

ATARNotes

Chemistry Units 3&4

Edition 2

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- Graduating with a 99.95, Thushan topped the state in Chemistry with a study score of 50 and has since tutored and lectured hundreds of VCE students.

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ATAR

Notes

VCE Chemistry Units 3&4
Complete Course Notes

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Preface

The VCE Chemistry Units 3&4 course is split into two units, each with a number of Areas of Study:

Unit 3 – How can chemical processes be designed to optimise efficiency?

- Area of Study 1 – What are the options for energy production?
- Area of Study 2 – How can the yield of the chemical product be optimised?

Unit 4 – How are organic compounds categorised, analysed and used?

- Area of Study 1 – How can the diversity of carbon compounds be explained and categorised?
- Area of Study 2 – What is the chemistry of food?
- Area of Study 3 – Practical Investigation

In the determination of your study score, the graded assessments (GAs) are weighted as follows:

Outcomes	Assessment	Weighting
GA1	Unit 3 SACs	16%
GA2	Unit 4 SACs	24%
GA3	Examination	60%

One resource that I would highly recommend is www.chemguide.co.uk. This website is geared towards Year 12 students in the United Kingdom, but much of the material is relevant to VCE, and this resource explains many complex concepts in a simple way.

Best of luck with your VCE, and I hope you enjoy Chemistry!

— Thushan Hettige

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Part I

Unit 3: How can chemical processes be designed to optimise efficiency?

Significant Figures

Before we get started, here are some brief notes on significant figures. In Units 3&4 Chemistry, when you do calculations, you are expected to express your answer to the appropriate number of decimal places or significant figures, depending on the calculation.

Significant figures are the number of digits in the number, starting from the **first non-zero digit**.

For example, the number 0.1392 has **4 significant figures**, starting from '1' (the second digit), which is the first non-zero digit. Also, the number 205 has **3 significant figures** ('2' being the first non-zero digit) and the number 0.0023920 has **5 significant figures**.

Decimal places are the number of digits after a decimal point, if there are any. For example, the number 0.0023920 has **7 decimal places** and the number 203 has **0 decimal places**.

The following general rules apply:

- If **adding or subtracting** numbers, the answer should be to the same number of **decimal places** as the number in the sum with the **lowest number of decimal places** (e.g. $20.01 + 21.4 + 1.200 = 42.6$ (42.610)). The number 20.01 has **2 decimal places**, 21.4 has **1 decimal place** and 1.200 has **3 decimal places**. Therefore, the answer should be to **1 decimal place** - hence 42.6 and not 42.610).
- If **multiplying or dividing** numbers, the answer should be to the same number of **significant figures** as the number in the sum with the **lowest number of significant figures** (e.g. $10.62 \times 0.50000 = 5.310$). The number 10.62 has **4 significant figures**, and 0.50000 has **5 significant figures**. Therefore, the answer should be to **4 significant figures** - so 5.310).
- If $10^a = b$, the number **b** must be to the same number of **significant figures** as **a** has **decimal places** (e.g. $10^{3.14} = 1.4 \times 10^3$. The number **3.14** has **2 decimal places**, therefore the answer has to be to **2 significant figures** - so 1.4×10^3).
- If $\log_{10}a = b$, the number **b** must be to the same number of **decimal places** as **a** has **significant figures** (e.g. $\log_{10}(0.0123) = -1.910$. The number **0.0123** has **3 significant figures**, hence the answer has to be to **3 decimal places** - so -1.910).

The data that you will use in your calculations include that in the question stem itself, and data from your **Data Book**. For instance, your Data Book quotes a molar mass.

Area of Study 1

What are the options for energy production?

1.1 Gases

To be able to understand fuels, you need to have a working knowledge about the physical properties of gases. A **gas** is a state of matter whereby the individual particles (whether they be single atoms, or molecules) are widely spaced apart and are moving independently of one another. There are no intermolecular interactions (e.g. dispersion forces) between gas molecules in general.

1.1 Properties of a gaseous system

Consider a vessel (a box) that is full of gas. We can talk about the various properties of this vessel of gas in terms of **volume, pressure, amount (in mol) of gas molecules, and temperature**.

Volume and pressure

The volume (measured in mL or L) is a measure of how much space the vessel takes up.

The pressure in the vessel is equal to the force of the gas on the walls of the vessel, per unit surface area (this is key knowledge in the study design) with the standard unit being the **Pascal (Pa)**. As a crude example, if the surface area of the walls inside the vessel were 10 m^2 (the standard unit for area) and the total force on the walls of the vessel by the gas is **60 Newtons** (the standard unit for force), the pressure inside the vessel is **6 Pa**.

Where does this force come from? Remember that the particles in the vessel are moving in random directions, repeatedly colliding with the wall of the vessel and trying to push the vessel outwards.

The gas pressure in the atmosphere (which can be considered a giant vessel) is approximately $101,300\text{ Pa} = 101.3\text{ kPa}$. Therefore, we can use the alternate unit, **atmospheres (atm)**, whereby $1\text{ atm} = 101.3\text{ kPa}$.

Another measure of pressure is **millimetres of mercury**. If you take some liquid mercury and pour a little bit of it into a cylinder sitting on a table, to a height of the measly 1 mm, the mercury in the cylinder will exert a force on the bottom of the cylinder (due to its weight), over the surface area of the bottom of the cylinder. Therefore, we can also calculate the pressure it exerts on the bottom of the cylinder, which is defined to be **1 millimetre of mercury, or 1 mmHg**.

It turns out that if you filled a cylinder with mercury to a depth of $76\text{ cm} = 760\text{ mm}$, the pressure exerted on the bottom of the cylinder (760 mmHg by definition) is actually equal to atmospheric pressure. Hence, $1\text{ atm} = 101.3\text{ kPa} = 760\text{ mmHg}$. Another highly important alternate unit – $100\text{ kPa} = 1\text{ bar}$.

Relationship between pressure, temperature, amount and volume

Firstly, it stands to reason that if we took two 1 L vessels (with same pressure and at the same temperature), the amount of gas molecules in both 1 L vessels will be the same. If we joined these vessels together to form a 2 L vessel, the total amount of gas molecules will be double the amount in one of the 1 L vessels. This suggests that **at a given temperature and pressure**, the amount of gas molecules in a vessel is **proportional** to the volume of the vessel. For example, if we took a 10 L vessel containing gas, and a 30 L vessel containing gas at the same temperature and pressure, the amount of gas molecules in the 30 L vessel will be **3 times** the amount of gas molecules in the 10 L vessel. This is known as **Avogadro's Law**.

Additionally, if we took a 1 L vessel containing O₂ gas, another 1 L vessel containing a different gas (say N₂ gas), and a third 1 L vessel containing a mixture of O₂ and N₂ gases, all at the **same temperature and pressure**, the amount of gas molecules in each vessel is the **same**.

Hence, we can say:

$$V = k_1 n \dots \dots \dots (1)$$

where V is the volume of the vessel, k_1 is some random constant and n is the **total amount of gas molecules (in mol) in the vessel**.

Now, if you took a vessel of gas, and then you expanded the vessel out (increasing the volume of the vessel), in much the same way as pulling the plunger out of a syringe, you would decrease the pressure inside the vessel. This is because expanding the volume of a closed vessel means the particles spread out more, and therefore collide less frequently with the sides of the vessel.

In fact, it has been experimentally determined that pressure is inversely related to volume (in a closed vessel at a constant temperature). This means that doubling the volume halves the pressure, tripling the volume divides the pressure by 3, etc. This is known as **Boyle's Law**.

Therefore, we can say that in a closed vessel at constant temperature:

$$pV = k_2 \dots \dots \dots (2)$$

where p is the pressure, V is the volume, and k_2 is some random constant.

How about in a vessel that is not necessarily closed? Now, we **also** have shown through Avogadro's law that **volume** is proportional to the **amount of gas** in the vessel! Therefore, combining the two equations (1) and (2) above leads to this equation:

$$pV = k_3 n \dots \dots \dots (3)$$

... where p is the pressure, V is the volume, n is the total amount of gas, and k_3 is some random constant.

And finally, suppose you increase the temperature in a closed and rigid vessel (constant amount of gas and constant volume). Remember that an increase in temperature means that the particles will be moving much faster. This, in turn, means that the particles will be bouncing off the sides of the vessel much harder; this would increase the total pressure in the vessel. In fact, it turns out that if you double the temperature in the vessel (**with the temperature measured in Kelvin**) from say 300 K (27°C) to 600 K (327°C), you will double the pressure in the vessel. It has been experimentally shown that the pressure in the vessel is proportional to temperature (in **Kelvin**). Hence we can say:

$$p = k_4 T \dots \dots \dots (4)$$

... where p is pressure and T is the temperature **in Kelvin**, and k_4 is some random constant.

Since we already know the relationship between pressure, volume and amount of gas, we can combine equations (3) and (4) to get a combined equation:

$$pV = k_5 nT$$

Now, we know the numerical value of k_5 , determined experimentally, and we refer to it as the **universal gas constant (R)**. If the pressure is in **kPa**, volume in **L**, amount of gas in **mol** and temperature in **Kelvin**, $R = 8.31$. Therefore, we end up with the final equation:

$$pV = nRT$$

This is called the **ideal gas equation**.

Example 1.1

What would be the pressure inside a 2.00 L vessel, containing a mixture of 0.300 mol of O₂ gas and 0.200 mol of N₂ gas, at a temperature of 25°C?

Substitute the relevant numbers into the ideal gas equation (V = 2.00, T = 298 K and n = 0.200 + 0.300 = 0.500 mol of total gas):

$$p \times 2.00 = 0.500 \times 8.31 \times 298$$

$$p = 619 \text{ kPa}$$

Example 1.2

What is the total amount of gas in a 10.0 L vessel at a pressure of 730 mmHg and temperature 27°C?

First, convert pressure to the appropriate units (101.3 kPa = 760 mmHg):

$$p = \frac{730}{760} \times 101.3 = 97.3 \text{ kPa}$$

Now, substitute into the ideal gas equation:

$$97.3 \times 10.0 = n \times 8.31 \times 300$$

$$n = 0.390 \text{ mol}$$

Standard molar volumes

On top of the ideal gas equation, we also have quick measurements of the volume occupied by 1 mole of gas (also known as the molar volume) at specified conditions, which are:

- **STP (standard temperature and pressure)**, which means a temperature of 0°C (273 K) and a pressure of 1 bar (100 kPa)
- **SLC (standard laboratory conditions)**, which means a temperature of 25°C (298 K) and a pressure of 1 bar (100 kPa)

KEY POINT :

Some older textbooks may say that the pressure in STP and SLC is 1 atm (101.3 kPa). This is part of the **old** definitions of STP and SLC, which were recently changed a few years ago.

VCAA has only officially changed their definition of STP and SLC as of 2017 to line up with the definition of IUPAC (who are the experts on these matters). Therefore, past VCAA and trial exams from 2016 and earlier will use the **old** conventions for SLC and STP. Keep in mind that now VCAA is using the **new** definitions outlined in these notes!

It is known that:

- At **STP**, the molar volume is 22.7 L mol⁻¹
- At **SLC**, the molar volume is 24.8 L mol⁻¹

This means that 1 mol of gas would occupy a volume of 22.7 L at STP, and 24.8 L at SLC.

Note that under the older definitions (now obsolete), the molar volumes were 22.4 L mol⁻¹ (at STP) and 24.5 L mol⁻¹ (at SLC).

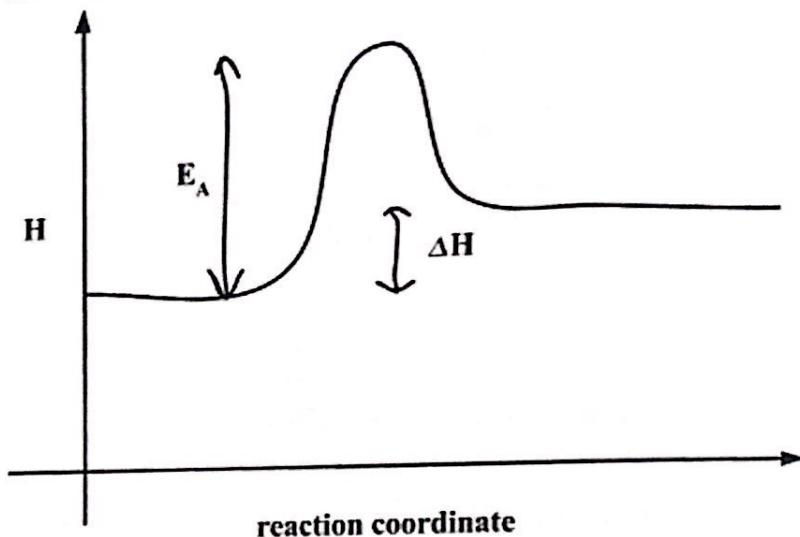
1.2 Energy Profiles

Another concept that is related to fuels which is essential to grasp is the **energy profile**.

The energy profile depicts the energy changes that occur during a chemical reaction. This is important because we use fuels as a source of energy. Before we talk about energy changes, however, we need to know what types of energy exist (in the context of this topic). The relevant types for this topic are:

- **Chemical energy** (also known as **enthalpy**): this is the energy contained within the various electric forces within and between species. The symbol for enthalpy is **H**.
- **Thermal energy**: this is what we often think as 'heat.' It is the kinetic energy that manifests in the speed of randomly moving particles. The higher the thermal energy contained within a set of molecules, the higher their speed, and therefore the higher the temperature of the system.
- **Kinetic energy**: this is an umbrella term for energy contained within the movement of particles. Thermal energy is a type of kinetic energy.

Now, let's have a look at what an energy profile looks like:



Regarding the axes:

- The vertical axis is the **chemical energy (enthalpy)** of the reacting particles.
- The horizontal axis is the **reaction coordinate** (i.e. how far along the process the particles have gone from reactants to products).

Let's go through the steps that occur throughout the reaction.

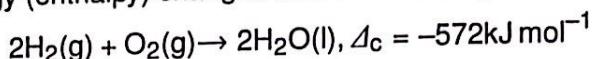
1. The reactant particles move close to one another.
2. The reactant particles move close enough to one another for their electrons to start repelling one another, slowing the particles down. The kinetic energy of the particles is being converted into **chemical energy** here - much like what happens when you squeeze a spring. Here, the **enthalpy starts to rise** - remember that it represents chemical energy.
3. The reactant particles collide and the reactant bonds break. Breaking the bond requires energy to be 'injected' into the chemical. Hence, the **enthalpy continues to rise**.
4. New bonds form to create the products. The formation of new bonds causes a decrease in chemical energy and conversion into kinetic energy. Hence, the **enthalpy will fall**.

A few terms need to be defined here.

- The **activation energy** is the minimum energy needed to commence the reaction. It is depicted by E_A on the energy profile and is sourced from the kinetic energy of moving reactant particles.
- The **change in enthalpy** is denoted as ΔH .
 - If ΔH is **positive**, then this means that the reaction is **endothermic**. There has been a net **absorption** of energy by the chemicals, usually decreasing the temperature of the surroundings.
 - If ΔH is **negative**, the reaction is **exothermic**. There has been a net **release** of energy by the reactants, usually increasing the temperature of the surroundings.

1.3 Thermochemical Equations

To understand the way we use fuels as a source of energy, we need some background knowledge about thermochemical equations. Thermochemical equations are chemical equations that also contain information about the chemical energy (enthalpy) changes that occur during the reaction. For example:



So, what information can we deduce from this equation? Well, we know that 572 kJ of heat energy is released per mole of **reaction**, that is, when 2 moles of hydrogen and 1 mole of oxygen react to form 2 moles of water. The subscript 'c' in Δ_{c} denotes that this is a combustion reaction. We also know that this value of 572 kJ is with the species at their standard states under standard conditions (i.e. 298 K, 1 bar).

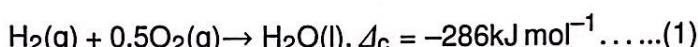
States are very important – you **MUST** include states in these equations because a change in state changes the enthalpy – for instance: $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$ has a different Δ_{H} value.

Coefficients

The coefficients also matter. If we multiply the equation by a number, we multiply Δ_{H} by that same factor. So, to take the previous equation as an example:



If we multiply the coefficients by 0.5, then we also have to multiply the Δ_{H} by 0.5 as well:



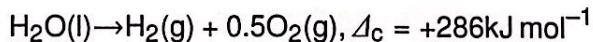
If you check your data book, it quotes the $\Delta_{\text{H}_{\text{c}}}$ for the combustion of hydrogen to be -286 kJ mol^{-1} – this is for 1 mole of hydrogen. If you quote a value direct from your data book, the coefficient next to your “fuel” reactant (H_2 , C, CH_4 etc.) **must** be 1. If it isn't, then you manipulate the H to fit the equation.

Sign of Δ_{H}

Let's take equation (1) and flip it:

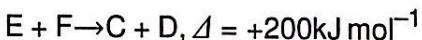
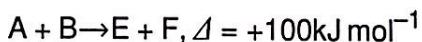


Now, if equation (1) – the forward reaction – releases 286 kJ of energy per mole, then it follows that the back reaction – equation (2) – must absorb 286 kJ of energy per mole. Hence, reversing the equation changes the sign of H, so we can complete equation (2):



Reaction pathways

This is best explained through an example. (I'm omitting states here, but just for the purpose of this exercise!) If we have the reaction: $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$ and we want to know Δ_{H} , but we are only given this data:



We can add the two equations, and adding two equations together means we add the H values:



Cancelling out:



To summarise:

- If you want to multiply the coefficients of a reaction by x, then multiply Δ_{H} by x.
- If you want to add two equations together, add their Δ_{H} values.
- If you want to reverse the direction of a reaction, change the sign of the Δ_{H} value.

1.4 Introduction to Fuels

Firstly, we need to establish what a fuel is; you must know the definition of a fuel for the exam as it is key knowledge in the study design. A fuel is a substance that can be reacted with other substances (often oxygen), leading to the release of energy (usually chemical) that can be harnessed for a specific purpose. There are a number of ways in which fuels are used in society, including to generate electrical energy (in the form of electricity to power electrical appliances), and to power engines of vehicles, lawnmowers, hedge trimmers, chainsaws etc.

One particularly important concept with relation to fuels is their **renewability**. A renewable fuel is one that can be replenished or replaced by natural processes within a relatively short period of time. Renewable fuels are considered a **sustainable source of energy**, since we can continually replenish the fuel, so the chances of us running out of these fuels are significantly smaller.

There are two main categories of fuels, **fossil fuels and biofuels**. You are expected to be able to distinguish between these two types with relation to their **renewability and origin**.

1.4.1 Fossil Fuels

Fossil fuels are chemicals that were produced by fossilisation of dead plant and animal matter. Fossilisation is a process whereby a dead organism is rapidly buried, usually in low-oxygen conditions, preventing decomposers from breaking down the organism's body. Over **millions of years**, the preserved dead organism is subject to extremely high pressures in the multiple layers of rock and sediment that form over it, and the chemicals that comprise the organism are broken down into a mixture of hydrocarbons and other organic substances. This leads to the formation of a mixture of solid **coal** (a mixture of large hydrocarbons and organic molecules that are solid), liquid **crude oil** (a mixture of semi-large hydrocarbons and organic molecules that are liquid) and **natural gas** (a mixture of small hydrocarbons such as methane and ethane).

Importantly, fossil fuels are considered **not a renewable source of energy**. This is because the rate at which fossil fuel production by fossilisation occurs is extremely slow, almost negligible compared to the rate at which we are consuming fossil fuels.

1.4.2 Biofuels

Biofuels are fuels that are derived from matter from **living or recently deceased plants**. To understand the general concept of why we love biofuels so much, we need to briefly delve into Biology to understand how plants develop.

Plants are borne out of fertilised seeds. Over time the seed develops into a small plant, which grows into a large plant. Where does the extra plant matter come from to allow the plant to grow like this? In humans and other animals, we develop from being a tiny infant into a big adult and we get the extra material to form human tissue from food (which contains organic molecules). However, plants cannot eat stuff. Instead, they synthesise their own organic molecules using carbon atoms from CO_2 and H_2O from the environment in a process known as **photosynthesis**.

Photosynthesis is the process by which plants produce glucose from CO_2 and H_2O , using sunlight as the source of energy here. The glucose is converted into other organic molecules such as oils, proteins and complex carbohydrates. Some of these organic molecules, including glucose and oils, can be extracted from the plants and chemically modified to form biofuels such as **bioethanol** and **biodiesel**.

Biogas is produced when plants die and start to decompose; bacteria break down these large molecules into smaller molecules, including methane gas. Importantly, these fuels are **renewable**. We can continuously grow plant matter to generate biofuels, harnessing energy from the sun. These fuels are also **carbon neutral**. This means that there is no net production of CO_2 into the atmosphere.

Why is this the case, even though burning biofuels leads to the release of CO₂ into the atmosphere (just like any other fuel)? It is because these crops will remove CO₂ from the atmosphere via photosynthesis to produce glucose and are the precursors to what will become our biofuels. The source of the carbon atoms to produce our biofuels in the first place is the carbon dioxide from the atmosphere. In short, the CO₂ released during the burning of the fuel is approximately equal to the CO₂ consumed during the production of the fuel (via growing of crops).

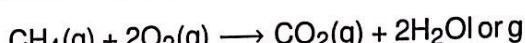
Burning of fuels

As per the definition of a fuel, when we react the fuel with another chemical, it leads to the release of energy.

The question is – what is the actual chemical reaction that occurs?

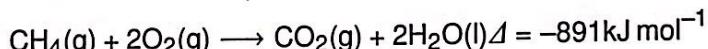
In the context of VCE Chemistry, we are going to talk about fuels that burn in oxygen – in other words, fuels that react with oxygen in a **combustion reaction** to produce carbon dioxide and water.

Let us have a look at the combustion of a simple fuel, methane (CH₄), in oxygen:



Now, combustion reactions are **exothermic reactions** (i.e. $\Delta H < 0$), where there is a net loss (release) of **chemical energy** throughout the reaction. The chemical energy released can be converted into a mixture of other forms of energy, for example **thermal energy** to increase the temperature of the surroundings, **light energy** in the formation of the fire you see from the burning of methane, and **mechanical energy** in certain circumstances such as in an internal combustion engine. In other words, **chemical energy** is converted into other forms of energy, such as **thermal energy** (mainly), **light energy**, and in some cases, **mechanical energy**.

We can therefore write a thermochemical equation for the above reaction:



From the previous section, we can glean from this information that if you burn **1 mole of methane in 2 moles** of oxygen to form 1 mole of CO₂ and 2 moles of H₂O, you will release 891 kJ of energy.

There are other units besides kJ mol⁻¹ that we can use for enthalpy change; we can also use:

- kJ g⁻¹
- MJ tonne⁻¹

Note that 1 MJ = 1000 kJ and 1 tonne = 1000 kg.

Just for illustrative purposes, let us convert 891 kJ mol⁻¹ into these other units:

kJ g⁻¹ :

Burning 1 mol of methane releases 891 kJ of energy.

Therefore, burning 16.0 g of methane (1 mol) releases 891 kJ of energy.

Hence, burning 1.00 g of methane releases $\frac{891}{16.0} = 55.7 \text{ kJ}$ of energy.

Therefore, $891 \text{ kJ mol}^{-1} = 55.7 \text{ kJ g}^{-1}$.

MJ/tonne:

Burning 1 mol of methane releases 891 kJ of energy.

Therefore, burning 16.0 g of methane (1 mol) releases 891 kJ of energy.

Therefore, burning 1.00×10^6 g of methane (1 tonne) releases:

$$891 \times 1.00 \times 10^6 / 16.0 = 5.57 \times 10^7 \text{ kJ} = 5.57 \times 10^4 \text{ MJ.}$$

Therefore, $891 \text{ kJ mol}^{-1} = 5.57 \times 10^4 \text{ MJ tonne}^{-1}$.

1.5 Complete and incomplete combustion

Complete combustion occurs when a fuel is burnt in excess oxygen to form CO_2 and H_2O .

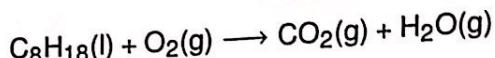
Incomplete combustion occurs when a fuel is burnt in limited amounts of oxygen. This can form a variety of products including a small amount of CO_2 sometimes, but the primary products are CO (carbon monoxide) and occasionally elemental carbon (C). You can also produce a variety of small molecules that are the products of 'cracking' of larger hydrocarbons such as octane (if octane was a component of the fuel), such as methane and ethane.

1.6 Thermochemical equations for combustion

1.6.1 Balancing combustion equations

You need to know how to balance combustion equations for various fuels, including hydrocarbons, methanol, and ethanol (both complete and incomplete combustion).

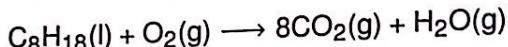
For example, let's balance the equation for the complete combustion of octane (C_8H_{18}), which is liquid at room temperature:



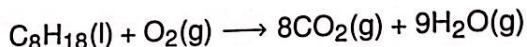
The best way of balancing these equations is to:

- Balance the C atoms by writing the appropriate coefficient next to the CO_2 .
- Balance the H atoms by writing the appropriate coefficient next to the H_2O .
- Finally, balance the O atoms by writing the appropriate coefficient next to the O_2 ; **you can write a fraction here as this is within the realm of convention.**

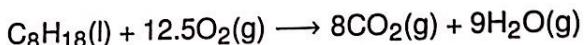
In the above example, there are 8 C atoms on the LHS, so you put an '8' next to the CO_2 :



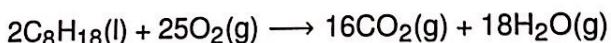
There are 18 H atoms on the LHS, so put a '9' next to the H_2O (remember H_2O has 2 H atoms each):



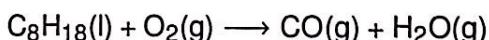
There are 25 O atoms on the RHS, so you write '25/2' or '12.5' next to the O_2 (which has 2 H atoms each):



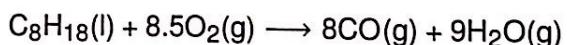
If you don't like fractions or decimals, you can get rid of the fraction by multiplying both sides by 2:



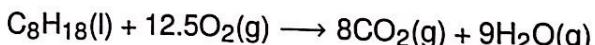
And now, let us follow the same process for the **incomplete combustion** of octane. Conventionally, when you write the equation for the incomplete combustion of a fuel, you write the equation of the **conversion of the fuel to CO**, even though in reality, multiple processes occur such as the formation of simpler alkanes, carbon, and a tiny amount of CO_2 . Writing down the equation:



If you follow the same steps, you will get this:



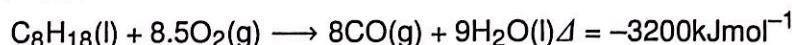
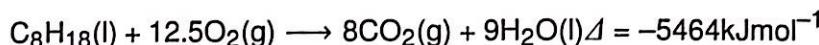
Compare this to the complete combustion equation:



You can see that in the incomplete combustion equation, less oxygen is used per mole of octane; this is consistent with the limited oxygen available in the conditions conducive to incomplete combustion.

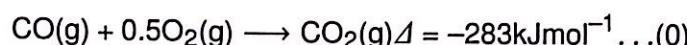
1.6.2 Thermochemical equations for complete and incomplete combustion

Let us compare the thermochemical equations for the complete and incomplete combustion of octane (putting water as a liquid because the values that data tables give for enthalpies of combustion conventionally assume water to be in the liquid state):

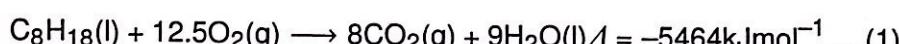


Importantly, the enthalpy of incomplete combustion of a fuel is always **less negative** than the enthalpy of complete combustion of the fuel. This is because the combustion of CO itself, the product of incomplete combustion, to CO₂, is also an exothermic reaction. One can consider the complete combustion reaction conceptually to occur in two steps – the incomplete combustion of the fuel to CO, releasing energy, and the combustion of the CO itself to CO₂, releasing additional energy.

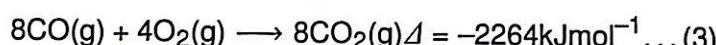
We can use the skills we developed earlier to infer the enthalpy of incomplete combustion of a fuel, if we are given the enthalpy of **complete combustion of the fuel** and the enthalpy of **combustion of CO**, the latter being illustrated below:



Suppose we were given only the thermochemical equation for the combustion of octane:



To determine the equation for the incomplete combustion of octane, we can break down the above equation into two equations:

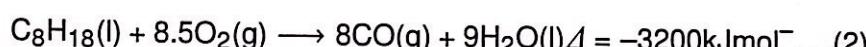


To get equation (3), we multiplied equation (0) by 8. Multiplying coefficients by 8 means we multiply the ΔH value by 8. Now, if you added equations (2) and (3), you will end up getting equation (1). Remembering that summing equations together means you add the ΔH values, we can get the following equation:

$$x + (-2264) = -5464$$

$$x = -3200$$

Therefore, equation (2) becomes:



Hence, the heat of incomplete combustion of octane is -3200 kJ mol⁻¹.

You can use this method with any fuel containing only carbon, hydrogen and/or oxygen.

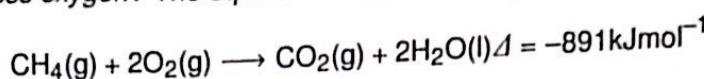
1.7 Stoichiometry

You are expected to be able to perform stoichiometric calculations involving combustion reactions to determine the amount, mass or volume of products and reactants in a reaction, as well as the heat generated during the reaction. The best way to go about this is via examples.

1.7.1 Mass-mass stoichiometry

Example 1.3

What would be the mass of CO_2 produced and amount of energy released in MJ if 1.00 tonne of methane were combusted in excess oxygen? The equation for the complete combustion of methane is:



Here, we know that if 1 mole of CH_4 were combusted (with 2 moles of O_2), we would release 891 kJ of energy. How about if we released 1.00 tonne?

Since we know the relationship between the amount of CH_4 and the amount of energy released, it is essential to determine the amount of 1.00 tonne of CH_4 . Hence:

$$\begin{aligned} n(\text{CH}_4) &= 1.00 \times 10^6 / 16.0 \\ &= 6.25 \times 10^4 \text{ mol} \end{aligned}$$

Therefore, the amount of energy released would be:

$$\begin{aligned} E &= 6.25 \times 10^4 \times 891 \\ &= 5.57 \times 10^7 \text{ kJ} \\ &= 5.57 \times 10^4 \text{ MJ} \end{aligned}$$

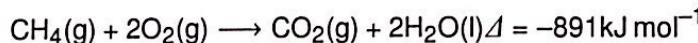
Now, to figure out the mass of CO_2 produced. We know that if 1 mole of CH_4 were combusted, 1 mole of CO_2 would be produced – going by mole ratios. Hence:

$$\begin{aligned} n(\text{CO}_2) &= n(\text{CH}_4) = 6.25 \times 10^4 \text{ mol} \\ &= n(\text{CO}_2) \times 44.0 \\ &= 2.75 \times 10^6 \text{ g} \\ &= 2.75 \text{ tonnes} \end{aligned}$$

1.7.2 Mass-volume stoichiometry

Example 1.4

What would be the volume of CO_2 produced at SLC if 2.50 kg of methane were combusted in excess oxygen? The thermochemical equation for the complete combustion of methane is:



Firstly, recall that SLC (standard laboratory conditions) means a temperature of 25°C and 100 kPa (1 bar). Also recall that 1 mol of gas occupies 24.8 L of volume. Therefore, we know a relationship between the volume of CO_2 and its amount at SLC. We also know that reacting 1 mole of CH_4 will produce 1 mole of CO_2 . Therefore, we should determine the amount of CH_4 in 2.50 kg:

$$\begin{aligned} n(\text{CH}_4) &= 2.50 \times 10^3 / 16.0 \\ &= 156 \text{ mol} \\ n(\text{CO}_2) &= n(\text{CH}_4) = 156 \text{ mol} \end{aligned}$$

Therefore, since 1 mole of CO_2 would occupy 24.8 L of volume:

$$\begin{aligned} V(\text{CO}_2) &= 156 \times 24.8 \\ &= 3.88 \times 10^3 \text{ L} \end{aligned}$$

Example 1.5

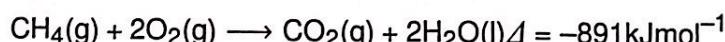
What if the CO_2 produced was at 95.3 kPa pressure and a temperature of 20°C ?

In this case, you would use the ideal gas equation ($pV = nRT$):

$$\begin{aligned} V(\text{CO}_2) &= nRT/P \\ &= 156 \times 8.31 \times 293 / 95.3 \\ &= 3.99 \times 10^3 \text{ L} \end{aligned}$$

1.7.3 Volume-volume stoichiometry**Example 1.6**

What would be the volume of CO_2 produced at SLC if 25.0 L of methane at SLC were combusted in excess oxygen? The thermochemical equation for the complete combustion of methane is:



We know that if we react **1 mole** of CH_4 with oxygen completely, we would produce **1 mole** of CO_2 , and that the amount of a gas is **proportional** to its volume (if temperature and pressure constant). We also know (from Avogadro's Law) that one mole of a gas, no matter which gas, would occupy the same volume every single time (given a constant temperature and pressure).

Therefore, we can say that if we react **1 L** of CH_4 under a given temperature and pressure, we would produce **1 L** of CO_2 under the same temperature and pressure!

The question gave a volume of a reactant at SLC, and asked for a volume of a product at SLC too! Therefore, the temperature and pressure are constant here!

Hence:

$$V(\text{CO}_2) = V(\text{CH}_4) = 25.0 \text{ L}$$

To illustrate this further, let's do another question:

Example 1.7

What would be the volume of CO_2 produced at SLC if 25.0 L of ethane at SLC were combusted in excess oxygen? The equation for the complete combustion of ethane is:



We know that:

- **1 mole** of ethane would combust to form **2 moles** of CO_2 .
- The amount of a gas is proportional to its volume at a given temperature and pressure; in other words, double the amount of a gas would occupy double the volume.
- Hence, **1 L** of ethane at SLC would combust to form **2 L** of CO_2 at SLC.

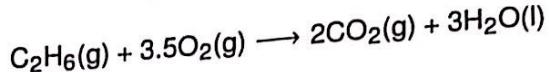
Hence, we can say:

$$\begin{aligned} V(\text{CO}_2) &= 2 \times V(\text{C}_2\text{H}_6) \\ &= 50.0 \text{ L} \end{aligned}$$

Now, let's go through a third example where the temperature and pressure are different. Here we will have to convert from volume to moles, and back to volume.

Example 1.8

What would be the volume of CO_2 produced at SLC if 25.0 L of ethane at a temperature of 20°C and 110 kPa were combusted in excess oxygen? The thermochemical equation for the complete combustion of ethane is:



Here, we have to determine the **amount** of ethane directly. We cannot use the trick because the temperature and pressure is different for reactant and product.

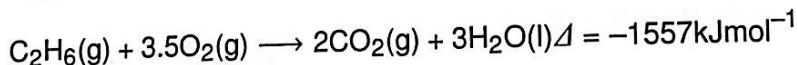
$$\begin{aligned} n(\text{C}_2\text{H}_6) &= pV/RT \\ &= 110 \times 25.0/(8.31 \times 293) \\ &= 1.13 \text{ mol} \\ n(\text{CO}_2) &= 1.13 \times 2 \\ &= 2.26 \text{ mol} \\ V(\text{CO}_2) &= 2.26 \times 24.8 \\ &= 56.0 \text{ L} \end{aligned}$$

1.7.4 Greenhouse gases

Now, the thing about fuels is that when you combust them, you produce **greenhouse gases**, which are gases that can absorb infra-red radiation, which warms up the planet. Greenhouse gases include CO_2 and CH_4 , as well as water vapour (H_2O). Excess production of greenhouse gases is problematic because they can cause global warming, also known as climate change. Therefore, an important property of a fuel is the amount of greenhouse gases produced per unit of energy that they release. You need to be able to calculate this.

Example 1.9

Calculate the volume of greenhouse gases released at SLC when methane is combusted as a fuel, to release 1.00 MJ of energy. Assume that H_2O is recovered as a liquid.



Given that H_2O is recovered as a liquid, CO_2 is the only greenhouse gas produced.

We know that if you combust **1 mole** of C_2H_6 , you would release 1557 kJ of energy. Therefore, how much C_2H_6 would you need to release 1.00 MJ (1000 kJ) of energy?

$$\begin{aligned} n(\text{C}_2\text{H}_6)_{1\text{MJ}} &= 1.00 \times 10^3 / 1557 \\ &= 0.642 \text{ mol} \end{aligned}$$

Therefore, given that 1 mole of C_2H_6 produces 2 moles of CO_2 :

$$\begin{aligned} n(\text{CO}_2)_{1\text{MJ}} &= 0.642 \times 2 \\ &= 1.28 \text{ mol} \end{aligned}$$

Hence, since 1 mole of CO_2 would occupy 24.8 L at SLC:

$$\begin{aligned} V(\text{CO}_2)_{1\text{MJ}} &= 1.28 \times 24.8 \\ &= 31.9 \text{ L} \end{aligned}$$

Therefore, 31.9 L of greenhouse gases are produced per MJ of energy released.

Example 1.10

What would be the mass of greenhouse gases produced in this scenario?

We know the amount of CO₂ to be 1.28 mol. Hence:

$$\begin{aligned} m(\text{CO}_2)_{1\text{MJ}} &= 1.28 \times 44.0 \\ &= 56.5\text{g} \end{aligned}$$

Therefore, 56.5 g of CO₂ are produced per MJ of energy produced.

1.7.5 Specific heat capacity of water

Recall from Chemistry Units 1&2 that the specific heat capacity of water is the amount of thermal energy required to heat up 1.00 g of water by 1.00°C, which is 4.18 J.

We can use the specific heat capacity of water to estimate the approximate amount of energy released as heat in a combustion reaction.

Example 1.11

Suppose we burnt a 1.56 g sample of a mixture of hydrocarbons (which include methane and ethane), and the heat was used to heat up a 2.00 L container full of water initially at 20°C. The final temperature of the water was 55°C. Determine the energy content of the fuel in kJ g⁻¹. The density of water is 1.00 g mL⁻¹. Assume all the energy released was transferred to the water.

To be able to solve this question, we need to determine the amount of energy required to heat up this 2.00 L of water from 20°C to 55°C, which will be the total amount of energy released by this 1.56 g sample of fuel. Now, since 1 mL of water weighs 1.00 g (density is given above), therefore 2.00 L of water will weigh 2.00 kg = 2.00 × 10³ g. Hence, the amount of energy released will be:

$$E = \text{mass of water} \times \text{specific heat capacity of water} \times \text{temperature change}$$

$$\begin{aligned} &= 2.00 \times 10^3 \times 4.18 \times 35 \\ &= 2.96 \times 10^3 \text{J} \\ &= 293\text{kJ} \end{aligned}$$

This is released by 1.56 g of the fuel. Therefore, the energy content of the fuel, the amount of energy released upon burning of 1.00 g of the fuel, is:

$$\begin{aligned} E_{1\text{g}} &= 293/1.56 \\ &= 188\text{kJ g}^{-1} \end{aligned}$$

1.8 Fossil Fuel Choices

In this section, we will compare and contrast the different fossil fuels with respect to their **energy content**, **renewability**, and **environmental impacts**. The fossil fuels that you need to know about are: **coal**, **crude oil**, **petroleum gas**, **natural gas**, and **coal seam gas**.

1.8.1 Coal

Coal, a black rock, is a fossil fuel that is composed of a variety of very large hydrocarbon molecules that, like any other hydrocarbon, can be combusted to release energy to generate electricity. The energy content of coal is approximately **30 MJ/kg**.

As a fossil fuel whose production by natural processes (fossilisation) is very slow, coal is a **non-renewable** source of energy.

Environmental impacts of coal (sourcing)

The mining of coal has numerous environmental impacts. Firstly, **wildlife habitat is destroyed** as land is cleared, trees felled and the ground upturned to get to the coal. Also, there can be **contamination of water within underground water deposits** that may be used as a source of potable water, as heavy metals and minerals in the rock dissolve in mine wastewater used and seep into the water table.

Sourcing of coal is also hazardous for the coal miners, who breathe **coal dust** (particles of coal) and can end up getting "**black lung disease**" from the coal dust that has built up in the lungs.

Environmental impacts of coal (combustion)

The most obvious environmental impact here is that combustion of coal leads to the production of the greenhouse gas CO_2 , which contributes to **global warming**.

Additionally, do not forget that coal is a mixture of substances, which include N and S atoms. Therefore, combustion leads to the production of NO and NO_2 (which are both toxic substances), as well as SO_2 and SO_3 .

The nitrogen and sulphur oxides, being acidic gases, can react with and dissolve in water to form **acid rain**.

Additionally, the nitrogen oxides can react with air at ground level, using sunlight as a catalyst, to form **ozone (O_3)**, which is a toxic gas and contributes to **photochemical smog**.

The burning of coal also leads to the release of particulate matter into the air, which are basically unburnt bits of coal. This contributes to air pollution and smog, and when inhaled can cause serious health effects.

1.8.2 Crude oil

Crude oil is a black tarry liquid that is composed of a series of large hydrocarbon molecules and other organic molecules containing some N and S atoms. These molecules are a little smaller than that found in coal, which is why they are found in a liquid form called crude oil. There are also small molecules such as propane and butane (usually gases) dissolved in the crude oil.

Crude oil is very rarely used in its raw form as a fuel. It is first **refined** – in other words, the different components of crude oil are separated by **fractional distillation**. The components are separated by boiling point and therefore by molecular size. The products of fractional distillation are:

- **Liquefied petroleum gas (LPG):** a mixture of propane and butane
- **Petrol:** liquids containing about 8-10 carbon atoms
- **Kerosene:** slightly more viscous liquids, used as **jet fuel**
- **Diesel:** a yet more viscous liquid (~15 carbon atoms)
- **Fuel oil:** a mixture of large hydrocarbon atoms, a black tarry liquid
- **Petroleum jelly, tar, bitumen**

LPG, petrol, kerosene and diesel are generally used as engine fuel, whereas fuel oil/diesel are used to generate electricity in some countries.

The energy content of the various distillates of crude oil are:

- **LPG 54 MJ/kg**
- **Petrol 46 MJ/kg**
- **Diesel 46 MJ/kg**
- **Fuel oil 48 MJ/kg**

These values are sourced from Wikipedia; do not attempt to memorise them! This is just to prove the point that the liquid distillates (not LPG) have very similar energy content, and importantly have a **greater energy content than coal**. As crude oil is derived from fossilisation (same as coal), it is also considered a **non-renewable** energy source.

Environmental impacts of crude oil (sourcing)

Crude oil is extracted by drilling a hole through the bottom of a seabed or landmass. In order to do this, sometimes land has to be cleared, leading to **habitat destruction**. However, the destruction is not nearly as bad as that of coal mining, given that only a small area needs to be cleared.

There are also environmental impacts related to a technique called **fracking**. Fracking is used where the oil is hidden within a type of rock deep in the ground called shale. In fracking, water is pumped deep into this rock under pressure to fracture the rock and extract the oil. Issues related to this are **water contamination** – the water used to fracture the rock can seep through the rock, dissolve heavy metals and toxic substances and seep into the water table and go into groundwater, which may be used as an aquifer (i.e. a source of drinking water).

A serious environmental impact is the **oil spill**, where during extraction of oil from below the seabed, the oil leaks and spills all over the sea. Oil is toxic, and therefore kills many animals within the sea, leading to a number of ecological impacts.

Environmental impacts of crude oil (combustion)

Given crude oil is formed in the same way as coal is and is composed of similar molecules, albeit smaller, it stands to reason that the environmental impacts are similar to that of burning coal. These include the fact that CO₂ – a major **greenhouse gas** – is emitted, and the acidic nitrogen oxides and sulphur oxides can also be emitted, leading to **acid rain** as well as **photochemical smog** (ground-level ozone).

1.8.3 Petroleum gas and natural gas

Petroleum gas, usually sold in liquid form as LPG (liquefied petroleum gas) is composed primarily of propane (C₃H₈) and butane (C₄H₁₀). It is generally used as vehicle fuel and for cooking (think barbecues!). Dry natural gas, which is primarily methane, is used for cooking as well as electricity generation.

This is derived mainly from **wet natural gas**, gaseous deposits of very small hydrocarbons, also formed from fossilisation, as well as from **crude oil**. Therefore, petroleum gas is generally **non-renewable**.

The energy content of petroleum gas is similar to that of petrol, diesel and oil – approximately **46 MJ/kg** (Wikipedia), and greater than that of coal.

The energy content of dry natural gas (primarily methane) is the **highest of all the fossil fuels**, sitting at about **56 MJ/kg**.

Environmental impacts of petroleum gas and natural gas (sourcing)

This section will talk about petroleum gas derived from **wet natural gas deposits**. The environmental issues with oil refining have been previously discussed.

In simple terms, a hole is drilled into the ground to extract the wet natural gas, which is a composition of methane primarily, with some heavier hydrocarbons such as propane and butane. The wet natural gas is refined further, separating the methane from the heavier hydrocarbons, as well as pollutants such as sulphur compounds (e.g. H₂S). The heavier hydrocarbons are collected and packaged as **petroleum gas (LPG)** whereas the methane is packaged as **dry natural gas**.

The main environmental issues include **habitat destruction** in clearing of surrounding land (again, not as bad as coal mines), as well as **gas leaks** – leakage of methane into the atmosphere. Methane is a very powerful greenhouse gas, tens of times as more potent than carbon dioxide at trapping heat.

Environmental impacts of petroleum gas and natural gas (combustion)

The production of CO₂, a **greenhouse gas**, as well as the production of nitrogen and sulphur oxides, with the associated **acid rain** and **smog** are issues here. However, the sulphur and nitrogen content is much lower in both dry natural gas and petroleum gas, and therefore the amount of nitrogen and sulphur oxides produced is much lower than that produced in the burning of oil and coal. This is why we consider natural gas and petroleum gas as a 'clean-burning' fuel.

Additionally, it is accepted that the burning of natural gas to generate electricity releases **less greenhouse gases per unit of energy** generated than coal and oil.

1.8.4 Coal seam gas

Coal seam gas is primarily methane, just like wet natural gas. The difference is the location in which they are found; wet natural gas is found in an underground deposit in a 'bubble' underneath some rock, whereas coal seam gas is found mixed within deposits of wet coal underground known as **coal seams**.

Coal seam gas, just like all fossil fuels, is a **non-renewable source of energy**. Its energy content, given that it is comprised mostly of methane, will be similar to that of dry natural gas (about 56 MJ/kg).

Environmental impacts of coal seam gas (sourcing)

Given drilling is involved in the extraction of coal seam gas (just like natural gas), there will be some issues with **habitat destruction**. Additionally, **gas leaks** of methane into the atmosphere is also a potential issue.

Fracking is also a practice that in some cases needs to be performed to allow extraction of the methane. As previously discussed, the contents of the fracking fluid, as well as the contents of the coal seam (which have been disturbed by the fracking process), can seep into aquifers and contaminate them.

One issue relatively unique to coal seam gas is that **sources of groundwater may be depleted**. This is because during the extraction of coal seam gas, the water mixed in the coal seam needs to be removed to allow the methane to flow into the inserted pipeline. This depressurises the coal seam and, if there is a nearby underground water body used as an aquifer, some of this water can be 'sucked' out of the aquifer into the coal seam, effectively depleting the water supply.

Environmental impacts of coal seam gas (combustion)

Given that coal seam gas has pretty much the same composition as natural gas, the environmental impacts of combustion are pretty much the same.

1.9 Biofuel Choices

The biofuels that you need to know about are **bioethanol**, **biodiesel**, and **biogas**.

1.9.1 Bioethanol

Bioethanol is quite literally ethanol ($\text{CH}_3\text{CH}_2\text{OH}$). The same ethanol that you can drink. We call bioethanol as such because of its source. Bioethanol is generally mixed with petrol to form a mixture called E10, which is 10% ethanol and 90% petrol.

Bioethanol is produced from the fermentation of glucose by yeast cells, via the following equation:



Where do we get the glucose from?

- **Sugar cane** – the sugar is extracted from sugar cane directly.
- **Wheat, corn, wood** – the cellulose (a polymer of glucose molecules) is broken down into glucose in a process known as saccharification, and then the glucose is fermented.

The energy content of bioethanol is **lower than petrol**, sitting at about **26-30 MJ/kg**, a value comparable to coal.

Environmental impacts of bioethanol (sourcing)

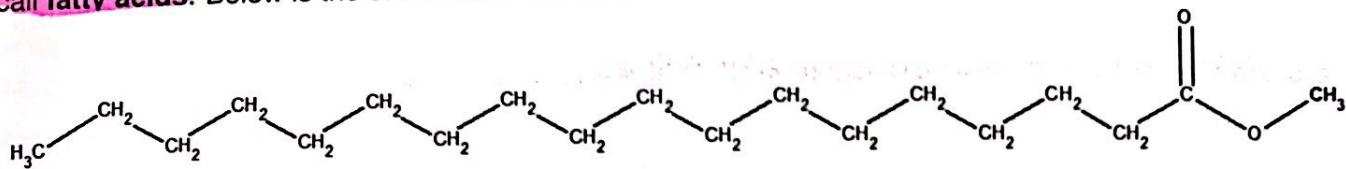
In many cases, natural habitat has to be cleared to grow these crops, leading to changes in the ecosystem that may be disadvantageous for wildlife. However, we can source bioethanol from existing crop plantations (whose purpose is for food) via their waste products, therefore minimising the amount of land that needs to be cleared.

Environmental impacts of bioethanol (combustion)

Whilst bioethanol is considered carbon-neutral as a biofuel, the balance between CO_2 consumption during production of crops and emission via combustion of ethanol is not perfect; usually there is more CO_2 that is produced. This is because processing the crops to produce ethanol requires electrical power which is generated, usually via coal, which itself produces CO_2 . So, if we include indirect CO_2 emissions, it is likely that bioethanol will have a net production of CO_2 into the atmosphere.

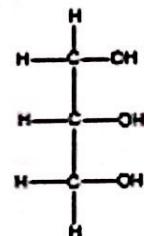
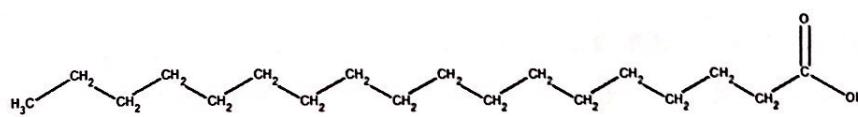
1.9.2 Biodiesel

Biodiesel is a mixture of **fatty acid methyl esters** (FAMEs). These are esters, and derivatives of what we call **fatty acids**. Below is the structure of a FAME:



These FAMEs are produced from modification of **triglycerides** (also known as triacylglycerols). As you will learn in Unit 4, triglycerides are fats and oils.

To have a proper understanding of biodiesel, it is best if you know a little bit about triglycerides (which you will learn more about in Unit 4). Triglycerides are molecules in our body that constitute fats and oils. They are produced from the combination of **glycerol** and **3 fatty acids**. The structure of a fatty acid and glycerol are shown below:

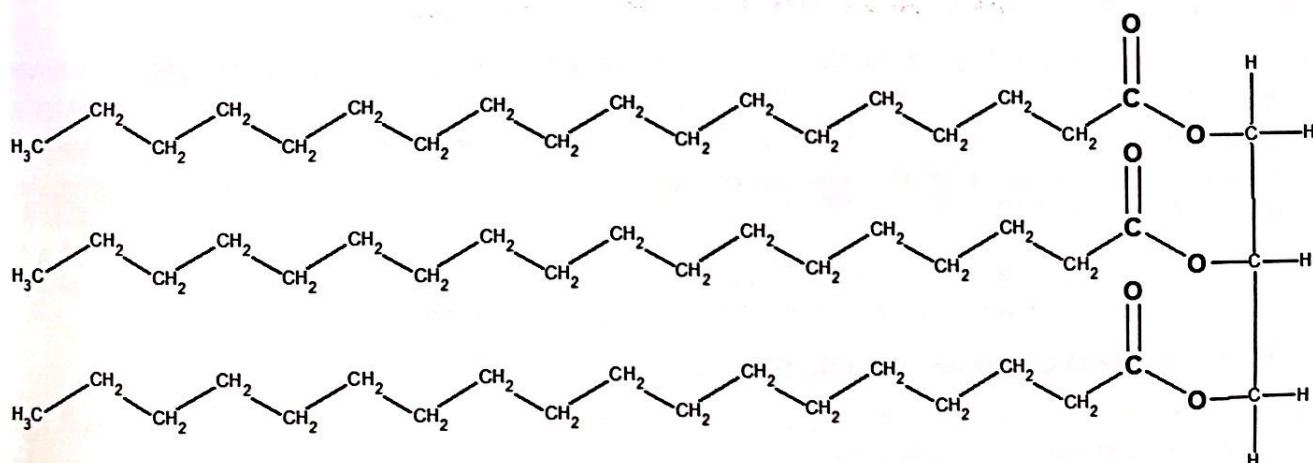


Fatty acids are **carboxylic acids** with a long hydrocarbon tail of varying length.

The fatty acid drawn above is an example of a fatty acid called stearic acid. Some fatty acids have C=C double bonds, whereas others do not.

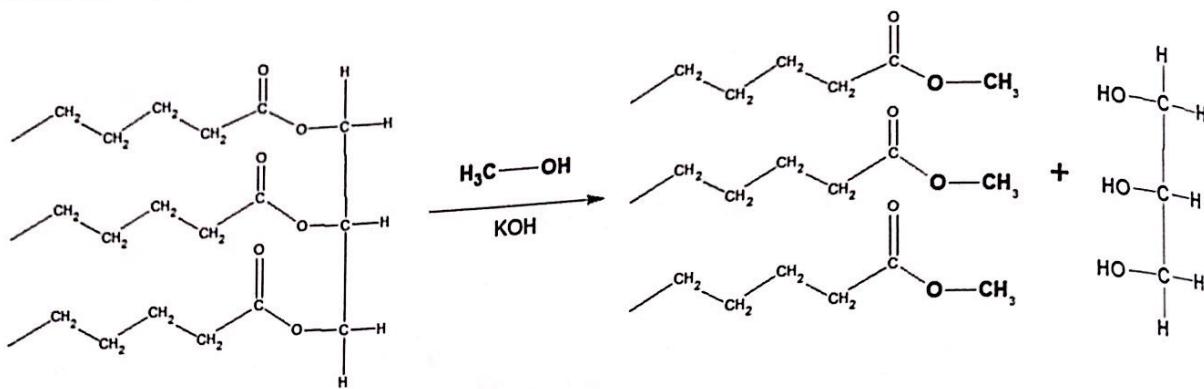
Glycerol is a three-carbon compound containing a hydroxyl group on each carbon atom.

From Units 1&2, you would have learnt that **hydroxyl** and **carboxyl** groups can react to form an **ester linkage** in a condensation reaction. If you took three fatty acids and reacted them with one glycerol molecule, you will end up with a triglyceride, as shown below – the ester linkages are emboldened:



Where do we get the triglycerides from? We get them from **vegetable oil**. Again, crops are grown and the vegetable oil is extracted from these crops and converted to FAMEs. How are they converted to FAMEs though?

Triglycerides are converted to FAMEs via a process called **transesterification**, whereby the triglycerides are mixed with a mixture of **potassium hydroxide (KOH)** dissolved in methanol. The KOH is a catalyst, whereas methanol is a reactant. The reaction is shown below:



Note that I have not drawn the full structures of the triglycerides (because they are very long molecules!). As a biofuel, biodiesel is a **renewable** source of energy. Its energy content is comparable to that of petrol and diesel (approximately 42 MJ/kg).

Environmental impacts of biodiesel (sourcing and combustion)

The environmental impacts of sourcing and combustion for the production of biodiesel are pretty much the same as that for bioethanol.

1.9.3 Biogas

Biogas is a mixture of gases, composed primarily of methane (CH_4) with a significant amount of CO_2 that is produced from the anaerobic metabolism of recently living plant material.

Biogas is sourced in Australia from:

- **Sewage treatment plants:** where the organic matter in sewage decomposes anaerobically to produce methane into the atmosphere. Scrubbers, which 'suck' the air above the sewage, extract the methane and use it to generate electrical energy.
- **Landfill:** the organic matter in landfill decomposes anaerobically to produce methane into the atmosphere, and is processed in a similar way.

Biogas can also be sourced from **biomass** as well, whereby organic matter from organisms that have recently died (e.g. felled trees, waste from sugar cane treatment) can be anaerobically digested by bacteria to form methane. Biogas, as a biofuel, can be considered a **renewable** source of energy, because the organic matter (e.g. food waste, paper, wood pulp) was ultimately sourced from living plant and animals which are easily replenished.

The energy content of the methane extracted from the biogas is the same as the energy content of the methane sourced from coal seam gas and natural gas – approximately **56 MJ/kg**.

Environmental impacts of biogas (sourcing)

If biogas is sourced from **biomass**, then we experience the same issues related to land clearance – destruction of natural habitat and loss of land that could have been used to produce food crops (the latter can be mitigated by using waste plant material from existing food plantations).

If biogas is sourced from landfill and sewage treatment plants, there is relatively little negative environmental impact that the actual extraction of biogas has. This is because the methane is captured from landfill and sewage treatment plants that would have been there anyway!

Whilst landfill and sewage treatment plants have their own issues (e.g. inadequate treatment of sewage leading to excess phosphate ions in waterways, leading to eutrophication), the actual extraction of biogas would not modulate this in a negative way.

Environmental impacts of biogas (combustion)

Carbon dioxide is the main product of biogas combustion, and is a greenhouse gas.

If the biogas were sourced from recently dead plant material as biomass, such as felled trees and waste products from sugar cane treatment, then we can consider biogas from these sources as carbon-neutral for the same reasons as outlined in the Bioethanol section.

Importantly, if the biogas were sourced from sewage treatment plants or landfill, the combustion of methane from biogas arguably **decreases** the impact of greenhouse gas emissions paradoxically.

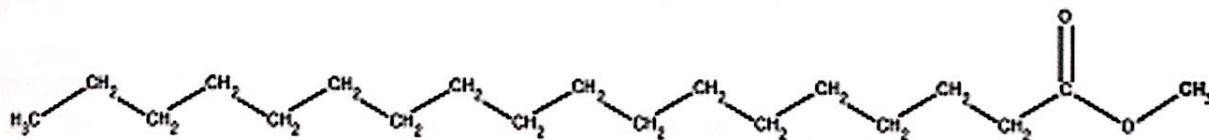
This is because had the methane not been extracted from the sewage treatment plants or landfill, it would have just escaped into the atmosphere anyway. Now, **methane itself is an extremely powerful greenhouse gas, much more potent than carbon dioxide**. Therefore, combustion of the methane here effectively replaces a potent greenhouse gas (methane) with one that is less potent (carbon dioxide).

1.10 Petrodiesel and Biodiesel Fuel Choices

In this section, we will compare and contrast the use of petrodiesel and biodiesel in vehicle engines (as a transport fuel). Let us review what biodiesel and petrodiesel are.

1.10.1 Biodiesel

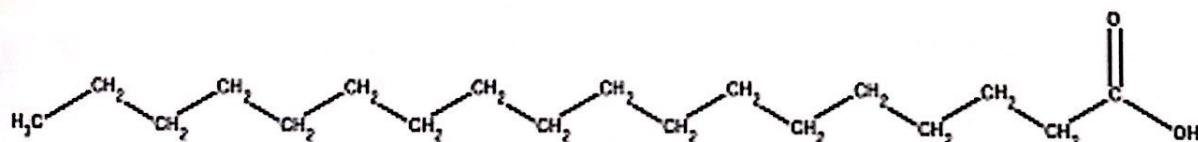
As discussed in the previous section, biodiesel is a mixture of FAMEs (fatty acid methyl esters), an example of which (methyl stearate) is shown below:



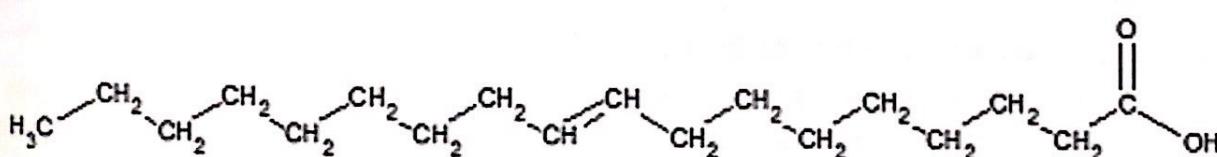
The length of the long hydrocarbon chain varies between approximately 12 carbons to 22 carbons, although usually C₁₆ and C₁₈ compounds are encountered.

An important property to talk about here is the concept of the **saturated** and **unsaturated** fatty acid, since this property will significantly affect the properties of biodiesel.

A **saturated fatty acid** is one that does **not** have any C=C double bonds. Below is **stearic acid**, an example of a saturated fatty acid:



An **unsaturated fatty acid** is one that has **at least one** C=C double bond. Below is **oleic acid**, an example of a saturated fatty acid:

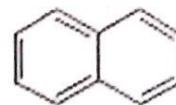
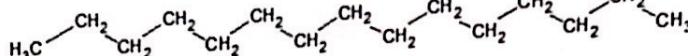


Biodiesel is composed of FAMEs derived from both saturated and unsaturated fatty acids. As you will learn later in this section, the relative composition of FAMEs derived from each of the saturated and unsaturated fatty acids will determine the physical properties of the biodiesel.

In practicality, biodiesel is sold as a **blend** with petrodiesel in Australia. For example, Caltex sells “B5”, a mixture of 5% biodiesel and 95% petrodiesel. As previously discussed, biodiesel is sourced from lots of different types of **vegetable oil**.

1.10.2 Petrodiesel

Petrodiesel is composed of a mixture of lots of different **hydrocarbons** ranging from C₁₀ to about C₂₀. These hydrocarbons are mixtures of **aliphatic** (straight chain or branched hydrocarbons) or **aromatic** (containing benzene rings). Two examples of molecules that can be found in petrodiesel, for illustrative purposes only, are pentadecane and naphthalene respectively (no need to memorise these):



As aforementioned, petrodiesel is sourced primarily from **fractional distillation of crude oil**, a fossil fuel.

1.10.3 Comparing biodiesel and petrodiesel

In this course, you are expected to be able to discuss the differences between biodiesel and petrodiesel with respect to:

- Chemical structure and sourcing (previously discussed)
- Combustion products
- Flow along fuel lines (impact of ambient temperature on viscosity of fuel, as well as hygroscopic properties of fuel)
- Environmental impacts

Note that in this section, we will be talking about B100 (pure biodiesel), whereas in reality, blends such as B5 are more commonly used. Generally, though, the higher the biodiesel content in the blended fuel, the greater the resemblance of the physical and chemical properties of the blend to the pure B100.

Biodiesel and petrodiesel (combustion products)

Both biodiesel and petrodiesel, containing mostly carbon atoms, would produce **carbon dioxide** as its major combustion product. Compared to **petrodiesel**, biodiesel produces **less carbon monoxide (CO)** and **more nitrogen oxides (NO_x)**.

Less carbon monoxide is produced due to the increased oxygen content of the biodiesel itself (as part of the ester groups), increasing the conversion of any CO to CO₂.

Both petrodiesel and biodiesel contain some sulphur atoms (within compounds), leading to the production of **sulphur dioxide (SO₂)** as a combustion product. Generally, biodiesel is considered to contain **less sulphur** than does petrodiesel. However, this is highly dependent on the composition of the biodiesel, and the way petrodiesel is refined. By law, the sulphur content of diesel in Australia has to be lower than 10 ppm, which makes comparisons of sulphur between petrodiesel and biodiesel/petrodiesel blends difficult, given that the composition of the biodiesel and refining of the petrodiesel are both manipulated to fall under the 10 ppm cap.

Biodiesel and petrodiesel (flow along fuel lines)

In transport vehicles, fuel is stored in a large tank, and then it flows through **narrow pipes** towards the engine. Little bits of the fuel are injected into the engine, which are each then mixed with air and combusted. The heat and pressure generated pushes the cylinders in the engine outwards, which turns a crankshaft causing the wheels of the vehicle to turn.

Viscosity is an important feature of a fuel. It is a measure of how 'thick' a fluid is. Water is a rather non-viscous liquid, whereas oil is a lot more viscous. This feature is important for two reasons; firstly, a high viscosity improves the **lubrication** of the cylinders on an engine, and secondly, it makes it **difficult to pump fluid through the narrow pipes and through the fuel pump and filter**.

Biodiesel is more viscous than petrodiesel, likely owing to the presence of additional dipole-dipole interactions between the C=O groups of different FAME molecules.

Importantly, the viscosity of fluids increases as the temperature decreases. If you do not believe me, next time you are in the kitchen, get some oil and pour it into a fry pan. Note how thick the oil is. Then, heat the oil, and after a couple of minutes when you see the oil start to smoke, pour the oil back into a cup and notice how runny the oil is; by increasing temperature, the oil becomes less viscous.

The implication here is that the ambient (outside) temperature being low could impair the flow of fuel along the fuel lines. This problem is significantly worse with biodiesel, given that it is a more viscous fluid.

Once the temperature is cold enough (below what is called the **pour point**), the fuel becomes so viscous that it is practically unable to flow, and assumes a gel-like structure. The **pour point** is significantly higher in biodiesel than it is in petrodiesel.

Aside from viscosity, another important feature of diesel fuels is its **hygroscopicity**, the ability of the fuel to absorb water from the atmosphere. **Biodiesel has a significantly higher hygroscopicity than petrodiesel**, because it can form hydrogen bonds with water molecules, using its C=O group as a hydrogen bond acceptor. When biodiesel absorbs water, it causes some of the biodiesel to undergo a series of oxidation reactions that produce numerous chemicals including free fatty acids. These free fatty acids can corrode the inside lining of fuel lines. Additionally, water in the biodiesel fuel can cause the growth of micro-organisms such as algae, which could end up clogging up fuel lines.

Biodiesel and petrodiesel (environmental impacts)

The environmental impacts of sourcing biodiesel and petrodiesel have been discussed previously.

With relation to combustion of the two fuels, combustion of **biodiesel** leads to:

- Lower production of **carbon monoxide (CO)**
- Lower emission of **particulate matter**
- Lower emission of **unburned hydrocarbons** (that could cause photochemical smog)
- Higher emission of **nitrogen oxides (NO_x)**
- Comparable (albeit lower) emission of **sulphur oxides**

Also, as previously discussed, biodiesel is carbon neutral, whereas petrodiesel is not.

1.11 Redox Chemistry and Galvanic Cells

Galvanic cells are a mechanism by which we can use chemical energy to generate electricity. You may know them by the name of **batteries**. However, to understand galvanic cells, you must know redox chemistry. Let us revisit redox chemistry from Unit 2, and extend some of the content.

Redox chemistry is based on two definitions:

- **Oxidation is the loss of electrons (OIL - oxidation is loss)**
- **Reduction is the gain of electrons (RIG - reduction is gain)**

This is very simple, when we talk about metals such as Cu that can lose 2 electrons to become Cu²⁺ and be oxidised. However, it is more complicated when it comes to molecules, because they don't generally physically lose electrons. For instance, SO₂ is deemed to have been oxidised to SO₃, but you can't really see where the electron loss is here. In this case, we use oxidation numbers in the following rules:

- A substance is oxidised if an atom within it encounters an **increase** in oxidation number.
- A substance is reduced if an atom within it encounters a **decrease** in oxidation number.

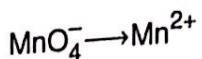
Oxidation numbers are like 'charges' of sorts. The rules are as follows:

- The oxidation number of an element is zero.
- The sum of oxidation numbers of the atoms is equal to the charge of the species.
- The oxidation number of a metal in a compound is equal to its charge.
- The oxidation number of H in a compound is always +1, except in hydrides (-1).
- The oxidation number of O in a compound is -2, except in peroxides (-1) and OF₂ (+2).
- The oxidation number of F in a compound is always -1.

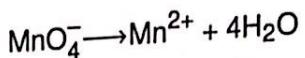
For instance, in the substance SO₃, each of the three O atoms has an oxidation number of -2 and S therefore has an oxidation number of +6, since the charge of the species is 0.

1.11.1 Balancing redox equations

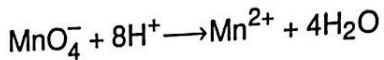
To balance redox half equations in acid - where there are lots of H⁺ running around - use the KOHES method. First, balance Key atoms:



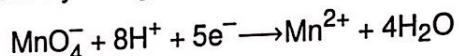
Then, balance O atoms by adding H₂O (remember, you're probably doing this reaction in solution so there will be H₂O around):



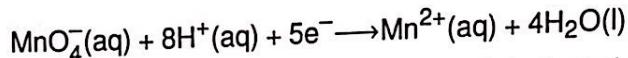
Now, since we are doing this in acid and there is lots of H⁺, you will have unbalanced the H balance by adding water. So, add H⁺ to balance the H atoms:



Now, balance charge by adding Electrons. In the above example, total charge on LHS is +7 (one MnO₄⁻ ion and 8 H⁺ ions), and RHS is +2 (one Mn²⁺ ion). Therefore, you add 5 electrons to the LHS to balance this - remember electrons are negatively charged:

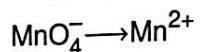


And don't forget States:

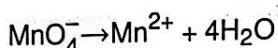


To do it in base, it's a little trickier; it is similar to the KOHES method, but a tad different:

First, balance Key atoms:

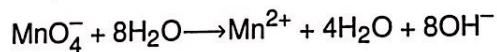


Then, balance O atoms by adding H₂O (remember, you're probably doing this reaction in solution so there will be H₂O around):

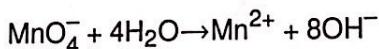


Since we are doing this in base we have OH⁻ and not H⁺. However, adding 1 H₂O to one side and 1 OH⁻ to the other side is equivalent to adding 1 H⁺ to the first side (the difference between the two species is a H atom - ignoring charges).

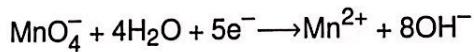
Normally we'd add 8 H⁺ to the LHS here. Instead, we are going to add 8 H₂O to the LHS and 8 OH⁻ to the RHS, like this:



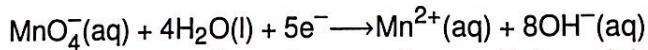
Don't forget to cancel out the water molecules!



Now, add Electrons:

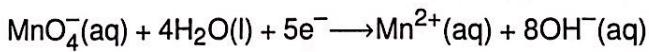


And the always important States:

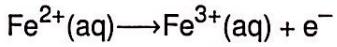


To combine redox half equations to an overall reaction equation, multiply each half equation by a number to get the number of electrons equal on opposite sides. When you add the equations together, the electrons should cancel out.

Let's take this redox half equation in combination with this one:



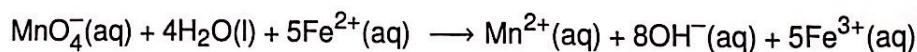
and



The top equation has 5 electrons, the bottom one has 1. Therefore, multiply the bottom equation by 5:



Both have the same number of electrons on each side. Now, add them and cancel out the electrons:



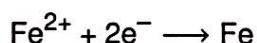
1.11.2 Electrochemical series

Below is a snapshot of the electrochemical series:

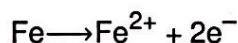
	E°
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	+0.15
$S(s) + 2H^+(aq) + 2e^- \rightleftharpoons H_2S(g)$	+0.14
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	-0.13
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	-0.14
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	-0.23
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	-0.28
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	-0.76
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	-0.83

The electrochemical series is a set of **reduction** half equations in order of increasing reactivity. (At this stage, ignore the funny looking arrows – they are equilibrium arrows and you will learn what they are later – it just means the reaction can go in either direction). The further up you go in the electrochemical series, the greater the tendency for the reduction half equation to occur. In other words, the reduction of I_2 to I^- has a greater tendency to occur than the reduction of Zn^{2+} to Zn .

It is important to note that these half equations can occur in either direction, depending on the conditions. For instance, if a solution of Fe^{2+} ions has a piece of Zn metal added to it, the Fe^{2+} can be reduced to Fe via the half equation as shown below:



However, if a piece of Fe metal was placed in a solution of Cu^{2+} ions, the Fe can be oxidised to Fe^{2+} as per the equation:



Notice how the second equation is just the first equation written backwards? Well, the first equation (Fe^{2+} to Fe) is a reduction half equation, as written in the electrochemical series; the second equation is the electrochemical series equation **going backwards**, and is the reverse (oxidation) equation.

An important point of the electrochemical series is this: **the greater the tendency for the reduction half equation to occur, the less tendency there will be for the reverse oxidation equation to occur**. For example, Cu^{2+} has a greater tendency to be reduced to Cu than Fe^{2+} is to Fe , and therefore Cu metal has a **lesser** tendency to be oxidised to Cu^{2+} than Fe is to Fe^{2+} .

So, what does the E° mean?

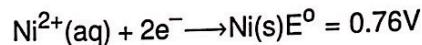
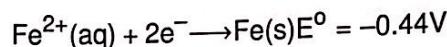
Effectively, the E° value (measured in volts – V) given is a measure of the relative **spontaneity** (the tendency of a reaction to 'go') of a particular reduction reaction relative to the H^+ / H_2 reduction reaction at standard conditions, also known as SHE (standard hydrogen electrode).

In other words, if a reduction reaction has a higher E° value than another, this means that the first reaction will go to the right, and the other to the left – generally to completion.

And since the further up the reduction reaction, the greater the tendency for it to occur, if we take two half-equations together, **the one on the top will be the reduction equation**. For example, Fe^{2+} will be reduced when it is reacted with Zn, as Fe^{2+} is higher in the series than Zn^{2+} .

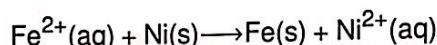
E°_{cell} is the relative potential of the two half-equations and gives an idea of the **extent (NOT rate)** of the reaction. How do we calculate E°_{cell} ? Take the difference in E values from electrochemical series.

For example, take the two half equations:



The top half equation would be going forward and the bottom half equation backward.

The overall reaction equation would be:



The E°_{cell} for this reaction would be:

$$E^\circ_{cell} = -0.44 - (-0.76) = -0.44 + 0.76 = +0.32V$$

Importantly, a reaction is said to be **spontaneous** if the E°_{cell} is **positive**.

Limitations of the electrochemical series

Firstly, the electrochemical series gives **no indication as to the reaction rate**. If we took two redox reactions with different E°_{cell} values, we would not be able to figure out which reaction occurred faster. The E°_{cell} is unrelated to the reaction rate. Additionally, you may not observe a reaction occurring between an oxidant and a reductant with an equation that has an E°_{cell} greater than 0, because the reaction rate **could** be so slow that you would not observe it occurring.

Secondly, the E° values written on the electrochemical series are written assuming specific conditions (called **standard conditions**). For the electrochemical series snapshot (an excerpt from the 2016 Data Book), the conditions are that solids are pure, solutions at 1 M concentration and pressure of gases at 101.3 kPa. However, changing the concentrations of the solutions and the pressure of the gases actually changes the E value (E° with the ' $^\circ$ ' means the E – voltage – value at standard conditions).

KEY POINT :

As of 2017, VCAA has adopted the new conventions for standard conditions, which are solids being pure, solutions at 1 M concentration and pressure of gases at **100 kPa** (1 bar). This would mean that the E° values in any data VCAA gives you will be very slightly different to those shown in the Data Books from 2016 and earlier.

1.11.3 Galvanic cells

Now that we know to interpret an electrochemical series, let us understand how cells work.

The galvanic cell supplies energy in that it utilises stored chemical energy to produce electrical energy.

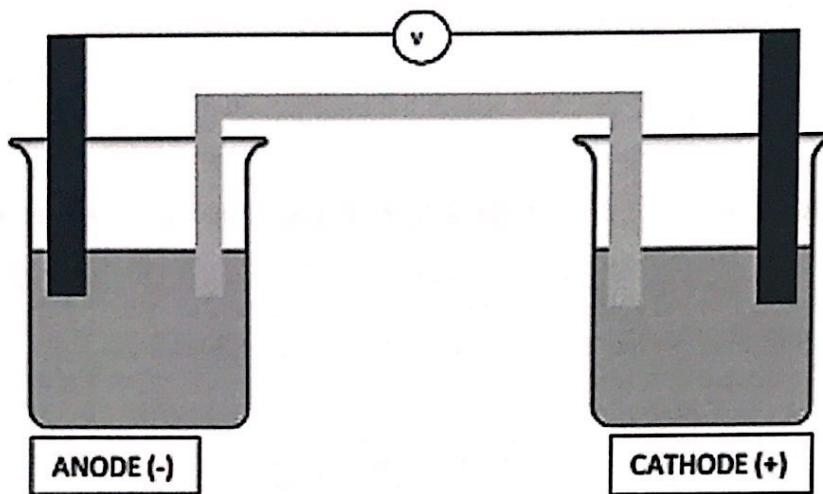
The main energy change is from chemical to electrical (key knowledge in study design).

Normally when a redox reaction occurs by the reactants coming into physical contact with one another, energy is released as heat. So, we have a **change of energy from chemical to thermal energy** (key knowledge). Well, that's no good, is it?

What we do is separate the half-equations out by making them occur in separate half-cells. Here

we can convert some of the chemical energy to electrical energy.

Let's draw a quick diagram of the galvanic cell.



By definition, the **anode** is the electrode in which **oxidation** occurs. The **cathode** is the electrode in which **reduction** occurs.

If you forget, remember the mnemonic:

AN OIL RIG CAT

Anode – Oxidation Is Loss – Reduction Is GCathode

The maximum potential difference (maximum cell voltage) between the two half cells, if each half cell were at standard conditions, would be... E^0_{cell} .

There are **three** types of electrode:

- **Electrodes made out of metal:** generally used for where the metal is the reduced form (eg Cu^{2+}/Cu)
- **Electrodes made out of an inert electrode:** (e.g. Pt, graphite) where both the oxidised and reduced form are aqueous (e.g. $\text{Fe}^{3+}/\text{Fe}^{2+}$)
- **Electrodes made out of an inert electrode and a gas chamber:** where one of the forms is gaseous (e.g. H_2/H^+)

The **salt bridge** (the grey thing in the diagram connecting the two half cells together) balances the charge in the cell. Without it, the cell will be polarised as electrons would accumulate in one half of the cell, preventing any further current passing through.

The salt bridge must have **free mobile charges** – a soluble salt – that is **Inert** in that it does not form a precipitate or react with one of the reactants. A very good one is KNO_3 (aq).

The cations in the salt bridge flow towards the cathode, where there would have been a build-up of negative charge. The anions flow towards the anode as electrons are being removed from the anode.

Which reaction occurs at each electrode?

The reaction that has the highest overall E_{cell} will occur.

In other words, the half-cell reactions with the highest positive difference in E will occur – that are the furthest apart from one another in the electrochemical series.

The simplest way to work this out is to, in the electrochemical series, look for the **strongest oxidant** – the substance on RHS closest to the top and the **strongest reductant** – the substance on RHS closest to the bottom.

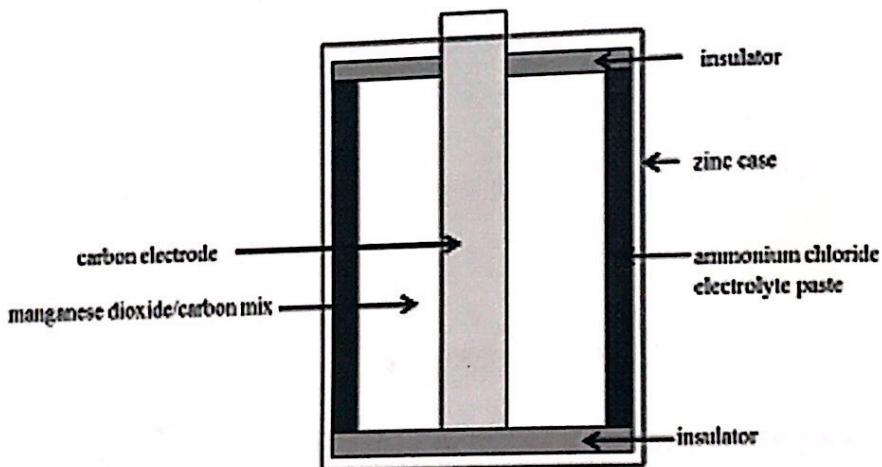
Now let's have a look at the specific types of galvanic cell.

There are three types of galvanic cell that we are going to learn about: **primary cells**, **secondary cells** (which we'll cover in Area of Study 2), and **fuel cells** (in the next section).

Primary cells

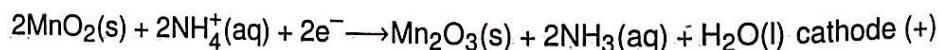
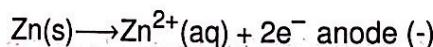
These are **non-rechargeable** because the products migrate away from the electrodes after reaction.

Let us examine an example of a primary cell. You do **NOT** need to memorise examples of primary cells, but you **DO** need to be able to interpret information about cells given to you and use your knowledge to solve problems in unfamiliar situations. Below is a **zinc-carbon (Leclanche cell)**:



On this occasion, the zinc case is the anode and the carbon electrode is the cathode. This is really two half-cells that are “stacked” on top of one another. The salt bridge completing the circuit here is the ammonium chloride electrolyte paste.

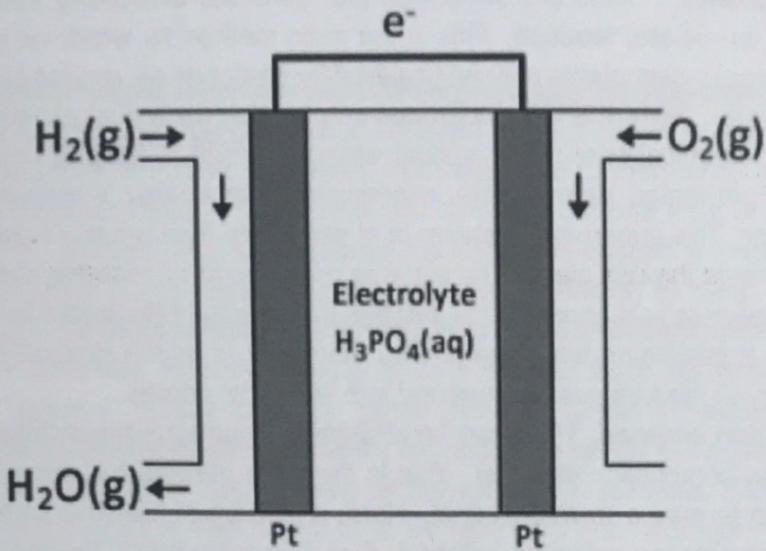
The reaction half equations are as shown:



Here, the electrons get sucked off the Zn at the anode, travel out of the (-) terminal, travel around the electrical circuit, arrive at the (+) terminal, and get accepted by MnO_2 .

1.12 Fuel Cells

Fuel cells are a type of primary galvanic cell whereby reactants are continuously supplied. The basic parts of a fuel cell are shown below:

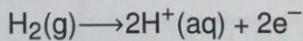


This is a **side on view** of the fuel cell; the two electrodes are, in reality, like wide sheets of paper.

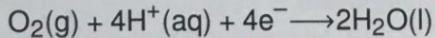
Just to help you get your head around this setup, this is a particular type of fuel cell called the **phosphoric acid fuel cell** (no need to memorise) This type of fuel cell contains two electrodes, which are like sheets of paper made out of a mixture of carbon (graphite) and platinum. The carbon acts as a conducting material, and the platinum acts as a **catalyst**.

In between the two electrodes is a porous 'matrix' of solid silicon carbide (SiC), onto which phosphoric acid is absorbed.

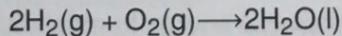
As a fuel cell, there is a constant supply of H₂ gas (the fuel) at the anode. The reaction that occurs at the anode, given that the electrolyte is **acidic**, is:



Simultaneously, oxygen (from air) arrives at the cathode to accept electrons, being reduced to water:



The overall reaction equation amounts to the combustion of hydrogen gas to form water:



1.12.1 Properties of fuel cells

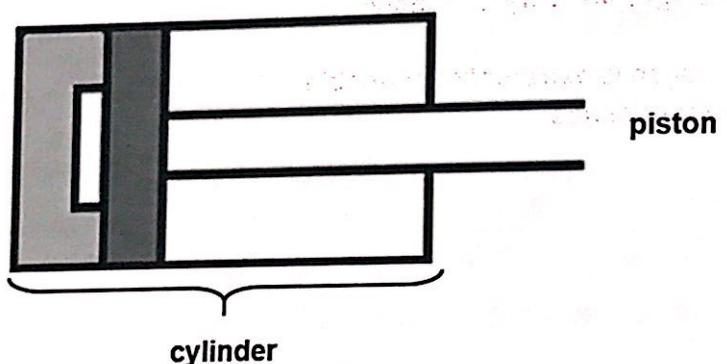
There are some specific features of fuel cells that you should be aware of:

- The electrodes are **porous**, which increases the efficiency of the cell. This is because porous electrodes have a higher **surface area**, increasing the rate at which the reactant can either donate or accept electrons.
- The electrodes contain a **catalyst**, which increases the potential performance (power output) of the cell. This is because the potential rate at which the reactants can donate electrons increases.
- Some fuel cells use hydrogen pumped into the fuel cell exogenously, whereas other fuel cells use another fuel (e.g. methanol), from which they produce hydrogen endogenously using a **reforming process**. Reforming is where you convert one type of fuel into another type of fuel. With some fuel cells, hydrogen is the fuel that is directly pumped into the fuel cell. With other fuel cells, another fuel such as methane or methanol is pumped into the apparatus, which then undergoes a chemical reaction that produces hydrogen gas as one of the products; the hydrogen gas is then pumped into the fuel cell for reaction.

1.12.2 Applications of fuel cells

Fuel cells can be used as an alternative method of extracting chemical energy for useful purposes. The methods that are currently employed widely to extract chemical energy from a fuel are:

- **Thermal power plants.** These are structures that generate **electricity** from the **heat** generated from a chemical (or nuclear) reaction. This is the main method by which we generate electricity for households. Thermal power plants may be powered by coal, fuel oil, natural gas or even uranium (for nuclear power plants). Here, the fuel undergoes combustion (or a nuclear reaction), which releases a vast quantity of chemical energy (or nuclear energy), which is used to heat some water nearby, converting it to superheated steam. Here, chemical/nuclear energy is converted to thermal energy in the nearby water. This superheated steam is at extremely high pressure (remember the ideal gas equation!), so it shoots through pipes. The extreme pressure turns massive turbines connected to the pipes – the thermal energy is converted to mechanical energy of the turbines. The massive turbines are connected to a generator, which generates electricity from the rotation of the turbines. Here mechanical energy of the turbines is converted into electrical energy.
- **Internal combustion engines.** These are structures that generate **mechanical energy** from chemical energy, via the combustion of a fuel. This is the main method by which vehicles are powered with the fuel being termed a **transport fuel**. Here, a little bit of fuel and some air are injected into a series of pre-compressed cylinders (either 4, 6 or 8 in most cars), leading to ignition, release of energy, production of high levels of heat and pressure, which pushes the pistons outwards. These pistons are connected to a shaft; pushing the pistons outwards leads to rotation of this shaft. The shaft happens to be connected, in most cars, to the rear wheels of the vehicle – pushing the vehicle forward. Below is a diagram of a cylinder-piston structure:



- In this context, fuel cells can be used as an alternative method to convert chemical energy to electricity (like a thermal power plant) or chemical energy to mechanical energy (like an internal combustion engine). Therefore, fuel cells can be used as an alternative to internal combustion engines to power cars. In fact, this is already being done with trials on buses powered via hydrogen fuel cells in Western Australia, and companies like Hyundai and Toyota developing hydrogen-powered cars. Fuel cells are also used to generate electrical power in **portable power generators** or **backup power generators**.

1.12.3 Advantages and disadvantages of fuel cells and fuel combustion

To assess the potential role of fuel cells as an alternative medium for energy conversion from chemical to mechanical or electrical on a large scale (e.g. cars or power stations), we need to be familiar with the advantages of fuel cells and the combustion of fuels.

Advantages include:

- **Fuel cells are more efficient than combustion engines and thermal power plants.** This is partly because there is only one energy conversion required to generate electricity from chemical energy with a fuel cell (whereas you have to convert from chemical to thermal to mechanical to electrical energy in a thermal power plant). Every time you convert from one form of energy to another, you lose energy as heat. Another reason is because the direct combustion of fuels in either a combustion engine or thermal power plants leads to significant losses of energy as heat.
- **Because fuel cells are more efficient, they lead to a lower production of greenhouse gases.** If hydrogen is the original fuel, the only waste product is H_2O , so there are no point-of-use greenhouse gas emissions. However, overall there are some greenhouse gas emissions because **as there is practically no elemental hydrogen on Earth**, the hydrogen needs to be generated from other substances, which requires energy that will likely be derived from fossil fuels. If substances like methane and methanol are the original fuel which is to be reformed into hydrogen, the reforming process produces CO_2 as well as hydrogen. However, the important thing here is that since fuel cells are more efficient at generating energy, we would need less of the fuel to generate the same amount of energy and therefore we would emit less CO_2 per amount of energy generated.
- **Fuel cells operate with minimal noise** due to the presence of fewer moving parts.

Disadvantages include:

- **Fuel cells, at this stage, are very expensive:** this is the main reason why we are still sticking to thermal power plants and combustion engines at this moment.
- **Safety Issues:** Hydrogen is **extremely flammable**. There are some... potential issues there.
- **Transport and storage Issues:** Hydrogen is a very light gas. Per unit mass, hydrogen has a very high energy density. However, per unit volume (given hydrogen gas has a very low molar mass), the energy density of hydrogen is very low. Therefore, storing enough hydrogen in a fuel tank in a car poses significant challenges. Currently, we try to store hydrogen as a compressed gas in a fuel tank. However, to pack sufficient amounts of hydrogen as a gas into a tank to power a car for a reasonable period of time requires extremely large tanks at high pressures, which is both logistically very difficult as well as very expensive. Emerging technologies is storing hydrogen as a cryogenic liquid, or in the form of another chemical such as ammonia borane (NH_3BH_3).

1.12.4 Comparing fuel cells and batteries

You are expected to be able to compare fuel cells with regular galvanic cells:

- Like regular galvanic cells, fuel cells are generally non-rechargeable and involve a conversion of chemical energy to electrical energy.
- In fuel cells, the reactants are **continuously supplied**, unlike in regular batteries, and the products are **continuously excreted**.
- In general, the electrodes in batteries are **not porous**, whereas the electrodes in fuel cells are.
- Fuel cells are **more efficient** than regular batteries.
- Both fuel cells and galvanic cells can be used to power cars and other appliances such as laptops. However, fuel cells can be used to **generate electricity de novo** whereas **secondary galvanic cells** are better suited to **storing energy for conversion to electrical energy** rather than **generating electricity de novo**.

Area of Study 2

How can the yield of a chemical product be optimised?

2.1 Reaction Kinetics

We know that increasing temperature increases the reaction rate - you may have learnt about this quite early on in school. We know that if you increase the surface area of a solid reactant, the reaction is faster. The question is - why is this the case? To understand this, we need to learn about **collision theory**.

2.1.1 Collision theory

For reactant species to be converted to product species, three criteria must be fulfilled:

- The particles must collide.
- The particles must collide with an energy equal to or higher than the activation energy.
- The particles must collide with the correct orientation.

If all three criteria are fulfilled, then a particular collision between reactants is termed a **fruitful** or **successful** collision. This shows that not all collisions are successful. The rate of any chemical reaction is dependent on the rate of successful collisions between reactants - the number of successful collisions per unit time. The higher the rate of successful collisions, the higher the reaction rate. This is the principle behind all the factors that affect rate of reaction.

2.1.2 Factors affecting reaction rate

Now, let us have a look at the factors that affect the reaction rate: **concentration, surface area, catalysts, and temperature**.

Concentration of reactants

If the concentration of the reactant were to be increased, there would be more reactant particles 'crammed' into the same volume. Hence, they would be colliding more often. Now, if they collided more often, assuming that a particular fraction of them are successful - this means that the frequency of successful collisions between reactants rises. Hence, **increasing concentration increases reaction rate**.

KEY POINT :

It is often said that increased **pressure** of the gas increases the reaction rate. This is true, but often they are talking about an increased pressure of the gas secondary to an increased concentration of the gas; remember that $P = cRT$ (where 'c' is the total concentration of gas), so pressure and concentration are proportional. It's the increased concentration of reactant gas that actually increases reaction rate.

Surface area of solid and liquid reactants

The important point here is that if you took a crystal of solid or a drop of liquid, only the surface of these will be exposed to the other reactant. Therefore, **increasing the surface area of a reactant increases the contact of the reactant to the other reactant and therefore increases the frequency of collisions between reactants**. Therefore, there is an increased frequency of successful collisions between reactants, leading to an elevated reaction rate.

Catalysts

A catalyst is a substance that **offers an alternative reaction pathway with a lower activation energy**. Therefore, if you add a catalyst to the reaction mixture, there will be a higher fraction of collisions that will have an energy equal to or above the activation energy. Hence, there will be a higher fraction of collisions that will be successful. Although the frequency of collisions will not change, the fraction of those that become successful increases. Thus, a catalyst will increase the frequency of successful collisions and therefore the reaction rate.

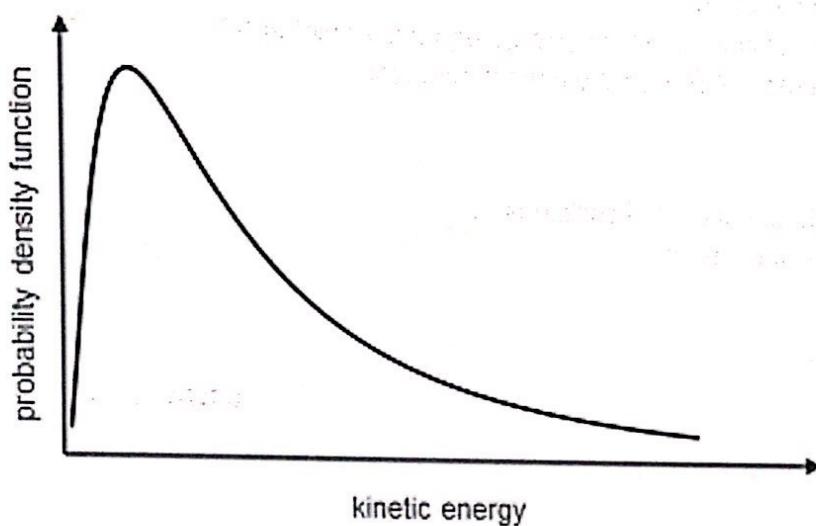
Temperature

Increasing the temperature of the system will imply that the reactant particles move faster (i.e. have higher kinetic energy). Therefore, they will collide more frequently. However, this is not the whole story. Since they are actually moving faster, they are 'smashing into each other harder.' In other words, the average kinetic energy contained within the reactant particles (the 'energy of the collision') will be higher.

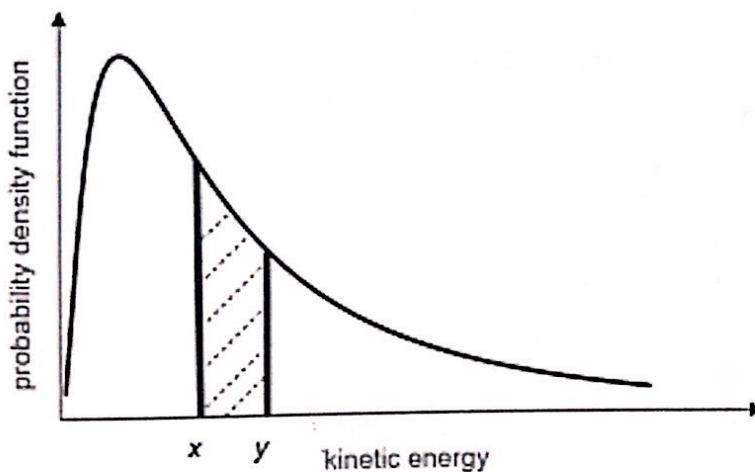
This means that a higher fraction of the collisions will have an energy equal to or above the activation energy. Given that increasing temperature makes the particles more frequently, increasing the total frequency of collisions, and that increasing temperature increases the fraction of collisions that are successful, it follows that increasing temperature increases the frequency of successful collisions and therefore increases the reaction rate.

2.1.3 Maxwell-Boltzmann distribution curve

You need to have a basic understanding of the Maxwell Boltzmann distribution curve and what it means. This is basically a representation of the distribution of kinetic energies of reactant particles. It looks a little like this:

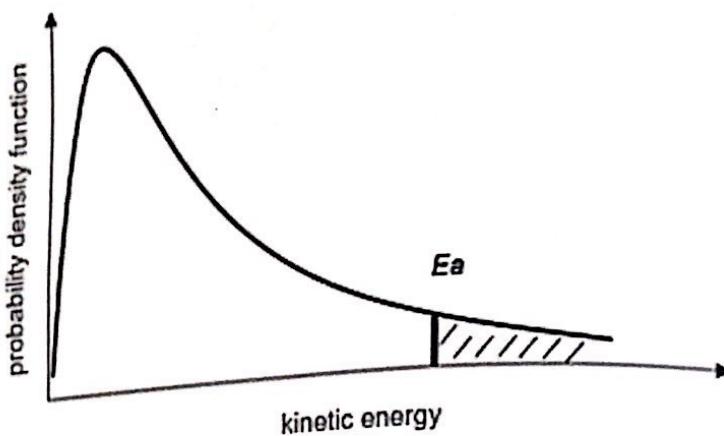


This is quite simply a probability density function, which will hopefully be familiar to any of you doing Maths Methods, though I'll explain this briefly here just in case. The function is drawn in such a way that the total area underneath the curve is 1. Also, if we took the area here:

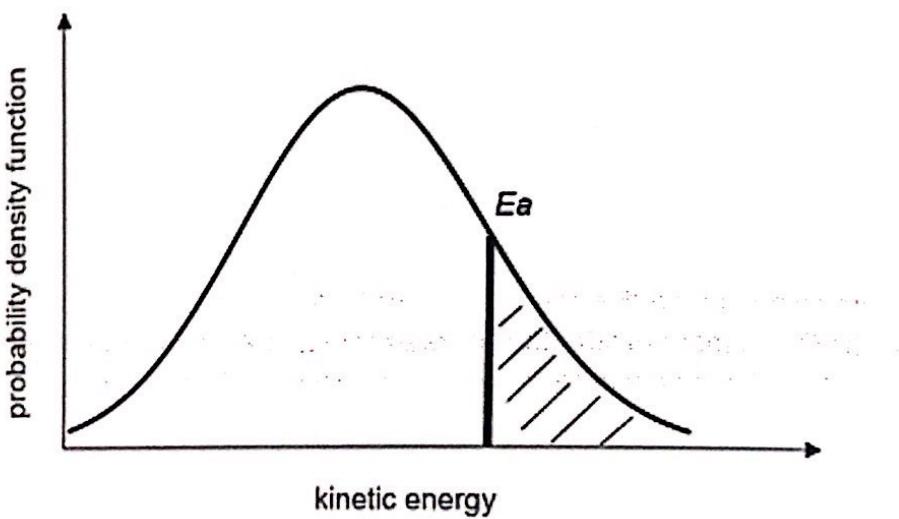


the shaded area is equal to the fraction of reactant particles that have a kinetic energy between x and y . If this area was 0.10, that means that 10% of the molecules have a kinetic energy between x and y .

Importantly, if we look at the kinetic energy of the particles with relation to the activation energy barrier, you can see that only a fraction of the particles have sufficient energy to breach the activation energy barrier.

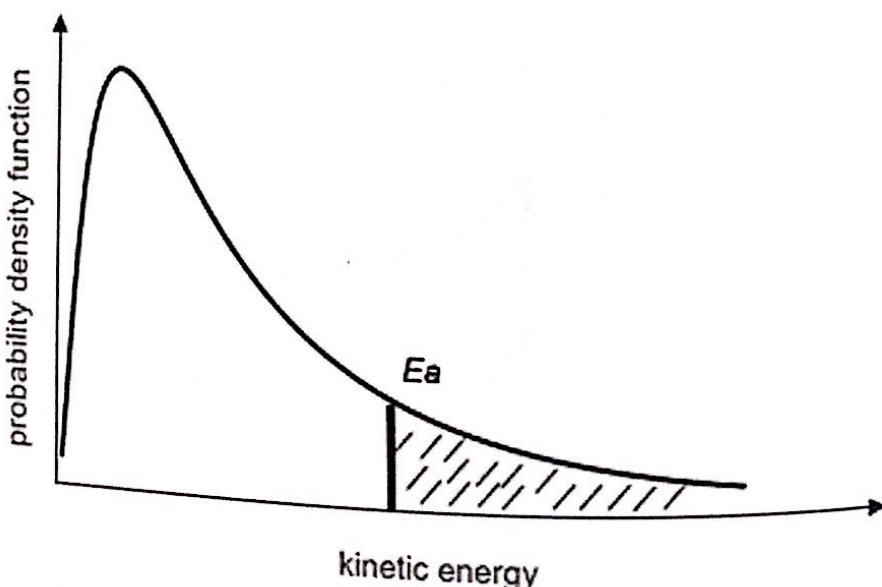


Now, remember that increasing the temperature **increases the average speed of the reactant particles**. Therefore, you'd expect a larger area of curve to span a higher kinetic energy, reflecting the higher fraction of particles that have a medium-high kinetic energy. Below is the curve you would expect if you were to increase the temperature:



See how the shaded area has increased? This shows how increasing the temperature increases the fraction of collisions between reactant particles that are successful.

Now see what happens if you were to, instead, add a catalyst:



The activation energy is **lower** and hence the fraction of collisions that are successful is higher.

2.2 Equilibria

Up until now, you will have learnt that reactions go in one direction only, from reactants to products. However, it turns out that much of the time, the reactants can be converted to products, and the products can be converted back to reactants at the same time. Let us entertain ourselves with the following hypothetical reaction: $A(g) + B(g) \rightleftharpoons C(g) + D(g)$. The harpoons (those funny looking arrow things) show that the reaction occurs in both directions. The reaction of A and B to form C and D is the **forward reaction**. The reaction of C and D to form A and B is the **back reaction**. Let's picture a scenario, where we throw some A and B into a 1 L container. This A and B starts to react to form some C and D. At this stage, A and B are still reacting to form C and D, but the C and D produced is starting to form A and B again. The forward reaction rate is **much faster** than the back reaction rate here; reaction rate is affected by concentration of whatever is reacting, and [C] and [D] have just reached above 0 whereas [A] and [B] are close to their original value. Since the forward rate is faster, the rate of production of C and D is greater than the rate of consumption of C and D; therefore, there is a **net production** of C and D here.

Subsequently, [A] and [B] drop further, and [C] and [D] rises further. The rate of the **forward reaction** drops from its high value, and the rate of the **back reaction** rises from its low value. This situation keeps occurring until the rate of the forward reaction is **equal** to the rate of the back reaction. Here, the rate of production of production of C and D is equal to the rate of consumption of C and D. In other words, [C] and [D], as well as [A] and [B], are **constant**. This state is referred to as **equilibrium**.

2.2.1 Reaction quotient and equilibrium constant

One can define some sort of number that will give us an index of how far towards completion the reaction has gone - and we call this the **reaction quotient** (Q), and for a reaction $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

A few notes here:

- The **products** go on the top, the **reactants** at the bottom.
- The higher the Q, the more **products** compared to **reactants** there are at the given time.
- The concentration of each chemical is taken to the power of its coefficient in the reaction equation.
- Solids and liquids do **NOT** appear in the expression, and Q is **variable** with time.

A couple of examples:

Reaction 1: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ (obviously at high temperatures):

$$Q = \frac{[HI]^2}{[H_2][I_2]}$$

Reaction 2: $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$:

$$Q = [Pb^{2+}][Cl^-]^2$$

Now, it also turns out that for a **given reaction** at a **given temperature**, no matter what the permutation of the concentration of the reactants and products are, the reaction quotient always seems to approach the same number as the system establishes equilibrium, and it actually ends up becoming the same number whenever the system does approach equilibrium. Therefore, we can define another quantity called the **equilibrium constant**; the equilibrium constant (K) is the value of the reaction quotient at equilibrium and for the hypothetical reaction shown in this question:

$$Q = \frac{[C]_{eq}^c[D]_{eq}^d}{[A]_{eq}^a[B]_{eq}^b}$$

The 'eq' subscript specifies that these are the concentrations when the system is at equilibrium. You do not HAVE to use this subscripts, but it is a good idea so you do not get confused between K and Q. When Q = K, the system is at equilibrium. The system (the collection of products and reactants) will always act as to make Q approach and equal K over time. In other words, if at a given time Q > K, the **back reaction** will be favoured (its rate will be greater than the forward reaction rate), which reduces Q so that Q = K eventually. If Q < K, the **forward reaction** will be favoured to as to increase Q so that Q = K eventually.

2.2.2 Position of equilibrium

The 'position of equilibrium' is a rather vague term that describes how far towards completion the reaction has gone. It can loosely be thought of as the percentage yield of product.

There are a number of reaction conditions that we can manipulate in order to change the position of equilibrium, to force the reaction to near completion. These manipulations involve:

- Increasing or decreasing the concentration of a particular reactant
- Changing the volume of the system
- Changing the temperature of the system

KEY POINT :

Note: Many textbooks will refer to changing the pressure of the system as a means of changing the equilibrium position. Personally, I think this is an easily misunderstood factor, which is why I did not include this. Remembering that $P = nRT/V$, pressure can be affected by **temperature** and **volume**, both of which are independent factors affecting equilibrium position. Therefore, I did not include pressure in the above list, since both temperature and volume can cause a change in pressure and that can lead to confusion.

We say that the position of equilibrium has been pushed **forward** if, after the manipulation, the forward reaction rate is faster than the back reaction rate, causing a net **forward** reaction and the net production of product. We say that the position of equilibrium has been pushed **backward** if, after the manipulation, the back reaction rate is faster than the forward reaction rate, causing a net **backward** reaction, and the net consumption of product. As a **shortcut** to work out whether the position of equilibrium has been pushed forward or backward after a manipulation, we can use **Le Chatelier's Principle**:

If a system in equilibrium is subject to a change, the system will act as to partially oppose that change.

There are a number of ways of figuring out **what** happens to the position of equilibrium when you perform a change onto the system, Le Chatelier's principle being the quickest of them. The other two ways (which are really the correct ways) of doing so is by using your knowledge of reaction kinetics to compare the forward and back reaction rates after you perform the change, or by comparing Q and K as you perform the change.

It should be noted that for an **endothermic reaction**, K **increases with temperature** and for an **exothermic reaction**, K **decreases with temperature**. The reason for this is well beyond Year 12 level. Also, **ONLY** temperature changes K. Below is a table summarising the effect of each of the changes:

Increasing the concentration of ONE species (also known as "adding or removing reactant or product"):

Le Chatelier's Principle	Changes to Q and K	Relative Reaction Rates
We increase the concentration of one species. System changes as to partially decrease the concentration of the species. System favours the reaction that consumes this species.	We increase the concentration of one species. K does NOT change. Q initially changes. Since Q 'wants' to equal K, Q will subsequently offset the change.	We increase the concentration of one species. There will be more fruitful collisions between this species and its other reactant. The rate of this reaction will increase and be higher than the reverse reaction. The position of equilibrium changes until the rate of both reactions are equal again.

Note that reciprocal changes would occur if you decrease the concentration of one species instead.

Decreasing the volume of the container (also known as "increasing the pressure of the system"):

Le Chatelier's Principle	Changes to Q and K	Relative Reaction Rates
We increase the pressure inside the vessel. System changes as to partially decrease the pressure. System favours the reaction that produces fewer particles.	We increase the concentration of all species by the same factor . K does NOT change. Q initially changes as the side (numerator or denominator) with more particles will increase more. Since Q wants to equal K, Q will subsequently offset the change.	The kinetics are well beyond Year 12 level. We increase the concentration of all the species. The rate of both the forward and the back reactions will both increase, by different amounts. The position of equilibrium will change until the rates of the forward and back reactions are equal.

Reciprocal changes occur if we increase the volume of the container.

Increasing the temperature (exothermic forward reaction):

Le Chatelier's Principle	Changes to Q and K	Relative Reaction Rates
We increase the temperature. System changes as to partially decrease the temperature. System favours the endothermic reaction – the back reaction.	We increase the temperature. K decreases . As Q always attempts to equal K, Q decreases subsequently. For Q to decrease, the back reaction must be favoured.	The kinetics are well beyond Year 12. If you increase the temperature, the rate of both the forward and the back reactions will both increase, by different amounts. Equilibrium position changes until both rates are equal.

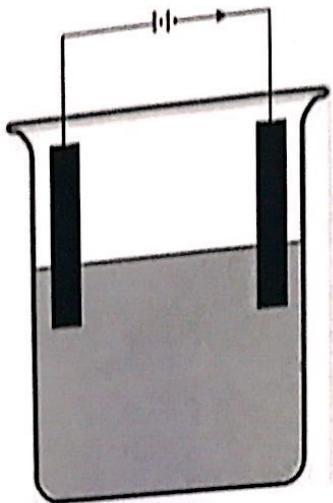
Increasing the temperature (endothermic forward reaction):

Le Chatelier's Principle	Changes to Q and K	Relative Reaction Rates
We increase the temperature. System changes as to partially decrease the temperature. System favours the endothermic reaction – the forward-reaction.	We increase the temperature. K increases . As Q always attempts to equal K, Q increases subsequently. For Q to increase, the forward-reaction must be favoured.	The kinetics are well beyond Year 12. If you increase the temperature, the rate of both the forward and the back reactions will both increase, by different amounts. Equilibrium position changes until both rates are equal.

Remember, again, that reciprocal changes occur if you **decrease** the temperature of the system.

2.3 Electrolysis and Secondary Cells

The electrolytic cell stores energy or uses electrical energy to produce new chemicals. The energy change is from electrical to chemical. Let's have a look at a diagram of a typical electrolytic cell.



Electrolysis forces non-spontaneous reactions to occur. Unlike a galvanic cell, the anode is positive and the cathode is negative. But, the definition still holds - the anode is the site of oxidation and the cathode is the site of reduction. The electrode could be made of reactive metals such as Fe, but could also be made of relatively inert metals such as Pt or even graphite (C).

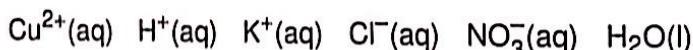
2.3.1 Predicting reactions

Remember, we are trying to force reactions to occur. We undertake the same process as we did with galvanic cells. We look for the easiest reaction that can occur (i.e. the one with the most positive E° value). We essentially need to find the species that is easiest to rip electrons from (i.e. the strongest reductant) and the species that is easiest to shove electrons into (i.e. the strongest oxidant). You can find out this information in the electrochemical series. It's the same thing as with galvanic cells, except with galvanic cells, the E° value has to be greater than 0, whereas with electrolytic cells, the E° value does not have to be greater than 0. (And don't forget to consider water!)

Example 2.1

A mixture of copper (II) nitrate and potassium chloride was electrolysed in acidic solution (hydrochloric acid) using inert graphite electrodes. Which species are produced at which electrode, assuming standard conditions?

Consider what is in the mixture:



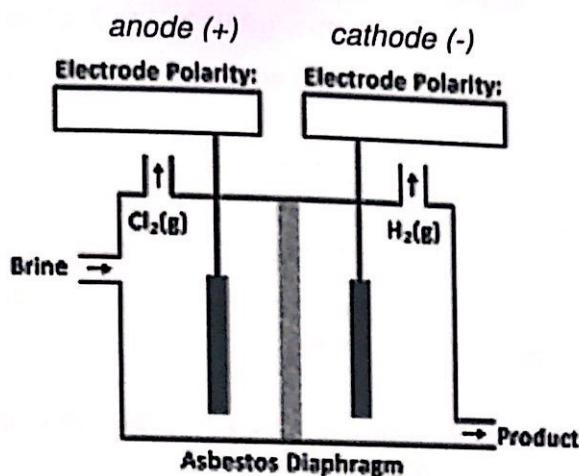
So, what can be oxidised and what can be reduced?

Cl^- and H_2O can be oxidised at the anode; note that at VCE level, NO_3^- (aq) never reacts at an electrode. Of the first two, which is more susceptible to being oxidised (can easily have electrons ripped off)? H_2O . When water becomes oxidised, it becomes O_2 .

Cu^{2+} , K^+ , H^+ and H_2O could be reduced at the anode. Of these, Cu^{2+} is the most susceptible to being reduced (having electrons shoved down its throat). Hence, O_2 (g) and Cu (s) are produced at the anode and cathode respectively.

2.3.2 Diaphragm cell

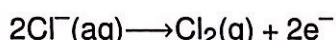
You are expected to know the general features of commercial electrolytic cells; you do not need to know specific examples. Below is an example of a commercial electrolytic cell for illustrative purposes. This cell produces chlorine (Cl_2) and sodium hydroxide (NaOH) from concentrated sodium chloride (NaCl) - brine.



Let's use the principles of electrolysis that we have learnt to determine what is going on.

We have Na^+ ions, Cl^- ions and H_2O . At the **anode (+)**, the site of **oxidation**, the possible species that could be oxidised are Cl^- and H_2O . Of these, H_2O is more susceptible to having electrons removed.

However, in this particular cell, there is an issue. Note that the above step, using the electrochemical series, is true under standard conditions, where $[\text{Cl}^-] = 1 \text{ M}$. If, however, we increase the $[\text{Cl}^-]$ to a very high level (like 6 M), then this will make Cl^- get discharged at the anode in preference. Increasing the concentration of a substance, whilst it does not guarantee it, increases the likelihood of the substance being reacted at an electrode. The reason this is possible, in this case, is because Cl^- and H_2O are so close together in the electrochemical series (on the right side). The half-equation at the anode is therefore:

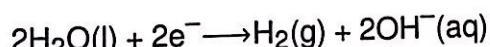


KEY POINT :

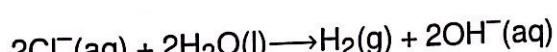
You will not be expected to predict when this sort of phenomenon occurs. You are, however, expected to know that changing the reaction conditions (e.g. concentration of the reactant) may, but not always, affect which substance is reacted at an electrode.

At the **cathode (-)**, the site of **reduction**, the possible species that could be reduced are Na^+ and H_2O . Of these - which is more susceptible to having electrons added? H_2O . In this case, H_2O is indeed reacted at the cathode. Although $[\text{Na}^+] \approx 6 \text{ M}$, Na^+ is so much weaker as an oxidant (accepting electrons) that even increasing its concentration to 6 M is ineffectual.

The equation at the cathode is:



The overall reaction equation is:



In essence, we are replacing Cl^- ions with OH^- ions, forming a mixture of NaCl and NaOH . The products are therefore H_2 , Cl_2 and NaOH . Note here that we have used **energy (electrical)** to generate useful chemicals such as H_2 , Cl_2 and NaOH from simple salt solution.

2.3.3 Faraday's laws

These laws help us answer the question: how much metal is deposited on the cathode when you electrolyse a solution for a specific period of time using a known current? Faraday's laws stipulate that:

- The mass of the metal is directly proportional to the charge passed through the cell.
- To produce one mole of metal, an integer number (usually 1 to 3) of moles of electrons must be used.

The data that we are generally given is the current (I) in amperes, which if you recall is the amount of charge (Q) in coulombs that passes into cathode per unit time (t) in seconds.

So, we can relate our data to the amount of charge that reached the cathode. How do we relate this to the amount of electrons that reach the cathode? It turns out that experimental data has shown that 1 mole of electrons have a total charge of 96,500 coulombs of charge. This is known as **Faraday's constant**.

We know how many electrons a metal ion consumes until it is reduced to the metal. For example, a silver (Ag^+) ion requires one electron to be reduced to silver metal.

Example 2.2

Using a current of 0.100 A for 10.0 seconds, how much silver (in grams) is deposited on a silver cathode in an electrolytic cell using silver nitrate as the electrolyte?

How much charge reached the cathode?

$$Q = It = 0.100 \times 10.0 = 1.00\text{C}$$

So, how many electrons reached the cathode?

$$n(e^-) = 1.00/96500 = 1.04 \times 10^{-5}\text{ mol}$$

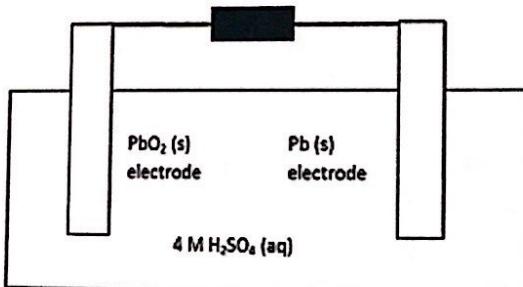
We know that a silver (Ag^+) ion requires one electron to be reduced to silver metal.

$$n(\text{Ag}) = 1.04 \times 10^{-5}\text{ mol}$$

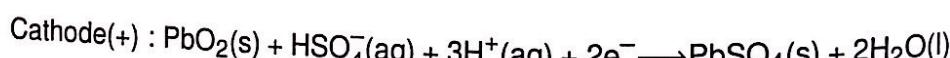
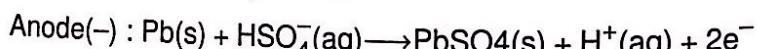
$$m(\text{Ag}) = 1.04 \times 10^{-5} \times 107.9 = 1.12 \times 10^{-3}\text{ g.}$$

2.3.4 Secondary cells

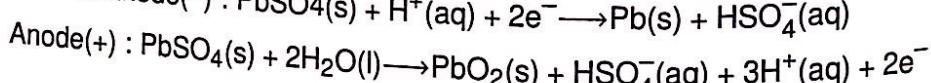
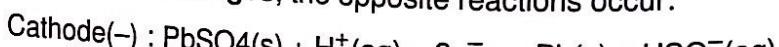
Now that we know about electrolysis, we can finally talk about rechargeable batteries. These are **rechargeable** because the products remain in contact with the electrodes after reaction. This recharging occurs through **electrolysis**. One prime example is the lead-acid accumulator, used for car batteries.



Whilst the cell is **discharging** - that is, the cell is being used as a galvanic cell, using its stored chemical energy to produce electricity, the reaction equations are:



Note that the reactants are **Pb (s)** and **PbO₂ (s)** in this battery. The product - **PbSO₄** - remains in contact with the electrodes. When the cell **recharges**, the opposite reactions occur:



Part II

Unit 4: How are organic compounds categorised, analysed, and used?

Area of Study 1

How can the diversity of carbon compounds be explained and categorised?

1.1 Elemental properties of organic compounds

Organic chemistry is the study of compounds of carbon. You can write an entire textbook on the chemistry of carbon. Many important molecules in the world, particularly in biology, are organic compounds. Organic compounds range from the smallest molecule – methane (CH_4) – to giant molecules of over 500 carbon atoms. Why is it that the simple element carbon can form such a variety of molecules of different sizes? The carbon atom has 6 protons in its nucleus, and an electron configuration of 2,4. The carbon atom has a **valency** of 4, and can therefore form 4 covalent bonds. The interesting thing about the carbon atom is that the C-C bond is **extremely strong and stable**, and carbon bonds with other atoms are also extremely strong and stable, particularly the C-H bond. This is part of the reason why carbon compounds can become so large without the molecule decomposing. In Unit 1, you would have been introduced to different classes of organic compounds, being the **hydrocarbons (alkanes, alkenes and alkynes)**, the **alkanols**, the **carboxylic acids** and the **esters**.

1.1.1 Alkanes

Alkanes are hydrocarbons where there are no double bonds or triple bonds between carbon atoms.

Name	Molecular formula	Semi-structural formula	Structural formula #1	Structural formula #2
methane	CH_4	CH_4	n/a	<pre> H H—C—H H </pre>
ethane	C_2H_6	CH_3CH_3	$\text{H}_3\text{C}—\text{CH}_3$	<pre> H H H—C—C—H H H </pre>

1.1.2 Alkenes

Alkenes are hydrocarbons whereby there exists at least one **double bond** between two carbon atoms, and there are no triple bonds. Below are the structures of the smallest alkenes:

Name	Molecular formula	Semi-structural formula	Structural formula #1	Structural formula #2
ethene	C_2H_4	$\text{CH}_2=\text{CH}_2$	$\text{H}_2\text{C}=\text{CH}_2$	<pre> H H C=C H H </pre>
propene	C_3H_6	$\text{CH}_3\text{CH}=\text{CH}_2$	$\text{H}_3\text{C}-\text{CH}=\text{CH}_2$	<pre> H H C=C H H </pre>

1.1.3 Alkynes

Alkynes are hydrocarbons where there is at least one triple bond between two carbon atoms.

Name	Molecular formula	Semi-structural formula	Structural formula #1	Structural formula #2
ethyne	C ₂ H ₂	HC≡CH	HC≡CH	H—C≡C—H
propyne	C ₃ H ₄	HC≡CHCH ₃	H—C≡C—CH ₃	H—C≡C—C—H H

1.1.4 Alkanols (alcohols)

Alcohols are organic molecules with an -OH (hydroxyl) group, somewhere in the molecule.

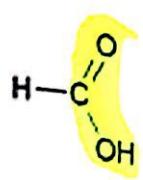
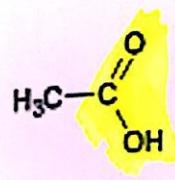
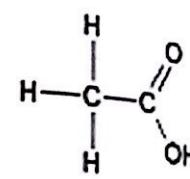
Name	Molecular formula	Semi-structural formula	Structural formula #1	Structural formula #2
methanol	CH ₄ O	CH ₃ OH	H ₃ C—OH	H—C—O—H H
ethanol	C ₂ H ₆ O	CH ₃ CH ₂ OH	H ₃ C—CH ₂ —OH	H—C—C—OH H H

There are three types of alkanols – primary, secondary and tertiary.

Type of alkanol	Description	Example
Primary (1°)	The hydroxyl (OH) group is on the terminal carbon atom.	H ₃ C—CH ₂ —CH ₂ —OH
Secondary (2°)	The hydroxyl (OH) group is on a carbon atom in the middle; this carbon atom is bonded to only 2 other carbon atoms.	H ₃ C—CH(OH)—CH ₂ —CH ₃
Tertiary (3°)	The hydroxyl (OH) group is on a carbon atom in the middle; this carbon atom is bonded to 3 other carbon atoms.	H ₃ C—C(OH)—CH ₂ —CH ₃

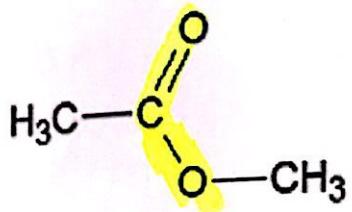
1.1.5 Carboxylic acids

This is another set of hydrocarbon derivatives that contain the moiety -COOH. Below is a set of the simple carboxylic acids:

Name	Molecular formula	Semi-structural formula	Structural formula #1	Structural formula #2
methanoic acid	CH ₂ O ₂	HCOOH	n/a	
ethanoic acid	C ₂ H ₄ O ₂	CH ₃ COOH		

1.1.6 Esters

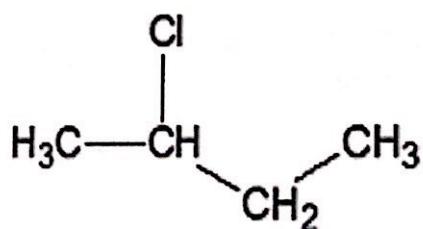
Esters are derivatives of carboxylic acids, which have a -COOC- moiety. Below is an example of an ester:



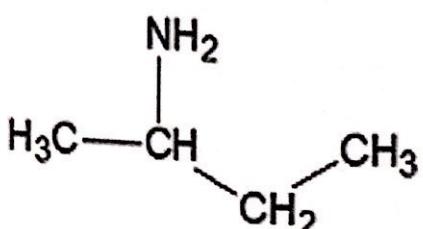
1.1.7 Other organic molecules

There are other types of organic compounds that you need to be familiar with, including:

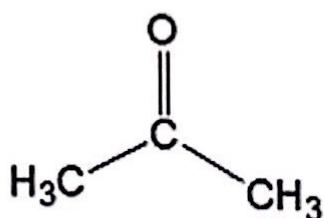
- **Haloalkanes:** these are organic compounds that are like alkanes, except have at least one C-Cl, C-Br, or C-I bond. The halogen replaces at least one of the H atoms in the molecule. The -Cl, -Br, and -I moieties are known as the **chloro**, **bromo** and **iodo** functional groups.



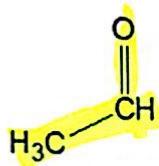
- **Primary amines:** these are molecules with an -NH₂ group in the molecule. The -NH₂ moiety is known as the **amino** functional group. Note that there must be **2 H atoms** bonded to the nitrogen atom for the amine to be considered a primary amine.



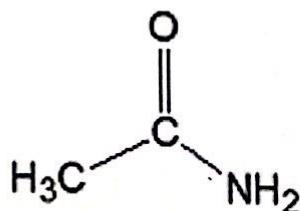
Ketones: these are new to the 2017 course and refer to groups with a C=O moiety (and are not part of a carboxyl or ester group). The C=O moiety is known as a **carbonyl** group. The C=O moiety must be in the **middle** of the molecule – ketones cannot have a C=O group at a terminal carbon atom.



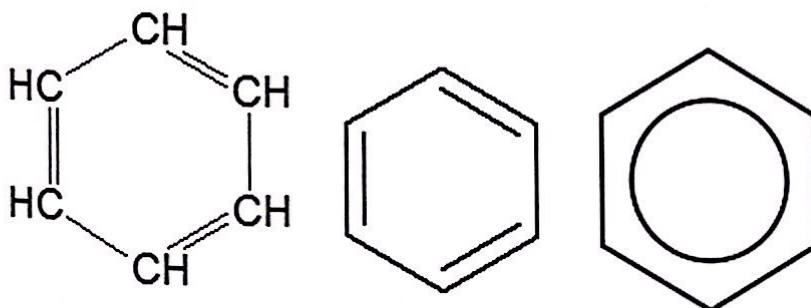
Aldehydes: these are also new to the 2017 study design, and are groups with a C=O moiety at the **terminal** carbon.



Primary amides: these are groups with a CONH₂ moiety at the **terminal** carbon. The CONH₂ moiety is known as an **amide** functional group.

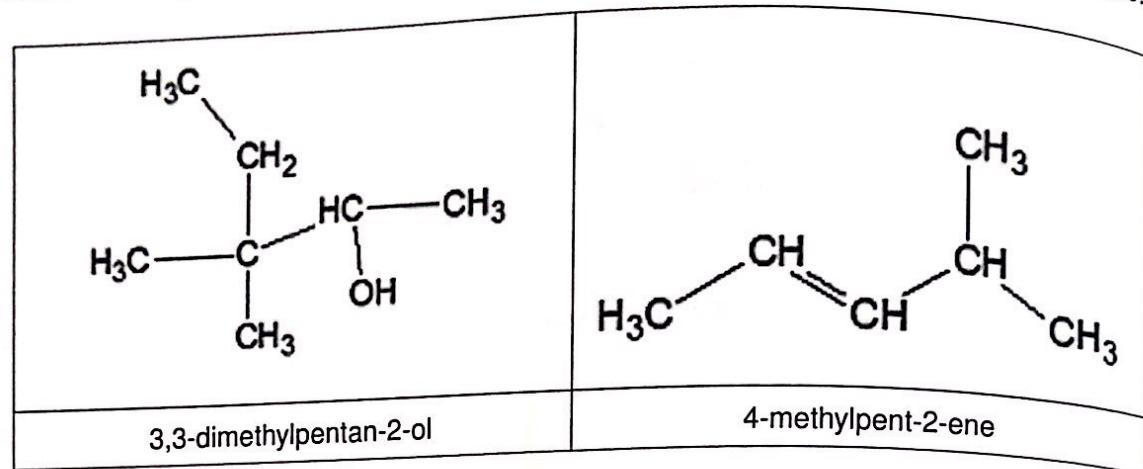


Benzene: this is an unusual molecule. It is a cyclic molecule with formula C₆H₆. At first glance, this looks like just a normal alkene (e.g. the first and second image below). However, the molecule does not behave like one with alternating double bonds and single bonds. Benzene does not undergo reactions that alkenes undergo. In fact, the bonds between every carbon atom are the same – each carbon atom can be said to have “1.5 bonds.” The electrons that form the second bond between carbon atoms in the proposed double bond actually roam around the entire molecule. The third image here is a more accurate representation of the molecule (though the second one is also valid).



1.2 Naming compounds

There is a systematic way that organic compounds can be named, and this is dictated by the International Union of Pure and Applied Chemistry (IUPAC). We will use the following compound as an example:



If you look at the names shown above, the name of the molecule is split into a set of affixes:

- [substituents][main part of molecule] – this can be further split to
- [substituent][substituent][substituent]...[no. of carbons][C=C bonds?][principal functional group]

In the left example:

- [substituent]= 3,3-dimethyl
- [no. of carbons]= pent (5 carbon atoms)
- [C=C bonds?]= an (used when there are no C=C bonds)
- [principal functional group]= ol (OH group)

How to systematically name a compound:

1. Identify the LONGEST carbon chain containing a principal functional group if possible; if there are none containing a principal functional group, try to identify the longest one with a C=C double bond. I will call this the **main carbon chain**.

At VCE Unit 3&4 level, the only **principal** functional groups that you need to worry about are:

- carboxyl (COOH)
- hydroxyl (OH)
- amino (NH₂)

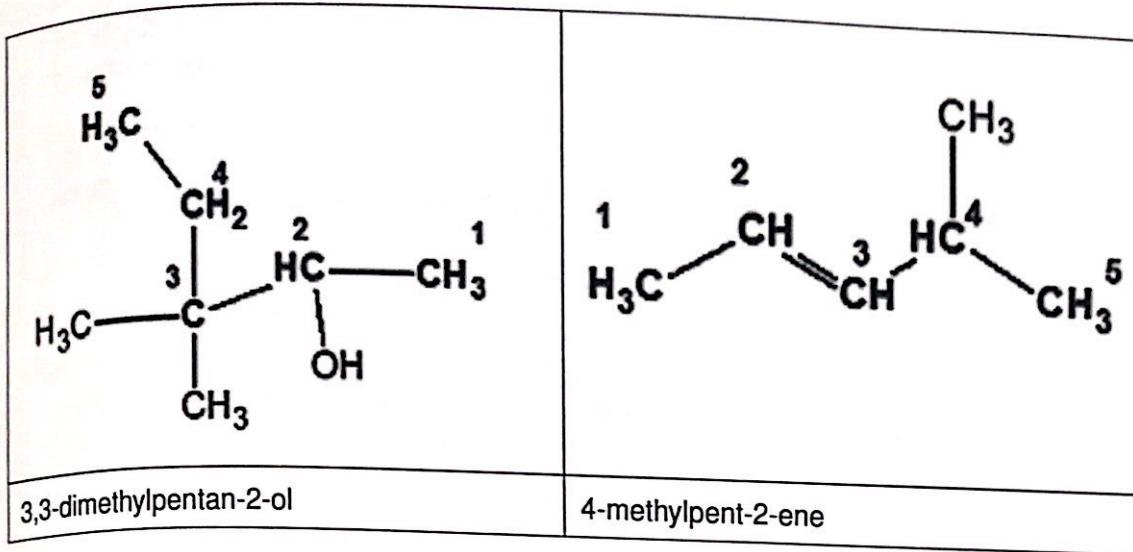
When you identify the longest carbon chain containing the principal functional group, you can then determine the [no. of carbons]. For [no. of carbons] you put the affix that corresponds to the number of carbon atoms in the longest carbon chain.

- 1: meth-
- 2: eth-
- 3: prop-
- 4: but-
- 5: pent-
- 6: hex-
- 7: hept-
- 8: oct-

2. NUMBER the carbon atoms in the main carbon chain. Ensure that you number in the direction that would give the lowest possible number on the carbon containing the principal functional group (or, if there is no principal functional group, then the double bond, or if there is no double bond, the substituent).

Many organic molecules have “substituents”, which are groups of atoms that replace a hydrogen atom in the main carbon chain. Substituents include methyl groups (CH₃-) and hydroxyl groups (-OH).

In a molecule, the name needs to convey where along the main carbon chain the substituents are. To do this, each carbon atom in the main chain is given a number.



Going back to our substances:

- The substance on the left has a principal functional group (the OH group). As you can see, the numbering was performed from right to left (1 on the right, 5 on the left). If numbering were instead performed from left to right, the OH group would be on carbon number 4 instead of carbon 2. Therefore, numbering direction in this molecule should be from right to left.
- The substance on the right has no principal functional group, but there is a double bond. If numbering were from right to left, the double bond would be between carbon atoms 3 and 4 (and the double bond designated as being at carbon 3 – the lower one by convention). In contrast, numbering from left to right as per the diagram has the double bond between carbons 2 and 3, and therefore the double bond is designated as being at carbon 2. Since $2 < 3$, the numbering will be from left to right here.

3. Determine [principal functional group] and/or [C=C bonds?].

For a principal functional group, the affixes used for [principal functional group] are:

Principal Functional Group	Affix
carboxyl (-COOH)	-oic acid
hydroxyl (-OH)	-ol
amino (-NH ₂)	-amine

To denote the carbon number that the functional group is in, you put a number before the functional group. For instance, if the principal functional group was an OH group on carbon 2, you write “-2-ol”. You use a dash whenever you are writing a letter and a number next to each other.

What is there is more than one potential principal functional group (e.g. a carboxyl and amino group) in the same molecule? Well, in that case, only one of these will be the designated principal functional group. The table written above has the potential principal functional groups written in order of priority, with the carboxyl being the highest priority. Therefore, if there is both a carboxyl and amino group in the same molecule, the carboxyl group will become the principal functional group, with the amino group becoming a mere substituent (described in step 4).

1.2 Naming compounds

The affixes used for [C=C bond?] are:

Category	Affix
Contains one or more C=C bonds	-en(e)-
Contains no C=C bond	-an(e)-

You have to locate where your C=C double bonds are. Examples of how to use this affix:

Situation	Affix
C=C bond at carbon 3	-3-en(e)-
C=C bond at carbon 1 and 3	-1,3-dien(e)-

For the two example molecules:

<p>There is an OH group on carbon-2, hence [principal functional group] = -2-ol. There is no C=C double bond, so [C=C double bond?] = -an(e)-.</p> <p>So far, we now have pentan-2-ol. We don't use -ane- here because "pentaneol" sounds gross and slow to say.</p>	<p>There is no principal functional group. There is a C=C double bond on carbon 2, so [C=C double bond?] = -2-ene.</p> <p>So far, we therefore have pent-2-ene.</p>

4. Determine substituents.

The affixes for each substituent are:

Substituent	Affix
CH ₃ -	methyl
CH ₃ CH ₂ -	ethyl
Cl-	chloro
Br-	bromo
I-	iodo
-OH (as a substituent)	hydroxy
-NH ₂ (as a substituent)	amino

You can guess what the bigger ones would be called.

Remember that you have to put the number of the carbon to which the functional group is bonded next to each substituent, for example "3-methyl". If there are 2 of the **same** substituent, you name them simultaneously, putting commas between the location of each of the duplicates/triplicates/etc. and adding 'di,' 'tri' or 'tetra' to denote 2, 3 or 4 copies of the functional group. For example, if there were a methyl group on carbons 1, 1 and 3 – you would write "1,3,3-trimethyl-".

<p>There are two CH_3 groups on carbon 3. We therefore get "3,3-dimethyl". The name of the molecule is therefore 3,3-dimethylpentan-2-ol.</p>	<p>There is a CH_3 group on carbon 4. We therefore get "4-methyl". The name of the molecule is therefore 4-methylpent-2-ene.</p>

KEY POINT :

Make sure that when there is a principal functional group in a molecule, that the principal functional group's affix is written at the end of the molecule where appropriate. For example, the compound $\text{CH}_3\text{CH}_2\text{NH}_2$ is **ethanamine**, NOT aminoethane. The reason I am writing this is because many past VCAA assessment reports have cited students continually writing names such as 'aminoethane' and being penalised for it. Names such as 'aminoethane' were old names for the molecule, and are not the new IUPAC systematic names.

1.3 Isomerism

1.3.1 Structural Isomerism

Structural isomers are molecules that have the **same molecular formula** but a **different structural formula**. In other words, the same number of each atom is present in both molecules, but the atoms are arranged differently, bonded to different sets of atoms. Below is an example of **two isomers with molecular formula C_4H_{10}** :

butane	methylpropane

1.3 Isomerism

There will be some questions in the exam that may ask you to figure out how many structural isomers exist for a particular molecular formula. Below is the method that I use:

1. Determine the number of double bonds in the molecule using the molecular formula.

You could either do this intuitively, or use the following formula (the double bond equivalent formula, which will give you the number of double bonds + rings):

$$\text{DBE} = \frac{2(\text{C} + 1) - [\text{1}] + [\text{3}]}{2}$$

In this formula:

1. C is the number of **carbon** atoms in the formula
2. [1] is the number of atoms that form 1 bond (e.g. H, Cl, Br, I)
3. [3] is the number of atoms that form 3 bonds (e.g. N, P)
4. Note that oxygen does not appear in this formula.

For the case of $\text{C}_3\text{H}_5\text{Cl}$:

$$\text{DBE} = \frac{2(3 + 1) - 5 + 0}{2} = 1$$

In this case, $\text{C}_3\text{H}_5\text{Cl}$ has 1 double bond.

2. Draw all the possible arrangements for all atoms that form more than one bond (eg. C, O, N, etc.) Don't forget to factor in double bonds!

In this case of $\text{C}_3\text{H}_5\text{Cl}$, there is only one arrangement for these atoms (which are all carbon atoms), that being the arrangement $\text{C}=\text{C}-\text{C}$.

3. Using the 'skeletons' you draw in step 2, draw all the possible arrangements of all atoms that form single bonds apart from hydrogen.

In this case of $\text{C}_3\text{H}_5\text{Cl}$, the Cl atom can go on any of the three carbon atoms.

4. Complete all the structures of the isomers by adding in all the hydrogen atoms.

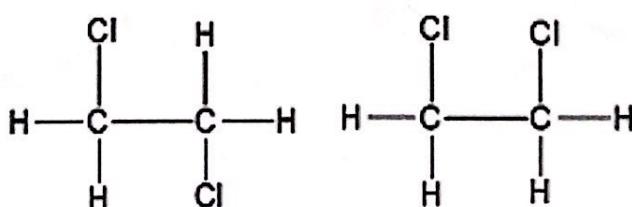
So the isomers would be:



1.3.2 Geometric isomerism

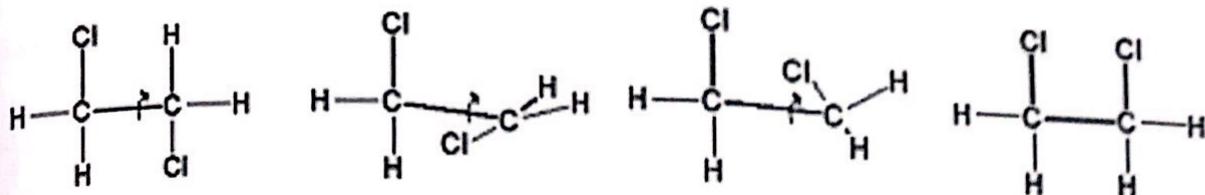
There is a second type of isomerism called **geometric isomerism**, which is a new addition to the study design as of 2017. Here, the two isomers have the **same** molecular **AND** structural formula, but the way the atoms are arranged in space is different.

To understand the implications of geometric isomerism, let us compare these two structures:



It goes without saying that these two are considered the same molecule. But have you ever thought of why? After all, these are two different spatial arrangements of the atoms. However, the important point is this: the molecule (1,2-dichloroethane) can adopt either configuration. If you follow a single molecule of dichloroethane, the molecule will oscillate between a number of configurations, including both the one on the left and the one on the right? Why? Because **single bonds can rotate**.

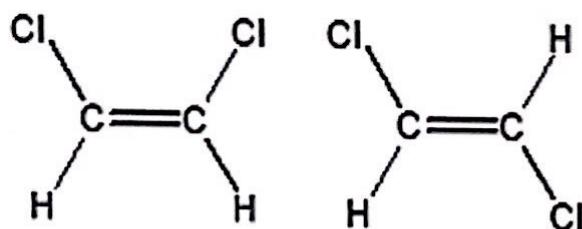
If you imagine the structure on the left rotating:



you will end up getting the structure on the right. In fact, these two structures are different configurations of the same molecule.

So, in what cases can we get **geometric isomers**? We get them when there are C=C double bonds involved. Why is this the case? Because **C=C double bonds cannot rotate** – the reasons for this are beyond the scope of this course.

Let us compare the following two structures:

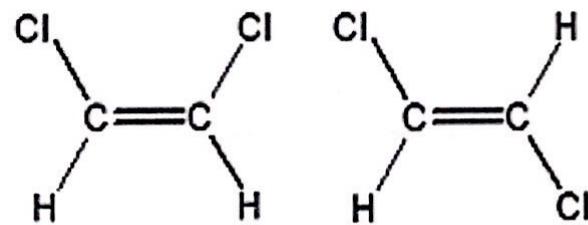


This is analogous to the previous example, except here the two C atoms are double-bonded. Now, theoretically to get from the structure on the left to the structure on the right, you would have to rotate the C=C bond. However, this bond cannot rotate (unless you put the molecule under really hot conditions where the double bond temporarily breaks). Therefore, since these two conformations are not interchangeable, the two molecules above are considered **different molecules**; they are **geometric isomers**.

How do we differentiate between these two isomers? At a VCE level,

- The geometric isomer where the two hetero groups (e.g. CH₃, Cl groups) are on the **same side** of the double bond is the **cis isomer**.
- The geometric isomer where the two hetero groups are on **opposite sides** of the double bond is the **trans isomer**.

Therefore, in the above example, the isomers will be classified as thus:



cis-1,2-dichloroethene trans-1,2-dichloroethene

Note that cis and trans isomers are **different molecules** with slightly different physical and chemical properties. For example, the trans isomer above has a higher boiling point than does the cis isomer.

Thus, geometric isomerism exists where there is a C=C double bond **AND** where, in each of the C atoms in the double bond, the two bonds each C atom forms are to different groups of atoms; in the above example, for each C atom, the groups to which the C atom was bonded were different – a H atom (group 1) and a Cl atom (group 2).

1.3.3 Optical isomerism

Optical isomerism is similar to geometric isomerism in that the atoms in the molecules are bonded in the same way, but are oriented differently in space. The feature specific to optical isomerism is the effect that optical isomers have on light that passes through them.

Some substances have two optical isomers, which are called **enantiomers** of that substance. Importantly, each enantiomer rotates the plane of polarised light in opposite directions.

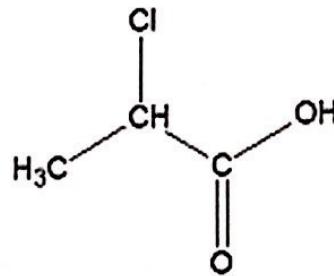
Remember, light can be considered to be a wave. If we imagine a stream of light hitting your eye, some of the light waves will be oscillating up and down (vertically), others oscillating left and right (horizontally), and yet others diagonally. Polarised light is light that is only oscillating in one particular direction (e.g. vertically). **Polaroid sunglasses** do this – when the light hits the glass, the glass is designed so that light waves oscillating in a particular direction get through. The resulting light is **polarised light**.

The **plane** of polarised light is related to the path traced by the wave as it is travelling and oscillating. For example, if the wave is travelling towards you and is oscillating vertically (up and down), the plane is basically a sheet of paper held vertically/sideways (as if you were about to drop it from one hand), with you looking directly at the edge of the paper.

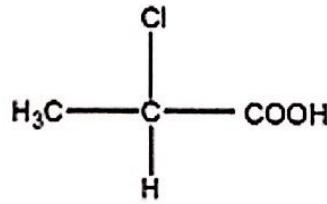
If vertically polarised light passes through a solution containing only a single enantiomer of a molecule, then that plane rotates; the light coming out would oscillate diagonally, not up and down. If vertically polarised light passes through a solution contains the other enantiomer of the same molecule, the plant will rotate equally, but in the **opposite** direction.

Chiral centres

What sort of molecules have optical isomers? The answer is that molecules that have at least one **carbon atom** that is bonded to **four different substituents**. Carbon atoms with this property are called **chiral centres**. Let us consider the molecule 2-chloropropanoic acid:



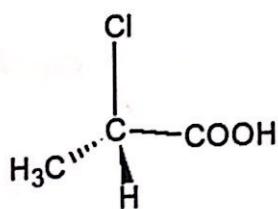
This molecule looks innocuous enough. However, let's redraw this molecule in a different way:



Notice how this carbon atom has **4 different substituents**? A H atom, a Cl atom, a CH₃ group and a COOH group. This makes this carbon atom a chiral centre. However, why does this lead to isomerism? Well, **optical isomers or enantiomers are mirror images of one another**.

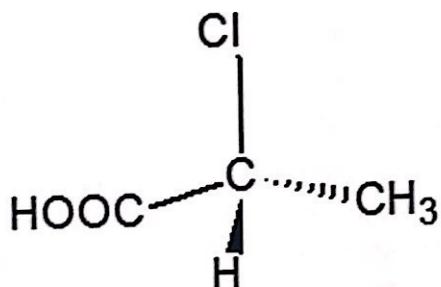
Let's take the second structure of the molecule and draw it a little more accurately. The second drawing suggests that the molecule has a planar structure.

However, remember from Unit 1 Chemistry that if there are 4 electron sites and no lone pairs about an atom, the substituents adopt a tetrahedral structure:



If you have not seen these weird lines before:

- A wedge (—) means the bond is coming out of the page towards you.
 - A dashed line (.....) means the bond is going into the page away from you.
- Now, what we are going to draw is an alternate structure for this molecule – a **mirror image** of the original structure:

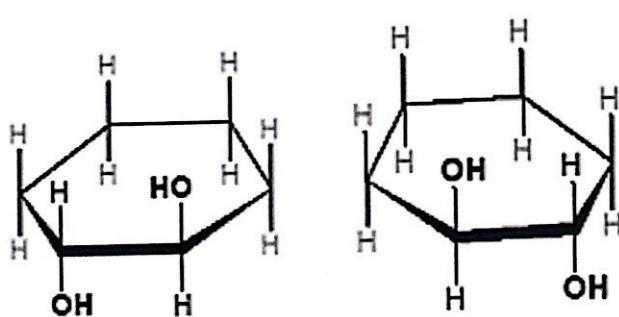


Now, I have a task for you. Either using a model or in your mind, try and rotate this third structure to superimpose it onto the second structure. You will find that you cannot do it. These two structures are **enantiomers or optical isomers**.

Note that for all intents and purposes, **optical isomers have pretty much the same physical and chemical properties**. This is because in practice, most substances that have optical isomers exist as mixtures of the two optical isomers; these substances are called **racemic mixtures**.

The only situations where different optical isomers of the same chemical have different chemical properties is in environments where only one optical isomer of chemicals is found. This happens mainly in **biological contexts**. You will learn later that **enzymes** (molecules that catalyse biological reactions) only work on one optical isomer of a particular substance.

Below is another example of two optical isomers (each vertex is a carbon atom):



If a molecule has optical isomers, the molecule is said to be **chiral**; molecules without optical isomers are called **achiral**.

To determine whether a molecule is chiral or achiral, the test is this: **if you can draw a line of symmetry somewhere in the molecule, the molecule is achiral**.

1.4 Physical properties of organic compounds

In the scope of this course, you will need to be able to compare organic compounds with respect to **boiling point**, **viscosity**, and the **flashpoint**. In order to compare organic compounds via these parameters, we need to define what these parameters mean:

- **Boiling point:** this is the temperature at which a liquid is converted into a gas.
- **Viscosity:** this is effectively the 'thickness' of the fluid. Viscosity is the degree of resistance a liquid has to flow. For example, oil is more viscous than water.
- **Flashpoint:** this is the lowest temperature at which a substance would ignite (combust) given an ignition source, such as a spark.

Boiling point

When a liquid is converted into a gas, the molecules have to break their intermolecular bonds so that they can enter the gaseous phase and move around independently. Now, if the intermolecular bonding (the sum of dispersion forces, dipole-dipole interactions and hydrogen bonds) is very strong, you need the molecules to vibrate really fast and move very quickly to break these strong intermolecular bonds. In other words, you need **higher temperatures**. Therefore, the stronger the intermolecular bonding within a substance, the higher the boiling point.

This explains, for example, why octane (C_8H_{18}) has a higher boiling point than pentane (C_5H_{12}). Since octane is a larger molecule, it exhibits stronger dispersion forces. Additionally, there is no hydrogen bonding in either substance. Therefore, octane has stronger intermolecular forces.

Note that it is not just the size of the molecule that matters, but also the ability of the molecules to 'pack' together. This explains why **straight-chain hydrocarbons** (e.g. octane) would have a higher boiling point than **branched hydrocarbons of a similar size** (e.g. 2,3,4-trimethylpentane, which has a molecular formula of C_8H_{18} as well). Straight chain hydrocarbons have a better ability to pack closely together and therefore exhibit strong dispersion forces, which require that the atoms are very close to one another.

Viscosity

The main factors that increase viscosity of a liquid are the **degree of intermolecular bonding** as well as the **size and shape of the molecule**.

Strong intermolecular bonding tends to hold the molecules close to one another, preventing them from separating from one another too easily, which would impede flow. This is analogous to taking some sand and letting it flow out of your hands, and then mixing sand with some glue, and trying to let that mixture flow out of your hands.

The size and shape of the molecule matters for two reasons: large and narrow molecules tend to exhibit stronger dispersion forces (i.e. stronger intermolecular bonding), and large molecules tend to get 'entangled' in one another, preventing the molecules from flowing in an ordered fashion. Imagine a set of super long trucks travelling along the Monash Freeway, and trying to change lanes repeatedly – that would cause a giant traffic jam.

This is why **oil** (which is made out of giant long molecules of about 54 carbon atoms in size) is more viscous than **water** (H_2O). The molecules of oil can become entangled very easily, and also oil exhibits very strong dispersion forces.

Flashpoint

The determinant of the flashpoint is how **volatile** a liquid is. Generally, the lower the boiling point, the more volatile the liquid, and therefore the lower the flashpoint.

The flashpoint is related to volatility because the more volatile a liquid is, the more vapours that tend to form around the liquid. It is generally the vapour part of the liquid that tends to ignite.

For example, ethanol has a lower flashpoint than does diesel (a mixture of large hydrocarbons).

1.5 Reactions of Organic Compounds

Here, you will learn about the different reactions organic compounds can undergo. Importantly, in organic chemistry, the **functional groups** have their own individual chemistries; for example, if a molecule has an amino group and a carboxyl group, the amino and carboxyl group will tend to react independently of one another. The amino group would undergo the same reactions that amines undergo, and the carboxyl group would undergo the same reactions that regular carboxylic acids would undergo. (Note that this section will not go into the combustion reactions, which we've already gone through in Unit 3.)

1.5.1 Alkanes

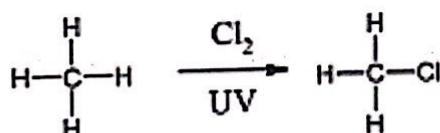
Alkanes are rather boring and unreactive compounds, owing to the stability and strength of the C-H bond. Therefore, it takes some rather reactive substances to react with alkanes. Normally, alkanes tend to react with highly reactive oxidising agents, such as O₂ gas, F₂ gas, Cl₂ gas as well as Br₂ to an extent.

We already know that alkanes can react with O₂ gas to form CO₂ and H₂O in a combustion reaction. For your information, alkanes **can** also combust in F₂ and Cl₂ gas (F₂ will combust alkanes even in the cold and dark) to form elemental carbon and the hydrogen halide.

The reaction involving alkanes you need to know about is the **photochemical substitution** of alkanes. If you react an alkane with Cl₂ in bright sunlight, or in very hot conditions – the alkane can combust in Cl₂ to form elemental carbon and HCl. However, if you mix the alkane with Cl₂ and expose the mixture to mild sunlight, you get the following reaction (methane is used as an example):



Another way of writing this reaction is shown below – this is the organic chemist's shorthand:

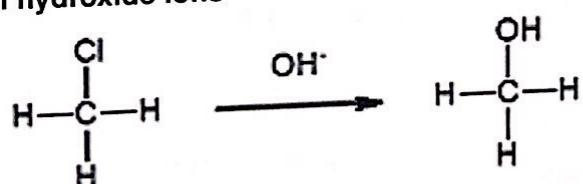


The second representation is just as valid as the first, but it omits accessory products that we do not care about (e.g. HCl). This is a **substitution** reaction since a H atom from the alkane is replaced by a Cl atom. Now, note that you can react the chloroalkane with more Cl₂ to produce molecules such as CH₂Cl₂, CHCl₃ and even CCl₄. In reality, when you mix methane and Cl₂ and expose to sunlight, you will produce a mixture of CH₃Cl, CH₂Cl₂, CHCl₃ and CCl₄, depending on the ratio of methane to Cl₂ you mixed in the first place. The same reactions occur with Br₂, but not so much with I₂.

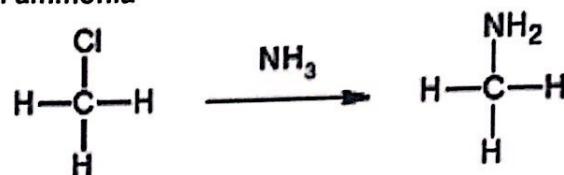
1.5.2 Haloalkanes

Haloalkanes are substances with a hydrocarbon chain with halo functional groups such as -Cl (chloro), -Br (bromo) and -I (iodo). Haloalkanes undergo **substitution** reactions, where the halogen atom is replaced by another functional group.

Reaction of haloalkane with hydroxide ions



Haloalkanes can react with hydroxide ions to form the equivalent alkanol; note that there is no catalyst needed. This is a **substitution** reaction.

Reaction of haloalkane with ammonia

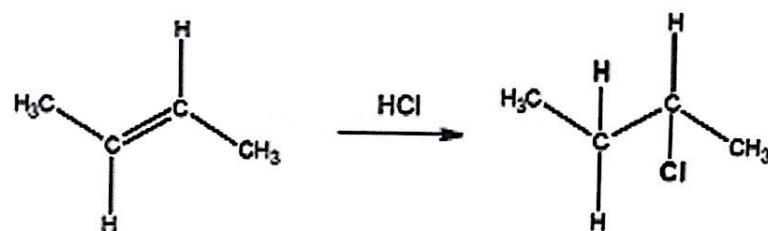
Haloalkanes can also react with **ammonia** to form the equivalent amine – again, there is no catalyst required. This is also a substitution reaction.

1.5.3 Alkenes

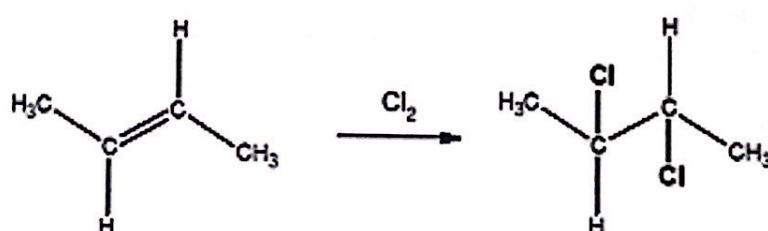
Alkenes are very highly reactive substances, owing to the C=C double bond. You don't need to know why, but the C=C double bond has electrons in the double bond which are highly 'exposed' – left hanging out to dry for chemicals that love electrons (electrophiles) to react with them. In particular, acidic substances (substances that form an acidic solution when dissolved in water) tend to react with alkenes very well. Examples of acidic substances are:

- HCl, HBr and HI – goes without saying, these are strong acids
- Cl₂, Br₂ and I₂ – when dissolved in water, will form some H⁺ ions as a product

Alkenes generally undergo **addition** reactions. These are reactions where the two reactants combine to form a single product; alternatively, the atoms of the smaller molecule are incorporated into the structure of the larger molecule with no second product formed.

Reaction of alkene with HCl

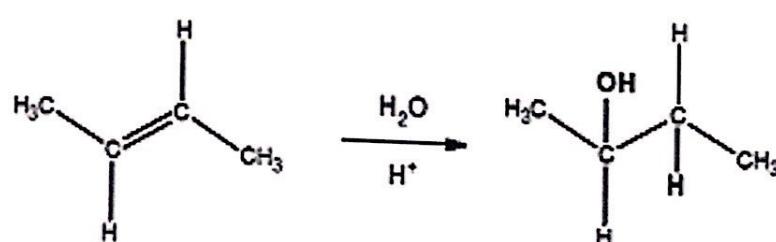
These reactions will work with HBr and HI as well.

Reaction of alkene with Cl₂

These reactions will work with Br₂ and I₂ as well.

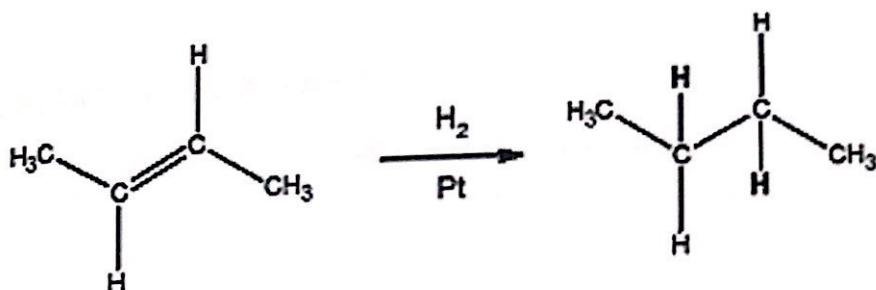
Reaction of alkene with H₂O (hydration of an alkene)

Water, being a very weak acid, does not react well with alkenes alone. Therefore, water requires an acid catalyst (usually H₃PO₄, although other acids may be used).



Reaction of alkene with H₂ (hydrogenation of an alkene)

H₂ is not known for its acidic properties; as such:

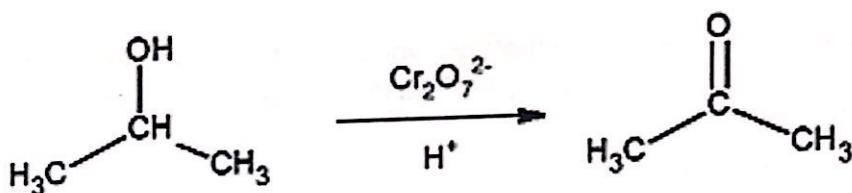


1.5.4 Alkanols

Alkanols can undergo a variety of organic chemical reactions. The main reaction you need to know involving alkanols is the oxidation of the alkanol, using oxidising agents such as acidified dichromate ions (a mixture of Cr₂O₇²⁻ ions and H⁺ ions) or acidified permanganate ions (a mixture of MnO₄⁻ ions and H⁺ ions). The product formed depends on the type of alkanol that is reacted:

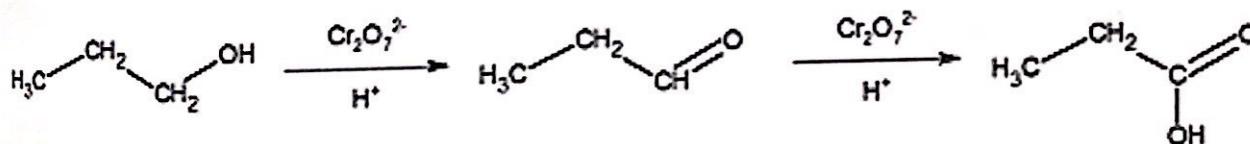
Oxidation of secondary alkanols

Oxidation of a secondary alkanol leads to the formation of a **ketone**:



Oxidation of primary alkanols

Oxidation of a primary alkanol yields the **aldehyde**, but if you use an excess of the oxidising agent and you ensure the aldehyde stays in the reaction mixture (aldehydes are volatile, with some aldehydes being gases at room temperature), then you can produce the carboxylic acid:



Oxidation of primary alkanols

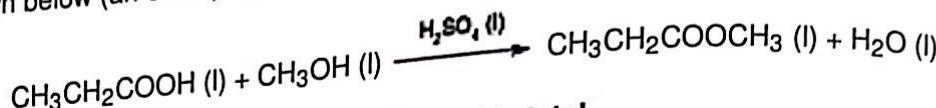
Tertiary alkanols cannot be oxidised to either a ketone, aldehyde or a carboxylic acid.

Carboxylic acids and their derivatives

Carboxylic acids can react as an acid (like any other acid), with **alkanols** to form an **ester**, OR with **amines** to form an **amide**.

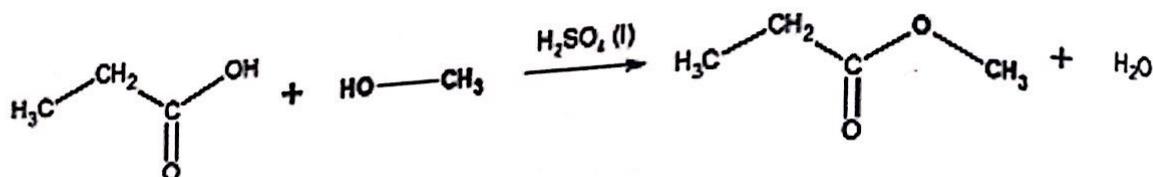
1.5.5 Esterification

A carboxylic acid can react with an alkanol, in the presence of concentrated sulfuric acid, to form an ester, as shown below (an example):



Note here that all the substances have to be in liquid state!

A more intuitive way of representing the reaction is below:



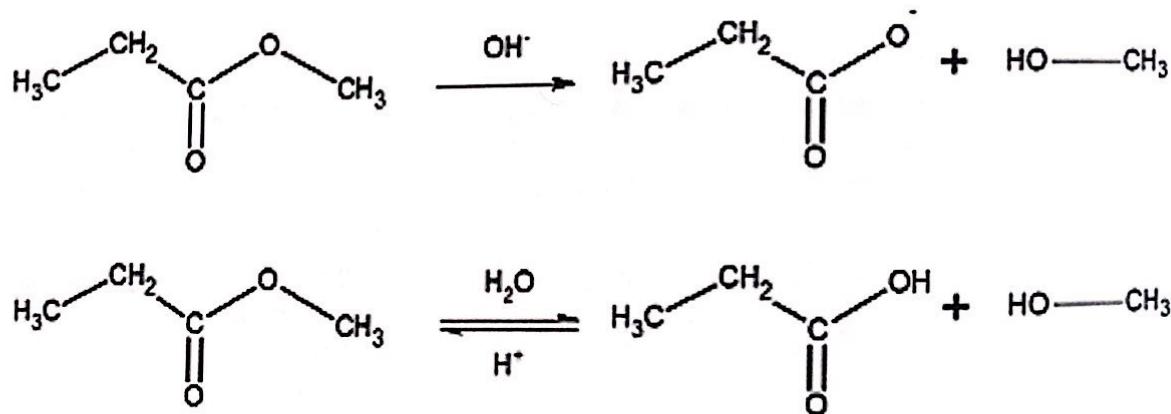
The methanol (CH_3OH) was bolded to highlight the arrangement of the atoms from each reactant in the product. Note that the ester looks like a “hybrid” between the carboxylic acid and the alkanol. This is the way you can figure out that you can form an ester by reacting a carboxylic acid and an alkanol together.

The ester is a derivative of a carboxylic acid.

You also need to know how to **hydrolyse** an ester – break an ester apart into the constituent carboxylic acid and alkanol. To do this, you could either:

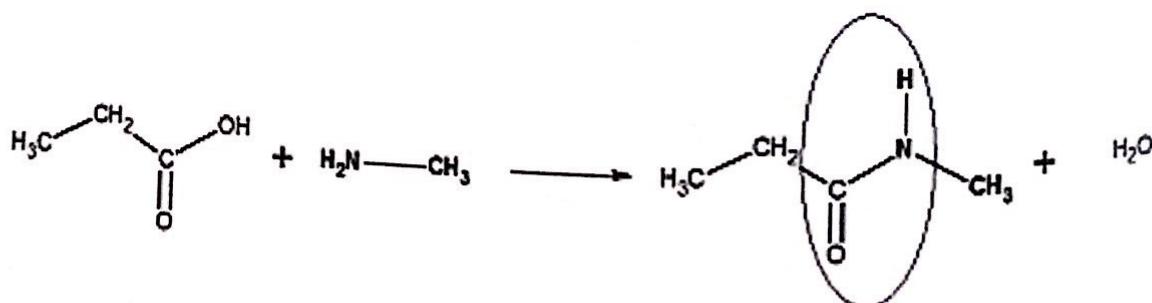
- Use OH^- ions, which is a one-way reaction, but would form the carboxylate instead of carboxylic acid.
- Use H_2O and a H^+ catalyst (dilute acid, NOT concentrated), which would form the carboxylic acid, but is a **reversible** reaction.

Below are schematics of both reactions:



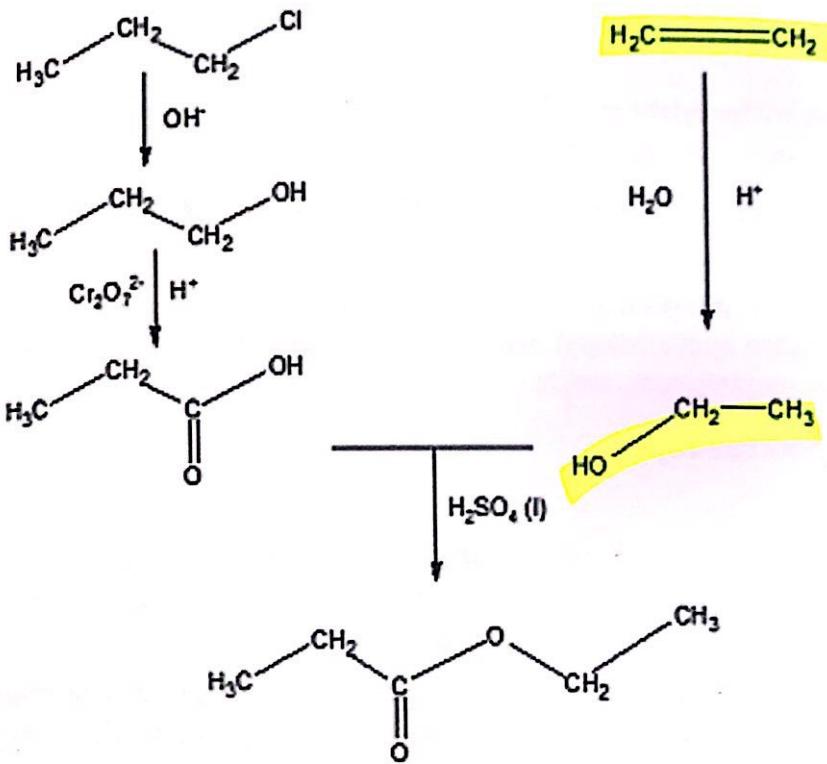
Formation of an amide (secondary amide)

You also need to be aware that carboxylic acids can react with amines to form amides. In reality, the direct reaction between a carboxylic acid and an amine to form an amide is not a reaction that tends to occur very easily; however, you are expected to know that this reaction is possible:



1.5.6 Reaction pathways, atom economy, and yield

Using what you know about reactions, we can combine multiple chemical reactions together to synthesise a particular organic compound from a set of other organic compounds. For example, suppose we were given some **1-chloropropane** and some **ethene** and you were told to synthesise **ethyl propanoate**. You might come up with a pathway looking like this:



There is a related concept called **atom economy**, which provides an indication as to the "green-ness" of the process. The atom economy is a value representing the percentage of the mass of the atoms used as reagents that is present in the final product. In other words:

$$\text{atom economy} = \frac{M(\text{useful product(s)})}{M(\text{all reagents})}$$

KEY POINT :

Importantly, **catalysts** do **NOT** count as a 'reagent' in this context, and are excluded from the equation. Another thing is that we do not care about the **stoichiometry** – in other words, in the context of organic chemistry, we don't care about the mole ratio of the reactants used. Yes, this makes the calculation of atom economy crude and perhaps almost meaningless, but we'll stick with it for now.

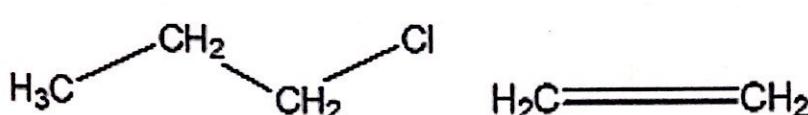
For example, let us calculate the atom economy of the synthesis of ethyl propanoate shown previously.

1. Work out the molar mass of the useful product(s).

In this synthesis, the useful product is ethyl propanoate. Its molar mass is 102.0 g mol^{-1} .

2. Work out the total molar mass of the reagents used.

What were the original reagents that were used? Let's start with the organic chemicals that we started with:



1-chloropropane ethene

$M(1\text{-chloropropane}) = 78.5 \text{ g mol}^{-1}$
 $M(\text{ethene}) = 28 \text{ g mol}^{-1}$

Now, don't forget the reagents (NOT catalysts) that were used throughout the synthesis:

- $\text{OH}^- \text{ M} = 17 \text{ g mol}^{-1}$
- $\text{Cr}_2\text{O}_7^{2-} \text{ M} = 216 \text{ g mol}^{-1}$
- $\text{H}_2\text{O} \text{ M} = 18 \text{ g mol}^{-1}$

Therefore, $\text{M}(\text{all reagents}) = 78.5 + 28 + 17 + 216 + 18 = 357.5 \text{ g mol}^{-1}$. Hence:

$$\text{atom economy} = \frac{102.0}{357.5} = 28.5\%$$

On a final note, the percentage yield in a synthesis is the mass of the product produced in reality over the maximum mass of the product (based on stoichiometric calculations).

1.6 Organic Structural Analysis: IR, NMR, and MS

You would have learnt about atomic absorption spectroscopy and UV-visible spectroscopy in the quantitative analysis of substances. Now, you will learn two more spectroscopic techniques (infra-red spectroscopy and nuclear magnetic resonance spectroscopy), as well as mass spectrometry, which are used to determine the structure of unknown organic compounds.

1.6.1 Infra-red spectroscopy

Mechanics

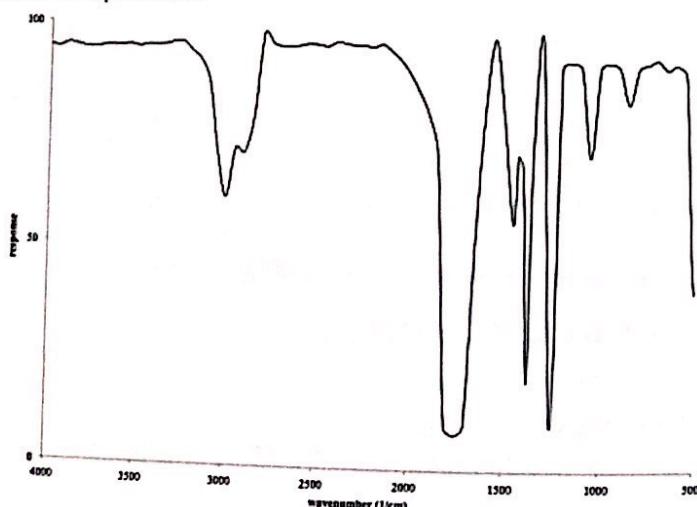
Bonds within molecules have "vibration states", just as electrons in an atom are arranged in energy levels. Just as an electron can absorb a photon to move up an energy level to a higher shell, bonds can absorb photons in the infra-red range and move up a vibration level.

The energy (and therefore the wavenumber) that the bond absorbs is dependent on **mass** of the atoms and the **bond length**. Therefore, specific bonds absorb specific wavenumbers. For instance, the bond C=O always absorbs light of a $\sim 1700 \text{ cm}^{-1}$ wavenumber.

In an infrared spectrum,

- The vertical axis is the **transmittance**, the amount of light that passes through the sample.
- The horizontal axis is the **wavenumber**, which is the reciprocal of wavelength, where the wavelength is measured in centimetres.

Now, let's have a look at an IR spectrum:



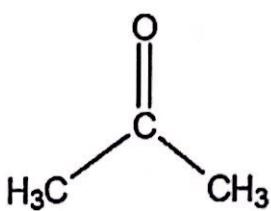
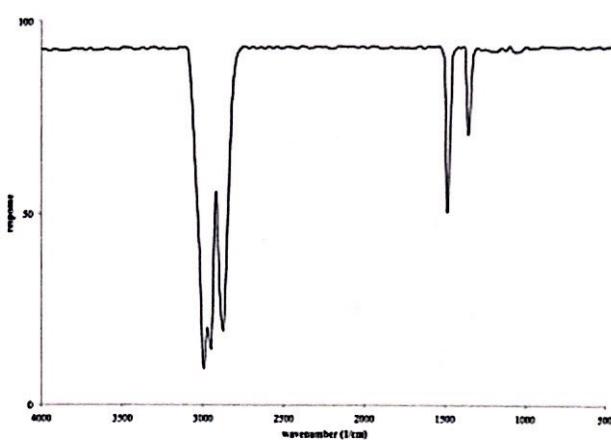
How do we analyse an IR spectrum?

Firstly, anything that is at 1500 cm^{-1} or under – ignore. Hardly any useful information here, except for identifying compounds like a fingerprint would identify a person. This is called the **fingerprint region**. The IR spectrum will tell you **which bonds** are present in the organic molecule in question. Although this will be in your Data Book, it is useful to recognise some characteristic absorption bands, which are shown in the following pages.

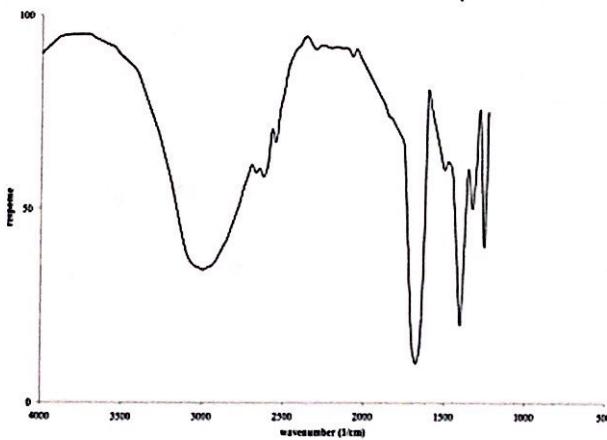
$\sim 1670\text{-}1750\text{ cm}^{-1}$

A strong absorption here indicates the presence of a C=O.

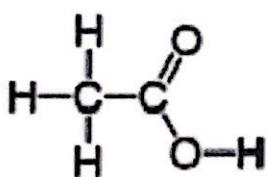
The IR spectrum shown previously is that of propanone (acetone), the structure of which is shown below:

 $\sim 2800\text{-}3000\text{ cm}^{-1}$ 

A strong absorption here shows the presence of a C-H bond, but it is generally always going to be there, although it COULD indicate an O-H (acid) bond. The O-H (acid) bond tends to be **fat** and somewhat fused with the C-H stretch. If it is due to a C-H bond, the absorption band tends to be **sharp**. Note that **practically every organic compound** will have this absorption band. Above is the IR spectrum of hexane ($\text{CH}_3(\text{CH}_2)_4\text{CH}_3$), which only contains C-C and C-H bonds. Compare this to an ethanoic acid:

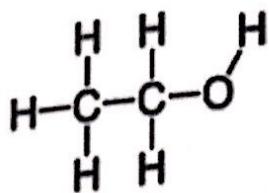


Note above how the trough at $\sim 3000\text{ cm}^{-1}$ is **fat**. Also, note the slight sharp end on the right side of the trough - that's the C-H bond absorbing energy, and you can view this property as the O-H (acid) and the C-H bond troughs as superimposed on each other. The structure of ethanoic acid is shown below:

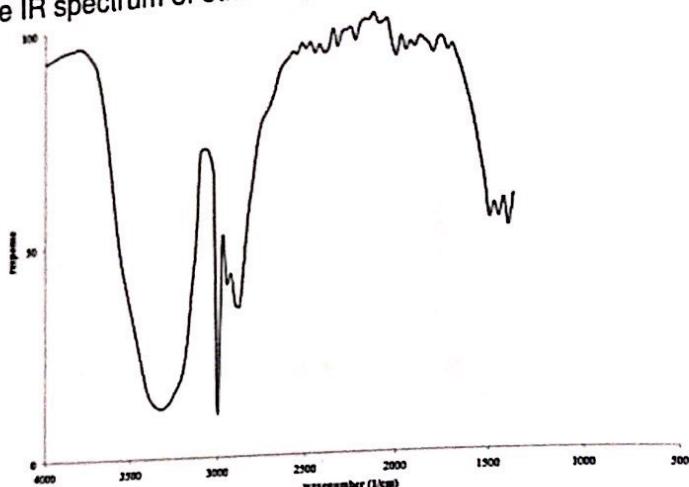


$\sim 3000\text{-}3500 \text{ cm}^{-1}$

A strong and fat band here indicates O-H (alcohol). A medium-strong and sharp, sometimes two-pronged band indicates the presence of an NH₂ group (this was asked in the 2016 exam).

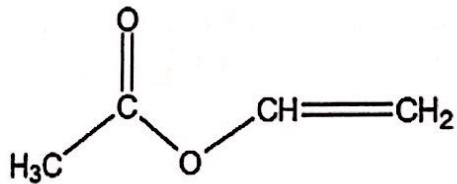


For example, consider the IR spectrum of ethanol (structure shown above):

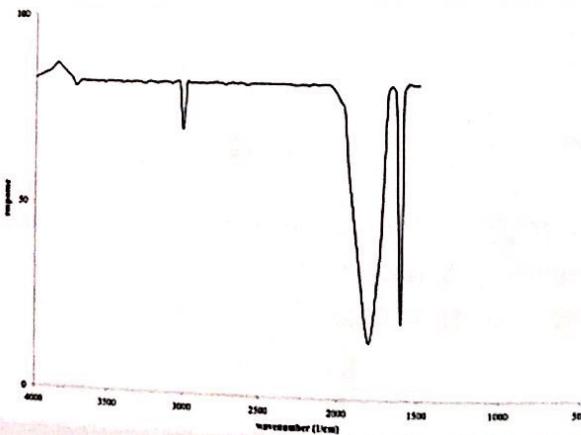


Note that there is a **strong** band at around 3200 cm^{-1} , **distinct** from the C-H stretch band at 3000 cm^{-1} . The fact that they're separate helps us differentiate between the O-H of a carboxylic acid and an alcohol.

C=C stretch



This hasn't come up on the exam, but it might. It's a **thinner, sharper** absorption band than the one corresponding to the C=O bond, and it tends to be further to the right. Let's look at the IR spectrum of vinyl acetate (structure above), which has a C=O bond on the left and a C=C bond on the right.



KEY POINT :

The locations of the absorption bands corresponding to their bonds are found in the data book. However, use this only when desperate, because it is much easier to recognise the shape of the peak to differentiate between bonds. I found that the Data Book only confused me!

1.6.2 NMR spectroscopy

Background information

NMR takes advantage of the fact that every nucleus with **an odd number of nucleons** has a magnetic moment - they respond to magnetic fields. If you put a compass needle on a table and place a magnet nearby, the needle will spin in the direction of the field. These certain nuclei do the same thing.

Two nuclei with an odd number of nucleons are the ^1H nucleus and the ^{13}C nucleus. We use these nuclei to analyse organic compounds through NMR.

Now, let's go through some basic mechanics. Note that ^1H nuclei are basically little magnets. Think of them as little 'arrows'. Stick in a strong magnetic field, and the 'arrows' will all 'point' in the one direction – with the field. With this strong field, the arrows can be in one of two 'directions': with the field, and against the field. Stick in radio waves of a specific frequency (and hence a specific energy), say 300 MHz, and shoot them at the nuclei. Radio waves can cause nuclei spin to 'flip' if they have enough energy to break the magnetic field. When spin flips, the radio waves are absorbed, and a peak is generated.

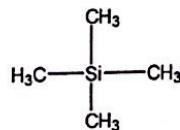
The stronger the magnetic field experienced by the nucleus, the more energy required to force nucleus to flip. Vary magnetic field, keep radio waves constant. A high magnetic field means radio waves are not enough to allow arrows to spin away from field. A low magnetic field means radio waves are enough to make arrows spin away from field.

So what causes the variation in the required magnetic field to cause a flip? Well, just because I throw say 300 units of 'magnetism' on a nucleus doesn't mean the nucleus experiences 300 units. What's around the nucleus that stops it from experiencing the full 300 units? Electrons. They shield nuclei from the magnetic field. Hence, we can generalise:

- The more 'exposed' the nucleus is, the lower the magnetic field required to force the nuclei arrows to spin towards the field.
- Nuclei that are next to more electronegative atoms are generally more 'exposed' because there is less electron density around them.

In a molecule, different nuclei are surrounded by different things – protons and electrons. How do we describe this location of protons and electrons relative to the nucleus? We call it a 'chemical environment.' So, nuclei in different chemical environments need different strength magnetic fields to force them to flip against the field. How can we tell whether two nuclei are in the same chemical environment? Protons are in the same chemical environment if and **only if** they are bonded to **exactly** the same things (not just locally, but considering the whole molecule).

Let us keep the frequency (and hence the energy) of the radio waves constant and vary the magnetic field. Remember that an 'exposed' nucleus requires a lower magnetic field to allow it to 'rebel'. But how do we measure a scale for the 'magnetic field'? We need a reference point; otherwise how can we perform measurements? For this, we use TMS - tetramethylsilane.



Why? All the protons are in the same chemical environment, bonded to same things, hence one peak. Silicon is *less* electronegative than carbon (refer to the structure above) hence the ^1H nuclei are most shielded as the electron density is closer to carbons than towards silicon. Since nuclei are most shielded, it requires a *big* magnetic field to force the nuclei to 'behave,' to turn towards field; in fact, few organic compounds have environments that need a higher magnetic field for flipping. Hence, we can designate the peak at TMS = 0.

Now, the units for the 'magnetic field' are 'chemical shift' measured in parts per million. A peak at x ppm means that the magnetic field required to cause flipping of the nucleus is x millionths less than that for the ^1H nuclei of TMS. So, a higher chemical shift means a more 'exposed' nucleus – in general.

How do we analyse proton NMR spectra?

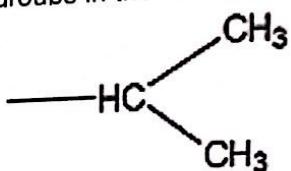
When analysing a proton (^1H) NMR spectrum, there are a number of features to look out for:

- 1. Number of peaks:** number of chemical environments. This gives you an idea into whether there is any symmetry in the molecule, say if there are more carbons than environments.
- 2. Integration pattern:** if available, look at the relative **area** under the peaks. This gives you the relative number of hydrogen atoms in each particular environment. For example, if peak A has an area of 1.2 units and peak B has an area of 0.4 units, it means that the chemical environment that gave rise to peak A has 3 times the number of protons compared to the chemical environment that gave rise to peak B.

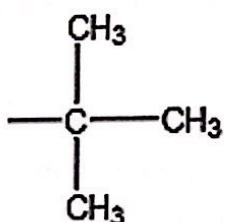
You can use this information to determine how many hydrogen atoms are in each chemical environment. For example, if you had a molecule with molecular formula $\text{C}_2\text{H}_6\text{O}$ that gave rise to three peaks of area 1.2 units, 0.8 units and 0.4 units, you can surmise that the ratio of the number of protons in each chemical environment is 3:2:1. Since there are 6 H atoms in the entire molecule, you can say that there are 3 protons in one chemical environment, 2 protons in a second chemical environment and 1 proton in a third.

Typical characteristics:

- If a peak represents **3 H atoms** in a chemical environment, it often indicates that the peak represents a **CH_3 (methyl)** group, which is found at the **end** of a molecule.
- If a peak represents **6 H atoms** in a chemical environment, it is **very likely** due to what is called an **isopropyl group** (which has 2 CH_3 groups in the same environment), shown below:



- A peak representing **9 H atoms** in a chemical environment indicates a **tert-butyl group** (3 CH_3 groups in same environment) as shown below:



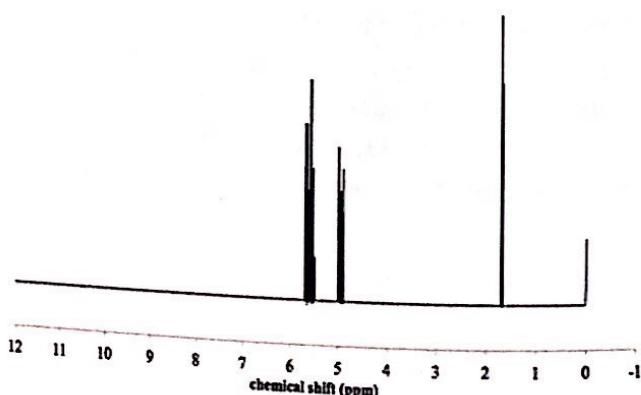
- 3. Location of peaks:** remember the principle that the more ‘exposed’ the nucleus is, the higher the chemical shift. In particular, look for and recognise these points:

~ 1.0 ppm

This generally indicates a CH_3 or $-\text{CH}_2-$ group. Check integration and splitting for confirmation.

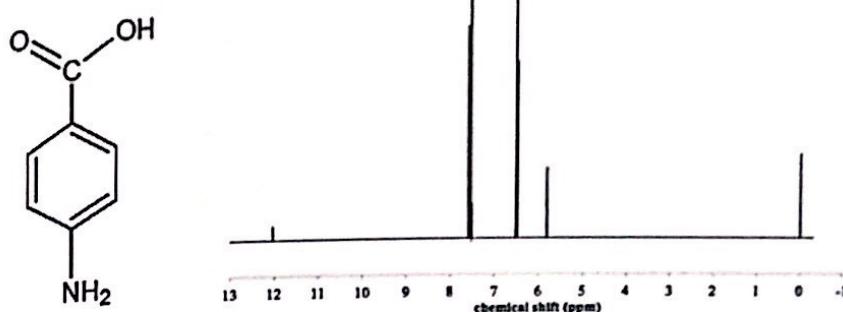
C=C

You may have a proton bonded to an alkenyl group ($\text{C}=\text{C}$) at a chemical shift of ~5-7 ppm. Consider the structure of propene ($\text{CH}_2=\text{CHCH}_3$) and its NMR spectrum (ignore the scary-looking splitting; alkenes undergo pretty nasty splitting). Note the peaks at ~5-6 ppm.



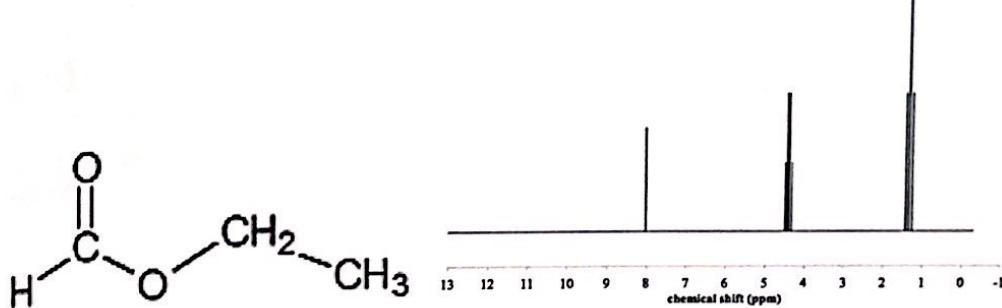
Aromatic Protons (H atoms bonded to benzene)

peaks due to these H nuclei are found at a chemical shift of around 7-8 ppm. If you see peaks at 7-8 ppm in an NMR spectrum, you can be sure that you have a benzene ring in the structure. VCAA have not sprung benzene for analysis yet though, but maybe this year...just keep that in the back of your head. Consider p-aminobenzoic acid (shown below) and its NMR spectrum:



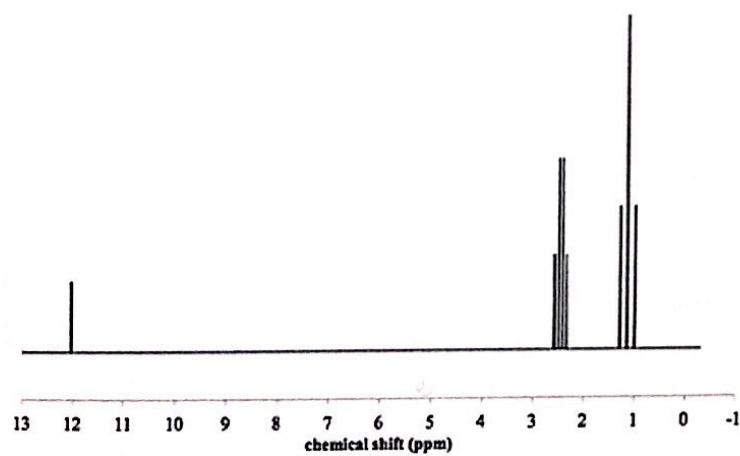
8-10 ppm

This indicates the presence of an **aldehyde** or **methanoate** (HCOOR or RCHO). Beware of the amide though (CONH_2) if nitrogen is present in the compound. Below is the structure and NMR spectrum of ethyl methanoate.



Carboxyl (-COOH) group

A peak at 11-13 ppm is unequivocally due to the H atom in the **carboxyl** (COOH) functional group. Consider the NMR spectrum of propanoic acid:



4. Splitting

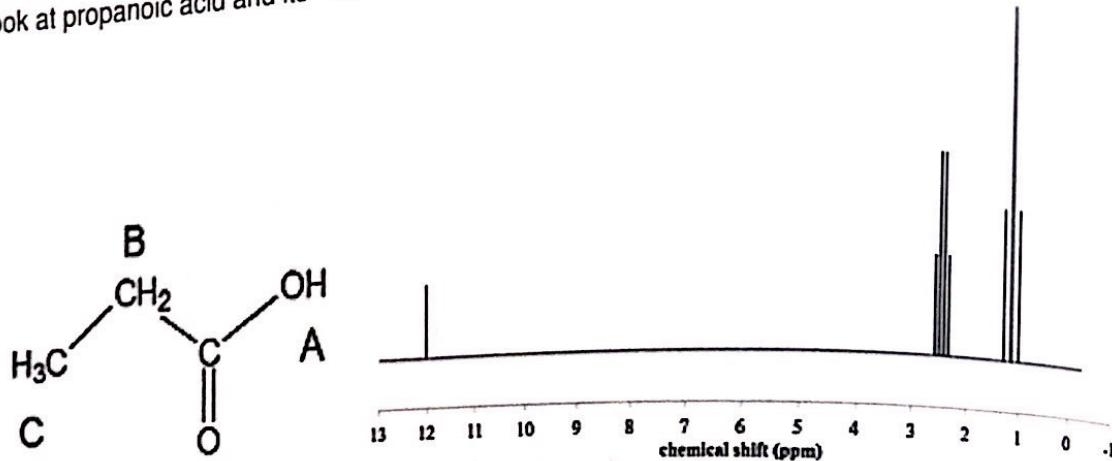
Notice how some of these peaks are 'split'? Individual peaks can be split into many different peaks. For example, in the ^1H NMR spectrum for propanoic acid, there are three peaks:

- At ~12 ppm, there is a single peak that is not split; we call this a **singlet**.
- At ~2.5 ppm, there is a peak that is split into 4; this is a **quartet**.
- At ~1.1 ppm, there is a peak that is split into 3; this is a **triplet**.

What determines whether a peak is a singlet, doublet, triplet, etc? There are a number of rules that apply. You are only expected to know one of these rules, and it is called the **$n+1$ rule**. The $n+1$ rule stipulates that if a chemical environment has n H atoms that are on the **neighbouring C atoms**, the peak that corresponds to that chemical environment is split into $n+1$. Regarding the n H atoms in the neighbouring carbons:

- These n H atoms need to be in a different environment to the original chemical environment (that gave rise to the peak)
- These n H atoms all need to be in the same chemical environment as one another.

Let's look at propanoic acid and its ^1H I



Each chemical environment is labelled with the labels **A**, **B** and **C**, and the corresponding peaks that give rise to each environment is labelled with the same letters. We will look at each environment in turn:

- **A:** this refers to the H atom as part of the COOH group. Something you **must know**: H atoms on COOH groups, OH groups and NH₂ groups will **always** give rise to a **singlet**.
- **B:** this refers to the H atoms on the CH₂ moiety. As you can see, the **neighbouring carbon** (the CH₃ carbon) has 3 H atoms. Therefore, $n = 3$. Hence, $n+1 = 4$, and this peak at B is split into a **quartet**.
- **C:** this refers to the H atoms on the CH₃ moiety. As you can see, the neighbouring carbon (the CH₂ carbon) has 2 H atoms. Therefore, $n = 2$. Hence, $n+1 = 3$, and the peak at C is split into a **triplet**.

There are characteristic splitting patterns to look out for, that would give you a strong indication as to what sort of groups are present in the molecule:

- A quartet with a 2H integration (2 hydrogens in environment) at a low ppm **and** a triplet with a 3H integration at a very low (1.0) ppm usually indicates the presence of an ethyl group (CH₃ – CH₂).
- Singlets at 1-6 ppm generally indicate –OH or –NH₂ (check integration trace to differentiate).
- Singlets at 11-13 ppm indicate carboxylic acid (or 8-10 ppm for aldehydes).

How do we analyse ^{13}C NMR spectra?

- Number of peaks:** number of chemical environments. This gives you an idea into whether there is any symmetry in the molecule, say if there are more carbons than environments.
- Location of peaks:** you do get a Data Book, but here is a little something that you can remember to make your analysis very quick:

- C-C → ~0-50 ppm
- C-O → ~50-100 ppm
- C=C → ~100-150 ppm
- C=O → ~150+ ppm

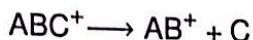
(This is a generalisation, but it's very useful!)

Luckily, ^{13}C NMR does not have splitting or integration traces.

1.6.3 Mass spectrometry

The mass spectrometer separates species based on their relative molecular mass by the following process.

The sample (say ABC) is injected, and electrons bombard the sample to knock off electrons to form ABC^+ . These ions can be unstable, and they split into 'fragment ions':



The positively charged ions are accelerated through the chamber using an electric potential. The ions are deflected by a magnetic field; smaller ions are deflected **more** than larger ions. The detector detects ions with particular m/z values (mass/charge, and generally charge ($z = 1$) – by adjusting its position to only detect ions that go through one particular path. The ion with the highest abundance produces a peak called the base peak and is **assigned** a relative value of 100. All other abundances are measured relative to that peak. Information you can get out of a mass spectrum:

- You can effectively only get the molar mass of the compound by looking at the peak with the largest m/z; this represents the molecular ion, the ion that has not been fragmented
- You can get an idea on how many atoms are in the compound based on the number of peaks; the more atoms there are, the more fragments, the more peaks.

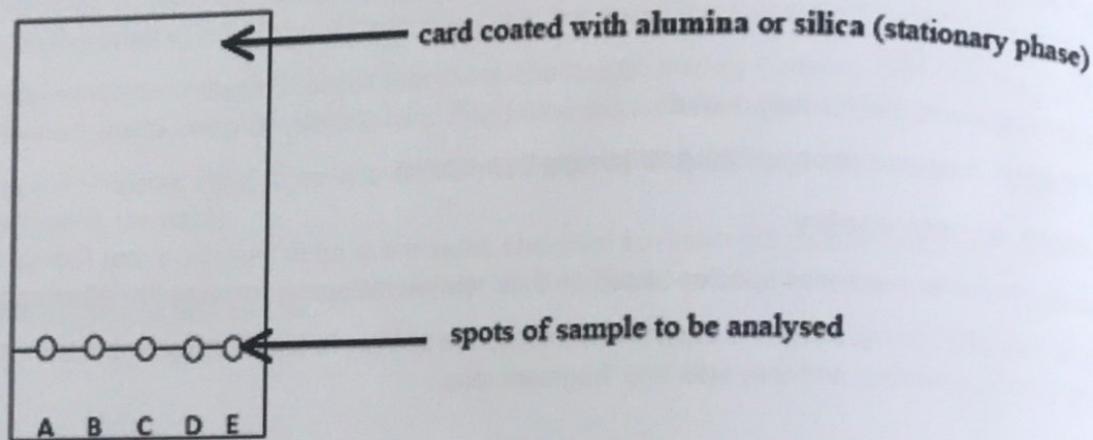
1.7 Organic Chemical Analysis: HPLC, Volumetric Analysis

This topic is pretty much an exact repeat of the topics covered in Unit 2. The only difference is that the HPLC and volumetric analysis will be specifically for organic compounds – you will only be analysing organic compounds. Therefore, these notes will be very similar to the Units 1&2 notes – the material is exactly the same; the only difference is that the problems will be about organic compounds.

1.7.1 Thin layer chromatography

In the study design, it is stipulated that you need only know about high performance liquid chromatography (HPLC). However, to understand HPLC, it is useful to learn about the simpler types of chromatography. You do NOT need to know about TLC for the exam.

Thin-layer chromatography is primarily a qualitative technique; using this technique we can identify compounds, but we cannot accurately determine their amount. The setup is as follows:



To prepare a TLC, we use a capillary tube to 'spot' tiny samples of each compound to be analysed on a pencilled line on the card. The card is then placed in a cylindrical container containing eluent – the solvent that acts as the mobile phase. The eluent starts to move up the plate, carrying the sample with it. **The spotted samples on the pencilled lines MUST be above the line of eluent initially, otherwise the samples will dissolve into the eluent instead of moving up the plate.**

After the eluent has moved up the plate a sufficient distance, the plate is removed from solution, a second pencilled line drawn where the eluent line (the solvent front) was, and the spots on the TLC plate observed under visible or UV light.

Now, how do we differentiate between compounds using TLC? We differentiate them by how fast they travel up the plate. Remember, the greater the affinity of the compound for the mobile phase and the less the adsorption of the compound to the stationary phase, the faster the compound will travel through the plate.

The measurement for how fast the compound travels through the column is the retardation factor (R_f) value. It is calculated as follows:

$$R_f = \frac{\text{distance travelled by component}}{\text{distance travelled by solvent}}$$

Note that the R_f value depends on the compound, the eluent, the stationary phase and temperature.

How do we use this R_f value? Well, suppose that we perform a TLC on an unknown compound, and after the development of the chromatogram we have the solvent front travelling a distance of 5.0 cm, and the substance travelling 3.0 cm. It is found that, in previous experiments, paracetamol has an R_f value the same as that calculated in this experiment. This means that it is **possible** that this compound is paracetamol. **Why cannot we definitively say that this compound is paracetamol?**

Often, the stationary phase is a polar substance such as silica or alumina and the mobile phase (eluent) is a non-polar organic solvent such as ethyl ethanoate. Now, remember that like dissolves like. This means that polar substances tend to adsorb onto the polar stationary phase to a greater degree and non-polar substances tend to dissolve into the mobile phase better. **Therefore, using these general principles, which substance will travel further up the plate – the polar or non-polar substances?**

1.7.2 Column chromatographic methods

Before we embark on HPLC, let us explore the simple setup of column chromatography:

This column is like a burette without markings. The sample is pipetted onto the packed silica column, eluent added on top of the sample, and the tap opened. The eluent is allowed to go through the column and drip out of the burette, carrying the sample with it. Just like in TLC, the sample will adsorb onto and desorb from the silica. Again, the stronger the intermolecular forces between the silica and the sample (and the weaker the intermolecular bonds between the eluent and the sample), the slower the sample goes through the column.

In TLC, we measured how fast the sample goes up the plate by measuring the retardation factor, a ratio of distances travelled by the eluent and the sample. In column chromatographic methods though, we measure the time taken for the sample to travel through the column. This is called the retention time.

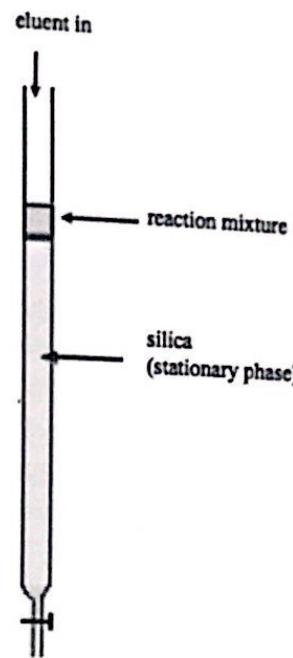
So if the intermolecular bonds between the sample and the stationary phase are stronger, is the retention time higher or lower?

The difference between this and TLC is that this method allows for quantitative analysis of the samples. We can actually collect the fractions of sample as it comes out of the column and perform analyses that will test for their amount.

Here, it would be better to use finer pieces of silica than coarse because there is a higher surface area of silica with which the sample can potentially adsorb. This means that the more adsorptive components of the sample will separate better from the less adsorptive; using finer pieces of silica has the same effect as using a longer column.

There's a downside to this though; imagine trying to pass water through a column packed with big gravel pieces, then passing water through a column packed with sand. The water will pass much more slowly through the sand, wouldn't it? Likewise, using finer pieces of silica takes longer than alternate methods.

However, there is a way to get around this. How about using a hand-pump to pump the eluent under pressure through the column? This will make the eluent pass through the column faster, saving time. Even then though, it would make sense if we could use extremely fine pieces of silica to increase separation – but hand pumps would not be able to pressurise the eluent to 14000 kPa (about 140 atmospheres of pressure). How about if we use a really powerful machine to pump the eluent at 14,000 kPa through a really robust column able to withstand such pressures – and use an electronic detector to measure how much of each compound in the sample is passed through the column? Well, we are doing this already: it's called high performance liquid chromatography (HPLC).

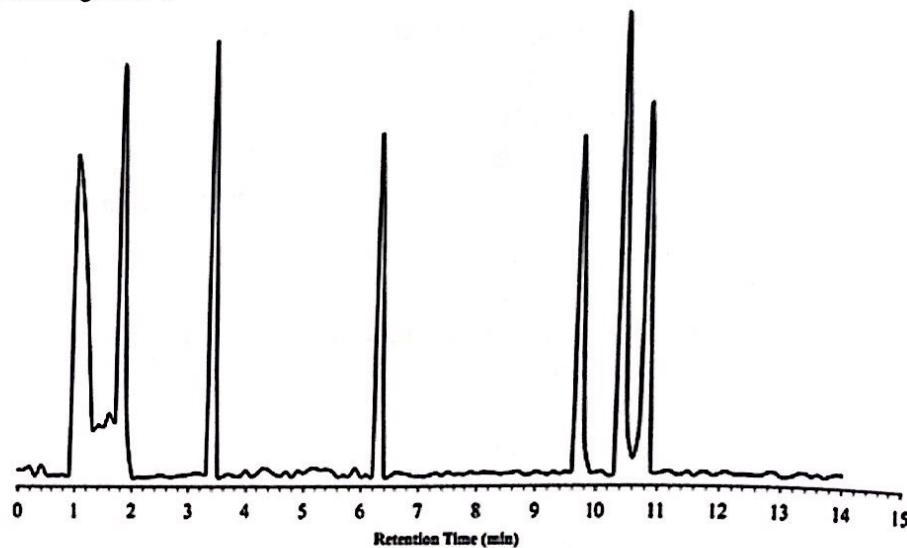


1.7.3 High performance liquid chromatography

High performance liquid chromatography is effectively identical to the basic form of column chromatography except that it is mechanised. The stationary phase is generally alumina or silica, and the mobile phase is generally a nonpolar organic solvent. As a method of column chromatography, the R_f value is used to identify compounds. How to interpret HPLC chromatograms will be discussed later.

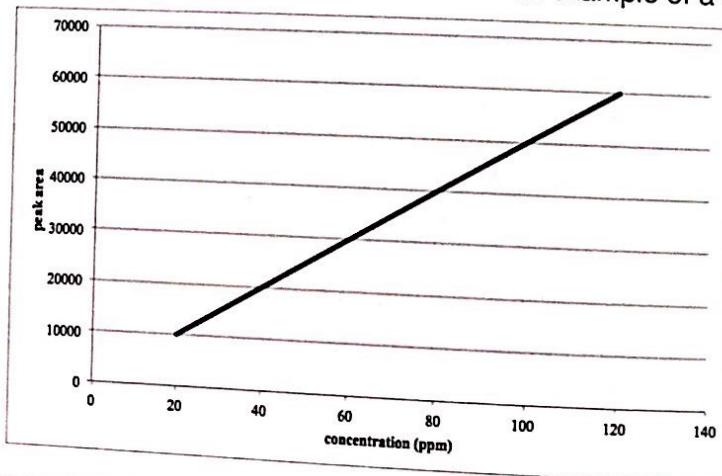
Analysis of chromatograms

Consider the following example of a chromatogram:



Area of Study 1 – Explaining and categorising carbon compounds

Remember that the retention time identifies the compound; therefore, the location of the peak identifies the compound. The area under the peak that the compound gives rise to gives information about the amount of that compound. It is found that, at low amounts, the area under the peak is proportional to the amount of compound. However, how do we know what amount corresponds to what area? If I get an area of 12,000 square units, how do I know whether that corresponds to 1 mol, or 2 mol, or 0.1 mol? This is where calibration curves come in. We can plot a calibration curve by taking samples of the compound of known amount and determining the area under the peak at its retention time. With this calibration curve, we now know a relationship between the area under the peak and the amount of compound – and therefore when we measure the area under the peak of an unknown amount of compound to be 12,000 square units, we can tell what amount of compound that corresponds to. Below is an example of a calibration curve.



KEY POINT :

Calibration graphs cannot be extrapolated outside its range accurately; if the area under the peak of an unknown amount is outside the range of the calibration curve, it is not valid to use that curve to determine the amount of compound in that sample.

1.7.4 Volumetric analysis

The basis of volumetric analysis is the titration, where we want to determine amounts or concentrations of stuff by using known amounts of substance. However, how do we make up this known amount of substance – a standard solution? A **standard solution** is one in which the concentration is **accurately known**. We need a primary standard, something that we can accurately weigh, dissolve in a known volume of water, and therefore accurately determine the concentration of this substance in the solution. The characteristics of a primary standard are that you **must have a known formula**, it **must have a relatively high molar mass**, it **must not react with the atmosphere**, and it **should be soluble in water**. Examples of good primary standards are sodium carbonate and oxalic acid. Let's visit the different pieces of glassware that you will encounter in volumetric analysis:

- **Volumetric flask:** this is used to measure **exact** volumes of solution. This is an excellent piece of glassware for making standard solutions and for performing dilutions.
- **Pipette:** this is used to transfer an **accurate** volume of solution from one vessel to another vessel.
- **Conical flask:** this is used as a vessel to perform a reaction. It is shaped as such as to make it easy to mix the contents. It is **NOT** used to measure out exact volumes.
- **Burette:** this is used to titrate one chemical against another, to accurately determine what volume of one solution is required to completely react with another.

In volumetric analysis, it is essential to understand the **acid base titration** and the **redox titration**.

Let's go through an example of an acid base titration.

Suppose you want to **standardise** (determine the accurate concentration) a solution of HCl with an approximate concentration of 0.1 M. Now, to be able to standardise this HCl, you need a **standard solution** in the first place. Let's make up a standard solution of sodium carbonate.

We weigh the sodium carbonate accurately, and **quantitatively** transfer into a 500.0 mL volumetric flask, which we add water to, up to the mark. This is called 'making it up to the mark'. We now have **exactly 500.0 mL** of a standard solution of sodium carbonate. Knowing the volume of solution and the accurate mass of the sodium carbonate, we can accurately determine its concentration.

With this standard solution, we can deliver a known volume (say 20.00 mL) of sodium carbonate into a conical flask for the titration. To do this, we use a 20.00 mL pipette - remember, a pipette is used to transfer an accurate volume of solution from one vessel to another vessel. The actual solution that is being extracted from a vessel via a pipette is known as an **aliquot**.

The HCl solution is loaded onto the burette (preferably via a funnel so that it doesn't spill everywhere). This solution in the burette is known as the **titrant**. Now, before we do all this, we need to have cleaned our glassware beforehand. But what do we wash our glassware with?

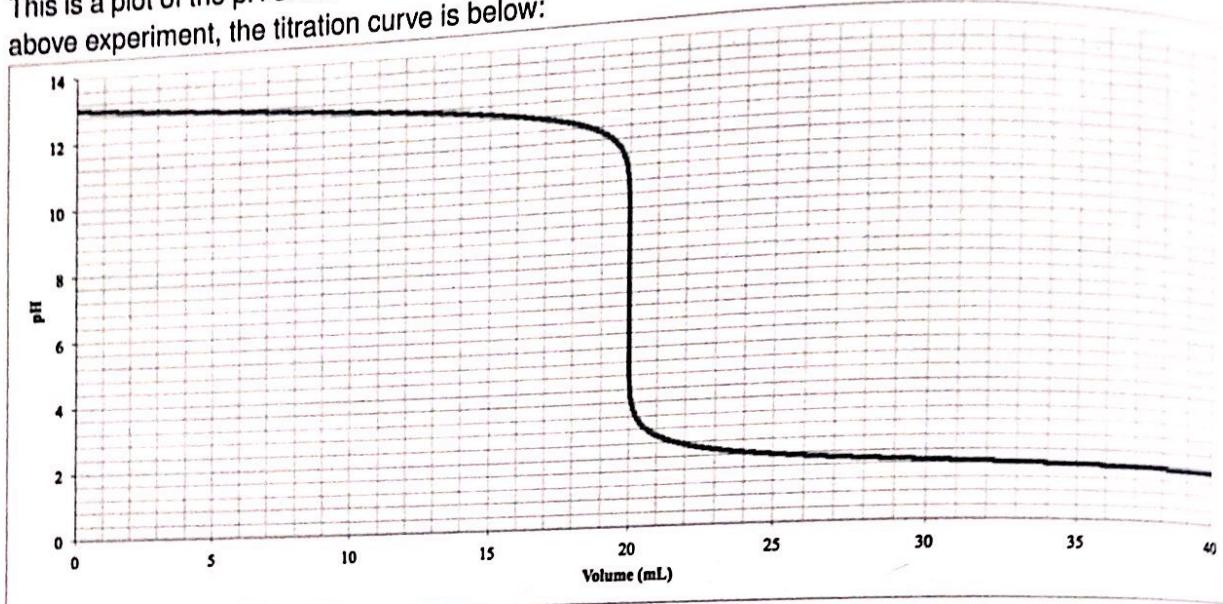
- **Burette:** you wash this with a little bit of the solution you are about to load into it. You do not wash with water, because if you do, there will be a few drops of water in the burette when you load the solution in. When this happens, the solution is diluted, and you will no longer get accurate results. Remember, **every drop counts**.
- **Pipette:** you wash this with a little bit of the solution that you are going to deliver as the aliquot. If you wash with water, the residual water will dilute that solution, whilst keeping the volume the same (since you suck up exactly, say, 20.00 mL of liquid). This means that you have extracted less than the 20.00 mL of solution that you thought you did, since some of that would be residual water. This will lead to inaccurate results.
- **Conical flask:** you wash this with water, **NOT** any solution. This is because if you wash with, say, the aliquot that you extracted, there will be residual drops of solution in the conical flask. When this happens, when you deliver the aliquot into the conical flask, you will have more solution than you think you have in the conical flask. This will lead to inaccurate results.

Now that you have set up the equipment, it is time to do the titration. But how in the world would you know when you have reacted exactly all of the sodium carbonate in the conical flask without adding excess HCl? After all, all the reactants and products are clear. This is where you need an **indicator**.

An indicator is a chemical that shows when the equivalence point has been reached by changing colour. This is where, during the titration as you are slowly adding the HCl into the conical flask to react with the sodium carbonate, you reach a point that all of the sodium carbonate has been reacted and there is no HCl in excess; this is the equivalence point. This is distinct from the endpoint, which is defined as the point in the titration whereby the indicator changes colour. What you need to do is select an indicator whose endpoint coincides with the equivalence point of the titration. In order to do this, we need to have an understanding of titration curves.

1.7.5 Titration curves

This is a plot of the pH of the solution against volume of titrant (HCl) delivered into the conical flask. For the above experiment, the titration curve is below:

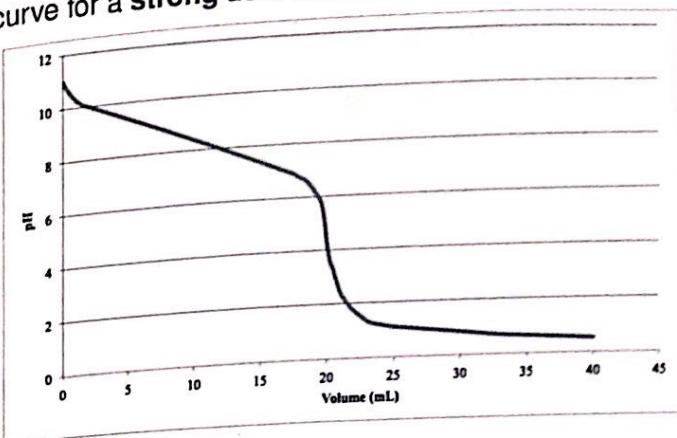


You can see that the pH of the solution is 13 (consistent with a 0.1 M solution of NaOH in the conical flask) before the titration. The pH slowly moves down and suddenly shoots from about 10 to 4 in a matter of a very small volume. For your interest, in the generation of this graph, the data points I have that are around the equivalence point are:

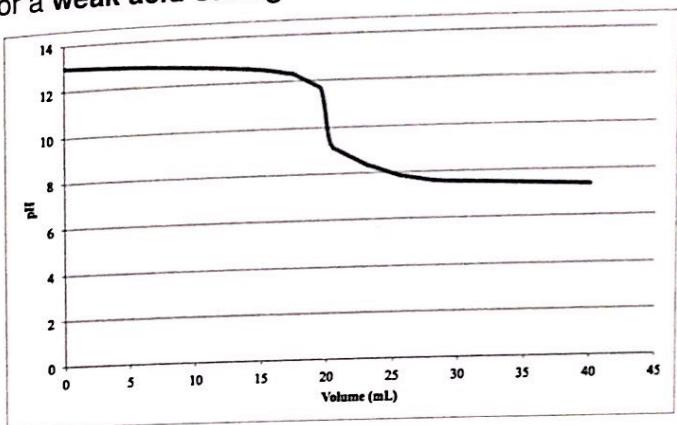
Volume (mL)	pH
19.96	10.00
19.97	9.88
19.98	9.70
19.99	9.40
20.00	7.00
20.01	4.60
20.02	4.30
20.03	4.13
20.04	4.00

The idea here is to choose an indicator that would change colour at ~ pH 4 - 10. If you have a look at your Data Book, there is a list of indicators along with the colour changes and the pH range at which the colour changes occur. You will see that you could use any indicator really (except perhaps thymol blue). If you chose thymol blue, the colour change (the endpoint) would occur well after the equivalence point. The above titration curve is typical for a **strong acid-strong base titration**. Let's have a look at the titration curves for a **strong acid-weak base** and a **weak acid-strong base titration**.

Below is a rough titration curve for a strong acid-weak base titration:



Note here that the equivalence point is **below** a pH of 7. I will explain why this is the case soon.
 Below is a titration curve for a **weak acid-strong base titration**:



Note here that the equivalence point is **above** a pH of 7. So why do different types of titrations have different pHs at equivalence point? Below are a couple of concepts that you should be able to remember:

- A strong acid has a conjugate base that is so weak that it basically accepts no protons.
- A weak acid has a conjugate base that is also a weak base.
- An acid so weak that it barely donates any protons (e.g. methane - CH_4) has a conjugate base that is strong.

Keeping this in mind, we get the following facts:

- Strong acid + strong base → extremely weak conjugate base + extremely weak conjugate acid. Here, both products do not accept or donate protons, so the equivalence point pH would be 7.
- Strong acid + weak base → extremely weak conjugate base + weak conjugate acid. We have a weak acid in solution at equivalence point, so the pH here will be < 7 .
- Strong base + weak acid → extremely weak conjugate acid + weak conjugate base. We have a weak base in solution at equivalence point, so the pH here will be > 7 .

Since different titrations have different pHs at equivalence point, we need to select the appropriate indicator for each titration. For example, methyl red, which changes colour at a pH < 7 , would be inappropriate for a titration between a strong base and a weak acid where the pH at equivalence point is > 7 .

1.7.6 Redox titrations

Redox titrations are very similar to acid-base titrations, except you are doing a redox reaction. Usually, **you do not need an indicator**, since in many cases the reactants and products exhibit different colours. For example, permanganate (MnO_4^-) ions are purple, whereas Mn^{2+} ions are clear.

Area of Study 2

What is the chemistry of food?

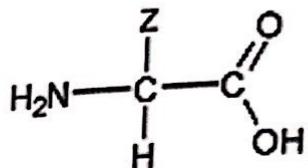
2.1 Food Molecules

In this topic, you will learn about the different macronutrients (proteins, carbohydrates and fats/oils), as well as a little bit about micronutrients (specifically vitamins).

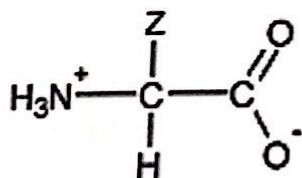
2.1.1 Proteins

Before we look at proteins, we should examine its monomer, the amino acid.

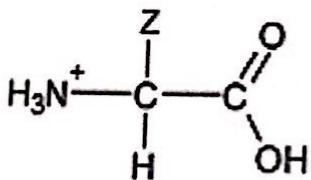
The general structure is shown below:



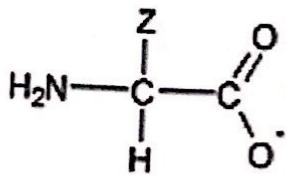
Each amino acid has a different Z group. All amino acids that comprise proteins in the human body are **2-amino acids** or α -amino acids as the amino group is connected to carbon 2. A carbon adjacent to a C=O group is known as an α -carbon. So, proteins have an amino group and a carboxyl group. The amino group is a base and the carboxyl group is acidic. Stick an amino acid into water, and you'll most likely get this species being dominant (as shown below):



These species are known as **zwitterions**. Zwitterions have a positive and negative charge at different parts of the molecule, but the **net charge is zero**. Now, add some HCl (aq) into this amino acid solution. We are now effectively forcing H⁺ onto the –COO[–] groups, and we get the species below (**at low pH**):



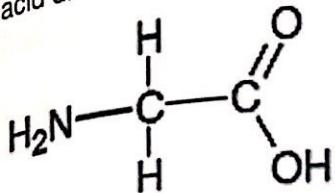
Now, add an excess of NaOH (aq) into the amino acid solution. The OH[–] ion is a very strong base; it likes ripping off protons. So it rips protons off the –NH₃⁺ group and the –COOH group, and you get the species below (**at high pH**):



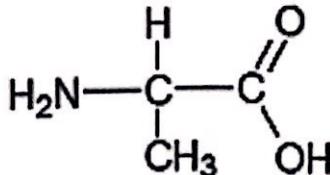
Also, just a note: the Z group could itself be acidic or basic; and this could affect its acid-base properties. However, the principles don't change.

Essential and nonessential amino acids

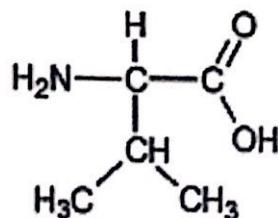
Every amino acid differs by the Z group they possess. For example:



glycine



alanine



valine

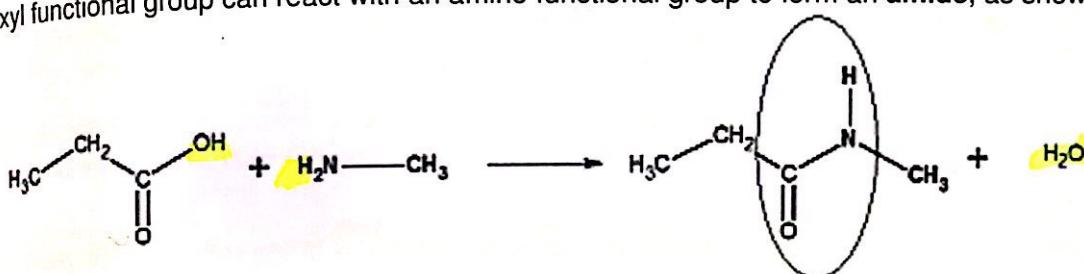
Some of the Z groups are nonpolar (e.g. the ones shown above). Other types of Z groups include:

- Polar: e.g. serine (-CH₂OH)
- Basic (and polar): e.g. lysine (-CH₂CH₂CH₂CH₂NH₂)
- Acidic (and polar): e.g. glutamic acid (-CH₂CH₂COOH)

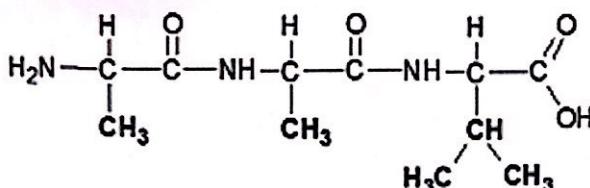
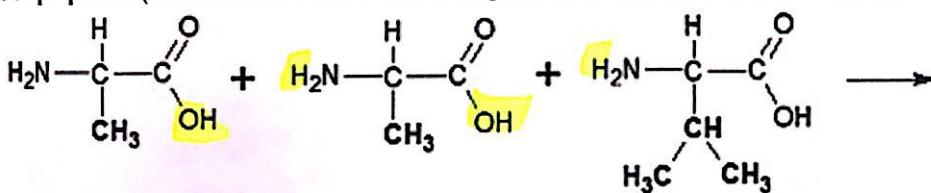
There are 20 amino acids (2-amino acids) that exist in our body, that are used as building blocks for our protein molecules that we synthesise. Some of these amino acids can be synthesised from other amino acids as well as other non-protein molecules in our diet such as fats and carbohydrates. These are called **non-essential amino acids**, of which there are 11. Other amino acids cannot be synthesised in our body – our bodies do not possess the enzymes to allow these synthesis reactions to occur. Hence, these amino acids have to be obtained in our diet, and are called **essential amino acids**, of which there are 9.

Amino acids to proteins

A carboxyl functional group can react with an amino functional group to form an **amide**, as shown below.



The carboxyl functional group of one amino acid can react with the amino functional group of another to form an amide linkage. Does this scenario look familiar? Polymerisation can occur here too! Here is another example of how biochemistry is just chemistry. This is a **condensation polymerisation reaction**. Let's see how a **tripeptide** (three amino acids linked together, in this case alanine-alanine-valine) is formed:



The tripeptide can also be written as H₂N-ala-ala-val-COOH. As you can see, individual amino acids can also polymerise to form polypeptides. Large polypeptides are called proteins. **Peptide linkages** occur when the amide linkage is between two amino acids.

KEY POINT :

When you want to refer to individual amino acid moieties in a larger dipeptide, tripeptide or polypeptide, you should refer to them as **amino acid residues**.

Protein levels of structure

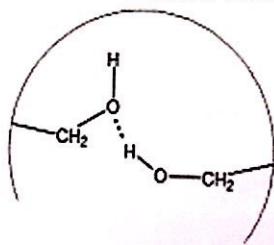
The structure of a protein molecule is a little more complex than just a simple linear chain of amino acids bonded together. This is because the protein molecule tends to coil and fold onto itself. An example of a protein molecule is shown here:



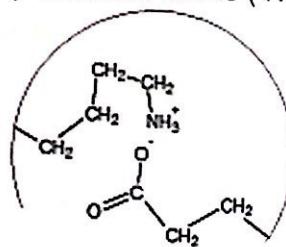
You can see that the molecule has an overall structure which, quite frankly, looks a bit like a blob. However, you can see little "micro-structures" within this big blobby structure, such as that small coil (represented by the thick sections of molecule), or even the chain of amino acids itself. Therefore, we say that proteins have different **levels of structure**. Many proteins have three levels of structure, with some proteins having four levels. We will go through these types of structure.

- Primary structure:** this is the **specific sequence of amino acids** in the polypeptide chain, held together by covalent bonds (peptide linkages). You can visualise the primary structure in the protein shown above by tracing from one end of the molecule to the other end.
- Secondary structure:** this is the **localised coiling and folding of segments of the polypeptide chain**. This is held together by **hydrogen bonding** between nearby peptide linkages, specifically the C=O moiety of one peptide linkage and the N-H moiety of the other peptide linkage. This localised coiling and folding can result in the formation of a few specific arrangements:
 - **Alpha-helices** (e.g. the thick lines in the image above)
 - **Beta-pleated sheets**
 - **Random coils**
- Tertiary structure:** this is the **overall 3-dimensional structure** of the entire protein molecule. The interactions that give rise to this structure are those between the **Z groups** in the protein molecule. So what sort of interactions can arise?

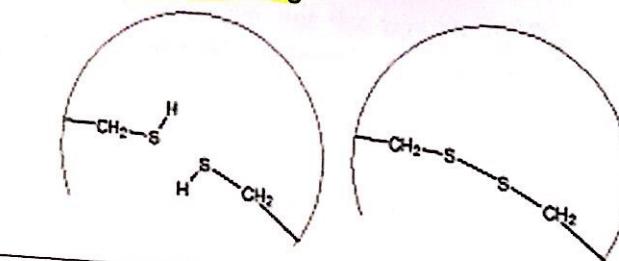
Hydrogen bonds: below is an example of hydrogen bonds between serine residues.



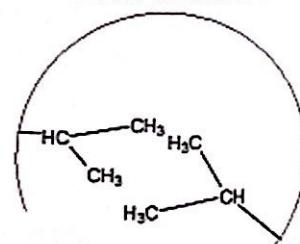
Ionic bonds: occur between deprotonated carboxyl (-COO^-) groups and protonated amino (-NH_3^+) groups.



Covalent bonds: occur specifically between **cysteine residues**, whereby they are oxidised to form a **disulphide linkage**.



Dispersion forces: occur between any two residues, but are the prominent interaction between non-polar residues.



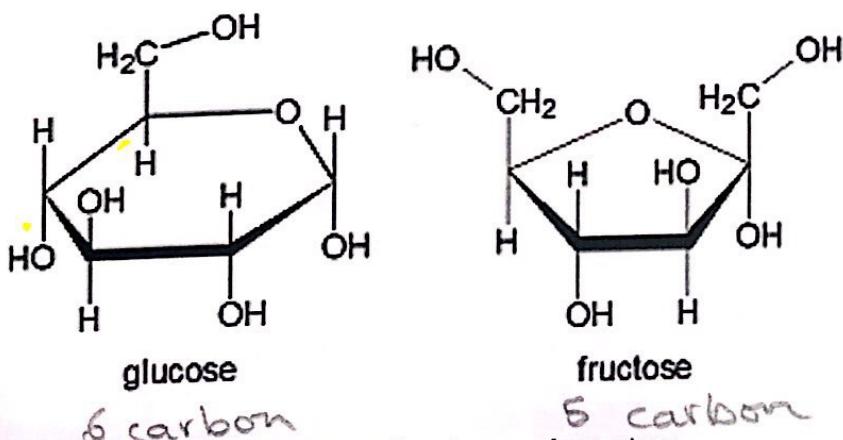
Quaternary structure: some proteins are made out of **more than one polypeptide chain**. In these sorts of proteins, the 3-D shape formed by **each** of these chains is referred to as the **tertiary structure** of the protein. The way each of these chains interact with one another to form a protein molecule (made out of multiple polypeptide chains) is referred to as the **quaternary structure**. For example, **haemoglobin** is made out of four polypeptide chains and therefore has a quaternary structure.



2.1.2 Carbohydrates

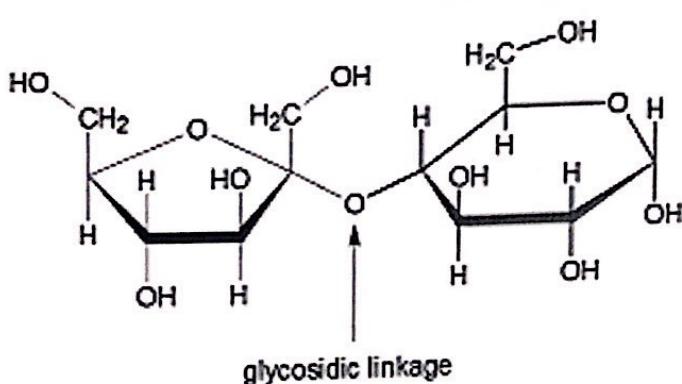
Carbohydrates are biomolecules that are composed of one or more rings of carbon and oxygen atoms, with an approximate (sometimes exact) empirical formula of CH_2O . There are three types of carbohydrates that you should be aware of – **monosaccharides**, **disaccharides** and **polysaccharides**.

Monosaccharides are composed of a single ring; there are a number of monosaccharides that exist, including **glucose** and **fructose** (whose structures you need to be familiar with):

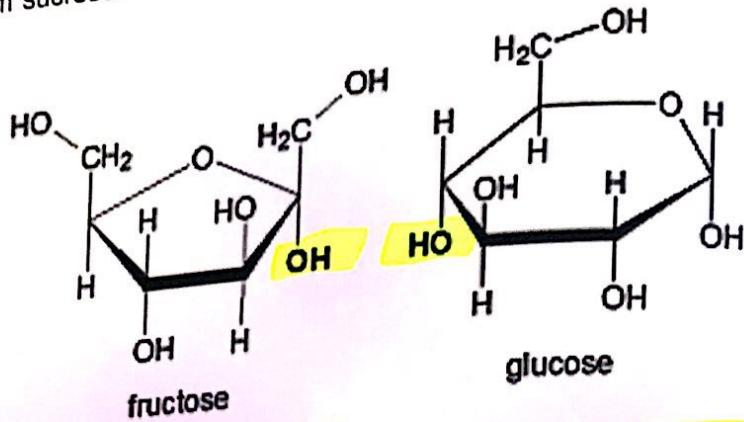


Note that this is a shorthand form – each vertex refers to a **carbon atom**.

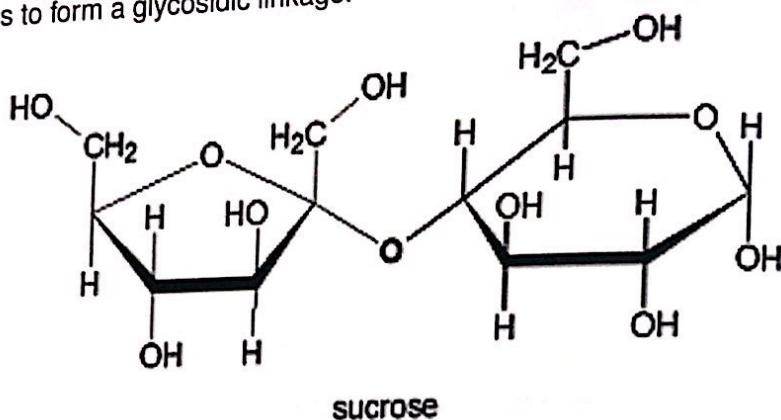
Disaccharides are composed of **TWO** rings that are bonded to one another via a **glycosidic linkage**. Of the disaccharides, you should be familiar with **sucrose**, which is a dimer of glucose and fructose:



Let's see how we form sucrose – let's have a look at fructose and glucose, this time, with the important atoms in bold:



The OH groups involved in the reaction are bolded. These two sugars will undergo a condensation reaction, whereby a H₂O molecule is produced in addition to the disaccharide. Therefore, of the 2 O and 2H atoms involved, 2 H atoms and an O atom combine to form water, and the other O atom is used to bridge the two carbon atoms to form a glycosidic linkage.



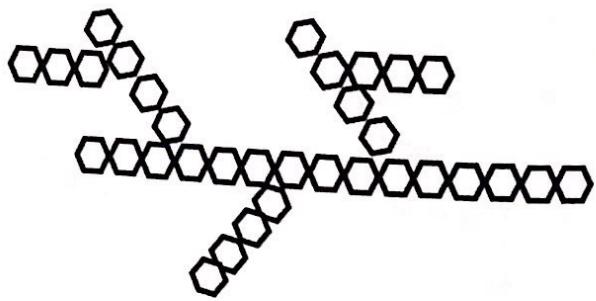
Polysaccharides

Polysaccharides (complex carbohydrates) are polymers of monosaccharides, composed of many monosaccharides bonded together via glycosidic linkages. There are three types of polysaccharides that you need to know about: **starch**, **glycogen**, and **cellulose**.

- **Starch:** this is a polysaccharide that is used as **energy storage in plants**. It is composed of a mixture of **two polysaccharides** (known as **amylose** and **amylopectin**). The structure of amylose is shown below:

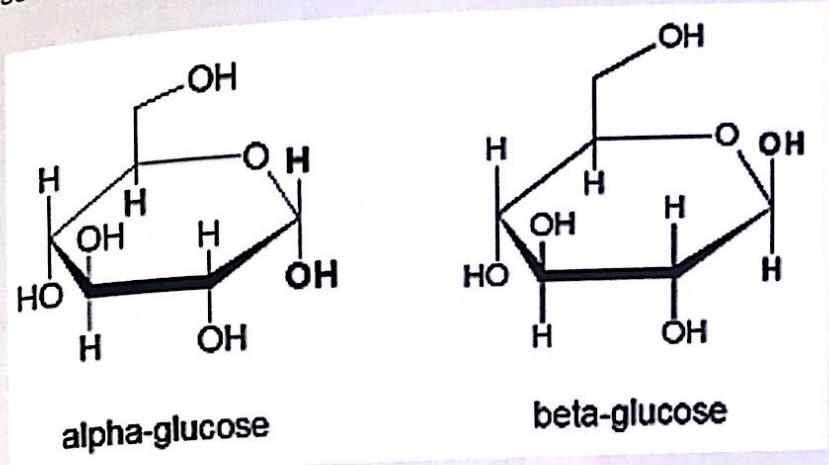


This is a sketch of amylose more than anything; note that each ring is connected via a glycosidic linkage. Amylose is **unbranched**, and this chain of glucose molecules forms a **helix** (not unlike the alpha-helix you see in proteins). Amylopectin is a **branched** polymer of glucose. The way branching occurs is if a glycosidic bond is formed via a different OH group than the ones usually used to form glycosidic linkages. Below is the structure of **amylopectin**:



- Glycogen:** this is another polysaccharide of glucose and is used as the **main energy storage for humans**. Whenever there is excess glucose in the body, it is transported into liver and muscle tissue and polymerised to form glycogen. This is key knowledge in the study design. The structure of glycogen is similar to that of amylopectin, except it is even more branched.
- Cellulose:** this is another polymer of glucose and is used for **structural support of plant cell walls**. It is made out of a particular type of glucose called **beta-glucose** (explained below):

KEY POINT:
Anomers of Glucose: there are two forms of glucose that exist in the human body – alpha-glucose and beta-glucose. These two forms of glucose can interconvert spontaneously (in a process called mutarotation). These two forms are called anomers, and are shown below:



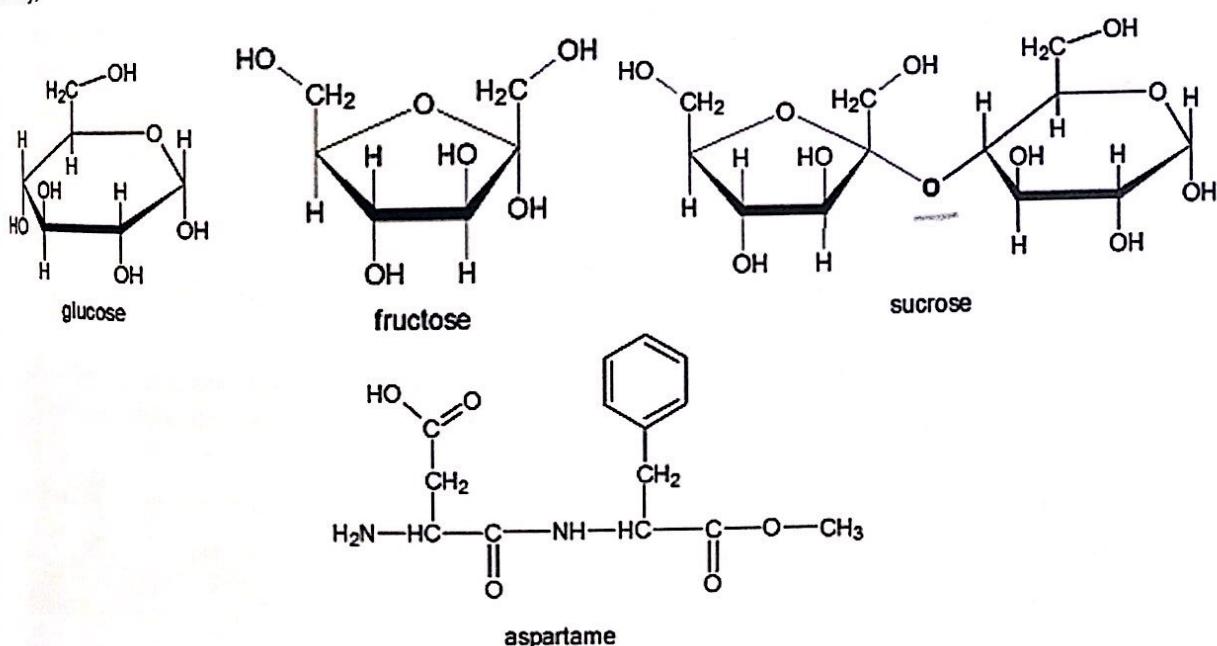
Starch and glycogen are polymers of **alpha-glucose** whereas cellulose is a polymer of **beta-glucose**.

Like amylose, cellulose is an **unbranched** polymer of glucose. The difference in position of the OH group that is part of the glycosidic linkage changes the geometrical arrangement of cellulose different from that of amylose. While amylose adopts a helical structure, cellulose forms a straight-chain structure.

Comparison of sweeteners

The study design stipulates that we need to compare the different types of sweeteners that we use in our food – namely **glucose**, **fructose**, **sucrose** and an artificial sweetener called **aspartame**.

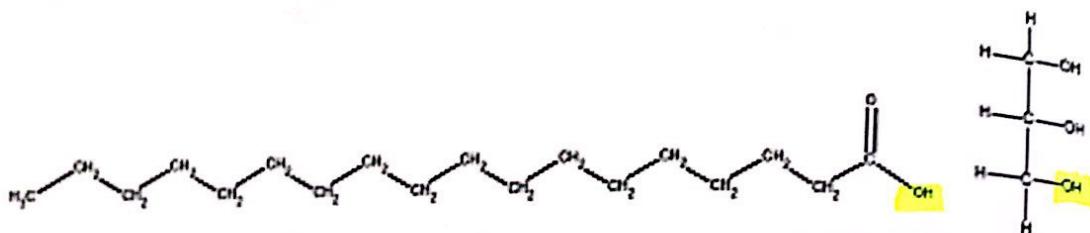
Firstly, let us have a look at the structure of these four molecules:



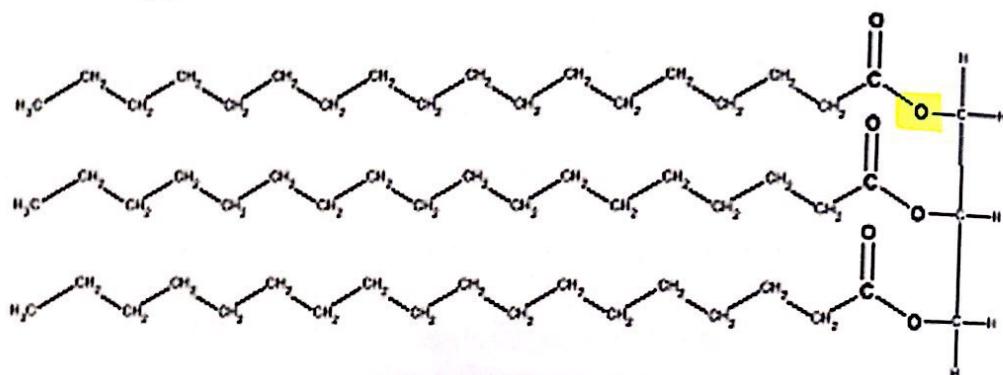
Glucose and fructose are naturally found in foods, with fructose being found in high quantities in some fruits. Sucrose is the table sugar we use in our tea and coffee. Aspartame is an artificial sweetener which is actually a modified dipeptide – a methyl ester of a dipeptide of aspartic acid and phenylalanine. The energy content of glucose, fructose, sucrose and aspartame per gram is pretty much the same as one another. However, we use aspartame in very, very tiny quantities because its sweetness is about 200 times higher than that of sucrose.

2.1.3 Fats and oils

We have covered triglycerides, to an extent, in the Biobiesel section of these notes. Now for a refresher, fats and oils are macronutrients and are collectively known as triglycerides. Triglycerides are relatively large molecules composed of glycerol and fatty acids bonded via ester linkages. The structure of stearic acid (a fatty acid) and glycerol are shown below:



As explained in the biodiesel section of the notes, the hydroxyl groups of the glycerol can react with the fatty acids to form a triglyceride:

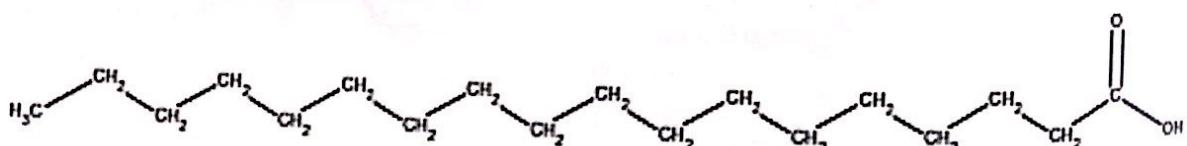


As you can see, fatty acids are basically long-chain carboxylic acids. They can be characterised based on the number of double bonds in the molecule:

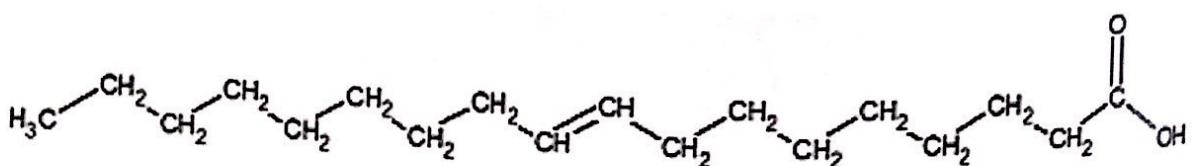
- Saturated fatty acids have no C=C double bonds.
- Monounsaturated fatty acids have exactly one C=C double bond.
- Polyunsaturated fatty acids have two or more C=C double bonds.

Below are examples of each type of fatty acid:

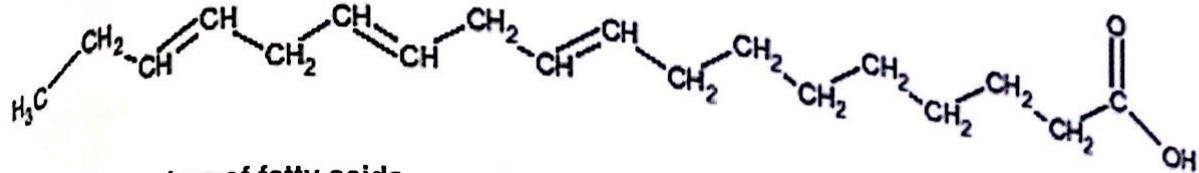
Saturated fatty acid



Monounsaturated fatty acid



polyunsaturated fatty acid

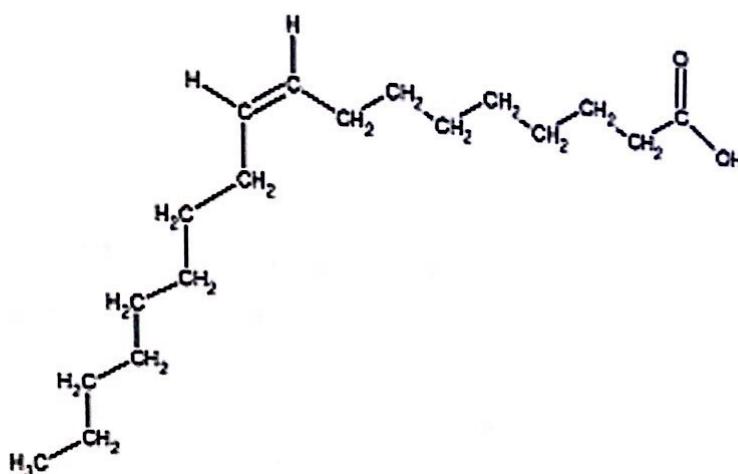


Geometric isomerism of fatty acids

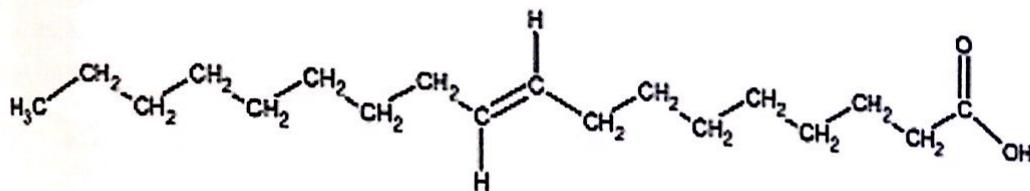
Given that unsaturated fatty acids have C=C double bonds, the issue of cis-trans isomerism comes into play. Generally, in nature, the C=C bonds in fatty acids are **cis** double bonds.

This has important implications for the molecule. Let us have a look at the cis and trans isomers of an 18-carbon fatty acid with a C=C double bond between carbons 9 and 10:

cis-isomer



trans-isomer



Notice how the shapes of the molecules are so different? This shows that the **trans** isomers are linear molecules, whereas the **cis** isomers have 'kinks' in the structure. Additionally, saturated fatty acids are also linear molecules.

This affects the melting point of these molecules; since **linear** molecules can align in an ordered fashion ('pack tightly together'), they can exhibit stronger dispersion forces and therefore will have a higher melting point than bent molecules.

Given that in nature, the C=C bonds in a fatty acid are almost always **cis** C=C bonds, we need not talk about the cases where there are **trans** C=C bonds.

What is the difference between a fat and an oil?

The only differences are this – fats are **solid** at room temperature whereas oils are **liquid** at room temperature. Generally, fats are derived from **saturated** fatty acids whereas oils are derived from **unsaturated** fatty acids.

This figures, because triglycerides derived from unsaturated fatty acids will have 'kinks' in the fatty acid tails that prevent the triglyceride molecules from packing very closely together. This would result in a lower melting point of the triglyceride (below room temperature), rendering the triglyceride a liquid at room temperature, and therefore an oil.

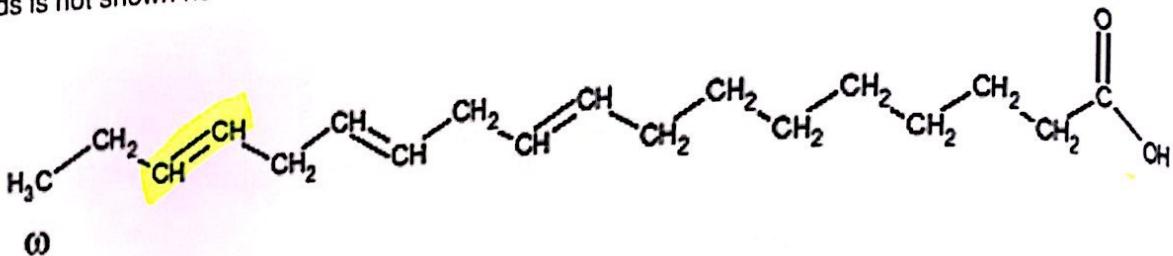
Nutritional concepts

The nutritional concepts related to fatty acids that you need to be aware of are:

- The difference between essential and nonessential fatty acids
- The difference between omega-3 and omega-6 fatty acids

Essential fatty acids are those that are important for the maintenance of health in an individual (as a metabolic reagent or for structural reasons), but cannot be synthesised from other precursors in the body. In humans, the essential fatty acids are **linoleic acid** and **alpha-linolenic acid** (both polyunsaturated fatty acids). All other fatty acids are **non-essential**.

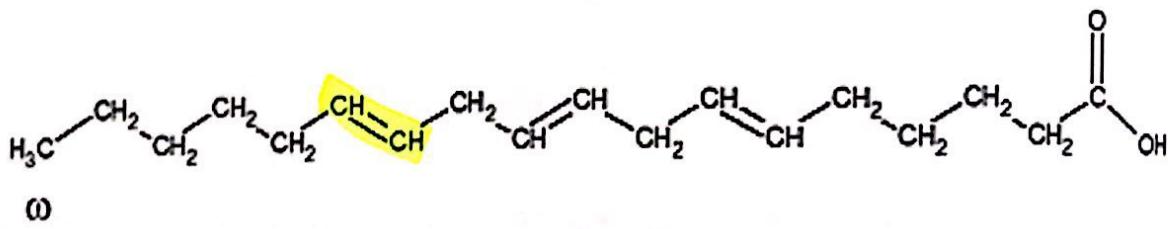
To explain the difference between omega-3 and omega-6 fatty acids, we need to look at what the term omega means. Let's consider the molecule alpha-linolenic acid (note that the cis nature of the C=C double bonds is not shown here for the sake of clarity!)



By convention, the **last** carbon in a fatty acid (away from the carboxyl group) is the omega (ω) carbon.

An **omega-3** fatty acid is one where if you count the carbon atoms on the fatty acid, **starting from and including the omega carbon**, the **3rd** carbon atom is where the **first** C=C bond starts. An **omega-6** fatty acid is the same, except the **first** C=C bond starts at the **6th** carbon atom.

If we look at alpha-linolenic acid again, we can see that the first C=C bond starts at the **3rd** carbon (from the omega carbon). This is therefore an **omega-3** fatty acid. Let us compare this with gamma-linolenic acid (another fatty acid):



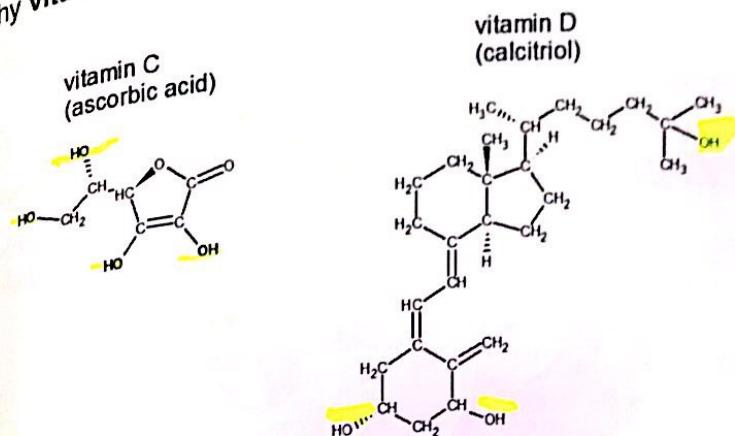
Count the carbon atoms from the omega carbon, and the C=C double bond starts at the **6th** carbon atom. This is an **omega-6** fatty acid. So why the hype about omega-3 and omega-6 fatty acids? Firstly, omega-3 and omega-6 fatty acids are **essential fatty acids**. Secondly, it is known that omega-6 and omega-3 fatty acids, when metabolised in the body, contribute to or detract from the general degree of inflammation in the body, which may have health consequences. Nonetheless, the evidence on the health benefits of omega-3 fatty acid supplementation (e.g. via fish oil pills) is conflicting.

2.1.4 Vitamins

Vitamins are **micronutrients** that are important in small quantities in maintaining the health of individuals. You will see in the next section exactly how vitamins are involved in maintaining health. There are many of these seemingly random chemicals that are important in the functioning in our body, such as retinol ($\text{C}_{20}\text{H}_{30}\text{O}$), thiamine ($\text{C}_{12}\text{H}_{17}\text{N}_4\text{OS}^+$), cobalamin ($\text{C}_{63}\text{H}_{88}\text{CoN}_{14}\text{O}_{14}\text{P}$), ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$), and calcitriol ($\text{C}_{27}\text{H}_{44}\text{O}_3$), or in simpler terms, Vitamins A, B₁, B₁₂, C, and D.

These compounds are very important in the normal functioning in our body and they are also very important in general parlance, since we need to maintain normal levels of each of these chemicals. The reason this is so important in general parlance is because all of these vitamins, **except vitamin D**, cannot be synthesised in the body so we need to obtain these vitamins in our diet.

Now, you are expected in this course to compare and contrast the structures of vitamin C and vitamin D and explain why vitamin C is water soluble and vitamin D is lipid soluble.



If you look at the structure of vitamin C, you can see the hydroxyl groups spread throughout the entire molecule, which can all hydrogen bond with water. Since there are a high number of polar hydroxyl groups spread throughout the entire molecule, vitamin C would be water soluble.

Contrast this to vitamin D. Vitamin D is a very large molecule, but there are only three sites of polarity (the three OH groups). Therefore, vitamin D would not be water soluble – it would be lipid soluble.

2.2 Metabolism of food

Now that we know a little about the different food groups that exist in our body, the question is – how does our body handle these food groups?

Our bodies are made out of a variety of compounds, ranging from water (we are about 60% water), to proteins (about 20%), to certain types of lipids, to DNA, etc. In fact food is a substantial contributing factor as it would not be possible for us to grow in size unless our bodies were synthesising lots of protein molecules as part of connective tissue, muscles, bones (since bones are basically calcium phosphate salt mixed with protein), and other structures. To synthesise such protein molecules, we need monomers of proteins (i.e. amino acids). And where do we get these from? Food – which itself contains protein which your gastrointestinal tract breaks down into amino acids and then absorbs.

Also remember – you need energy for some of these reactions – where do you get this energy from? You will have learnt through general knowledge and science that **glucose** is the primary source of energy. However, in our food we usually consume polysaccharides such as starch, which is broken down into glucose in our gastrointestinal tract, and absorbed. Furthermore, if we have too much glucose in our blood, our bodies transport the glucose into liver and muscle cells, and convert the glucose to **glycogen** (a polysaccharide).

Anyway, the point is that metabolic reactions can be divided into two groups:

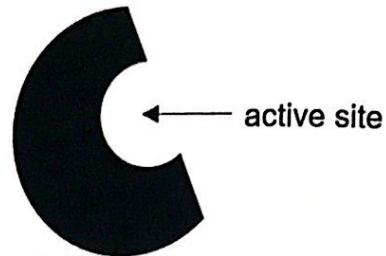
- **Catabolic reactions:** where large biomolecules are **hydrolysed** into smaller biomolecules (often occurs in food), e.g. the breakdown of starch and protein into glucose and amino acids respectively.
- **Anabolic reactions:** where large biomolecules are synthesised from smaller biomolecules via **condensation reactions**, e.g. the synthesis of protein from amino acids.

2.2.1 Enzymes

The issue with these metabolic reactions that are necessary to sustain life is that the activation energies of these reactions are fairly high, and body temperature is only 37°C . In other words, these reactions would usually be way too slow to sustain life.

However, our bodies have a series of catalysts which increase the rate of all these reactions; this ensures that the reactions are fast enough for life to be sustained. These catalysts are called **enzymes**.

Enzymes are **protein molecules**. The basic structure of an enzyme molecule is shown below:



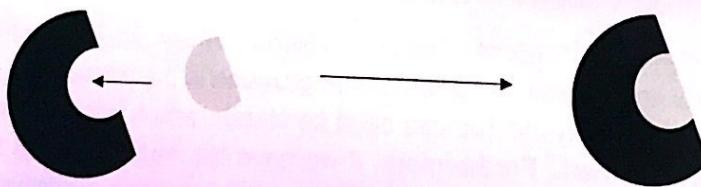
Note that the enzyme molecule has a specific shape (i.e. a specific tertiary structure). There is a particular section of the enzyme molecule called the **active site**. The active site is the region in the enzyme molecule that physically binds to the reactants (which, in this context, are known as the **substrates**).

Mechanism of reaction

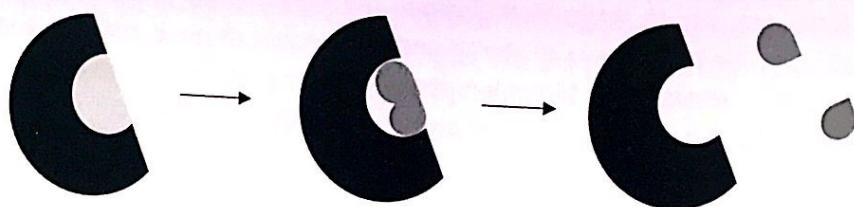
How do enzyme molecules work? Suppose we had a reactant molecule that can be broken down into two smaller product molecules. In pictorial form – this may be the reaction:



What is the enzyme's role in this reaction? Well, firstly, the substrate will bind to the active site of the enzyme, via hydrogen bonds and ionic interactions:



The active site of the enzyme will then catalyse the reaction, converting the substrate into the product(s):



Enzyme specificity, lock and key model and induced fit model

One important feature of enzymes is that each enzyme catalyses a specific reaction. For example, the enzyme alcohol dehydrogenase converts ethanol to acetaldehyde (CH_3CHO) in the body, and the enzyme glycogen synthase catalyses the polymerisation of glucose into glycogen. If you add the enzyme glycogen synthase to a solution containing ethanol, it would not be converted to acetaldehyde.

Why is this the case? The reason is attributed to the fact that the active site has a specific shape, and can therefore bind only to a substrate with a complementary shape.

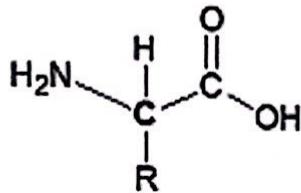
The lock and key model explains this phenomenon:



However, the lock and key model is a little bit crude. There is a second model that is proposed, and is considered to be more correct – known as the induced fit model. This is similar to the lock and key model, except in the induced fit model the active site is not perfectly complementary to the substrate. Only when the substrate approaches the active site of the enzyme, the active site changes shape slightly, making it perfectly complementary to the substrate molecule.

Enzymes and optical isomerism

Let's have a look at the general structure of an amino acid, the monomer of the enzyme:



Look at the bolded C atom. Notice how that this carbon atom has 4 different substituents? Therefore, this C atom is chiral – and therefore amino acids are chiral molecules and have optical isomers. In fact, in the body, only one optical isomer (which we call the L isomer) of each amino acid exists in the body. Therefore, enzyme molecules in the body are composed entirely of L-amino acids, and are themselves chiral molecules.

What does this tell us? This means that if the substrate is chiral (and has two optical isomers), the enzyme will tend to bind better to one optical isomer of the substrate than the other (much like the right hand fits perfectly into a right-hand glove, but not so much to the left-hand glove). Therefore, the enzyme is at least partially selective to one optical isomer of the substrate.

Relationship between temperature, pH and enzyme activity

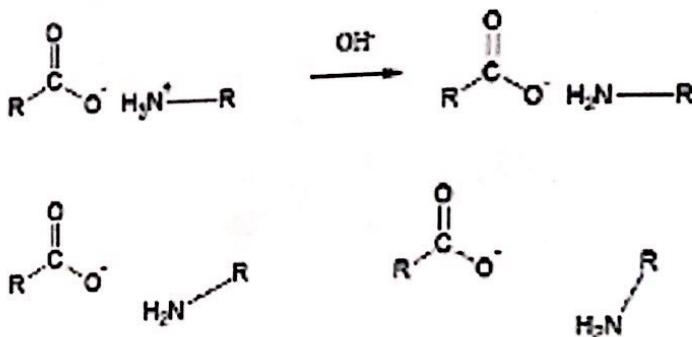
Enzyme activity and function is dependent on temperature and pH. In other words, there is a specific temperature and pH at which enzymes work optimally. Why is it that enzyme function is temperature and pH sensitive?

Recall that when the temperature is low, molecules move significantly more slowly. This means that the frequency of collisions between the enzyme and its substrate(s) would be much fewer, and the rate of formation of enzyme-substrate complexes significantly drops. Hence, the rate of product formation decreases. As the temperature increases, the activity of the enzyme increases as the rate of formation of enzyme-substrate complexes increases.

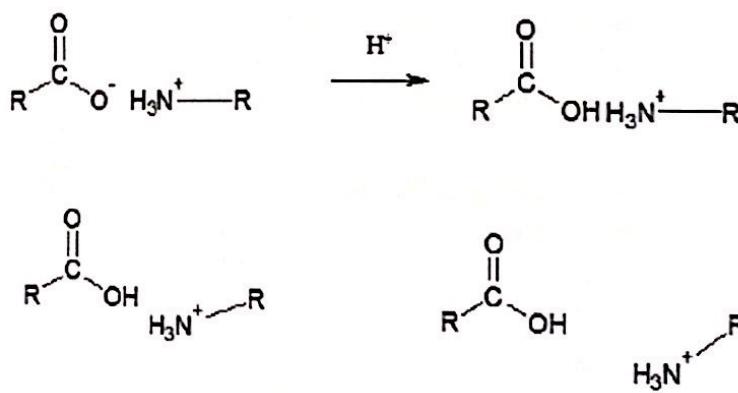
However, if the temperature is increased to too high a level, then the vigorous vibration of the enzyme molecules, as well as the high speeds at which the enzyme molecules move and collide with one another, can break the hydrogen bonds in the secondary and tertiary structure. This will change the shape of the enzyme and hence the shape of the active site. This prevents the substrate from being able to bind to the active site of the enzyme, and the enzyme therefore ceases to function. This change in shape of the active site and subsequent loss of function of the enzyme is called **denaturation**. Note that if the temperature of the environment is subsequently reduced, enzyme function does not recover, since the hydrogen bonds formed subsequently will be between different amino acid residues (as the protein had changed shape during the denaturation, changing the spatial arrangement of the amino acid residues). The shape of the active site will remain different here.

Furthermore, changing the pH from the optimal value also changes the shape of the active site because the **ionic interactions** between Z groups change as the pH changes. This is because when you change the pH from optimal, the distribution of protonated and deprotonated amino groups (-NH_3^+ and -NH_2) changes, as does the distribution of protonated and deprotonated carboxyl groups (-COOH and -COO^-). For instance, if the pH were decreased, more of the amino and carboxyl groups will tend to be protonated (-COOH and -NH_3^+). This means that some ionic interactions will break as certain acidic/basic groups lose their charge, and other ionic interactions may form as other acidic/basic groups gain a charge. The process of breaking ionic bonds is shown below:

Increase in pH (more OH^- ions)



Decrease in pH (more H^+ ions)



Now, keep in mind that when we talk about **denaturing** an enzyme, we refer to disrupting the secondary and tertiary structures – **not** the primary structure. The primary structure can be disturbed only by **hydrolysing the peptide bonds**. There are two ways of hydrolysing peptide bonds:

- Heating the protein in a solution of strong acid (e.g. 6 M HCl)
- **Protease enzymes** in solution, which catalyse the hydrolysis of peptide bonds

In fact, when we eat proteins as part of our diet, **protease enzymes** released from the pancreas catalyse

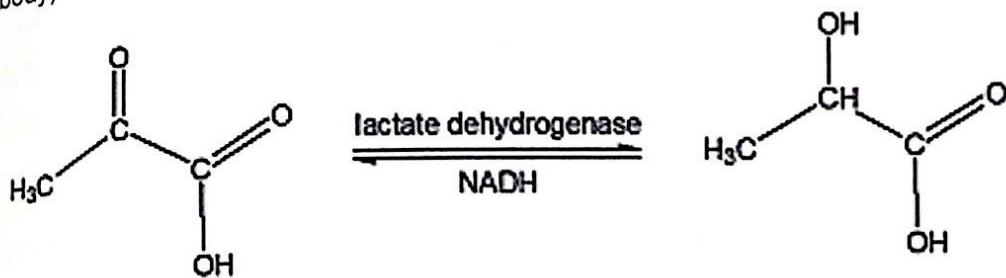
the hydrolysis of these proteins into amino acids for absorption by our gastrointestinal tract (GIT). The absorbed amino acids are subsequently used for the synthesis of proteins inside the body.

2.2.2 Coenzymes

Some enzymes require the action of chemicals called **coenzymes** to function. Coenzymes are small organic molecules that bind to the active site of an enzyme molecule along with the substrate. This may allow a change in the conformation of the active site to allow better binding with the substrate, or it may participate as an additional reactant in the enzyme-catalysed reaction.

Coenzymes can either accept electrons from or donate electrons to the substrate to form the product, or accept or donate groups of atoms such as acyl groups ($\text{CH}_3\text{C=O}$).

One example of a coenzyme is NADH (nicotinamide adenine dinucleotide), which acts as an electron donor, in the action of the enzyme lactate dehydrogenase, which converts a chemical called pyruvic acid (in the cells of the body) to lactic acid via the following reaction:



NADH binds to the active site of lactate dehydrogenase and donates electrons to pyruvic acid, which is reduced to lactic acid. NADH itself is oxidised to its oxidised form called NAD⁺.

Interestingly, the sole function of NADH is to act as an 'electron carrier', coupling oxidation and reduction reactions in cells which are spatially distinct from one another. For example, NAD⁺ (the oxidised form) acts as a coenzyme in the chemical reactions of cellular respiration whereby glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is oxidised to carbon dioxide (CO_2), collecting electrons from glucose to be reduced to NADH. The NADH then donates these electrons in enzyme-catalysed reduction reactions, as a coenzyme.

There are numerous molecules in biological settings that have these sorts of roles that we refer to as coenzymes, including NADH itself and a related molecule called NADPH and **vitamins**.

2.3 Metabolism of biomolecules

Now that we understand the way enzymes work, we can talk about what happens to the different macronutrients in the GIT as they are consumed in food.

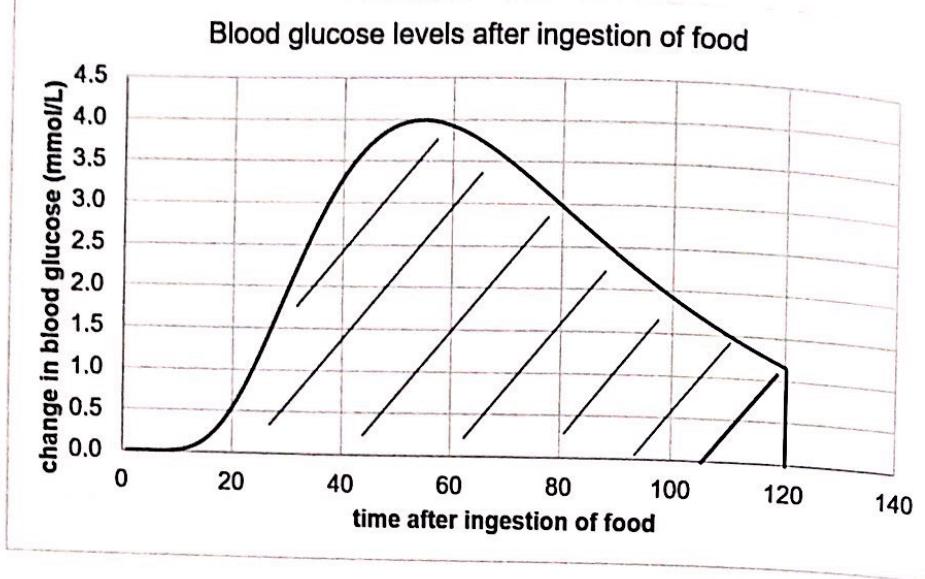
Metabolism of carbohydrates

As part of our diet, we consume both simple (monosaccharides and disaccharides) and complex (polysaccharides) carbohydrates. The disaccharides and polysaccharides have to be hydrolysed to form monosaccharides in the GIT before they can be absorbed.

Metabolism of polysaccharides

Now, both starch and glycogen in food can be broken down into glucose. However, **cellulose cannot be broken down** and is excreted as fibre. This is because starch and glycogen are both polymers of alpha-glucose whereas cellulose is a polymer of beta-glucose. Therefore, the glycosidic linkages in cellulose have slightly different geometries than those in starch and glycogen and therefore the enzyme in our GIT primarily responsible for the breakdown of polysaccharides into smaller oligosaccharides, **pancreatic amylase**, can catalyse the hydrolysis of **alpha glycosidic bonds** but not **beta glycosidic bonds**. This is an example of how specific the shape of the substrate has to be to bind properly to the active site of its corresponding enzyme.

Focus on a particular issue related to carbohydrate digestion and metabolism called **glycaemic index (GI)**.
Cellulose cannot, let us define as the relative area underneath a **change in blood glucose-time** curve over 2 hours after eating some food. This can be seen in the graph below:



The above graph shows the change in the blood glucose after food is ingested. You can see that at about the 20 minute mark the blood glucose starts to rise as the first amounts of glucose are taken up in the blood, continue to rise, and then subsequently fall as most of the glucose has already been absorbed, and glucose is leaving the blood and entering cells (due to the action of the hormone insulin).

To calculate the glycaemic index of a particular food, a standard amount of the food is ingested and blood glucose calculated at periodic intervals for 2 hours to generate the above graph. The area under the curve (AUC) (shaded above) is determined and compared to the AUC for a standard amount of pure glucose. The AUC for a standard amount of glucose is taken to be a value of 100, and based on this a numerical value is given to the AUC for this food; this numerical value is the **glycaemic index** of the food. Yes, this means that the GI for pure glucose is 100.

Foods that tend to have a high GI are those where either there is a high content of simple sugars that can be directly absorbed (or absorbed with minimal metabolism), or there is a high content of polysaccharides that can be broken down into glucose and ingested very quickly.

Different starch-containing foods differ in their GI, depending on the relative proportions of amylose and amylopectin. Why is this the case? Remember from previously that amylose is an unbranched polymer of glucose whereas amylopectin is a branched polymer of glucose. Because amylopectin is branched, the polar OH groups in the glucose moieties are more 'spread out' in the molecule, rendering amylopectin significantly more soluble in water than is amylose. This means that amylose tends to form 'clumps' (much like a precipitate), whereas amylopectin tends to be dissolved in the watery chyme (food mixture in intestines). Hence, the amylases and other glycolytic enzymes in the intestines get greater access to amylopectin and hydrolyse it much more quickly than they do amylose. The glucose is released and absorbed by the intestine much more quickly, leading to significant amounts of glucose being absorbed into the body at once and hence a higher GI.

For example, the starch in **lentils** has a high proportionate amount of amylose compared to amylopectin, contributing to its low GI (<55). Some white rices, such as the infamous Sri Lankan samba rice, have a very high proportionate amount of amylopectin, contributing to its high GI (>70).

Lactose metabolism

Lactose (milk sugar) is a disaccharide composed of **glucose** and **galactose**, and is primarily found in milk. Lactose is hydrolysed into glucose and galactose by the enzyme **lactase**, which is found in the small intestine. Babies all express lactase on the cells of their small intestine, and are hence able to metabolise milk sugar when they breastfeed or are bottle-fed.

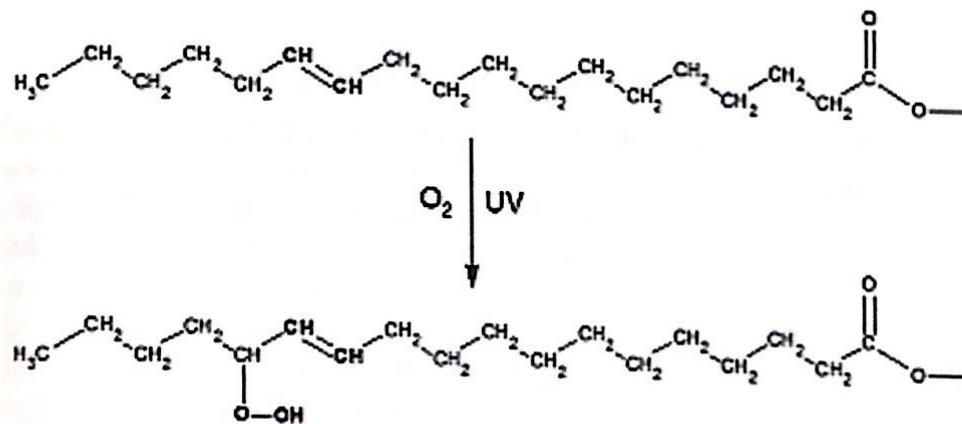
However, upon weaning in many individuals, the presence of functional lactase diminishes significantly whereas in other individuals, lactase persists in the small intestine. Therefore, some individuals are able to metabolise lactose as adults, whereas others are not and are considered **lactose intolerant**. If lactose is undigested, it draws water into the small intestine (via a process called osmosis), and upon entering the large bowel, bacteria in the large bowel metabolise the lactose and produce high amounts of gas. This leads to bloating (due to the gas), abdominal pain and cramps and diarrhoea (due to drawing of water into the small bowel).

2.4 Metabolism of fats and oils

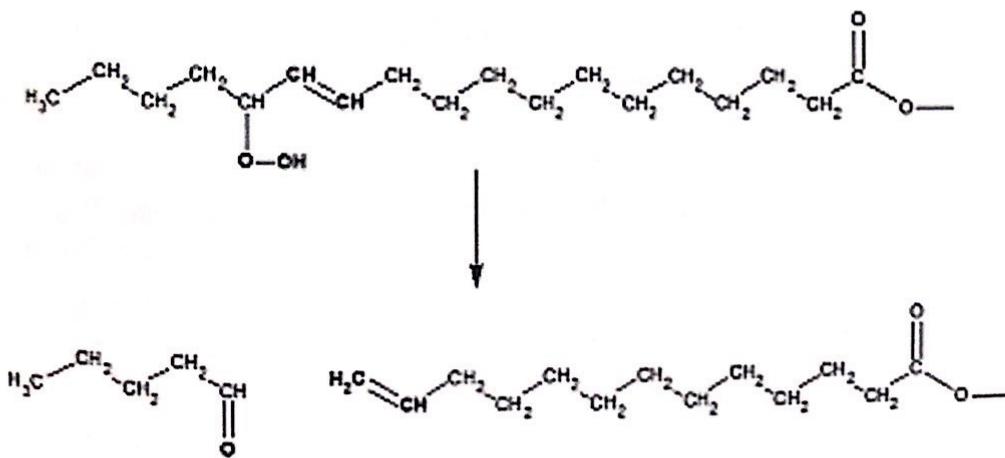
When fats and oils are consumed, they are hydrolysed by **lipases** in our mouth, stomach and small intestine to form their constituents: **glycerol** and **fatty acids** (in reality the lipases actually only release two fatty acids from the triglyceride, leaving the middle fatty acid tail intact – but for the sake of VCE Chemistry, ignore that!) Let us have a look at a particular nutritional issue with respect to fats and oils – **oxidative rancidity**.

What is oxidative rancidity?

If you are to leave any fatty foods out in the air, they tend to go “off” very quickly. You will find that this happens particularly with triglycerides that are comprised of unsaturated fatty acids (**particularly polyunsaturated fatty acids**). Unsaturated fatty acid tails tend to react with oxygen from the air, in the presence of UV light; this leads to the formation of **hydroperoxy** (-OOH) functional groups adjacent to C=C double bonds. This happens via a number of complex processes; one of the simpler processes is shown below – only a single fatty acid residue is shown for purposes of clarity:



These hydroperoxy residues, for example the one shown above, are extremely unstable and can degrade to form a number of other compounds including smaller aldehydes and ketones, which are volatile and have a very pungent smell. These **secondary peroxidation products** (the volatile aldehydes and ketones) are what contributes to the ‘off’ smell of spoilt fatty foods. The formation of the secondary oxidation products involves numerous very complex processes. One of the more simpler processes is shown below:



You can see on the left the formation of the volatile aldehyde – one of the many secondary oxidation products formed.

This entire process is called **rancidification** and we say that after these processes occur the oils exhibit **oxidative rancidity**.

How do we mitigate oxidative rancidity?

During processes, chemicals called **antioxidants** are added to foods and oils to slow down the rancidification processes. Antioxidants are essentially **reducing agents** that prevent the oxidation of fatty acid residues by letting themselves become oxidised instead. This is essentially a form of 'sacrificial protection' – the antioxidants 'sacrifice' themselves to protect the fatty acids from oxidation. There are natural antioxidants in foods such as vitamins C and E, and we also add synthetic antioxidants such as propyl gallate to foods to increase their shelf life.

2.5 Energy Content of Food

In this section, we talk about how much energy different foods contain. First, let's focus on the energy content of our major sources of energy – carbohydrates and fats/oils, and proteins in some situations.

2.5.1 Energy content of macronutrients

The energy content of a macronutrient is the maximum amount of energy that the body can extract from a given mass of the macronutrient. Importantly, the way the body extracts energy from the macronutrient is by oxidation to form CO_2 and H_2O (which is pretty much a combustion reaction, except it occurs over many, many steps). Therefore, the energy content of the macronutrient is basically the same as the energy released when you combust 1 g of the macronutrient.

The energy content of most carbohydrates (glucose, sucrose, starch, for example) is approximately 17 kJ/g (or 4 kilocalories/g).

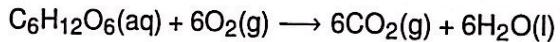
The energy content of proteins is very similar, again around 17 kJ/g.

The energy content of triglycerides is significantly higher, around 37 kJ/g. The reason for this is that much of the chemical energy released involves the breaking of C-C bonds within the nutrient and the resultant formation of C=O bonds in forming CO_2 . Triglycerides have a significantly higher percentage by mass of C atoms than do proteins and carbohydrates.

2.5.2 Energy sources in the body

Our cells need energy to function, and they use chemical energy from a variety of macronutrients (carbohydrates, lipids and proteins) to this end via oxidation to CO_2 , which are exothermic reactions that release significant amounts of energy.

The primary energy source for most cells is **glucose**. Glucose is oxidised to form CO_2 , which releases energy that is harnessed by cells to drive numerous metabolic reactions. The process by which glucose is oxidised to form CO_2 to release energy is called **cellular respiration**, and the reaction equation (which you need to know) is:

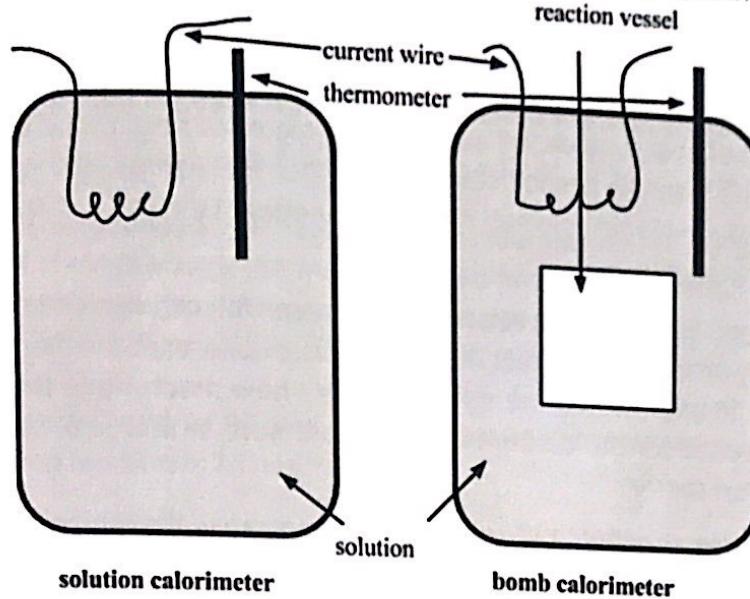


2.5.3 Calorimetry

How do we experimentally determine the energy content of a particular fuel – say glucose? We can use a technique called **calorimetry**. We can also use calorimetry to determine the enthalpy change associated with chemical reactions.

The idea here is to perform a chemical reaction in some sort of solution or vessel in an insulated container, and measure the change in temperature. Then, we use the temperature change to determine how much energy has been released as heat into this container, or absorbed from the container.

This insulated container is the **calorimeter**. The setup of the calorimeter is shown below:



There are two types of calorimeter, the first is a **bomb calorimeter**, which is used to determine the heat released in **combustion reactions**. There is a vessel (the bomb) inside the solution into which you put your fuel (could be a biscuit, or petrol, or something) which contains **oxygen** gas at high pressure. An ignition coil inside the bomb is used to ignite the fuel, and the heat generated dissipated into the surrounding water. The second type of calorimeter is a **solution calorimeter**, which is used to determine the heat released or absorbed when a reaction occurs in solution.

Before we learn how to interpret findings from calorimetry experiments, it would be a good idea to review the concept of specific heat capacity from Year 11.

Specific heat capacity

If you remember correctly, **thermal energy** is the energy contained within a chemical that is responsible for its temperature. The higher the thermal energy, the higher the temperature of the chemical. When you heat up a chemical to a higher temperature, you are giving this chemical more thermal energy. But the question is - how much does the thermal energy of the chemical need to increase to increase the temperature by 1 K? The increase in thermal energy required to increase the temperature of 1 g of a chemical by 1 K is the **specific heat capacity** of that chemical.

For instance, the specific heat capacity of **water** is $4.18 \text{ J K}^{-1} \text{ g}^{-1}$. This means that to increase the temperature of 1 g of water by 1 K, you need to transfer 4.18 J of energy into the water (as thermal energy). The symbol we use for this 4.18 is c .

Suppose you wanted to determine the energy required to heat up 20 g of water from 20 to 50 degrees Celsius. Remembering that **an increase in temperature by 1 K is the same as an increase in temperature by 1 degree Celsius**, we can say that we need to heat the water by 30 K.

Remembering that to increase the temperature of 1 g of water by 1 K, you need 4.18 J of energy, and you want to increase the temperature of 20 g of water by 30 K, we can conclude that:

$$E = 4.18 \times 20 \times 30 = 2.51 \times 10^3 \text{ J}$$

If you were to generalise this, with say an increase of the temperature of m g of water by ΔT K, and that the symbol we use for specific heat capacity is c , we can say that:

$$E = c \times m \times \Delta T = mc\Delta T$$

Now let us look at two examples of calorimetry in action. Suppose there is a chemical reaction like

$$A(\text{aq}) + B(\text{aq}) \rightarrow C(\text{aq})$$

and we want to determine its enthalpy of reaction.

We plan to take a solution calorimeter and dissolve 0.500 mol of A and an equivalent amount of B into this calorimeter. We will see a temperature change and measure it using a thermometer. From this we will determine the amount of energy released into the calorimeter as heat, or the energy absorbed from the calorimeter as heat. We will then use this to determine the chemical energy (enthalpy) change that occurred in the reaction. The energy transfer is between **chemical energy** of the chemicals, and the **thermal energy** of the calorimeter and its contents.

For all this to occur, we need to find out the relationship between the change in temperature of the calorimeter and the thermal energy change of the calorimeter, so we can determine the thermal energy change given the temperature change. In other words, we need to know - **how much does the thermal energy of the calorimeter need to increase for the calorimeter's temperature to increase by 1 K?** The answer to this is known as the **calibration factor**.

For example, a calibration factor of 300 J K^{-1} means that to increase the temperature of the calorimeter by 1 K, you need the calorimeter to absorb 300 J of thermal energy.

How do we measure the calibration factor physically of a particular calorimeter? After all, each calorimeter is different and the calibration factor is basically a weighted average of the specific heat capacity of all the substances in the calorimeter (the insulation material, the water, the thermometer, the components, etc.). We can measure a temperature change in the calorimeter by using a thermometer, easy. But how can we deliver a known quantity of thermal energy into the calorimeter? It turns out there is a very elegant method.

First, let's do a little revision of electronics:

- **Charge (Q)**: is a quantity carried by protons and electrons and is measured in **C** (coulombs).
- **Voltage (V)**: is the energy, in J, contained within **1 coulomb** of charge and is measured in **V** (volts)
- **Current (I)**: is the **rate of flow of charge** - the amount of coulombs of charge flowing through a particular point in a circuit in 1 second; it is measured in **A** (amperes).

Hence, a current of 1 A means that 1 C of charge passes through a point in the circuit in 1 second.

Suppose we dip some wiring into the calorimeter, through which we pass **Q** coulombs of charge via an electrical current with voltage **V**. We can conclude that, since the voltage is the energy contained within 1 C of charge, the energy delivered to the calorimeter will be $E = VQ$.

Note that **current** is the number of coulombs of charge passing through a point in 1 second. Therefore, if the current were **I** A and the time the current was flowing for was **t** seconds:

$$E = VQ = Vit$$

Now, we have a method by which we can calculate the exact amount of energy delivered to the calorimeter. So, back to the original problem. Before we perform the $A + B \rightarrow C$ reaction, we need to find the calibration factor. Suppose we passed a 5.00 A current for 120 seconds with a voltage of 3.00 V through the calorimeter, and the temperature increase was 2.50 K. To calculate the calibration factor, we need to determine the energy delivered to the calorimeter:

$$E = Vit = 3.00 \times 5.00 \times 120 = 1.80 \times 10^3 \text{ J}$$

We know that delivering 1.8×10^3 J of energy into the calorimeter as thermal energy increases the temperature by 2.50 K, we need to know how much energy is required to heat the calorimeter by 1 K (the calibration factor):

$$CF = \frac{1.80 \times 10^3}{2.50} = 720 \text{ J K}^{-1}$$

Now, we do the actual $A + B \rightarrow C$ reaction with 0.500 mol of A and 0.500 mol of B. Suppose the temperature rose by 3.50 K. Let's figure out what the enthalpy of reaction is.

We know the temperature change - an increase of 3.50 K. Here, chemical energy must have been converted to thermal energy throughout the reaction, which heated the calorimeter and caused its temperature to rise.

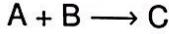
The question is - how much thermal energy was gained? We know the calibration factor is 720 J K^{-1} ; increasing the temperature by 1 K requires 720 J of thermal energy. However, the temperature increase was 3.50 K, therefore the increase in thermal energy is:

$$E_{\text{thermal}} = 7.20 \times 3.50 = 2.52 \times 10^3 \text{ J}$$

Now, the thermal energy has increased by 2.52×10^3 J. This thermal energy originated as chemical energy (enthalpy). An increase in thermal energy means a decrease in chemical energy. Therefore, the change in chemical energy is the negative value of the increase in thermal energy:

$$E_{\text{chemical}} = -E_{\text{thermal}} = -2.52 \times 10^3 \text{ J}$$

When 0.500 mol of A is reacted with 0.500 mol of B, the change in chemical energy is -2.52×10^3 J. Now, the enthalpy of the following reaction in kJ mol^{-1} :



will be the chemical energy change when **1 mol** of A reacts with **1 mol** of B (as per the coefficients). Since 0.500 mol of A reacting led to a change in chemical energy is -2.52×10^3 J, the chemical energy change when 1 mol of A reacts is $-2.52 \times 10^3 \text{ J} \times 1/0.5 = -5.04 \times 10^3 \text{ J}$.

Hence the $\Delta H = -5.04 \times 10^3 \text{ J mol}^{-1} = -5.04 \text{ kJ mol}^{-1}$.

Errors in calorimetry

Now, calorimetry is not an **exact** technique for various reasons. Sometimes, the enthalpy of reaction determined during the calorimetry is not exactly equal to the enthalpy of reaction in real life. There are a number of reasons for this:

- There may be **heat transfer** between the calorimeter and the surroundings – the walls of the calorimeter may not be perfectly insulated. This means that as the reaction occurs, any temperature change away from ambient (room) temperature will be mitigated, and any temperature change towards room temperature will be exacerbated.
- The solution may **not be homogeneous** - it may be hotter in some parts of the calorimeter than in others; this means that when you measure the temperature using a thermometer, you may inadvertently measure the temperature of a hotter or a cooler part of the calorimeter, leading to an inaccurate value for the increase in thermal energy. A **stirrer** inside the calorimeter is used to make the solution homogeneous.
- The equipment with which you are measuring your data will have an uncertainty - the balance with which you weigh your reactants, the thermometer with which you measure the temperature changes.
- One interesting reason that you could throw in is the fact that the **calibration factor changes after the reaction is complete**. The calibration factor, if you remember, is the amount of thermal energy required to be absorbed by the calorimeter to increase its temperature by 1 K. Therefore, it is a weighted average of the specific heat capacities of all the components in the calorimeter, including the chemicals. Now, after the reaction occurs, the substances that are present in the calorimeter are different - there are no longer reactant species present, but product species (which have a different specific heat capacity).

Another interesting reason is that **enthalpies of reaction** are dependent on **temperature**; the enthalpy of a reaction at 298 K will be different from the enthalpy of the same reaction at 310 K, for example.

Area of Study 3

Practical Investigation

This section is new to the 2017 course. The purpose of this section is because being proficient in the scientific method is absolutely essential, not just for being a good scientist and contributing to the wealth of knowledge that we have amassed, but also because the critical thinking skills you gain are extremely valuable.

The knowledge that we are taught today has itself been discovered through experimental investigation. The way scientists obtain knowledge is by using information that is already known to make conjectures or hypotheses. For instance, if it is known already that acidified permanganate ions can oxidise primary alkanols to carboxylic acids, one could hypothesise that another oxidising agent such as periodic acid (HIO_4) could also oxidise ethanol to ethanoic acid. The scientist would develop an experiment to determine whether periodic acid indeed oxidises ethanol to ethanoic acid. The experiment would be conducted and data collected. The scientist would then interpret the findings and discuss the meaning of these findings, and come to a conclusion based on these findings. This experimental data, should the scientist wish, can be published and become part of the **literature** (this term will be explained later).

You will be expected to conduct your **own experiment** in this course, from start to finish. You will be designing the experimental method, conducting the experiment and collecting data, interpreting the results and obtaining a conclusion. You will then be presenting your results in a **scientific poster of 1000 words** consisting of the following sections:

- Introduction
- Methodology
- Results
- Discussion
- Conclusion

These notes will give you some suggestions as to how to conduct your experiments and poster.

3.1 Introduction

Here, you need to **explain the background information**, to give some context to your experiment. To do so, you need to consult the current **literature** (i.e. published information available in books, academic journal articles and websites). For the purposes of Year 12 though, the only literature that most people would be able to understand is material from textbooks and websites. In other words, you need to do some **independent research**.

Some questions that you need to answer:

- What background information does the reader need to know to be able to understand your experiment?
- Has your experiment been performed before? If so, what was the methodology and the findings?
- Why is your research question pertinent – what are the implications should your research question be answered?

Keep in mind that at Year 12 level, your research is likely (not definitely!) limited to small, rather inconsequential research questions, or confirming the findings of existing literature or experimentally verifying theory that you have learnt.

For your poster, I suggest your introduction be between **150-200 words**. Keep things succinct, and only discuss pertinent information.

3.2 Methods

For illustrative purposes, suppose we were investigating the effect of temperature on the rate of reaction of CaCO_3 with HCl. The setup will have some CaCO_3 dissolved in HCl in a reaction flask connected to a gas syringe, which will measure the volume of CO_2 produced.

When designing the methodology of your experiment, ensure the following:

- Have **experimental groups** and a **control group** of set-ups where appropriate. In the above example, a single flask with CaCO_3 dissolved into HCl, connected to a gas syringe that measures CO_2 production, would be a single setup. In the (negative) control group, you modify the setup to guarantee you a negative result. This is so you have a setup against which you can compare your experimental groups and you know what a fully negative result (i.e. no production of CO_2) would look like experimentally.
- Have a **large sample size** if appropriate. The sample size refers to the number of experimental setups. Having multiple setups would decrease the effect of a freak result or random error leading to incorrect conclusions.
- Make sure you vary the **independent variable** and explain how you are measuring the independent variable. The independent variable is the variable you are manually changing. In the above example, the independent variable is temperature. You would use multiple sets of reaction flasks, each at different temperatures (eg. one at 10°C , one at 20°C , one at 30°C , etc.). Explaining how the independent variable is measured is important because to draw accurate conclusions, you want to ensure that your independent variable has been varied (eg. the temperature of the flasks are what we think they are).
- Make sure you **control** other variables – i.e. keep them constant. This ensures that if there is a positive result in your experimental setup, it cannot be attributed to other variables. For example, you want to ensure that the amount of CaCO_3 , the surface area of CaCO_3 , the concentration of HCl, are kept constant. If you do not keep them constant – and you see an increased reaction rate in a flask that has both a high temperature and a higher $[\text{HCl}]$, then how would you know whether the increased reaction rate is due to increased temperature or an increase in $[\text{HCl}]$?
- Explain how the **outcome will be detected**. In the previous example, you would explain that the volume of CO_2 produced in the gas syringe would be measured in say 10 second intervals over 2 minutes.

For the poster, about 100 words are advised for the methods.

3.3 Results

When presenting results, think about the most succinct way to present them. Would a table be illustrative? If you are trying to show a trend – then a graph would be most appropriate. Ensure quantitative data are collected to the **appropriate accuracy**. For example, if you are eyeballing the volume of CO_2 produced over the 10 second intervals, it may not be appropriate to say e.g. 20.0 seconds (because by the time you read the volume of CO_2 produced it might be 20.5 seconds already) – in that case writing “20” instead of “20.0” would be prudent.

About 100 words are advised for the results section.

3.4 Discussion

This is the most important section of your poster. Here, you need to analyse your data and extract meaning from it. In particular – answer these questions:

- Does the data support or negate your hypothesis?
- If your data supports your hypothesis, are there any **other** explanations for your positive findings, besides your independent variable?
- If your data negates your hypothesis, is it possible for you to have generated this data **given the hypothesis were in fact true** (e.g. could it be due to experimental error)?

3.4 Discussion

The study design also stipulates that you must know and be familiar with the terms **accuracy**, **precision**, **validity**, **reliability**, **uncertainty**, **random error** and **systematic error**.

- Is your data accurate and precise?

For illustrative purposes, suppose that the experiment has been conducted, and the data collected states that for a flask at 30°C , 20 mL of CO_2 was collected at the 20 second mark.

Accuracy: refers to the degree to which your data matches what has actually happened. The data presented in the above example is considered accurate if 20 mL of CO_2 was indeed produced at the 20 second mark. It would be considered inaccurate if say 21 mL of CO_2 were produced in reality.

Precision: refers to how sensitive your data is to slight differences in the outcome or the experimental variable. For instance, your data quotes 30°C as the temperature, 20 mL of CO_2 as the volume of CO_2 and 20 seconds as the time. Your data is able to differentiate between say 30°C and 31°C (if you were using a thermometer), but not between say 30°C and 30.05°C . In the experiment, your data has to be precise enough to ensure that you can detect differences between your variables in different experimental setups. For example, if you are expecting one flask to produce 20.0 mL of CO_2 at the 20 second mark and a second flask to produce 20.1 mL of CO_2 , your experimental design is not precise enough to pick up these minute differences.

Validity is a property of the experiment; the experiment is considered valid if the data generated is by and large accurate. An experiment is said to be **reliable** if, upon replication of the experiment, you pretty much get the **same** results every single time – i.e. your results are **consistent**. Note that validity and reliability are independent descriptions; an experiment can be both valid and reliable, valid but unreliable, invalid yet reliable, and invalid and unreliable.

Valid but unreliable means that by and large, the data you generate is accurate, but there is too much variation in your experimental outcome between identical experimental setups. For example, if one setup says you produce 20 mL of CO_2 gas at the 20 second mark, yet other identical experimental setups say you produce 30 mL, 15 mL, and 27 mL – these results may be correct results, but there is some unknown factor in the experiment that is causing this heterogeneity of results. If you were to average these results out, you would obtain an accurate expected volume (i.e. **validity** is maintained), but you would not be able to take any of the individual results (e.g. the 20 mL result) and say that this reflects the true reality (i.e. **the result is unreliable**). It is analogous to having a cricketer who, on average, scores about 60 runs per innings (a very high average), yet his scores range wildly from scores of 0, 1, and 6 to scores of 160, 200 and 300. This cricketer is pretty skilful, but you cannot *rely* on him to make a good score on a particular innings when you really need him to.

Invalid but reliable means that the data you generate is inaccurate, but the variation in the experimental outcome is very minimal. For example, if the reality is that 30 mL of CO_2 would be produced (say from numerous past experiments), yet your identical setups generate values of 20, 20, 21, 19, 21 mL, these results would be **invalid but reliable**. If you average out these results, you would end up getting an inaccurate average value. This is analogous to having Glenn McGrath or Chris Martin (New Zealand bowler) batting. These people would have very bad averages of say 1.50 (Chris Martin's one-day batting average is 1.50). However, if you were to follow his last few batting scores, you would likely see something like 1, 1, 1, 0, 1, 0, 1, 1, 2, 1, 2, 1, 1, 2, 3, 2, 1, 1, 1, 1. All of these scores are bad, but they're consistent. Therefore, when Chris Martin is called out to bat, you can *rely* on him to get a score of 1.

Random errors are factors in the experiment that would cause a **high variation in results**. For example, if you were to do a titration 4-5 times and get titre volumes of 20.05 mL, 20.07 mL, 20.02 mL, 20.01 mL and 20.04 mL – why are these results ever so slightly different? This is likely due to factors such as parallax (where your eye level when reading the burette will be ever so slightly different), the fact that the size of each drop of titrant may be ever so slightly different between titrations and the fact that you are eyeballing the colour change in the titration. **To mitigate the effect of random errors, we use a high sample size, and average results wherever we can.**

Systematic errors are factors in the experiment that would, alone, cause a **consistent yet inaccurate result**. For example, if you were titrating samples of baking soda to determine the percentage by mass of NaHCO_3 via titration against HCl solution, and the baking soda was contaminated with some CH_3COONa (a weak base), this CH_3COONa would **consistently** be titrated along with the NaHCO_3 , leading to a similar/same percentage by mass of NaHCO_3 every single time the experiment is conducted, which will consistently be higher than the true value.

- Are there any sources of bias?

As humans, we are very good at consciously or unconsciously rigging the experiment to get the result that we want; this has been demonstrated in numerous studies. The parts of the experimental design that give us scope to rig the experiment are what we call **sources of bias**.

There are different types of bias in experimental research; the common sources of bias are:

- **Biases in conducting the experiment:** this is where you consciously or unconsciously treat your different experimental or control groups differently in conducting the experiment in order to get the outcome you want. For example, when you add the CaCO_3 to the HCl, you would have the tendency and the temptation to close the rubber stopper and gas syringe over the flask a little more quickly in the high temperature groups than you would in the low temperature groups, if you wanted to show that temperature is positively correlated with reaction rate.
- **Biases in measuring experimental outcomes:** this is where you may measure outcomes differently in different experimental groups to get the outcome you want. For example, when you read the volume of CO_2 produced at each 10 second interval and you could not properly tell if the volume was 20 mL or 22 mL, you would be more likely to write down "22 mL" as your data if the temperature were higher.

The central message is that **the scientific method is amazing, but science is ultimately performed by humans, who are inherently human and biased**.

- What suggestions could I make to improve the experiment?

To answer this question, think about what you could do to mitigate each of the random and systematic errors that you have identified. To eliminate **bias**, where possible it would be good to **blind** the researcher to which groups of setups are in which experimental or control group.

- Based on the findings, what **new** questions arise that deserve experimental investigation?

Remember, each experiment should raise **more questions than answers**.

The conclusion should be about **500-600 words**.

3.5 Conclusion

When you write your conclusion, ensure that you **directly** answer your research question in a **succinct** manner. Also, ensure that no further details are given (because it is not appropriate for a conclusion). For example:

This study shows that temperature is strongly positively correlated with the rate of reaction of calcium carbonate and hydrochloric acid.

Part III

Exam Tips

Doing well in your examinations is not just about learning the content and understanding it. It is essential that you express yourself **clearly and logically**, and that you **set out your working with good notation**. You want to show the examiner that you know what you are talking about, and you are not just trying to vaguely fudge an answer. Be strict with your wording. In the following sections I will give you a good technique that I use in preparing for my exams, and give you pointers on how to answer exam questions.

Advice for setting out working:

- **Specify your species.** When you are working out the amount, in mol, of for example SO₂, write n(SO₂), not simply 'n'. This way, you know exactly what you are calculating and you can read and understand your working when you go back to check your work. More importantly, the examiner will understand your working and will be able to award partial marks if you do make a mistake.
- **Make use of subscripts.** If you want to calculate, say, the amount of NaOH in excess after reaction with HCl in some chemical reaction, write n(NaOH)_{excess} instead of just n(NaOH). This way, you can differentiate between the amount of NaOH that has reacted with the HCl, the amount of NaOH that is in excess, and the amount of NaOH that was present before the reaction. Again, this makes your working more clear to you and to the examiner.
- **Be strict with your significant figures and decimal places.** Write every piece of data, including that from your data book, to the number of significant figures/decimal places that is given in the question or data book, when you do your working. With every step of working, keep each intermediate step to the appropriate number of decimal places or significant figures, **whilst using the value on your calculator to perform subsequent steps** so as to ensure you don't get rounding error. This way, you don't get tricked in terms of significant figures, and to work out the number of significant figures your final answer needs to be to, all you need to do is to look at the previous step.

KEY POINT :

If you have not done this before, it will seem slow and tedious at the start. You will find, however, that once you practise being strict with your significant figures like this, it will become second nature to you and you will make fewer mistakes.

- **Have legible handwriting.** As a person who has marked practise exams as a tutor, it gets extremely frustrating when it is extremely difficult to discern handwriting. This would put me in a bad mood and be less inclined to give you marks when it's touch and go.
- **For each step, use a new line.** This will make your working a lot more clear and easy for you to follow, and for the examiner to follow. Let's do an example together.

Question X (3 marks)

The phosphorus content of some washing powder is determined by precipitating the phosphorus as magnesium pyrophosphate (Mg₂P₂O₇). A 4.05 g sample of washing powder was treated, and 0.204 g of magnesium pyrophosphate was produced.

Determine the percentage, by mass, of phosphorous in the washing powder.

*For this question, assume all phosphorus atoms are present in the magnesium pyrophosphate.

It's always a good idea to highlight key terms. So let's do that:

Question X (3 marks)

The phosphorus content of some washing powder is determined by precipitating the phosphorus as magnesium pyrophosphate ($Mg_2P_2O_7$). A 4.05 g sample of washing powder was treated, and 0.204 g of magnesium pyrophosphate was produced.

Determine the percentage, by mass, of phosphorous in the washing powder.

Now, we know that it's 4.05 g of washing powder that has been treated and we have 0.204 g of magnesium pyrophosphate after the reaction, and we have to determine the percentage by mass of phosphorous (not phosphate or magnesium pyrophosphate).

The thinking process now is - what do we want to know to get to the answer we need? We want to determine the percentage by mass of phosphorous in the powder. I have the total mass of the powder, which is 4.05 g. That's half the information we need. The other half: what is the mass of phosphorous in the powder? Well, we know that all the phosphorous atoms originally in the powder are present in the pyrophosphate. Therefore, we need to determine the amount, in mol, of magnesium pyrophosphate. Firstly, though, we need to determine the molar mass of magnesium pyrophosphate. For this, we need to go into the periodic table. In the periodic table, you may notice that the molar masses are to 1 decimal place. If you recall, when you sum numbers, they have to be to the same number of decimal places as the least accurate piece of data. Therefore:

Question X (3 marks)

The phosphorus content of some washing powder is determined by precipitating the phosphorus as magnesium pyrophosphate ($Mg_2P_2O_7$). A 4.05 g sample of washing powder was treated, and 0.204 g of magnesium pyrophosphate was produced.

Determine the percentage, by mass, of phosphorous in the washing powder.

$$\begin{aligned} M(Mg_2P_2O_7) &= 24.3 \times 2 + 31.0 \times 2 + 16.0 \times 7 \\ &= 198.3 \text{ g mol}^{-1} \end{aligned}$$

Notice that even numbers like 31.0 I quoted to 1 decimal place, because that is exactly what was written on the periodic table. Again, quote all data exactly as per your source, whether it be the question stem or the data book. From here, you can determine the amount of magnesium pyrophosphate:

Question X (3 marks)

The phosphorus content of some washing powder is determined by precipitating the phosphorus as magnesium pyrophosphate ($Mg_2P_2O_7$). A 4.05 g sample of washing powder was treated, and 0.204 g of magnesium pyrophosphate was produced.

Determine the percentage, by mass, of phosphorous in the washing powder.

$$\begin{aligned} M(Mg_2P_2O_7) &= 24.3 \times 2 + 31.0 \times 2 + 16.0 \times 7 \\ &= 198.3 \text{ g mol}^{-1} \\ n(Mg_2P_2O_7) &= \frac{0.204}{198.3} \\ &= 1.03 \times 10^{-3} \text{ mol.} \end{aligned}$$

Note here that I specified my species (i.e. by writing ' $n(Mg_2P_2O_7)$ ' instead of just 'n'), and that I was strict with my significant figures. Every piece of data I quoted to the appropriate accuracy, and my answer so far is to the correct number of significant figures. My calculator says $1.028744327\dots \times 10^{-3}$ for this step. You use this calculator value in your subsequent steps, even though you wrote 1.03×10^{-3} in your intermediate step. This way, you avoid rounding error, yet you remember that the $1.028744327\dots \times 10^{-3}$ is really only accurate to 3 significant figures in this question.

Determining the amount and mass of phosphorous atoms:

Question X (3 marks)

The phosphorus content of some washing powder is determined by precipitating the phosphorus as magnesium pyrophosphate ($Mg_2P_2O_7$). A 4.05 g sample of washing powder was treated, and 0.204 g of magnesium pyrophosphate was produced.

Determine the percentage, by mass, of phosphorous in the washing powder.

$$M(Mg_2P_2O_7) = 24.3 \times 2 + 31.0 \times 2 + 16.0 \times 7 \\ = 198.3 \text{ g mol}^{-1}$$

$$n(Mg_2P_2O_7) = \frac{0.204}{198.3}$$

$$= 1.03 \times 10^{-3} \text{ mol.}$$

$$n(P) = 2n(Mg_2P_2O_7) \\ = 2.06 \times 10^{-3} \text{ mol.}$$

$$m(P) = 2.06 \times 10^{-3} \times 31.0 \\ = 0.0638 \text{ g.}$$

Again, I am specifying all my species, every piece of data (even the 31.0 on the second last line) is quoted exactly and every step is to the appropriate number of significant figures, whilst avoiding rounding error. Note that all my equal signs are in line - that's just a neatness thing, and it makes it easy for me and the examiner to follow. Now, the fact I highlighted the "percentage by mass of phosphorus" makes me realise I haven't finished the question! So, let's do the last part:

Question X (3 marks)

The phosphorus content of some washing powder is determined by precipitating the phosphorus as magnesium pyrophosphate ($Mg_2P_2O_7$). A 4.05 g sample of washing powder was treated, and 0.204 g of magnesium pyrophosphate was produced.

Determine the percentage, by mass, of phosphorous in the washing powder.

$$M(Mg_2P_2O_7) = 24.3 \times 2 + 31.0 \times 2 + 16.0 \times 7 \\ = 198.3 \text{ g mol}^{-1}$$

$$n(Mg_2P_2O_7) = \frac{0.204}{198.3}$$

$$= 1.03 \times 10^{-3} \text{ mol.}$$

$$n(P) = 2n(Mg_2P_2O_7) \\ = 2.06 \times 10^{-3} \text{ mol.}$$

$$m(P) = 2.06 \times 10^{-3} \times 31.0 \\ = 0.0638 \text{ g.}$$

$$\%(\text{P}) = \frac{0.0638}{4.05}$$

$$= 1.57\%.$$

Again, I am utilising the same techniques that I have been doing in the previous steps.

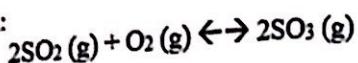
Advice for wording:

- **Use key terms.** Show the examiners that you can speak 'Chemistry'.
- **Linking words are helpful here.** Words like 'initially', 'subsequently', 'in addition' and 'however' are very useful words to use when showing relationships between the sentences you are using to explain your answer.
- **Either dot points or prose is fine,** so long as the language is clear. Personally, I prefer prose though.
- **Be concise and straight to the point.** Examiners love a beautifully worded and concise answer that hits the bullseye with one shot instead of an answer that looks like an archer had aimed millions of arrows indiscriminately at the target, hoping to get one bullseye.

Here is an example:

Question Z (3 marks)

Consider this chemical reaction:



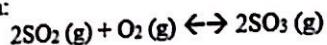
Use your understanding of reaction rates to explain what happens to the position of equilibrium when some extra oxygen is added to a closed reaction vessel containing a mixture of these three gases, initially in equilibrium.

In your head, you are aware that extra oxygen added to the reaction vessel increases the concentration of oxygen in the vessel, thereby increasing the forward reaction rate; the forward reaction rate is faster than the rate of the back reaction, and therefore the equilibrium position moves forward.

Now, how to express this clearly and concisely? This is what I would have written on the exam:

Question Z (3 marks)

Consider this chemical reaction:



Use your understanding of reaction rates to explain what happens to the position of equilibrium when some extra oxygen is added to a closed reaction vessel containing a mixture of these three gases, initially in equilibrium.

Addition of oxygen would increase its concentration in the vessel, thereby increasing the forward reaction rate (by increasing the frequency of collisions and hence successful collisions between O₂ and SO₂). The forward reaction rate is thereby faster than the rate of the back; hence, the position of equilibrium moves forward.

Notes: I used the words thereby and hence to show the logical progression between my ideas. Other words you could use are 'therefore' and 'it follows that'. I used key terms such as 'frequency of...successful collisions' to show that I understand the relationship between the concentration and the reaction rate.

Thus concludes our discussion of exam advice; hopefully this has given you some idea of how to tackle your assessment tasks. Best of luck with your VCE studies!

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