trend in volatility of the group 17 elements in terms of instantaneous dipole-induced dipole attraction

Table 5. Physical states, melting and boiling points of halogens

Element	No. of electrons	Melting point/ °C	Boiling point/ °C	Physical state at 20 °C
F_2	18	−220	−188	Gas
Cl_2	34	−101	−35	Gas
Br_2	70	−7	59	Liquid
I_2	106	114	184	Solid

The following table on the colour of halogens can be found in the *Data Booklet*:

Halogen	Colour of element	Colour in aqueous solution	Colour in hexane
Chlorine, Cl_2	Greenish yellow gas	Pale yellow	Pale yellow
Bromine, Br_2	Reddish brown gas/liquid	Orange	Orange-red
Iodine, I_2	Black solid/purple gas	Brown	Purple

The Group 17 elements, also known as the halogens, exist as simple, **non-polar diatomic** molecules with **dispersion forces** existing between molecules.

Down the group, the size of the electron cloud and hence, the polarisability of the halogen molecule increases. More energy is needed to overcome the stronger dispersion forces between the molecules. Hence, the **volatility of the halogens decreases** down Group 17, and the melting and boiling points **increase** down the group.

**The volatility of a substance refers to how easily the substance in the liquid phase may be converted to the gas phase.*

The increase in strength of dispersion forces down the group explains the change in physical state of the elements down Group 17.

8.2 Relative strength of Group 17 elements as oxidising agents

LO 5(f)(ii): describe and deduce from $E^\ominus$ values the relative reactivity of elements of Group 17 as oxidising agents

The outermost electron shell of halogens contains 7 electrons, i.e. $ns^2\ np^5$. As such, their chemistry is dominated by a tendency to gain a completely filled outermost electron shell. Hence, halogens tend to be **reduced** in a redox reaction, and their oxidising power can be measured by the value of the standard reduction potential $E^\ominus$ for the process:

$$X_2(std) + 2e^- \rightleftharpoons 2X^-(aq)$$

The $E^\ominus$ values become less positive down the group, as shown in Table 6. Hence, the **oxidising power** of the halogens **decreases** down the group and they become less likely to be reduced in a redox reaction.

Table 6. Standard reduction potentials of the halogens

Element	F_2	Cl_2	Br_2	I_2
$E^\ominus$/ V	+2.87	+1.36	+1.07	+0.54

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8.3 Redox reactions of Group 17 elements

LO 5(f)(ii): describe and deduce from $E^{\ominus}$ values the relative reactivity of elements of Group 17 as oxidising agents

This section describes some of the redox reactions that Group 17 elements undergo. In each of these reactions, the relative oxidising abilities of the halogens are further emphasised.

8.3.1 Displacement reactions

In general, a halogen higher in the group can oxidise a halide **below** it. A more reactive halogen will hence displace a less reactive one from its compounds.

Exercise 8.1 (Worked Example)

Describe the observations in each of the following. Explain your answer with the aid of chemical equations, where appropriate.

(a) Aqueous chlorine is added to a solution of KI.

Pale yellow $Cl_2(aq)$ solution turns brown.

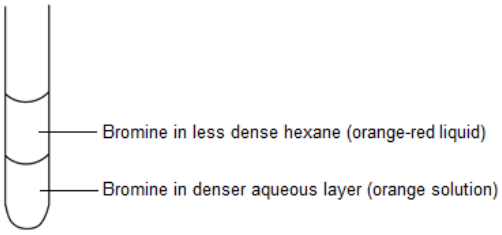
Chlorine is a stronger oxidising agent than iodine. Hence, it displaces I^- to form Cl^- and I_2.
$Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$

The brown solution is due to a reaction between I_2 and the excess I^- to form I_3^-.
$I_2 + I^-(aq) \rightleftharpoons I_3^-(aq)$

(b) Potassium bromide solution is added to hexane (colourless liquid with a density of 0.659 g/cm^3 at 25 °C) in a test tube. Chlorine is bubbled through the potassium bromide layer.

Chlorine is a stronger oxidising agent than bromine, and hence it displaces Br^- to form Cl^- and Br_2.
$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$

The Br_2 formed may dissolve in the top organic layer to form an orange-red liquid, or in the bottom aqueous layer to form an orange solution.



8.3.2 Reactions with aqueous solutions containing iron(II) ions

In the presence of a halogen oxidising agent, an aqueous solution of Fe^{2+} ions can be oxidised to Fe^{3+}.

Exercise 8.2

By calculating the $E^{\ominus}_{cell}$ for the reaction between Fe^{2+} and the halogen, show that only chlorine and bromine are able to oxidise Fe^{2+} while iodine will not oxidise Fe^{2+}. (Given $E^{\ominus}(Fe^{3+}/Fe^{2+})$ = +0.77V)

Equation	$E^{\ominus}_{cell}$
$Cl_2(aq) + Fe^{2+}(aq) \rightarrow 2Cl^-(aq) + 2Fe^{3+}(aq)$	
$Br_2(aq) + Fe^{2+}(aq) \rightarrow 2Br^-(aq) + 2Fe^{3+}(aq)$	
$I_2(aq) + 2Fe^{2+}(aq) \rightarrow 2I^-(aq) + 2Fe^{3+}(aq)$	

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8.3.3 Reactions with thiosulfate, $S_2O_3^{2-}$

The decrease in oxidising power of the halogens can also be illustrated by their reaction with an aqueous solution of thiosulfate.

Chlorine and bromine would oxidise thiosulfate to sulfate, SO_4^{2-} while iodine oxidises thiosulfate to tetrathionate, $S_4O_6^{2-}$.

$$4Cl_2(aq) + S_2O_3^{2-}(aq) + 5H_2O(l) \rightarrow 8Cl^-(aq) + 2SO_4^{2-}(aq) + 10H^+(aq)$$
$$\quad\quad\quad\quad +2 \quad\quad\quad\quad\quad\quad +6$$

$$4Br_2(aq) + S_2O_3^{2-}(aq) + 5H_2O(l) \rightarrow 8Br^-(aq) + 2SO_4^{2-}(aq) + 10H^+(aq)$$
$$\quad\quad\quad\quad +2 \quad\quad\quad\quad\quad\quad +6$$

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$
$$\quad\quad +2 \quad\quad\quad\quad +2.5$$

Iodine is a weaker oxidising agent than chlorine and bromine, and hence the oxidation number of sulfur only increases from +2 to +2.5, as compared to from +2 to +6 in the reactions with chlorine or bromine.

8.4 Thermal stability of Group 17 hydrides

LO 5(g)(ii): describe and explain the trend in thermal stability of Group 17 hydrides in terms of bond energies

Upon heating, the Group 17 hydrides (also called "hydrogen halides"), HX, can decompose to give hydrogen and the corresponding halogen.

$$2HX(g) \rightarrow H_2(g) + X_2(g)$$

The thermal stability of the hydrogen halide depends on the **strength of the H–X bond**.

Table 7. Relationship between decomposition behaviour and H–X bond energy

Compound	HF	HCl	HBr	HI
Decomposition behaviour	Does not decompose even on strong heating	Does not decompose even on strong heating	Strong heating yields brown fumes of Br_2	Violet fumes of I_2 obtained when red-hot rod is plunged into jar of HI
H–X bond energy/ kJ mol^{-1}	562	431	366	299

- Down the group, as atomic radius increases from F to I, the bond length of the H–X bond increases and thus bond strength decreases.
- Hence, less energy is needed to break the H–X bond. Thus, the thermal stability of the hydrogen halides **decreases** down the group.

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9 APPLYING THE PRINCIPLES OF CHEMICAL PERIODICITY

LO 5(h) predict the characteristic properties of an element in a given Group by using knowledge of chemical periodicity
LO 5(i) deduce the nature, possible position in the Periodic Table, and identity of unknown elements from given information of physical and chemical properties

The principles of chemical periodicity discussed in this topic can be used to predict characteristic properties of an element in a given Group. Given the physical and chemical properties, we can also deduce the nature and position of unknown elements in the Periodic Table.

Exercise 9.1
Use of Data Booklet is relevant to this question

Indium, $_{49}$In, is used in solar cells and transistors, and to coat high-speed bearings.

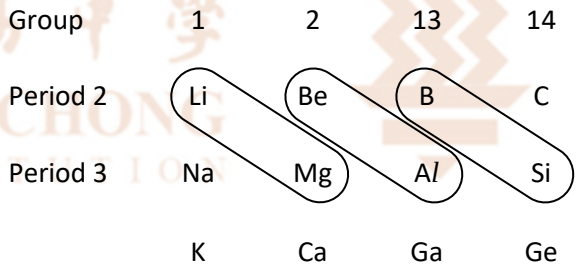
From its position in the Periodic Table, which properties will it be expected to possess?

1 In the vapour phase, the chloride has the formula In_2Cl_6.
2 Its oxide dissolves in aqueous acid.
3 Its ionic salts are highly coloured.

N13/P1/36

Diagonal Relationships in the Periodic Table (Useful Tool)

In the periodic table, certain pairs of diagonally adjacent elements in Period 2 and Period 3 (shown below) show similarities in their properties. They are said to have a diagonal relationship. As a result, the first element of some groups can be seen to have slightly different properties to the rest of the group.



Examples of diagonal relationships:

- Li is the only Group 1 element that can form a nitride salt; all Group 2 elements form nitrides; etc.
- BeO and Al_2O_3 are both amphoteric; aqueous solutions of Be^{2+} and Al^{3+} are both weakly acidic due to hydrolysis; etc.
- B and Si tend to form covalent compounds rather than forming cations; both B and Si are semiconductors; etc.

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Explanation

As we move across the period and down the group, the properties tend to have **opposite trends**:

For example, moving across the period, atomic radius decreases, but down the group, atomic radius increases. Similarly, moving across the period, electronegativity increases, while down the group, it decreases.

- Thus, moving *simultaneously* across the period and down the group by one element results in the combined effects of the opposing trends "cancelling out".

Note that diagonal relationships become less noticeable as we move beyond the B/Si pair, or below Period 3.

Exercise 9.2 (Worked Example)

Which element is likely to have an electronegativity similar to that of aluminium?

A barium **B** beryllium **C** carbon **D** chlorine

Answer: B

In general, electronegativity increases across the period and decreases down the group. Recall diagonal relationship. Electronegativity: C*l*(3.0) > C(2.5) > Be=A*l*(1.5) > Ba(0.9)

LOOKING AHEAD

You have seen both physical and chemical trends of the elements and their compounds across Period 3. Moving on to the next topic on Transition Elements, it is helpful to bear in mind the properties of the metals in Group 1, 2 and 13 (e.g. Na, K, Mg, Ca, A*l* etc.) and to compare them to the properties of transition metals.

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22 An Introduction to the Chemistry of Transition Elements

GUIDING QUESTIONS

- What are transition elements?
- What are the characteristic properties of transition elements? How are these properties similar or different from a typical s-block element?
- Are there any trends/patterns in the properties of transition elements?
- What are some examples/applications of transition elements/their compounds?

LEARNING OUTCOMES

Students should be able to:

For the first set of transition elements, titanium to copper

13 (a) explain what is meant by a transition element, in terms of d-block elements forming one or more stable ions with partially filled d subshells

13 (b) state the electronic configuration of a first row transition element and its ion (Refer to Topic 1 Atomic Structure and Physical Periodicity)

13 (c) explain why atomic radii and first ionisation energies of the transition elements are relatively invariant (Refer to Topic 1 Atomic Structure and Physical Periodicity)

13 (d) contrast, qualitatively, the melting point and density of the transition elements with those of calcium as a typical s-block element

13 (e) describe the tendency of transition elements to have variable oxidation states

13 (f) predict from a given electronic configuration, the likely oxidation states of a transition element

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 (Refer to Topic 20 Electrochemistry)

13 (h) predict, using $E^{\ominus}$ values, the likelihood of redox reactions (Refer to Topic 20 Electrochemistry)

13 (i) define the terms *ligand* and *complex* as exemplified by the complexes of copper(II) ions with water, ammonia and chloride ions as ligands (including the transition metal complexes found in the Qualitative Analysis Notes)

13 (j) explain qualitatively that ligand exchange may occur, as exemplified by the formation of the complexes in (i), including the colour changes involved, and CO/O_2 exchange in haemoglobin

13 (k) describe, using the shape and orientation of the d orbitals, the splitting of degenerate d orbitals into two energy levels in octahedral complexes

13 (l) explain, in terms of d orbital splitting and d-d transition, why transition element complexes are usually coloured [knowledge of the relative order of ligand field strength is **not** required]

13 (m) explain how some transition elements and/or their compounds can act as catalysts (Refer to Topic 6 Reaction Kinetics)

REFERENCES

1. P. Cann & P. Hughes, *Chemistry*, 2nd Edition, Hodder Education, Chapter 24.
2. P. W. Atkins, M. T. Weller, T. L. Overton, J. P. Rourke & F. A. Armstrong, *Inorganic Chemistry*, 6th Edition, Oxford University Press, Chapter 7, 20 and 21.
3. P. Amateis & M. Silberberg, *Chemistry: the molecular nature of matter and change*, 7th Edition, McGraw-Hill Education, Chapter 23.

LOOKING BACK

In this topic, you will learn about the chemical and physical properties of the first row transition elements and compare them with the main group metals, applying knowledge from earlier topics such as Atomic Structure, Chemical Bonding, Physical Periodicity, Equilibria and Electrochemistry.

1 INTRODUCTION

1.1 Definition of Transition Elements

LO 13(a): explain what is meant by a transition element, in terms of d-block elements forming one or more stable ions with partially filled d subshells

Transition elements are d-block elements that form one or more stable ions with partially filled d subshell.

By this definition, both scandium and zinc are **excluded** from the class of transition elements, even though they are part of d-block elements. This is because:

- Scandium forms only Sc^{3+} ion, which has no electron in the 3d subshell ($3d^0$).
- Zinc forms only Zn^{2+} ion which has 10 electrons in the 3d subshell ($3d^{10}$).

1.2 Electronic Configurations of First Row Transition Elements and its ions (covered in Topic 1 Atomic Structure and Physical Periodicity)

LO 13(b): state the electronic configuration of a first row transition element and its ion

Atom	No. of electrons	Full electronic configuration	Electron-in-box representation (3*d* / 4*s*)
Sc *Scandium* ^	21	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^1\,4s^2$	[Ar] ↑ ‖ ‖ ‖ ‖ ‖ ‖ ↑↓
Ti *Titanium*	22	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^2\,4s^2$	[Ar] ↑ ‖ ↑ ‖ ‖ ‖ ‖ ↑↓
V *Vanadium*	23	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^3\,4s^2$	[Ar] ↑ ‖ ↑ ‖ ↑ ‖ ‖ ‖ ↑↓
Cr *Chromium**	24	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s^1$	[Ar] ↑ ‖ ↑ ‖ ↑ ‖ ↑ ‖ ↑ ‖ ↑
Mn *Manganese*	25	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s^2$	[Ar] ↑ ‖ ↑ ‖ ↑ ‖ ↑ ‖ ↑ ‖ ↑↓
Fe *Iron*	26	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^6\,4s^2$	[Ar] ↑↓ ‖ ↑ ‖ ↑ ‖ ↑ ‖ ↑ ‖ ↑↓
Co *Cobalt*	27	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^7\,4s^2$	[Ar] ↑↓ ‖ ↑↓ ‖ ↑ ‖ ↑ ‖ ↑ ‖ ↑↓
Ni *Nickel*	28	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^8\,4s^2$	[Ar] ↑↓ ‖ ↑↓ ‖ ↑↓ ‖ ↑ ‖ ↑ ‖ ↑↓
Cu *Copper**	29	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^1$	[Ar] ↑↓ ‖ ↑↓ ‖ ↑↓ ‖ ↑↓ ‖ ↑↓ ‖ ↑
Zn *Zinc* ^	30	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2$	[Ar] ↑↓ ‖ ↑↓ ‖ ↑↓ ‖ ↑↓ ‖ ↑↓ ‖ ↑↓

Table 1. Electronic configuration of first row elements from d-block.

^ Sc and Zn are not transition elements.

* Cr and Cu atoms are two exceptions to the general pattern of electronic configurations.

Ion	No. of electrons	Full electronic configuration	Electron-in-box representation						
				3*d*					4*s*
Sc^{3+}	18	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^0$	[Ar]						
Ti^{2+}	20	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2$	[Ar]	↑	↑				
V^{3+}	20	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2$	[Ar]	↑	↑				
Cr^{3+}	21	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$	[Ar]	↑	↑	↑			
Mn^{2+}	23	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$	[Ar]	↑	↑	↑	↑	↑	
Fe^{2+}	24	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$	[Ar]	↑↓	↑	↑	↑	↑	
Co^{2+}	25	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7$	[Ar]	↑↓	↑↓	↑	↑	↑	
Ni^{2+}	26	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$	[Ar]	↑↓	↑↓	↑↓	↑	↑	
Cu^{2+}	27	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$	[Ar]	↑↓	↑↓	↑↓	↑↓	↑	
Zn^{2+}	28	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	

Table 2. Electronic configuration of selected ions of first row d-block elements.

1.3 Physical Properties of Transition Elements

LO 13(c): explain why atomic radii and first ionisation energies of the transition elements are relatively invariant (Refer to Topic 1 Atomic Structure and Physical Periodicity)
LO 13(d): contrast, qualitatively, the melting point and density of the transition elements with those of calcium as a typical s-block element

The atomic radii and first ionisation energies of the transition elements are relatively invariant. These concepts have been covered in Topic 1 Atomic Structure and Physical Periodicity.

The melting points of transition elements are higher than s-block elements, as both 3d and 4s electrons are involved in the metallic bonding in transition element.

The densities of transition elements are higher than s-block elements because the atomic radii of transition elements are smaller than s-block elements.

Exercise 1.1

Calcium is a fairly soft, silvery-grey metal which quickly tarnishes in air. Vanadium is a hard grey metal which is resistant to corrosion at ordinary temperatures. Metallic calcium has no commercial uses; vanadium is widely used as an alloying element in steels. Data about calcium and vanadium are given below.

	calcium	**vanadium**
electronic configuration	[Ar] $4s^2$	[Ar] $3d^3$ $4s^2$
atomic radius/nm	0.197	0.135
melting point/°C	843	1710
density/g cm^{-3}	1.54	6.07

(Worked Example)

a) The melting point of vanadium is significantly higher than that of calcium. Explain this in terms of the type and strength of bonding in each metal. (Worked Example)

Answer:

Both metals contain metallic bonding.

In Ca, only the 2 valence electrons (from 4s subshell) are contributed to the 'sea' of delocalised electrons.

For V, the 4s and 3d electrons are close in energy, therefore all these electrons could be involved in metallic bonding. In addition, vanadium cation has higher charge and smaller radius than Ca2+. Hence, metallic bonding in V is significantly stronger than that in Ca.

More energy is needed to overcome the metallic bonding in V during melting and thus it has higher melting point.

Comments:

This question is asking about the physical properties of metals. You should now recall relevant knowledge of metallic bonding from the Chemical Bonding chapter and the structure and bonding affects specifically melting point of the metal. The relevant properties are the charge density of the cations and the number of delocalised electrons.

The firs part of your answer should be to describe the metal structure and bonding within vanadium and calcium, followed by linking the relevant properties to the melting point.

b) Explain why the density of vanadium is significantly higher than that of calcium.

1.4 Chemical Properties of Transition Elements

The transition elements and their compounds display the following chemical properties that are different from s-block elements and their compounds.

Properties	Examples
Tendency to have variable oxidation states	• Manganese: +2 in Mn^{2+}, +4 in MnO_2, +7 in MnO_4^- • Iron: +2 in Fe^{2+}; +3 in Fe^{3+}
Catalytic properties (Heterogeneous and homogeneous)	• Iron, Fe, in the Haber process (manufacturing of ammonia) • Nickel, Ni, in hydrogenation of alkene • Vanadium(V) oxide, V_2O_5, in the Contact process (manufacturing of sulfuric acid) • Fe^{2+} ion in $I^-/S_2O_8^{2-}$ reaction
Formation of complex ions	• $[Cu(NH_3)_4(H_2O)_2]^{2+}$, $[Fe(CN)_6]^{3-}$, $[Ag(NH_3)_2]^+$
Formation of coloured ions	• $Cu^{2+}(aq)$: pale blue, $Cr_2O_7^{2-}(aq)$: orange • $Fe^{3+}(aq)$: yellow

Table 3. Chemical properties of transition elements.

2 VARIABLE OXIDATION STATES

LO 13(e): describe the tendency of transition elements to have variable oxidation states

The transition elements show variable oxidation states due to the close similarity in energy of the 4*s* and 3*d* electrons. Hence, once the 4*s* electrons are removed, some or all the 3*d* electrons may also be removed without requiring much more energy.

In contrast, the *s*-block elements are limited to form compounds with oxidation states of +1 (Group 1) or +2 (Group 2). This is because once the outermost electrons in the *s* orbital are removed, subsequent removal of electrons would be from the inner quantum shell which requires too much energy.

				+7					
			+6	+6	+6				
		+5	+5	+5	+5	+5			
	+4	**+4**	+4	**+4**	+4	+4	+4		
+3	+3	+3	**+3**	+3	**+3**	**+3**	+3	+3	
	+2	+2	+2	**+2**	**+2**	**+2**	**+2**	**+2**	**+2**
	+1	+1	+1	+1	+1	+1	+1	**+1**	
Sc scandium	**Ti** titanium	**V** vanadium	**Cr** chromium	**Mn** manganese	**Fe** iron	**Co** cobalt	**Ni** nickel	**Cu** copper	**Zn** zinc

Table 4. Known oxidation states of d-block metals. The more familiar oxidation states are shaded. Other oxidation states can only be stabilised under special conditions.

Scandium and zinc, which are not part of transition elements, can only form one oxidation state, as shown in Table 4 above.

2.1 General trends in oxidation states of transition elements

LO 13(f): predict from a given electronic configuration, the likely oxidation states of a transition element

- In their elemental states, the elements are assigned an oxidation number of zero.
- The value of the maximum oxidation number for the elements suggests that in each element, all the **available 3*d* and 4*s* electrons** may be used for bonding to form various compounds (either ionic bond by losing electrons or covalent bond by sharing electrons).
- The lower oxidation state metals are usually found in ionic compounds, e.g. $FeSO_4$ and $MnCl_2$.
- The higher oxidation state metals tend not to exist as free ions, e.g. Mn^{7+} or Cr^{6+} do not exist. However, they are involved in covalent bonds, such as TiO_2, V_2O_5, Mn_2O_7 and oxo-anions (e.g. VO_3^-, CrO_4^{2-}, $Cr_2O_7^{2-}$, MnO_4^-).
- The number of available oxidation states of the elements increases from Ti to Mn and decreases from Mn to Cu. After Mn ($3d^5$), **pairing of *d*-electrons occurs** such that there is a decrease in the number of electrons available for bond formation. This results in the decrease in the number of oxidation states exhibited by the elements with more than five *d*-electrons (from Fe to Cu).

Exercise 2.1

(Worked Example)

1. The table shows the possible oxidation states of five d-block elements in the Periodic Table. (The elements are represented by letters which are not their symbols.)

element	possible oxidation numbers						
P	–	–	3	–	–	–	–
Q	–	2	3	4	–	–	–
R	1	2	3	4	5	–	–
S	–	–	3	4	5	6	–
T	–	2	–	4	5	6	7

Which of the following ions is likely to exist?

A PO^{2+} **B** QO_3^- **C** RO_4^{2-} **D** TO_2^{2+}

Students should work out the oxidation states of P, Q, R, T in the options given and compare them to the possible oxidation numbers given in the table.
This can be done by using the overall charge of the ion and assuming the oxidation state of Oxygen is –2.
Option A: For the anion to have an overall charge of +2, with 1 oxygen atom, P needs to have an oxidation state of +4.
Using this same logic, we can work out that Q has a +5 oxidation state, R and T has +6 oxidation state. Hence only Option D is correct, where T has a possible oxidation state of +6 in the table given.

2. Titanium has the electronic structure $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$. Which of the following compounds does **not** exist?

A K_2TiO_4 **B** K_3TiF_6 **C** $TiCl_3$ **D** TiO

3. The electronic configuration of vanadium is [Ar] $3d^3\ 4s^2$. Which of the following ions does **not** exist?

A VO^{2+} **B** VO_2^+ **C** VO_3^{2-} **D** VO_4^{2-}

2.2 Redox reactions involving transition elements

LO 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
LO 13(h): predict, using $E^\ominus$ values, the likelihood of redox reactions

One of the applications of transition metal compounds is in the field of redox chemistry. In general, ions that have the transition metal in a high oxidation state tend to be oxidising agents (e.g. $Cr_2O_7^{2-}$, MnO_4^-) while transition metal in low oxidation state tends to be reducing agents (e.g. Cr^{2+}, V^{2+}). When transition metal ions undergo redox reactions, a colour change is usually observed.

Common redox systems involving transition elements include:

$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ yellow pale green	As a homogeneous catalyst in the redox reaction between iodide ions and peroxodisulfate ions.
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$ purple colourless	As an oxidising agent for organic compounds such as oxidation of primary alcohols to carboxylic acids.
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$ orange green	

To predict whether a redox reaction is feasible, or to explain colour changes due to redox reactions, we can make use of $E^\ominus$ values of the relevant species to find overall $E^\ominus_{cell}$, as learnt in Topic 20 Electrochemistry.

If $E^\ominus_{cell} > 0$, redox reaction is feasible.

Exercise 2.2

By quoting and using relevant $E^{\ominus}$ values from the *Data Booklet*, explain each of the following observations. Write balanced equations for the reactions.

(Worked Example)

(i) The green precipitate obtained when aqueous sodium hydroxide is added to aqueous iron(II) sulfate rapidly turns brown on exposure to air.

Answer:

The green precipitate is $Fe(OH)_2$.

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$ $\quad E^{\ominus} = +0.40$ V

$Fe(OH)_3 + e^- \rightleftharpoons Fe(OH)_2 + OH^-$ $\quad E^{\ominus} = -0.56$ V

$Fe(OH)_2$ is oxidised by O_2 in the air to form brown $Fe(OH)_3$

$O_2 + 2H_2O + 4Fe(OH)_2 \rightarrow 4Fe(OH)_3$ $\quad E^{\ominus}cell = +0.40 - (-0.56) = +0.96$ V > 0

Comments:

Students should first recall their QA knowledge and realise the green precipitate is iron(II) hydroxide and give the relevant equation for precipitation.

Students should then consider what would cause the green ppt to turn brown on standing, in this case it would be atmospheric oxidation. Hence to show this, students need to extract the relevant electrode potentials from the Data Booklet to prove that this is the case. In this case, oxygen is the oxidising agent.

Students should then use this information to formulate the overall balanced equation, AND calculate the standard cell potential.

(ii) The blue solution, containing $Cr^{2+}(aq)$, obtained by dissolving chromium metal in dilute sulfuric acid slowly turns green even in the absence of air.

3 CATALYTIC PROPERTIES

LO 13(m): explain how some transition elements and/or their compounds can act as catalysts

Transition elements, both in the elemental form and in their compounds, are important catalysts. We have learnt about catalysts and their mode of action in Topic 6 Reaction Kinetics. In this section, pay attention to the part played by transition elements and why they are able to act as catalysts. Also learn to apply your knowledge of $E^{\ominus}$ values to explain the mechanism of homogeneous catalysis.

A **catalyst** is a substance that increases the rate of a reaction by providing an alternative reaction pathway that requires lower activation energy than the uncatalysed reaction. The catalyst does not undergo any permanent chemical change during the process.

Transition elements and their compounds can act as heterogeneous catalysts as well as homogeneous catalysts:

Type	Homogeneous Catalyst	Heterogeneous Catalyst
phase of catalyst vs. phase of reactants	Catalyst operates in the same phase as the reactants	Catalyst operates in a different phase as the reactants (most commonly the catalysts are solids, and the reactants are gases)
reason why the transition metal or its compound could act as this type of catalyst	Variable oxidation states of the transition metal in its ions	Availability of partially filled 3d orbitals to accept electron pairs from, or donate electrons pairs to reactant molecules, for adsorption of reactant molecules onto the surface of the catalyst.

3.1 Heterogeneous Catalysis

In heterogeneous catalysis, the catalyst and the reactants are in different physical phases.

- The catalyst is usually in the solid phase and it provides active sites at which the reaction can take place.
- The reactants are usually gases or liquids.

Example: Haber process (manufacturing of ammonia)

Reaction:	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
Catalyst:	finely divided Fe(s) or $Fe_2O_3(s)$

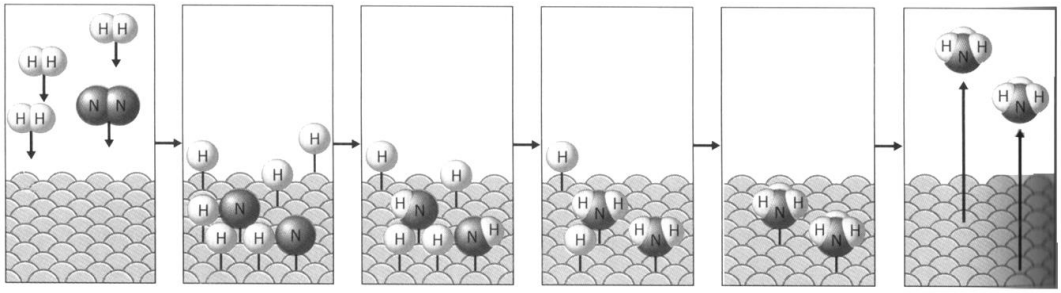


Figure 1. Heterogeneous catalysis in the Haber Process

Mode of action of the catalyst

- Adsorption: Gaseous reactant molecules, N_2 and H_2, diffuse towards surface of the Fe catalyst. N_2 and H_2 adsorb onto the active sides of Fe catalyst by formation of weak attraction forces.
- The adsorption process brings reactant molecules closer together, thus increasing their concentration on the catalyst surface, increasing frequency of collisions; the process also weakens the N≡N and H–H covalent bonds within the molecules; and allows these molecules to be orientated in the right positions for reaction to form new bonds between N and H. All these lower the activation energy of the reaction.
- Desorption: Product molecule, NH_3, desorbs and diffuses away from catalyst surface so that active sites are exposed for further reaction.

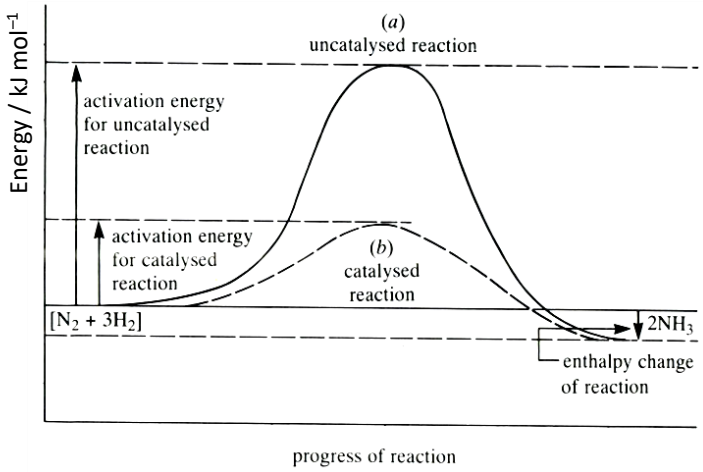
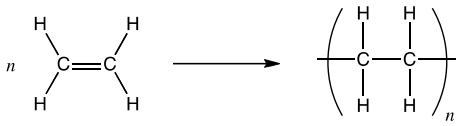


Figure 2. Energy profile diagrams for the catalysed and uncatalysed reactions.

Figure 2 shows the energy profile diagram for the catalysed and uncatalysed reactions.
Important points to note:

- A catalyst speeds up the forward and the reverse reactions.
- A reaction with a catalyst does not yield more product than one without a catalyst, but it yields the product more quickly.
- A catalyst provides a different mechanism for the reaction, with a new, lower activation energy pathway.
- A catalyst does not alter the enthalpy change of reaction.

Other heterogeneous catalysts used in the chemical industry

Heterogeneous catalyst	Reaction catalysed
V_2O_5	Contact process $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
Ni	Hydrogenation of vegetable oils to make margarine $RCH{=}CH_2 + H_2(g) \rightarrow RCH_2CH_3$
$TiCl_3$, $Al_2(C_2H_5)_6$ Ziegler-Natta catalyst	Polymerisation of ethene to poly(ethene) 

3.2 Homogeneous Catalysis

In homogeneous catalysis, the catalyst and the reactants are dispersed in the same phase (either liquid or gaseous).

The relative ease of inter-conversion between the different oxidation states of transition metals enables them to act as homogeneous catalysts, typically for redox reactions. Overall, the transition metal ions act as intermediaries for the electron(s) transfer between the oxidising and reducing agents.

We shall use the same example of homogeneous catalyst given in Topic 6 Reaction Kinetics: the oxidation of iodide ion, I^-, by peroxodisulfate ion, $S_2O_8^{2-}$.

Reaction:	$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$
Catalyst:	aqueous iron(III) ions

$I_2 + 2e^- \rightleftharpoons 2I^-$ $\quad E^\ominus = +0.54$ V

$S_2O_8^{2-} + 2e^- \rightleftharpoons SO_4^{2-}$ $\quad E^\ominus = +2.01$ V

Based on the data above, the reaction is found to have $E^\ominus_{cell} = +1.47$ V, which is expected to occur spontaneously. However, the electrostatic repulsion between the two negatively charged ions causes the reaction to have a high activation energy and hence to proceed at a very slow rate.

Aqueous iron(III) ions can catalyse this reaction via an alternative pathway involving 2 steps:

Step 1: Fe^{3+} oxidises iodide, itself reduced to Fe^{2+}, taking electrons from the I^-

$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$ $\quad E^{\ominus}_{cell} = E^{\ominus}_{red} - E^{\ominus}_{ox} = +0.77 - (+0.54) = +0.23$ V

Step 2: Fe^{2+} transfer electrons to, and reduces peroxodisulfate, itself oxidised to Fe^{3+}, thus Fe^{3+} is regenerated

$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$ $\quad E^{\ominus}_{cell} = E^{\ominus}_{red} - E^{\ominus}_{ox} = +2.01 - (+0.77) = +1.24$ V

This 2-step alternative pathway requires a lower activation energy because both steps involve collision between two oppositely charged ions. Fe^{3+} is regenerated at the end of the reaction.

If Fe^{2+} were present at the start instead, the two steps above will take place in the reverse order and the net effect will still be the same.

Note that the $E^{\ominus}_{cell}$ value for both steps must be positive, because:
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $\quad E^{\ominus} = +0.77$ V

Other redox couples of transition metal cations could also be used as catalysts in this reaction as long as their $E^{\ominus}$ values were between +0.54 V and +2.01 V, such that each of the two steps in the alternative pathway are feasible.

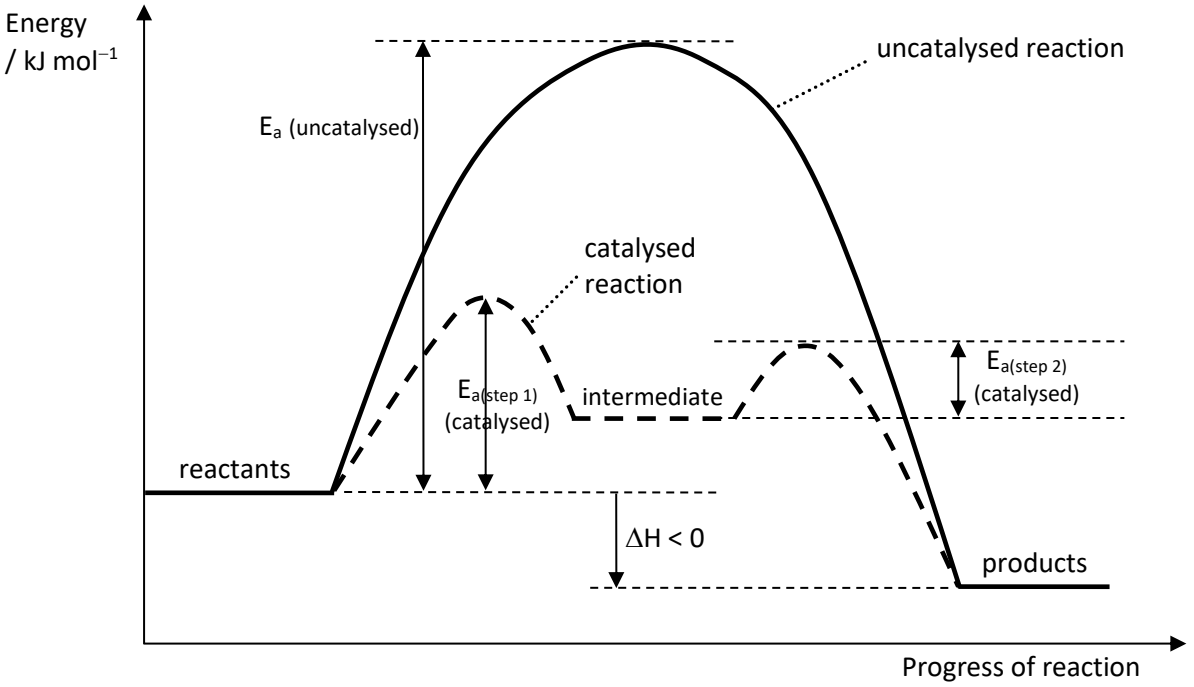


Figure 3. Energy profile diagrams for a catalysed and uncatalysed reaction

Exercise 3.1

The rate of the reaction between iodide and peroxodisulfate(VI) ions

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

is increased by the presence of small concentrations of $Co^{2+}(aq)$. Suggest how $Co^{2+}(aq)$ ions are able to participate in this reaction.

Hint: In this question, students need to demonstrate that the Co^{2+} is acting as a homogeneous catalyst to aid the transfer of electrons from the I^- ions to the $S_2O_8^{2-}$ ions. Extract 3 relevant half equations and their electrode potential from the Data Booklet and construct 2 balanced equations for each step of the homogeneous catalyst mechanism. The standard cell potential for each step should be positive.

4 TRANSITION ELEMENT COMPLEXES

LO 13(i): define the terms ligand and complex as exemplified by the complexes of copper(II) ions with water, ammonia and chloride ions as ligands (including the transition metal complexes found in the Qualitative Analysis Notes)

4.1 Introduction

Transition elements and their ions tend to form complexes.

A **complex** is a molecule or ion formed by a central metal atom or ion surrounded by one or more *ligands.

**Refer to Section 4.2 for the meaning of ligands*

When white anhydrous $CuSO_4$ solid is dissolved in water, a pale blue solution is formed. In water, Cu(II) exists as the aqua complex, with formula $[Cu(H_2O)_6]^{2+}$. When we write "$Cu^{2+}(aq)$", it refers to $[Cu(H_2O)_6]^{2+}(aq)$.

$$CuSO_4(s) + 6H_2O(l) \rightarrow \underset{\text{pale blue solution}}{[Cu(H_2O)_6]^{2+}(aq)} + SO_4^{2-}(aq)$$

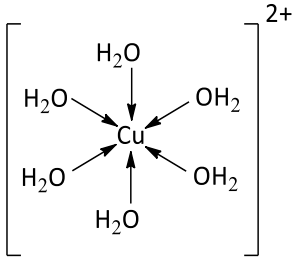


Figure 4. Copper(II) complex with water

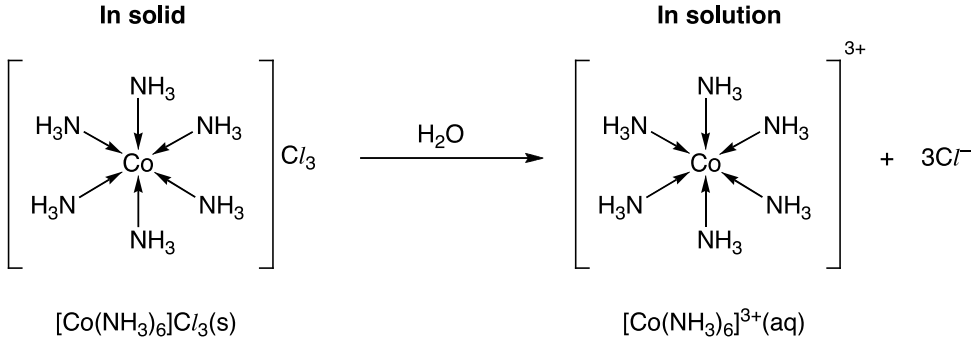
- In this complex, the central metal ion is Cu^{2+}, with six H_2O molecules acting as ligands.
- Each H_2O molecule bonds to the Cu^{2+} ion by forming a **coordinate (dative) bond**.
- Notice that the formula of a complex ion is usually written with a square bracket, the charge of the complex is indicated outside the square bracket.
- This complex is called the 'aqua complex' since its ligands are water.

A complex can be neutral, cationic or anionic. The net charge on the complex is the sum of the oxidation number of the central metal ion and the total charges of the ligands that surround it. The charge on the central metal is the oxidation number of the metal in that complex ion.

Type of complex	Central ion / atom	Ligands	Complex
Neutral	Ni	CO	$Ni(CO)_4$
Cationic	Cu^{2+}	H_2O	$[Cu(H_2O)_6]^{2+}$
Anionic	Fe^{2+}	CN^-	$[Fe(CN)_6]^{4-}$

To maintain charge neutrality, complex ion is typically associated with **counter ions**, as in the case of the compound $[Co(NH_3)_6]Cl_3$, in which the complex ion is $[Co(NH_3)_6]^{3+}$, the six NH_3 molecules acting as ligands, and the three Cl^- ions are counter ions. So the whole compound is like a salt.

When $[Co(NH_3)_6]Cl_3$ dissolves in water, the complex ion and counter ions separate from each other. The complex ion behaves like a polyatomic ion with **the ligands remaining attached to the central metal ion/atom**.



The tendency of transition metal ions to form complex ions rather than simple ions is due to two main factors:

- The "bare" cations of transition elements, with their incomplete 3d subshells are relatively small and highly charged. The resulting **high charge density** and hence **high polarising power** of the transition metal cations, produces a strong tendency towards covalent bond formation with ligands.
- The transition metal cations have **vacant 3d orbitals** (as well as 4s and 4p orbitals) which can be used to accommodate the lone pair of electrons from the ligands, resulting in dative bond formation.

4.2 Ligands

A **ligand** is an ion or molecule with one or more lone pairs of electrons available to be donated into the vacant orbitals of transition metal atom or ion.

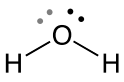
Ligands can be classified according to the number of dative bonds that it forms with the central metal atom or ion.

- Monodentate ligands bond using the electron pair of a single donor atom.
- Bidentate ligands bond using electron pairs on two donor atoms.
- Polydentate ligands bond using electron pairs on more than one donor atom (which includes bidentate ligand).

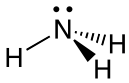
Polydentate ligands are sometimes called **chelating agents** (pronounced as *key-late-ting*) because of their ability to hold a metal ion like a claw. Chelating ligands form a stable complex ion with the central metal ion as the pincer-like grip of these polydentate ligands are able to hold the cation more securely. They typically form rings in the complex ion.

Monodentate Ligands

It is a ligand that forms one dative covalent bond to a central metal atom or ion.



Water



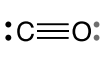
Ammonia



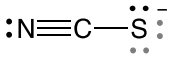
Chloride ion



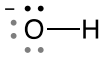
Cyanide ion



Carbon monoxide



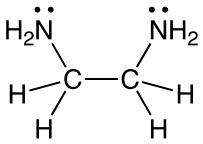
Thiocyanate ion



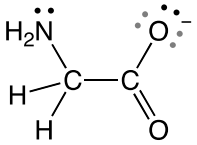
Hydroxide ion

Bidentate Ligands

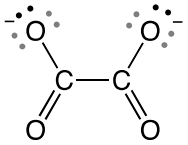
It is a ligand that forms two dative bonds to a central metal atom or ion.



Ethane-1,2-diamine (en)



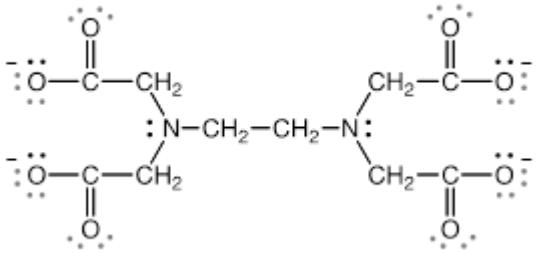
Glycinate ion (gly^-)



Ethanedioate ion

Hexadentate Ligands

It is a ligand that forms six dative bonds to a central metal atom or ion.



Ethylenediaminetetraacetate ion ($EDTA^{4-}$)

4.3 Coordination Number and Geometry

The **coordination number** indicates the **number of dative bonds** around the central atom or ion. The most common values are 4 and 6, but 2 is also observed and is particularly important in the chemistry of copper(I) and silver(I) compounds.

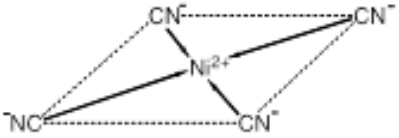
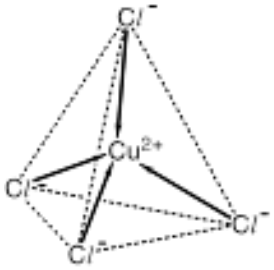
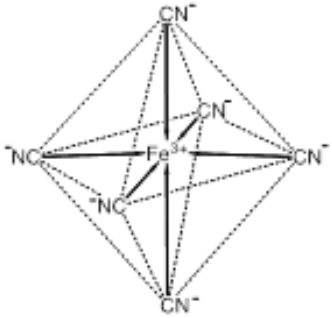
Formula	Coordination number	Geometry	Shape
$[Ag(NH_3)_2]^+$	2	linear	
$[Ni(CN)_4]^{2-}$	4	square planar	
$[CuCl_4]^{2-}$	4	tetrahedral	
$[Fe(CN)_6]^{3-}$	6	octahedral	

Table 5. Coordination number and shape of some complex ions

The shape (geometry) of the complex ion depends on the coordination number.

For coordination number of 4, the geometry can be square planar or tetrahedral depending on the transition metal and ligands involved. The determination and reasons for this is not in syllabus.

Exercise 4.1

1. Complete the missing information in the table below.

Complex ion	Oxidation no. of central metal ion	No. of ligands per complex ion	Coordination number	Net charge
(Worked Example) $[Cr(CN)_6]^{3-}$	**+3**	6	**6**	–3
$[Cu(Cl)_4]^x$	+2		4	
$[Fe(C_2O_4)_3]^{3-}$	+3			–3
$[Cu(EDTA)]^x$	+2		6	

There are 6 monodentate CN^- ligands in the complex, so a total of 6 dative bonds formed. Hence the coordination number is 6. The overall charge of the complex is –3, so to balance out the 6 CN^- ligands, the Cr must have an oxidation number of +3.

2. A complex is obtained by reacting aqueous cobalt(III) chloride with ammonia. It is found that the co-ordination number of cobalt is 6 and that only one third of the total chloride is precipitated as AgCl when the complex is treated with an excess of aqueous silver nitrate. What is the formula of the compound?

A $Co(NH_3)_6Cl_3$ **C** $Co(NH_3)_4Cl_3$

B $Co(NH_3)_5Cl_3$ **D** $Co(NH_3)_3Cl_3$

4.4 Acidity of aqua complexes

In aqueous solution, the transition metal ions exist as aqua complexes. Aqua complexes containing high charge density transition metal cations like Fe^{3+} and Cr^{3+}, undergo **hydrolysis** in water to give a **mildly acidic solution**.

$$[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$$
$$[Cr(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Cr(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$$

This is due to the **high charge density** on the central transition metal cation and these aqua complexes undergo appreciable hydrolysis in a similar fashion to the $[Al(H_2O)_6]^{3+}$ ion. The mechanism for this reaction was covered in the salt hydrolysis section in Topic 15 Acid-Base Equilibria.

However, for oxidation states higher than +3, the polarising power of the central metal cation is so great that the release of protons and loss of water molecules results in the **formation of oxoanions**.

For instance, $[Cr(H_2O)_6]^{6+}$ ions do not exist in aqueous solution. Instead, Cr(VI), occurs in two well-known oxoanions, the chromate (VI) ion, CrO_4^{2-}, and the dichromate (VI) ion, $Cr_2O_7^{2-}$.

4.4.1 Chromium complexes and oxoanions

When aqueous sodium hydroxide or aqueous ammonia is added dropwise to aqueous solution of chromium(III) ion, a grey-green ppt is formed. This is due to the formation of $Cr(OH)_3$. This is an acid-base reaction as chromium(III) ion is acidic.

$$[Cr(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \rightarrow [Cr(H_2O)_3(OH)_3](s) + 3H_2O(l)$$

or

$$Cr^{3+}(aq) + 3OH^-(aq) \rightarrow Cr(OH)_3(s)$$

When aqueous sodium hydroxide is added in excess, a dark green solution is formed. This is due to the formation of $[Cr(OH)_6]^{3-}$ complex ion.

$$[Cr(H_2O)_3(OH)_3](s) + 3OH^-(aq) \rightarrow [Cr(OH)_6]^{3-}(aq) + 3H_2O(l)$$

dark green solution

When acid is added to yellow solution of chromate(VI) ion, an orange solution of dichromate(VI) is formed. Notice that the oxidation state of the chromium ion remains the same.

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

yellow orange

4.5 Ligand exchange reaction

LO 13(j): explain qualitatively that ligand exchange may occur, as exemplified by the formation of the complexes in (i), including the colour changes involved, and CO/O_2 exchange in haemoglobin

The ligands in a complex ion can be exchanged for other ligands. This reaction is known as **ligand exchange reaction**. This reaction will happen readily if the new complex formed is more stable than the original complex. A change in colour of the solution is usually observed.

Ligand exchange reactions are largely reversible reactions, and therefore, are represented by the equilibrium sign '⇌'. For example, the ligand exchange reaction between the water ligands in $[Fe(H_2O)_6]^{3+}$ and SCN^- (thiocyanate) ions is represented by:

$$[Fe(H_2O)_6]^{3+}(aq) + SCN^-(aq) \rightleftharpoons [Fe(SCN)(H_2O)_5]^{2+}(aq) + H_2O(l)$$

yellow blood-red

A colour change from yellow to blood-red will be observed in this ligand exchange reaction.

The equilibrium constant of this reaction is given by $K_c = \dfrac{[Fe(SCN)(H_2O)_5^{2+}]}{[Fe(H_2O)_6^{3+}]\,[SCN^-]}$.

Note that although water is a reacting species (in the reverse reaction), it is also a solvent. Hence, $[H_2O]$ is almost constant and excluded from the K_c expression.

If the new complex formed is much more stable than the original complex, K_c would be large, the equilibrium position will lie very much to the right, and a single arrow may be used in the equation.

$$[Fe(H_2O)_6]^{3+}(aq) + SCN^-(aq) \rightarrow [Fe(SCN)(H_2O)_5]^{2+}(aq) + H_2O(l)$$

yellow solution blood red solution

4.5.1 Ligand exchange reactions involving copper complexes

This section concerns some common complexes of Cu(II) and the reactions in which they can be formed (often seen in Inorganic QA tests).

- To a solution of $Cu^{2+}(aq)$, add aqueous ammonia dropwise then in excess.
  Observation: pale blue ppt formed, which dissolves in excess ammonia to give dark blue solution.
  Explanation:
  $Cu(OH)_2$ is first precipitated when aqueous ammonia is added dropwise.

$$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow \underset{\text{pale blue ppt}}{Cu(OH)_2(s)}$$

  When excess ammonia is added, ligand exchange reaction takes place, with NH_3 ligands replacing H_2O ligands to form a dark blue solution. The $Cu^{2+}(aq)$ is equivalent to the hexaaqua cation $[Cu(H_2O)_6]^{2+}(aq)$.

$$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightarrow \underset{\text{dark blue solution}}{[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)} + 4H_2O(l)$$

  This causes the concentration of $Cu^{2+}(aq)$ to drop, thus the equilibrium below will shift to the right. Thus the ppt will dissolve to give a dark blue solution.

$$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$$

- To a solution of $Cu^{2+}(aq)$, add concentrated hydrochloric acid dropwise.
  Observation: solution turns from pale blue to green then yellow
  Explanation:
  When conc. HCl is added, ligand exchange reaction takes place, with Cl^- ligands replacing H_2O ligands.

$$\underset{\text{pale blue solution}}{[Cu(H_2O)_6]^{2+}(aq)} + 4Cl^-(aq) \rightarrow \underset{\text{yellow solution}}{[CuCl_4]^{2-}(aq)} + 6H_2O(l)$$

  The green colour is observed due to the mixture of both the blue aqua complex and the yellow chloro complex present.

4.5.2 Effects of ligand exchange on reduction potential (Application Example)

Ligands interact differently with the central metal ion, which will result in some change in reduction potential. For example, when water (H_2O) ligands are replaced by cyanide ligands (CN^-) for Fe^{3+}, we can see that there is a change in redox potential for the complex ions.

			$E^\ominus$/V
$[Fe(H_2O)_6]^{3+} + e^-$	$\rightleftharpoons$	$[Fe(H_2O)_6]^{2+}$	+0.77
$[Fe(CN)_6]^{3-} + e^-$	$\rightleftharpoons$	$[Fe(CN)_6]^{4-}$	+0.36

With the replacement of water ligands by cyanide ligands, $E^\ominus$ for the reduction of Fe(III) to Fe(II) becomes less positive. This is significant in the reaction with iodide ions.

$I_2 + 2e^-$	$\rightleftharpoons$	$2I^-$	+0.54V

$[Fe(H_2O)_6]^{3+}$ is able to oxidise I^- to I_2 and a dark brown solution is obtained.

$2[Fe(H_2O)_6]^{3+} + 2I^-$	$\rightarrow$	$2[Fe(H_2O)_6]^{2+} + I_2$	$E^\ominus_{cell}$ = +0.23 V

On the other hand, $[Fe(CN)_6]^{3-}$ is unable to oxidise I^- to I_2.

$$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox}$$
$$= +0.36 - 0.54$$
$$= -0.18 \text{ V (not feasible)}$$

4.5.3 Ligand exchange reaction in haemoglobin

Haemoglobin is the iron-containing protein in red blood cells that transports oxygen in blood. It consists of four protein chains loosely held together in a cluster. Each chain has a haem molecule within its folds. Iron (in the +2 oxidation state) is located in the centre of a plane of four nitrogen atoms. A haemoglobin molecule in the lungs picks up an O_2 molecule, which forms a dative bond with the iron to form a species called *oxyhaemoglobin*. This binding is reversible and enables haemoglobin to carry oxygen around the body and release it where it is needed.

Carbon monoxide, CO, can replace O_2 as the ligand attached to the iron(II). This is a **ligand exchange reaction**. The new complex is called *carboxyhaemoglobin*. The binding between CO and the iron(II) is irreversible, thus making carboxyhaemoglobin a very stable complex. The affinity of human haemoglobin for CO is about 210 times greater than that for O_2. As a result, a relatively small quantity of CO can inactivate a substantial fraction of the haemoglobin for oxygen transport. If the concentration of CO is high and the level of carboxyhaemoglobin becomes too high, oxygen transport is effectively shut down and death occurs.

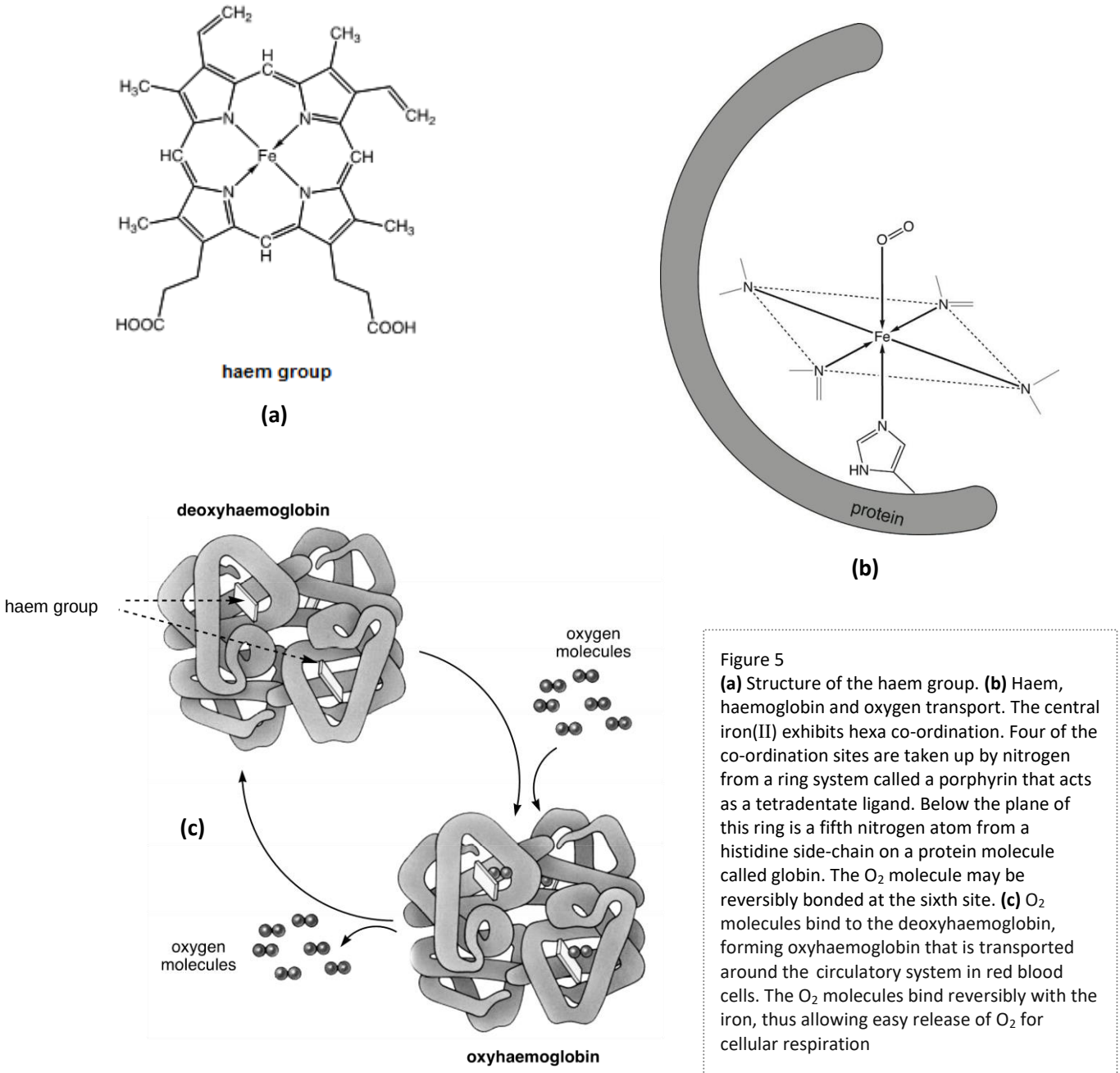


Figure 5
(a) Structure of the haem group. **(b)** Haem, haemoglobin and oxygen transport. The central iron(II) exhibits hexa co-ordination. Four of the co-ordination sites are taken up by nitrogen from a ring system called a porphyrin that acts as a tetradentate ligand. Below the plane of this ring is a fifth nitrogen atom from a histidine side-chain on a protein molecule called globin. The O_2 molecule may be reversibly bonded at the sixth site. **(c)** O_2 molecules bind to the deoxyhaemoglobin, forming oxyhaemoglobin that is transported around the circulatory system in red blood cells. The O_2 molecules bind reversibly with the iron, thus allowing easy release of O_2 for cellular respiration

5 COLOURED COMPOUNDS AND COMPLEXES

Transition metal compounds are frequently coloured, both in the solid state and in solution. This is due to absorption of part of the visible spectrum by the solution. The reason behind the observed colour can be explained using crystal field theory.

5.1 Light and Colour

White light is an electromagnetic radiation consisting of all wavelengths in the visible range. It can be dispersed into a spectrum of colours, each of which has a narrower range of wavelengths. For example, it can be dispersed into seven colours commonly known as the rainbow by using a prism.

Each colour has a complementary colour. For example, green and red are complementary colours. This is shown as opposite wedges in the colour wheel diagram below.

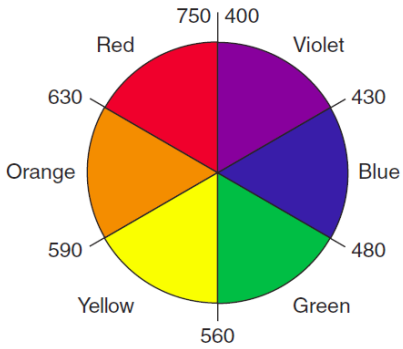


Figure 6. A diagram of the colour wheel, with approximate wavelength ranges (in nm), shown as wedges.

The energy of the light is inversely proportional to its wavelength. Therefore, red colour, with longer wavelength is lower in energy as compared to blue light, which is shorter in wavelength.

Objects appear coloured in white light because they absorb certain wavelengths and reflect or transmit others: an opaque object reflects light, whereas a clear one transmits it. The reflected or transmitted light enters the eye and the brain perceives a colour. If an object absorbs all visible wavelengths, it appears black; if it reflects all, it appears white.

5.2 Crystal Field Theory

The crystal field theory was first developed to account for the properties of transition metal ions in solids. In this theory, the lone pair on ligand is modelled as a point negative charge that attracts the positive central metal ion, which provides the stability to the complex. They also repel the electrons in the d orbitals of the metal ion.

Recall from Topic 1 Atomic Structure that the d orbitals have five different orientations and they are degenerate (same energy level).

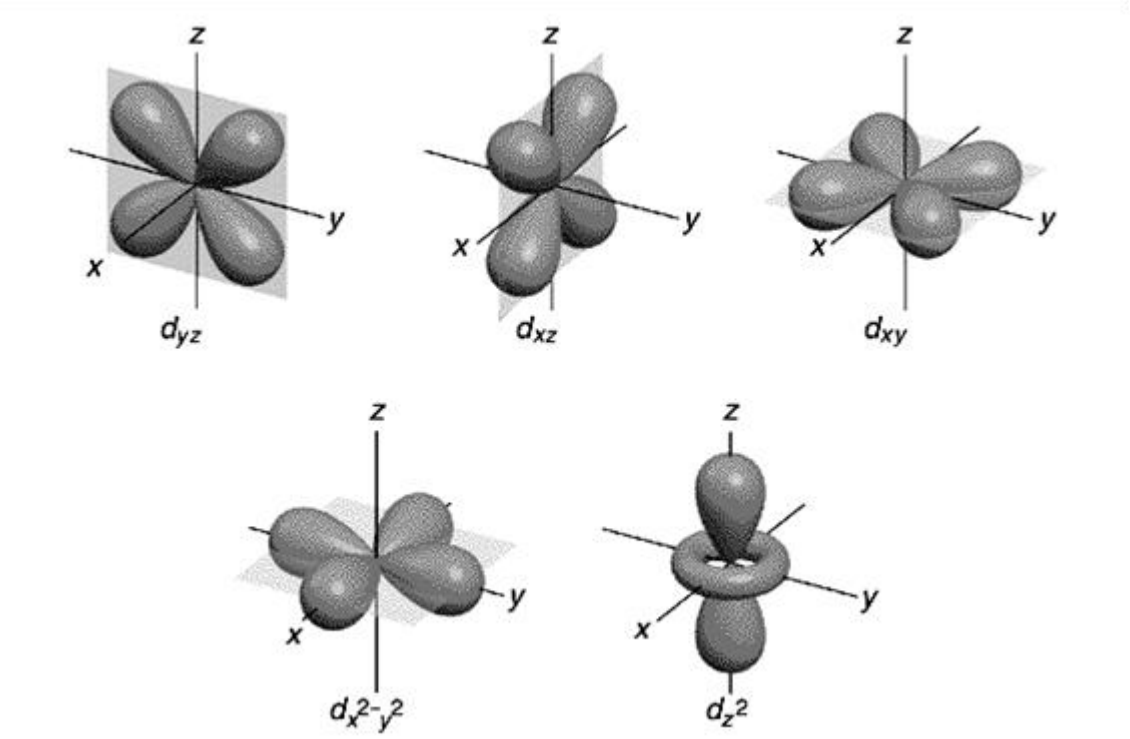


Figure 7. The shapes and orientations of the 3d orbitals

5.2.1 Splitting of degenerate d orbitals in octahedral complex

LO 13(k): describe, using the shape and orientation of the d orbitals, the splitting of degenerate d orbitals into two energy levels in octahedral complexes

- In a free transition metal ion, all five orbitals are degenerate (have the same energy).
- In the presence of ligands in an octahedral field, the ligands approach the metal ion along the mutually perpendicular *x*, *y*, and *z* axes.

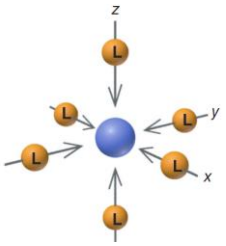


Figure 8. Ligands approach along the mutually perpendicular axes.

- As the ligands approach, their electron pairs repel electrons in the five *d* orbitals of metal ions, causing all five d orbitals to increase in energy.
- However, the d electrons are repelled unequally due to the different orientations of d orbitals. As the ligands move along the *x*, *y* and *z* axes, they approach directly toward the lobes of the $d_{x^2-y^2}$ and d_{z^2} orbitals but between the lobes of the d_{xy}, d_{yz} and d_{xz} orbitals. Thus, the electrons in $d_{x^2-y^2}$ and d_{z^2} orbital experienced stronger repulsion, which causes the energy of these orbitals to be higher than the d_{xy}, d_{yz} and d_{xz} orbitals.
- The five *d* orbitals therefore are no longer degenerate, but are split into two groups with an energy gap (ΔE) between them.

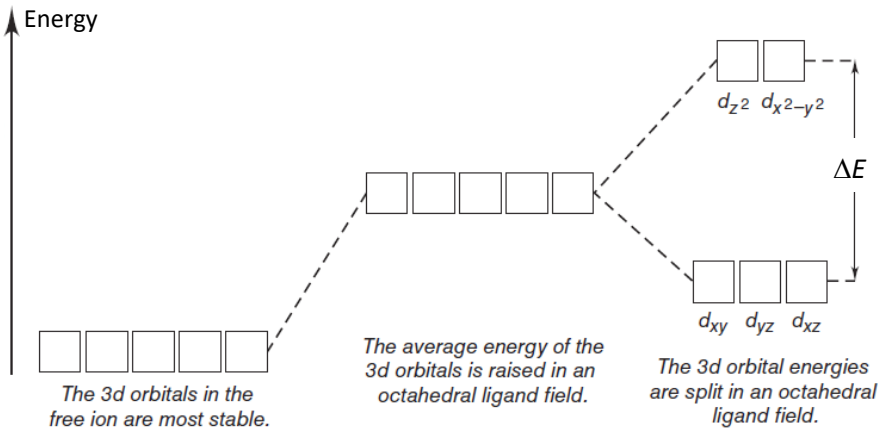


Figure 9. Splitting of d orbitals by an octahedral field of ligands.

5.2.2 Electronic d-d transition

- Let us consider the $[Ti(H_2O)_6]^{3+}$ ion, which appears purple in aqueous solution. $Ti^{3+}(aq)$ is a d^1 ion, with the *d* electron in one of the three lower energy orbitals.

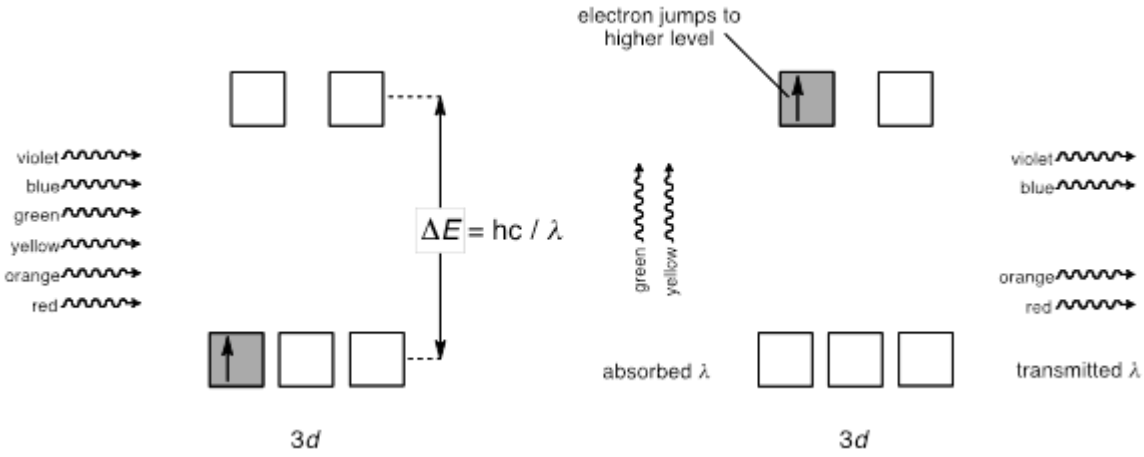


Figure 10. Orbital diagram depicting d-d electron transition.

- When white light shines on the solution, the electron at the lower energy level will absorb energy from the light and jump to one of the higher energy orbitals. Since the electron jumps from one d-orbital to another d-orbital, this movement is called a d-d transition.
- The energy gap (ΔE) between the two levels corresponds to the energy of photons with a range of wavelength in the visible spectrum. For $Ti^{3+}(aq)$, it happens to be in the green and yellow range.
- The complementary colours red, orange, blue and violet lights are transmitted, thus the solution looks purple.

LO 13(l): explain, in terms of d orbital splitting and d-d transition, why transition element complexes are usually coloured [knowledge of the relative order of ligand field strength is not required]

In the presence of ligands, the partially filled degenerate 3*d* orbitals of a transition metal ion are split into two different energy levels with a small energy gap ΔE between them. There are vacancies in the higher energy *d* orbitals. The promotion of an electron from the lower to the higher of these *d* orbitals requires the absorption of radiation in the visible spectrum with energy corresponding to the energy gap. Such a d-d transition is responsible for the colour of the complex ion. The colour observed is the complement of the colours absorbed.

5.3 Factors affecting the colour of complexes

5.3.1 Oxidation state of the metal

Different number of electrons in the *d* orbitals of the transition metal ion will result in different interactions with the electrons from the ligands. This will give rise to different energy gap (ΔE) thus the wavelengths of light absorbed will also be different. The table below shows the example of vanadium complexes.

Formula of ion	V^{3+}(aq)	V^{2+}(aq)
Oxidation state of vanadium	+3	+2
Electronic configuration	[Ar] $3d^2$	[Ar] $3d^3$
Colour	green	violet

The absence of colour in Sc^{3+}, Ti^{4+}, Cu^+ and Zn^{2+} is due to them having either no *d* electrons ($3d^0$ for Sc^{3+} & Ti^{4+}) or fully filled *d* orbitals ($3d^{10}$ for Cu^+ & Zn^{2+}). In such cases, no *d-d* electronic transition is possible.

5.3.2 Nature of ligand

Different ligands have different effects on the splitting of the *d* orbitals. The difference in magnitude of ΔE will lead to different colours observed. The diagram below shows the example of some nickel octahedral complexes.

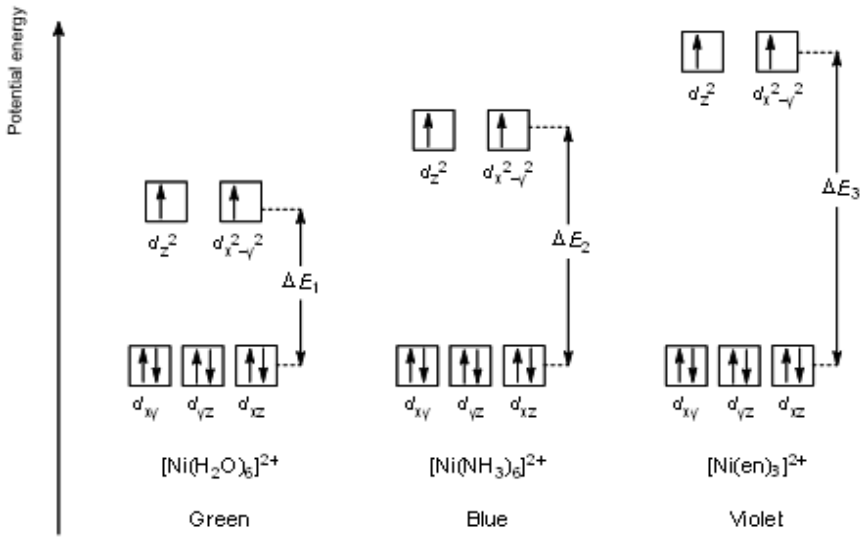


Figure 11. *Size of d orbital splitting – the energy gap between the two groups of d orbitals depends on the ligand*

Note: Other splitting patterns exist (and may appear as application questions) but student are only expected to be able to recall splitting of d-orbitals for octahedral complexes.

5.4 Common transition metal ions/compounds and their corresponding colours

Transition metal	Oxidation number of transition metal	Formula	Colour
Chromium	+3	$[Cr(H_2O)_6]^{3+}$	green
	+6	CrO_4^{2-}	yellow
	+6	$Cr_2O_7^{2-}$	orange
Manganese	+2	Mn^{2+}	faint pink / colourless if dilute
	+4	MnO_2	dark brown ppt
	+6	MnO_4^{2-}	dark green
	+7	MnO_4^-	purple
Iron	+2	$[Fe(H_2O)_6]^{2+}$	pale green
	+2	$Fe(OH)_2$	green ppt
	+3	$[Fe(H_2O)_6]^{3+}$	yellow
	+3	$[Fe(SCN)(H_2O)_5]^{2+}$	blood red
	+3	$Fe(OH)_3$	reddish brown ppt
Copper	+2	$[Cu(H_2O)_6]^{2+}$	pale blue
	+2	$[Cu(NH_3)_4(H_2O)_2]^{2+}$	dark blue
	+2	$[CuCl_4]^{2-}$	yellow
	+2	$Cu(OH)_2$	pale blue ppt

Not all colours of transition metal compounds originate from d-d transition. Some colours in the table above can be due to other electronic transitions which are not in the A Level syllabus (only d-d transition is required).

5.5 Using colorimetry in experiments

5.5.1 Determining the concentration of complex ions by colorimetry

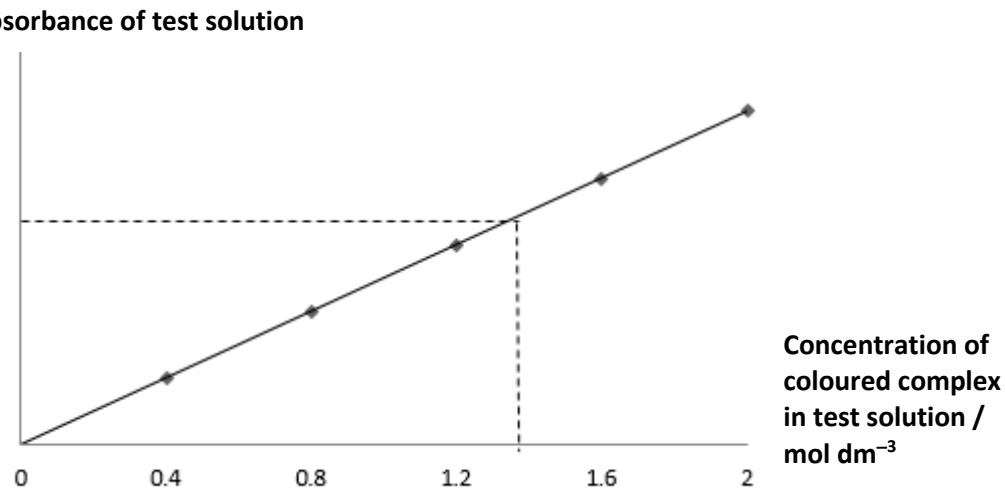
To determine the concentration of a coloured complex using colorimetry

Example: N2013/P2/Q1 (Planning Question)

Approach:
A calibration graph is first obtained by measuring the absorbance of a series of solutions containing the coloured complex at various known concentrations. Then measure the absorbance of the unknown solution and read its concentration off the calibration graph.

Generic procedure

1. A suitable filter (of a complementary colour) is selected.
2. A 'blank' absorbance reading is taken using water as a reference.
3. A series of solutions of known concentrations of (the coloured complex) are made up (usually by dilution from a stock solution).
4. The absorbance of the solutions are measured in turn with the colorimeter.
5. A calibration graph of absorbance against concentration is plotted.
6. The absorbance of the test solution is now measured, and the calibration curve is used to determine the unknown concentration.



- If the UV-VIS spectrophotometer is used instead of the colorimeter, the absorbance readings are measured at a fixed wavelength (usually at the wavelength where absorbance is the greatest or the complementary colour), instead of using a filter in Step 1.

5.5.2 Investigating the stoichiometry of complex ions by colorimetry

The formula of a complex ion can be determined by measuring the colour intensity of the complex ion, provided the colour of the complex is quite different from the colours of the separate aqueous ions.

E.g. When $Fe^{3+}(aq)$ react with thiocyanate ions $SCN^-(aq)$, a deep red (blood red) colour is produced:

$$Fe^{3+}(aq) + x\,SCN^-(aq) \rightarrow [Fe(SCN)_x]^{3-x}(aq)$$

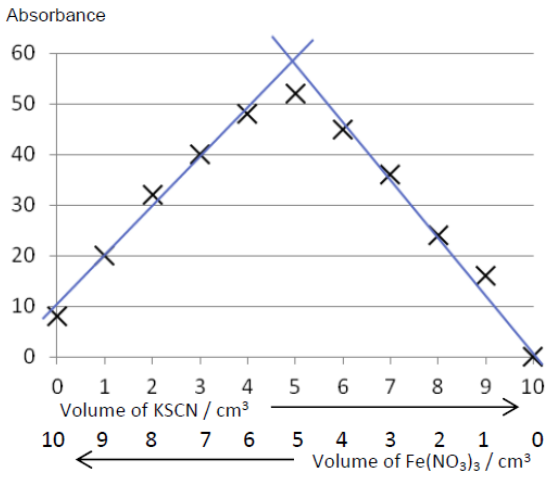
The stoichiometry of the complex can be determined by the **method of continuous variation**. Mixtures of Fe^{3+} and SCN^- with Fe^{3+} : SCN^- in molar proportions of 10:0, 9:1, 8:2, 7:3, 6:4, etc. is made. In other words, the relative proportions of Fe^{3+} : SCN^- are continuously varied from 10:0 to 0:10.

Clearly, the mixture with the most intense coloured solution corresponds to molar proportions of Fe^{3+} and SCN^- which just react completely leaving neither in excess. In some cases, it might be possible to tell by eye which mixture contains the darkest-coloured solution, but the judgment can be done much more reliably and accurately using a spectrophotometer. The spectrophotometer measures the absorbance of the test solution, which is proportional to the concentration of the complex.

The table below shows a typical set of results for the Fe^{3+} / SCN^- investigation.

Tube number	1	2	3	4	5	6	7	8	9	10	11
Volume of 5.00×10^{-3} mol dm^{-3} $Fe(NO_3)_3$ /cm^3	10	9	8	7	6	5	4	3	2	1	0
Volume of 5.00×10^{-3} mol dm^{-3} KSCN /cm^3	0	1	2	3	4	5	6	7	8	9	10
Absorbance	8	20	32	40	48	52	45	36	24	16	0

The results are represented graphically below.



Extrapolate the two straight lines to find the maximum absorbance (which corresponds to the highest concentration of the complex).

- In what molar proportions do Fe^{3+} and SCN^- react to form the blood red complex ion?
- Write the balanced equation for the formation of the complex ion by ligand exchange.



Planning an experiment involving qualitative analysis

You may be asked to propose a sequence of test-tube reactions to identify inorganic ions. This means you need to review your Inorganic Chemistry Qualitative Analysis notes. **Inorganic QA tests** are based on four main types of chemical reactions that produce precipitates, gases, and colour changes. Try to identify these four main types of inorganic reactions in your QA notes:

- Ionic precipitation reactions
- Acid-base reactions
- Redox reactions
- Complex forming reactions including ligand exchange

When planning a qualitative analysis experiment, you may be asked to:

- Present the sequence of tests. You may use a flowchart or table.
- Write the procedure with essential details of quantities and conditions for each test.
- State the expected observations for both positive and negative tests.
- Explain the chemistry underlying each test e.g. type of reaction, identity of species responsible for precipitate / gas / colour change.

The unknown ions might be present in a mixture, and you might be required to plan a filtration to separate the ions or precipitates. For example, **FA1** contains **two cations** (Fe^{2+} and Zn^{2+}). NaOH(aq) and NH_3(aq) are common test reagents for cations: Fe^{2+} forms an insoluble basic hydroxide while Zn^{2+} forms a soluble amphoteric hydroxide, which can be separated by filtration. A sample plan is shown below.

Test	*Observations*	*Location of ions*
To 1 cm^3 of **FA1** in a test tube, add excess NaOH(aq).	Green ppt insoluble in excess NaOH	Fe^{2+} – $Fe(OH)_2$ ppt
Filter the mixture and collect the filtrate in a separate test tube.	Colourless filtrate	Zn^{2+} – in the filtrate as $[Zn(OH)_4]^{2-}$
	Green residue turns reddish brown on contact with air	$Fe(OH)_2$ oxidised to $Fe(OH)_3$

You may also present your plan as a flowchart.

LOOKING AHEAD

You have completed the last topic in 9729 H2 Chemistry. Do spend some time to consolidate all that you have learned and be able to see how basic chemistry principles are applied in different topics throughout the syllabus. All the best!