Edexcel

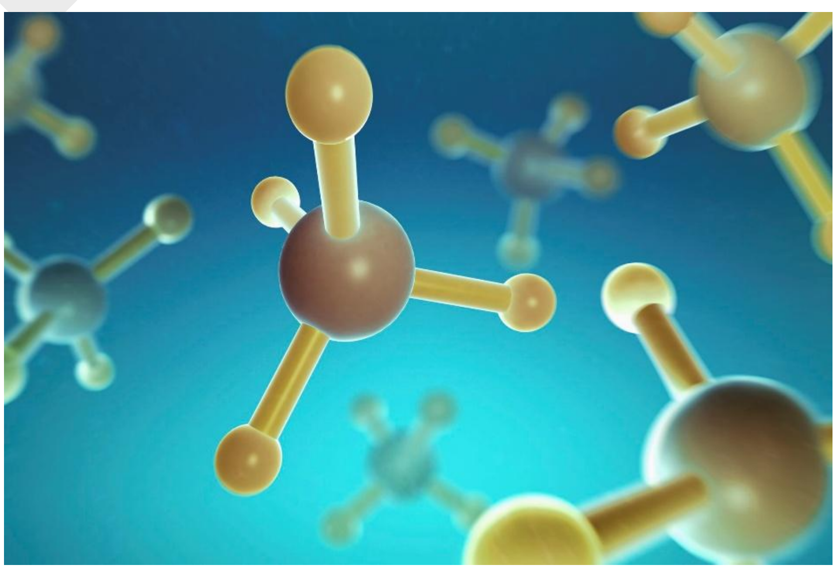
AS - Level

Chemistry

CODE: (WCH11)

Topic 4

Introductory organic chemistry and alkanes



4A – 1 What is organic chemistry?

EARLY DAYS

Since the 1800s, chemistry has been divided into inorganic, organic, and physical categories. Organic chemistry, which includes millions of compounds, has evolved to include farming and food. In the 1800s, people believed certain substances were only made in plants or animals. However, in 1828, German chemist Friedrich Wöhler discovered that urea could be made from non-organic compounds.

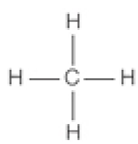
HYDROCARBONS

The main feature of an organic compound is that it contains carbon. Almost all of these compounds also contain hydrogen. Some of the most important compounds contain elements such as nitrogen and oxygen as well. In this topic, we look at some of the large numbers of compounds that contain only carbon and hydrogen. These compounds are called **hydrocarbons.**

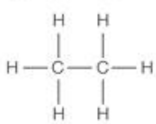
SATURATED OR UNSATURATED?

Although there are many thousands of different hydrocarbons, most of them are classed as saturated or unsaturated. Like many chemical terms, these words have a very different meaning in everyday life. Someone who has been caught in a heavy rain shower may say that their clothes are saturated, which means that they have absorbed as much water as they possibly can.

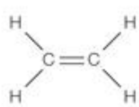
The formula of the simplest hydrocarbon, containing only one carbon atom, is:



There is a hydrocarbon that contains two carbon atoms and six hydrogen atoms, but also one that contains two carbon atoms and only four hydrogen atoms. The formulae of these hydrocarbons are:



saturated



unsaturated

You can see that in all three examples, each carbon atom has four bonds to other atoms. This is a general rule for organic compounds. In most cases, every carbon atom has four bonds. The difference between a saturated hydrocarbon and an unsaturated hydrocarbon is to do with whether or not there is room, for more hydrogen atoms.

• If there is no room, then the hydrocarbon is saturated.
• If there is room, then the hydrocarbon is unsaturated.

One easy way to decide whether a hydrocarbon is saturated or unsaturated is to look at structures like the ones above.

• If there are two bonds (a double bond) drawn between one or more carbon atoms, then the hydrocarbon is unsaturated.
• If there are only single bonds, then the hydrocarbon is saturated.

ALKANES AND CYCLOALKANES

Look at the formulae in **fig B**. These are alkanes.

▲ **fig B** Propane and butane.

Both structures have only single bonds and so are saturated.

Now look at the formulae in **fig C**. These are cycloalkanes.

▲ **fig C** Cyclopropane and cyclobutane.

SUBJECT VOCABULARY

hydrocarbon a compound that contains only carbon and hydrogen atoms
saturated a compound containing only single bonds
unsaturated a compound containing one or more double bonds

4A – 2 Different types of formulae

USING DIAGRAMS TO REFER TO ORGANIC COMPOUNDS

There are many millions of organic compounds, so making clear which ones we are referring to can be challenging. There are two main ways to refer to organic compounds. We can use:

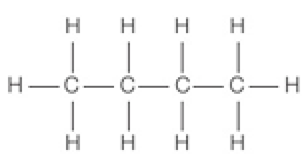
- formulae
- names.

In this topic we will consider how to refer to organic compounds using formulae.

DISPLAYED FORMULAE

The formulae you saw in Topic 4A.1 are all displayed formulae. They show (display) every atom and every bond separately. In many situations, these are the best type of formulae to use, but sometimes it is better to simplify them.

Consider the hydrocarbon with this displayed formula, its name is butane:



STRUCTURAL FORMULAE

One way to simplify this displayed formula is to group all the atoms joined to a particular carbon atom together. We can choose to show the bonds between the carbons, or we can leave them out. These are both structural formulae of butane:

$CH_3-CH_2-CH_2-CH_3$ and $CH_3CH_2CH_2CH_3$

SKELETAL FORMULAE

Another way to represent a compound is by a skeletal formula. The word skeletal is connected with the word skeleton, which, as you know, shows only the bones in a human or animal body.

A skeletal formula is a zig-zag line that shows only the bonds between the carbon atoms. Every change in direction and every ending means that there is a carbon atom (with as many hydrogen atoms as needed). Atoms other than carbon and hydrogen need to be shown.
This is the skeletal formula of butane:

The start and end both represent CH_3, and the two junctions between lines each represent CH_2.

MOLECULAR FORMULAE

The displayed, structural and skeletal formulae above show the structures of the molecules unambiguously. In other words, each formula represents only one compound. With a displayed formula, this is very clear. With a structural formula, you have to imagine how the atoms are joined together in groups such as CH_2 and CH_3, but that is very straightforward. With a skeletal formula, once you know the rules, you can be sure how every atom is arranged in the molecule.

Formulae like these are called molecular formulae. They only show the numbers of each type of atom in the molecule, and not its structure. Of course, in very simple molecules such as CHCI, the molecular formula can be used to work out the displayed, structural and skeletal formulae because there is only one way in which these five atoms can be joined together.

EMPIRICAL FORMULAE

Another type of formula is an empirical formula. This shows the compound like a molecular formula, but the numbers of each atom are in their simplest possible whole-number ratio. This means that butane (molecular formula C4H10) has an empirical formula of C2Hs.
In chemistry, the word empirical usually means 'as found from practical evidence'. You would normally work out this type of formula mathematically from the results of an experiment. You can see how we do this in Topic 1D.1.

DIFFERENT TYPES OF FORMULA FOR CHLOROETHANE

Until now, we have only considered the different types of formula using a hydrocarbon as the example.
Consider an example containing a third element (chlorine) - chloroethane. Table A shows the different types of formula for chloroethane.

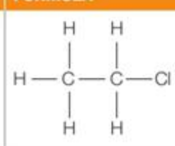
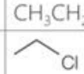
TYPE OF FORMULA	FORMULA
displayed formula	
structural formula	CH_3-CH_2-Cl or CH_3CH_2Cl
skeletal formula	
molecular formula	C_2H_5Cl
empirical formula	C_2H_5Cl

table A Different types of formula for chloroethane.

SUBJECT VOCABULARY

displayed formula shows every atom and every bond
structural formula shows (unambiguously) how the atoms are joined together
skeletal formula shows all the bonds between carbon atoms
molecular formula shows the actual numbers of each atom in the molecule
empirical formula shows the numbers of each atom in the simplest whole-number ratio

4A – 3 Functional groups and homologous series

FUNCTIONAL GROUP

A functional group in a molecule is an atom or group of atoms that gives the compound some distinctive and predictable properties. For example, the functional group of atoms shown as COOH gives substances such as vinegar a sour, acidic taste.

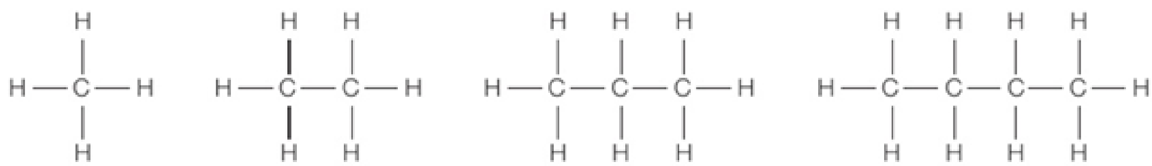
There are many organic compounds containing this group. Here are some examples:

$HCOOH$ CH_3COOH CH_3CH_2COOH $CH_3CH_2CH_2COOH$

If you look at the formulae above, you can see that each formula has one more carbon atom and two more hydrogen atoms than the previous one, they differ by CH_2.

ALKANES

The organic compounds that are mainly used as fuels are the alkanes (you will learn more about alkanes in Topic 4B). Alkanes are not considered to contain a functional group, but otherwise they form a homologous series. The displayed formulae of some alkanes are:



GENERAL FORMULAE

H-C-CC-C-H

In Topic 4A.2, we looked at five different types of formulae. Now we are going to look at another type of formula. For the compounds in a homologous series, we can use a general formula to represent all of them. This is done by using the letter n for the number of carbon atoms, excluding any in the functional group. For the compounds with formulae ending in COOH, the general formula is $C_nH_{2n+1}COOH$

Table A shows the formulae for some of the homologous series in this book.

NAME	GENERAL FORMULA	EXAMPLE
alkane	C_nH_{2n+2}	CH_4
alkene	C_nH_{2n}	C_2H_4
halogenoalkane	$C_nH_{2n+1}X$	CH_3CH_2Br
alcohol	$C_nH_{2n+1}OH$	CH_3CH_2OH

table A Examples of homologous series used in this book.

PROPERTIES OF A HOMOLOGOUS SERIES

ALKANES

We can use the alkanes to illustrate the similarity in chemical properties of a homologous series. For example, when alkanes are burned completely in air, they all form the same two products: carbon dioxide and water.

The commonest alkane is methane. The equation for the complete combustion of methane is:

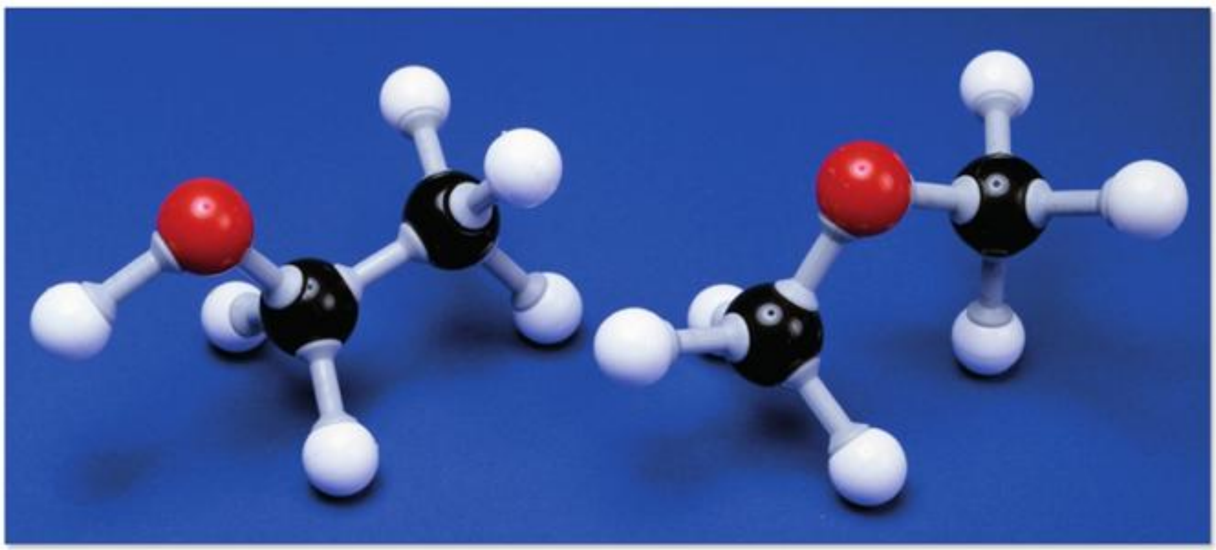
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

ALCOHOLS

We can use the alcohols to illustrate the gradation in physical properties of a homologous series. For example, the boiling temperatures of the first four alcohols are shown in **table B**.

FORMULA	BOILING TEMPERATURE / °C
CH_3OH	65
CH_3CH_2OH	79
$CH_3CH_2CH_2OH$	97
$CH_3CH_2CH_2CH_2OH$	117

table B You can see that as the number of carbon and hydrogen atoms increases, so does the boiling temperature.



▲ **fig A** Molecular models are very useful in organic chemistry. Both of these structures contain an oxygen atom (shown in red), but you can see that they belong to different homologous series.

SUBJECT VOCABULARY

functional group an atom or group of atoms in a molecule that is responsible for its chemical reactions

homologous series a family of compounds with the same functional group, which differ in formula by CH_2 from the next member

4A – 4 Nomenclature

WHY DO WE NEED RULES FOR NAMING ORGANIC COMPOUNDS?

As the number of known organic compounds has increased, it has become harder to continue to find new names for them. In Topic 4A.3, we referred to the simplest organic compound (CH4) as methane, but it was originally known as marsh gas (because it was found in marshes, where it was formed by the decay of plants). Many other organic compounds were named in similar ways.

An organisation called the International Union of Pure and Applied Chemistry (usually abbreviated to IUPAC ('eye-you-pack')) made some rules about how to name organic compounds. These rules are known as 'nomenclature'. The detailed rules needed for naming very complicated compounds are complex, but the simpler rules for the compounds described in your IAS course are much easier to understand and apply.

THE SIMPLE RULES OF NOMENCLATURE

Table A summarises the principles of naming organic compounds, including rules for **prefixes, suffixes and locants.**

THE PART OF THE NAME	HOW TO WRITE IT	EXAMPLE
Number of carbon atoms	This is shown by using a letter code (usually three or four letters).	meth = one carbon atom
Prefixes Suffixes	The presence of atoms other than carbon and hydrogen is shown by adding other letters before or after the code for the number of carbon atoms.	bromo = an atom of bromine ol = a hydroxyl group (OH)
Multiplying prefixes	The presence of two or more identical groups is shown by using the prefixes di-, tri-, etc.	di = two
Locants	Where atoms and groups can have different positions in a molecule, numbers and hyphens are used to show their positions. The numbers represent the carbon atoms in the longest chain that the atoms and groups are attached to.	2- = the atom or group is attached to the second carbon atom in the chain

table A The principles of naming organic compounds.

The letter codes for the number of carbon atoms (up to ten) are shown in **table B**.

NUMBER	CODE	PREFIX
1	meth	methyl
2	eth	ethyl
3	prop	propyl
4	but	butyl
5	pent	pentyl
6	hex	hexyl
7	hept	heptyl
8	oct	octyl
9	non	nonyl
10	dec	decyl

table B

APPLYING THE RULES TO WRITE NAMES

ALKANES

We can see how these rules work for some of the alkanes (**table C**). The names of all the alkanes end in *-ane*.

STRUCTURAL FORMULA	NAME
$CH_3-CH_2-CH_3$	propane
$CH_3-\underset{\displaystyle CH_3}{\underset{\mid}{CH}}-CH_3$	methylpropane The locant 2- is not needed because if the methyl group below the horizontal chain were attached to one of the carbon atoms at either end of the chain, then there would be a sequence of four carbon atoms, and the compound would be named butane.
$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{\mid}{CH}}-CH_2-CH_3$	3-methylpentane The longest carbon chain contains five carbon atoms, and there is a methyl group attached to the third one.
$CH_3-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{\mid}{CH}}-CH_3$	2-methylpentane This is not 4-methylpentane because another rule is that the lowest locant numbers should be used.
$CH_3-\overset{\displaystyle CH_3}{\overset{\mid}{CH}}-\underset{\displaystyle CH_3}{\underset{\mid}{CH}}-CH_3$	2,3-dimethylbutane This example shows the use of a comma between the locants when the attached groups are the same.
$CH_3-CH_2-\overset{\displaystyle CH_2-CH_3}{\overset{\mid}{CH}}-\underset{\displaystyle CH_3}{\underset{\mid}{CH}}-CH_3$	3-ethyl-2-methylpentane This example illustrates the rule about prefixes being in alphabetical order. Ethyl comes before methyl because e comes before m in the alphabet. Notice also that it is not called 3-ethyl-4-methylpentane because these numbers (3 + 4) total more than the numbers 3 + 2 in the correct name.

table C Naming alkanes from structural formulae using the rules of IUPAC nomenclature.

ALCOHOLS

Next, look at the alcohols in **table D**. The rules for these are a bit different because the presence of the alcohol functional group is indicated by a suffix, not a prefix. The names for all the alcohols end in *-ol*.

STRUCTURAL FORMULA	NAME
CH_3-CH_2-OH	ethanol
$CH_3-CH_2-CH_2-OH$	propan-1-ol This time, the locant appears near the end of the name, but, as before, it appears directly before the letters representing the group.
$CH_3-\underset{\displaystyle OH}{\underset{\mid}{CH}}-\underset{\displaystyle CH_3}{\underset{\mid}{CH}}-CH_3$	3-methylbutan-2-ol This example illustrates the use of both a prefix and a suffix. This is not called 2-methylbutan-3-ol because the lowest number locant should be used for the suffix functional group (-2-ol not -3-ol).
$CH_3-\overset{\displaystyle CH_3}{\overset{\mid}{\underset{\displaystyle CH_3}{\underset{\mid}{C}}}}-CH_2-CH_2-OH$	3,3-dimethylbutan-1-ol This example shows the use of prefixes, a suffix, locants and a comma. As with alkanes, the name uses locants that add up to the smallest possible number.

table D Naming alcohols from structural formulae using the rules of IUPAC nomenclature.

APPLYING THE RULES TO WRITE FORMULAE

Table E gives some examples of applying the rules the other way round, i.e. writing a structural formula for a compound from its IUPAC name.

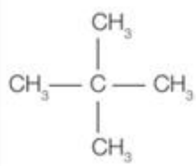
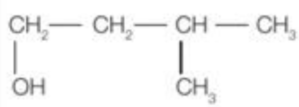
NAME	STRUCTURAL FORMULA
dimethylpropane	*prop* indicates a chain of three carbon atoms *dimethyl* indicates two methyl groups attached to the chain No locants are used, so the two methyl groups must be attached to the carbon chain in a way that does not make the longest carbon chain any longer than three carbon atoms. So the structural formula is: 
3-methylbutan-1-ol	*but* indicates a chain of four carbon atoms *methyl* indicates a CH_3 group *1-* and *3-* indicate attachments to the first and third carbon atoms in the chain So the structural formula is: 

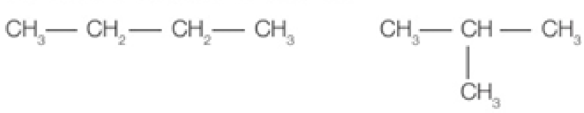
table E Writing structural formulae from IUPAC names.

SUBJECT VOCABULARY

prefix a set of letters written at the beginning of a name
suffix a set of letters written at the end of a name
locant a number used to indicate which carbon atom in the chain an atom or group is attached to

4A – 5 Structural isomerism

Consider these two structures:



butane methylpropane

You can see that they are different compounds because their names and structures are different. However, their molecular formulae are the same. They can both be represented by C_4H_{10} These two compounds are simple examples of **structural isomers.**

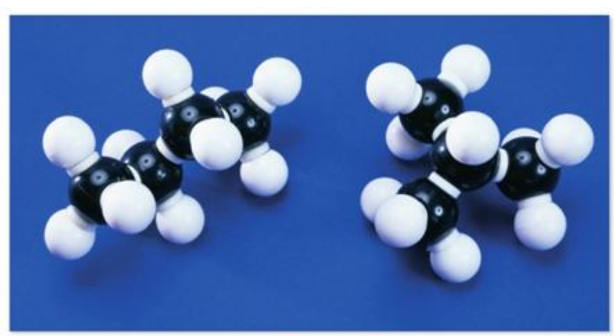


fig A By counting the atoms you can see that both structures have the molecular formula C_4H_{10}.

TYPES OF STRUCTURAL ISOMERISM

There are two important types of structural isomerism.

CHAIN ISOMERISM

Chain isomerism refers to molecules with different carbon chains. Butane and methylpropane (shown in fig A above) are examples of chain isomers because their carbon chains are different.

POSITION ISOMERISM

Position isomerism refers to molecules with the same functional group attached in different positions on the same carbon chain. Propan-1-ol and propan-2-ol are simple examples of position isomerism:

propan-1-ol propan-2-ol

They are examples of position isomers because the carbon chains are the same, but the OH groups are attached to different carbon atoms in the chain.

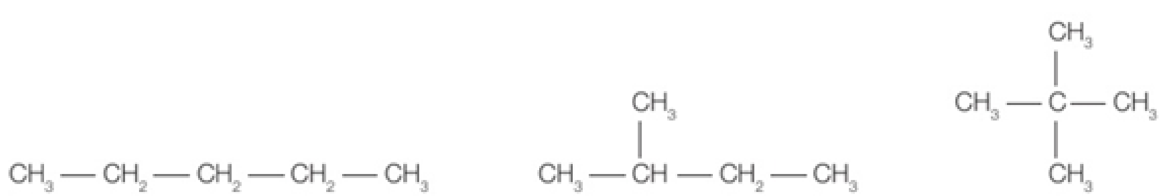
You might see examples where both of these types of isomerism are present:

DRAWING STRUCTURAL ISOMERS FROM MOLECULAR FORMULAE

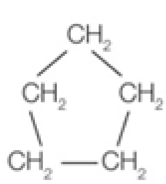
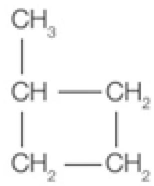
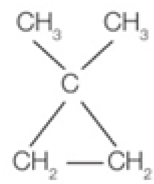
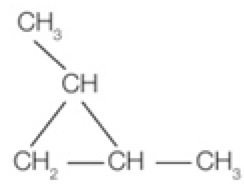
Molecular formulas display the atoms' actual arrangement, but not their arrangement. To draw a structure, use structural formulae, which show carbon and other atoms separately with bonds. Group hydrogen atoms together for simplicity. Start by showing carbon atoms in a straight line, then show other atoms in various ways, starting with atoms other than hydrogen. Consider using shorter chains with branches for additional atoms.

ALKANES AND CYCLOALKANES

You need to be able to draw the structures of all the alkanes and cycloalkanes with up to six carbon atoms. You have already seen structures of some examples of these homologous series, but now let us adapt the method we used for the structures of C_4H,Cl_2.



Now for the cycloalkanes. There can be a ring of 5 carbon atoms; or a ring of 4 carbon atoms with the 5th carbon atom attached to any one of the 4; or a ring of 3 carbon atoms with the 4th and 5th attached to the same or different carbons in the ring. Remember that each carbon atom must have 4 bonds, and the total number of hydrogen atoms must be 10. These are the possibilities.

SUBJECT VOCABULARY

structural isomers compounds with the same molecular formula but different structural formulae

4A – 6 Types of reaction

REACTIONS IN ORGANIC CHEMISTRY

In later topics of this book, you will learn about many different reactions and see many equations to represent these reactions. It will help if you can recognise these reactions as belonging to one of five main types. There is much more detail about these reactions in later topics (for example, Topic 10).

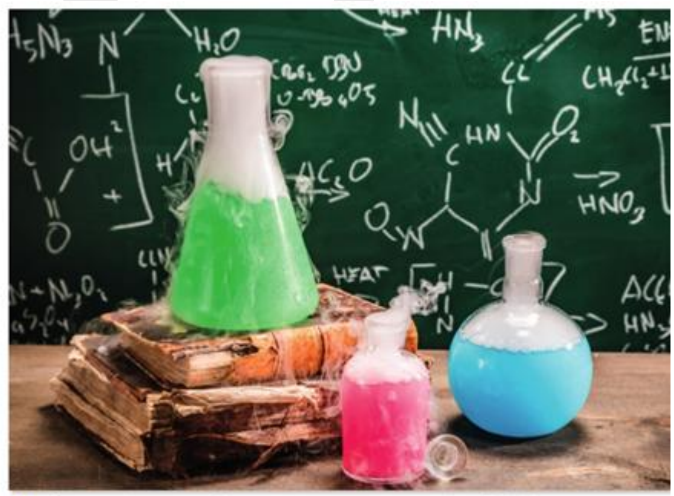


fig A What types of reaction are occurring in these flasks?

ADDITION REACTIONS

In an addition reaction, two reactant species combine together to form a single product species. Usually all the species are molecules. A general equation for this type of reaction is:

$$A + B \rightarrow C$$

One example is the reaction between ethene and bromine:

$$C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$$

SUBSTITUTION REACTIONS

In a substitution reaction, two reactant species combine together to form two product species. Usually all the species are molecules or ions. A general equation for this type of reaction is:

$$A + B \rightarrow C + D$$

OXIDATION REACTIONS

In an oxidation reaction, one organic compound is oxidised, usually by an inorganic reagent. This means that the organic compound can either lose hydrogen or gain oxygen. There is not a suitable general equation that can be used for this type of reaction, but here is one example you will find in Topic 10- the oxidation of ethanol by a mixture of potassium dichromate (VI) and sulfuric acid. The equation is not written to include the inorganic reagent as it would be very complicated. Usually, the oxygen atoms produced by the oxidising agent are shown using the symbol [O], so the equation then becomes:

$$C_2H_5OH + [O] \rightarrow CH_3CHO + H_2O$$

This reaction is classified as oxidation because the ethanol molecule loses two hydrogen atoms.

REDUCTION REACTIONS

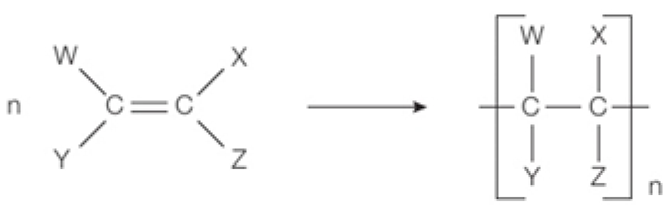
In a reduction reaction, one organic compound is reduced, sometimes by hydrogen gas and a catalyst and sometimes by an inorganic reagent. This means that the organic compound can either gain hydrogen or lose oxygen. There is not a suitable general equation that can be used for this type of reaction, but here is one example you will find in Topic 5A.3. This is the reduction of an alkene to an alkane by hydrogen gas and a nickel catalyst. The equation for the reaction is:

$$C_2H_4 + H_2 \rightarrow C_2H_6$$

You can now see why this reaction is classified as reduction. The ethene molecule gains two hydrogen atoms. Note that this is also an example of an addition reaction.

POLYMERISATION REACTIONS

In this book, all the polymerisation reactions you will meet are examples of addition polymerisation. In addition polymerisation, very large numbers of a reactant molecule (sometimes of two different reactant molecules) react together to form one very large product molecule. A general equation for this type of reaction is:



A familiar example of this type of reaction is the polymerisation of ethene to poly(ethene).

BOND BREAKING IN ORGANIC REACTIONS

Organic compounds contain covalent bonds, for example between

- two carbon atoms
- a carbon atom and a hydrogen atom
- a carbon atom and a halogen atom.

There are two different ways for the covalent bond to break. These are homolytic fission and heterolytic fission.

HOMOLYTIC FISSION

Like many other scientific terms, 'homolytic' comes from Greek: 'homo' indicates 'same' and 'lytic' indicates 'splitting'.

In homolytic fission, the shared pair of electrons in the covalent bond divide equally between the two atoms. This can be shown like this:

$$\mathrm{C}\overset{\times}{\bullet}\mathrm{C} \longrightarrow \mathrm{C}^{\times} + {}^{\bullet}\mathrm{C}$$

Each product species keeps one of the electrons from the covalent bond. These species are called free radicals. Each free radical has an unpaired electron and is uncharged.

Homolytic fission usually occurs when the two atoms bonded together are identical or when they have similar electronegativities.

HETEROLYTIC FISSION

'Heterolytic' is another term from Greek: 'hetero' indicates 'different' and 'lytic' indicates 'splitting'.

In heterolytic fission, both electrons of the shared pair in the covalent bond are kept by one of the atoms. This can be shown like this:

$$\mathrm{C}\overset{\times}{\bullet}\mathrm{C} \longrightarrow \mathrm{C}\overset{\times}{\bullet} + \mathrm{C}$$

The left-hand product species keeps both of the electrons from the covalent bond. This species is a negative ion. The right-hand product species does not keep either of the electrons from the covalent bond. This species is a positive ion.

$$\mathrm{C}\overset{\times}{\bullet}\mathrm{C} \longrightarrow \mathrm{C} + \overset{\times}{\bullet}\mathrm{C}$$

Here there are still two ions formed, but this time the right-hand product is the negative ion.

ELECTROPHILES

The origin of the term electrophile is 'electron', which indicates negative charge, and 'phile', which means liking. You may have come across the word 'bibliophile', which means a person who likes books. An electrophile refers to a chemical species that 'likes negative charge'. So how does this term fit in with this topic? You remember that opposite charges (positive and negative) attract each other. The positive ion produced by heterolytic fission will be attracted to a region of high electron density in another molecule. This region is often labelled with the symbol 8-. You will learn much more about electrophiles and their importance in reaction mechanisms in Topic 5A.4.

SUBJECT VOCABULARY

addition reaction reaction in which two molecules combine to form one molecule

substitution reaction reaction in which one atom or group is replaced by another atom or group

oxidation reaction reaction in which a substance gains oxygen or loses hydrogen

reduction reaction reaction in which a substance loses oxygen or gains hydrogen

polymerisation reaction reaction in which a large number of small molecules react together to form one very large molecule

homolytic fission the breaking of a covalent bond where each of the bonding electrons leaves with one species, forming a free radical

heterolytic fission the breaking of a covalent bond so that both bonding electrons are taken by one atom

free radical a species that contains an unpaired electron

electrophile a species that is attracted to a region of high electron density

4A – 7 Hazards, Risks and risk assessment

SAFETY IN CHEMISTRY LABORATORIES

Incidents that cause harm to people are rare in school and college laboratories. One of the reasons for this is that laboratories need to consider the hazards of doing chemistry experiments and use safe methods of working.
This applies to all chemistry experiments, but especially to those involving organic compounds. It is particularly important in experiments that you plan yourself, but also for those where you are following a method you have been given.
When you plan an organic synthesis, you need to consider the hazards associated with the reactants, the substance you are synthesising, and also any intermediates formed.

HAZARD AND RISK

The hazard of a chemical substance relates to the inherent properties of the substance. The risk is more to do with how you plan to use it and the chance of it causing harm. Most people would consider that water is completely safe and has no hazards. In most situations, this is the case. However, consider a beaker of water being boiled on a tripod and gauze. The steam coming from the water, and the boiling water itself, could both cause harm if they came into contact with your skin.

HAZARD WARNING SYMBOLS

A long time ago, bottles containing certain chemicals were labelled with the word POISON. This early attempt to prevent harm to laboratory workers was well-intentioned, but some people might think that bottles without such a label contained harmless substances.

Older ones are often square in shape with an orange background such as these:

The symbols in current use are red diamond shapes. One department of the United Nations Organisation has developed these GHS labels for international use. 'GHS' is an abbreviation for Globally Harmonised System of Classification and Labelling of Chemicals, and the use of these labels is spreading throughout the world.

Table A shows some of the more common ones, and includes a short description of their meanings.

SYMBOL	MEANING	
	Health hazard	includes warning on skin rashes, eye damage and ingestion
	Corrosive	can cause skin burns and permanent eye damage
	Flammable	can catch fire if heated or comes into contact with a flame
	Acute toxicity	can cause life-threatening effects, even in small quantities

table A Some pictograms used for chemical hazards.

In some cases, the substance may have more than one symbol, especially when it is an aqueous solution. For example, you are likely to use hydrochloric acid in three different concentrations:

- in a titration, it may have a concentration of about 0.1 mol dm-3
- as a general laboratory reagent, it may have a concentration of 1 or 2 mol dm-3

- for some purposes, you may use concentrated hydrochloric acid with a concentration of more than 10 mol dm3.

These very different concentrations have different hazards.

RISK ASSESSMENTS AND CONTROL MEASURES

The person in charge of a laboratory (or any other place of work) is responsible for making risk assessments. First, they look at the hazards of all the chemical substances, being guided by the hazard symbols. Then they consider the ways in which these substances will be used (this is assessing the risk). Finally, they write some guidelines for those who use the laboratory (these are the control measures).

Such guidelines will consider many different factors, including:

- the amount used
- the age and experience of the person using it
- whether it will be heated
- whether ventilation or a fume cupboard should be used.

The control measures may refer to:

- the type of eye protection that should be worn
- the need to wear gloves
- keeping the cap on the bottle after removing some of the substance
- keeping the substance away from a source of heat
- what to do if some of the substance is spilled on the floor or gets on the skin.

Remember that there are also hazards and risks in your home. Many cleaning materials contain hazardous materials. Fig A shows a warning label for a household oven cleaner.

fig A You may find examples of hazards, risks and control measures in your home.

Apparatuses

In chemistry laboratories, certain apparatuses may pose hazards, such as mercury thermometers containing hazardous substances, and heating methods like Bunsen burners and tripods. Electrical heating mantles are safer and easier to use. Glass apparatuses, used for techniques like distillation, have evolved from traditional tubing to ground glass joints, making them less hazardous due to assembly risks.

SUBJECT VOCABULARY

hazard something that could cause harm to a user
risk the chance of a hazard causing harm
risk assessment the identification of the hazards involved in carrying out a procedure and the control measures needed to reduce the risks from those hazards

4B – 1 Alkanes from crude oil

THE NEED FOR FUELS

The worldwide demand for energy is huge and steadily rising. At present, most of this energy comes from burning fossil fuels, in the form of coal, crude oil and natural gas. Most compounds in crude oil and natural gas are alkanes. fig A Petrol is just one product of crude oil but is perhaps the best known.

In this topic we will look at the three main processes used to convert crude oil into fuels.
They are:

- fractional distillation
- cracking
- reforming.

These processes are used in oil refineries located all over the world. You will already know something about fractional distillation, but you may be less familiar with cracking and reforming.

FRACTIONAL DISTILLATION

Crude oil is a complex mixture of compounds, mostly hydrocarbons. The composition of the mixture varies quite a lot depending on which part of the world the crude oil comes from. The process is sometimes called 'fractionation' because it involves converting the crude oil into a small number of fractions. The number of fractions varies between different refineries but is typically six. Fractionation is done in a distillation column.

THE PROCESS

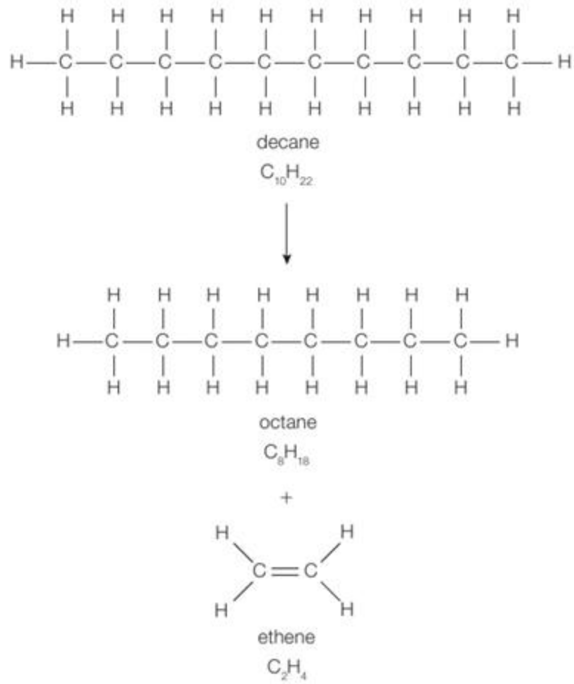
The crude oil is first heated in a furnace, which turns most of it into vapour, which is then passed into the column near the bottom. There is a temperature gradient in the column: it is hotter near the bottom and cooler near the top.
As the vapour passes up the column through a series of bubble caps, different fractions condense at different heights in the column, depending on the boiling temperature range of the molecules in the fraction.
• Near the bottom of the column, the fractions contain larger molecules with longer chains and higher boiling temperatures.
• Near the top of the column, the fractions contain smaller molecules with shorter chains and lower boiling temperatures.
• Some of the hydrocarbons in crude oil are dissolved gases, and they rise to the top of the column without condensing.
Some fractions still contain many different compounds, so they may undergo further fractional distillation separately.

CRACKING

The world has fewer uses for longer-chain hydrocarbons so there is a surplus of these. The demand for shorter-chain hydrocarbons is much higher because they are better fuels and can be used to make other substances such as polymers. Unfortunately, there are not enough of these to satisfy the demand. The solution is to convert the longer chains into shorter chains, which is what happens in cracking.

THE PROCESS

Cracking is done by passing the hydrocarbons in the heavier (longer chain) fractions through a heated catalyst, usually of zeolite, which is a compound of aluminium, silicon and oxygen. This causes larger molecules to break up into smaller ones. From one large molecule, at least two smaller molecules are formed. A good example is the cracking of decane into octane and ethene:

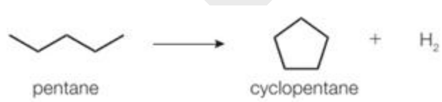


REFORMING

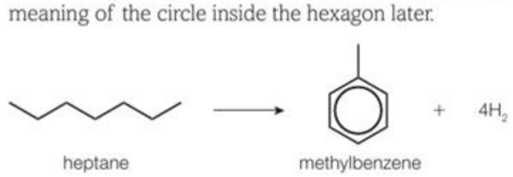
So far, we haven't mentioned one important point about the alkanes used as fuels. During the very rapid combustion that occurs in vehicle engines, not all hydrocarbons of the right size burn in the same way. Those with straight chains burn less efficiently than those with branched chains and those with rings (cyclic compounds). The process of reforming is used to convert straight-chain alkanes into branched-chain alkanes and cyclic hydrocarbons by heating them with a catalyst, usually platinum. This helps them to burn more smoothly in the engine.

EXAMPLES

Here are some examples of reforming reactions, using skeletal formulae.
In the first one, pentane (C,H12) is converted into a cyclic alkane:



In the second one, heptane (C_7H_{16}) is converted into methylbenzene, which is a cyclic hydrocarbon but not an alkane. You will learn the meaning of the circle inside the hexagon later.



In each example, hydrogen is formed. It is a useful by-product.

SUBJECT VOCABULARY

fractional distillation the process used to separate a liquid mixture into fractions by boiling and condensing
cracking the breakdown of molecules into shorter ones by heating with a catalyst
reforming the conversion of straight-chain hydrocarbons into branched-chain and cyclic hydrocarbons
temperature gradient the way in which the temperature changes up and down the column

4B – 2 Alkanes as fuels

THE COMPLETE COMBUSTION OF ALKANES

As we mentioned earlier, alkanes can burn. They are burned in vast quantities to provide the world's energy. For example, propane is sold in containers at high pressure for use as a fuel, both in homes and when camping. The equation for its **complete combustion** is:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

THE PRODUCTS OF COMBUSTION

One of the products of combustion is water, which is not a problem as it simply adds to the total quantity of global H_2O.

The other product is carbon dioxide. As you know, this is a greenhouse gas and most scientists consider its increasing production to be responsible for global warming, climate change and other problems.

INCOMPLETE COMBUSTION

Sometimes the combustion of an alkane is incomplete because there is not enough oxygen present, or because the combustion is very rapid. All of the hydrogen atoms in an alkane molecule are converted into water, but some of the carbon atoms can form gaseous carbon monoxide or solid carbon. These products can cause problems.

CARBON

You can often see when **incomplete combustion** forms solid carbon. This can be seen as smoke in the air or soot on the burner. One example of an equation for a reaction in which carbon is formed is:

$$C_3H_8 + 4O_2 \rightarrow C + 2CO_2 + 4H_2O$$

Notice that in this reaction two of the carbon atoms in propane undergo complete combustion and one does not. Tiny particles of carbon in the atmosphere can be harmful, but there is another product of combustion that can be fatal.

CARBON MONOXIDE

Carbon monoxide is a toxic gas that causes the death of many people each year. It acts by preventing the transport of oxygen around the body. It is colourless and odourless, so people breathe it into their lungs without knowing, which is why it is sometimes described as 'the silent killer'. Here is an example of an equation for a reaction in which carbon monoxide is formed:

$$C_3H_8 + 4O_2 \rightarrow 2CO + CO_2 + 4H_2O$$

UNBURNED HYDROCARBONS

The ultimate example of incomplete combustion is when the hydrocarbon does not burn at all. A small proportion of the hydrocarbons in a fuel are released into the atmosphere unchanged. They are known as unburned hydrocarbons (sometimes abbreviated to UHC).

OXIDES OF SULFUR

Some of the molecules in crude oil contain atoms of sulfur, and these may not be removed by the fractional distillation, cracking or reforming processes. During the combustion of alkanes, these atoms of sulfur form sulfur dioxide gas, and then can react in the atmosphere to form sulfur trioxide gas. The equations for these reactions are:

$S + O_2 \rightarrow SO_2$ and $2SO_2 + O_2 \rightarrow 2SO_3$

Both sulfur gases are acidic oxides. When they dissolve in water in the atmosphere, they form sulfurous acid and sulfuric acid:

$SO_2 + H_2O \rightarrow H_2SO_3$ and $SO_3 + H_2O \rightarrow H_2SO_4$

Both acids contribute to the formation of acid rain. Acid rain is responsible for a lot of environmental damage, including damage to aquatic life in lakes and rivers, and damage to crops and forests.

OXIDES OF NITROGEN

Although very few molecules used as alkane fuels contain atoms of nitrogen, their combustion occurs at very high temperatures. Under these conditions, especially around the spark plugs in cars, these very high temperatures cause nitrogen molecules in the air to react with oxygen molecules.

At very high temperatures, the main reaction is:

$$N_2 + O_2 \rightarrow 2NO$$

However, nitrogen monoxide can then react with more oxygen in the atmosphere as follows:

$$2NO + O_2 \rightarrow 2NO_2$$

Nitrogen dioxide is acidic and can dissolve in water in the atmosphere, forming nitrous acid and nitric acid:

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

Both acids contribute to environmental damage in the same way as sulfurous acid and sulfuric acid.

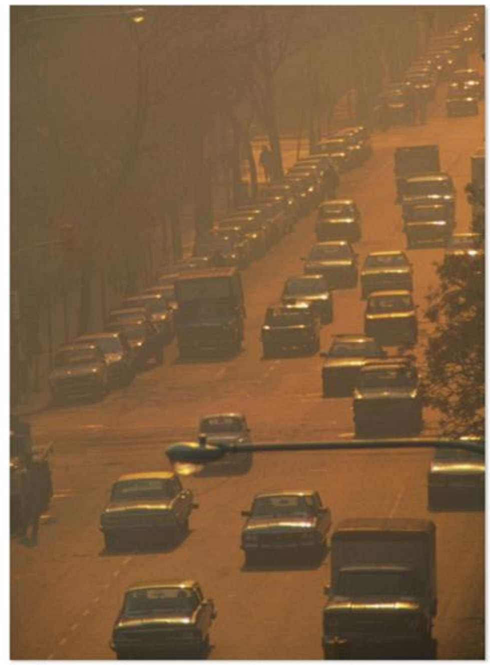


fig A Air pollution is a growing problem in many cities.

CATALYTIC CONVERTERS TO THE RESCUE

Cars and other road vehicles are responsible for a lot of air pollution. The widespread use of catalytic converters fitted to exhaust systems has made pollution less of a problem.

There are different types of catalytic converter, but they all use small quantities of precious metals such as platinum, rhodium and palladium. These metals are spread thinly over a honeycomb mesh to increase the surface area for reaction (and also to save money).

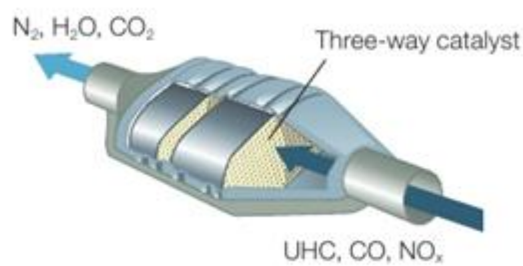


fig B A three-way catalytic converter.

Examples are the oxidation of the carbon monoxide and the oxidation of unburned hydrocarbons:

$$2CO + O_2 \rightarrow 2CO_2 \quad \text{and} \quad C_8H_{18} + 12\tfrac{1}{2}O_2 \rightarrow 8CO_2 + 9H_2O$$

Here is another useful reaction that removes two pollutants at the same time:

$$2NO + 2CO \rightarrow N_2 + 2CO_2$$

SUBJECT VOCABULARY

combustion a chemical reaction in which a compound reacts with oxygen

complete combustion reaction in which all of the atoms in the fuel are fully oxidised, producing only carbon dioxide and water

incomplete combustion reaction in which some of the atoms in the fuel are not fully oxidised, producing carbon dioxide, carbon monoxide and soot (unburnt carbon)

4B – Alternative fuels

THE NEED FOR ALTERNATIVE FUELS

There are serious concerns about relying on the combustion of fossil fuels to produce energy. We have already considered the pollution caused by the combustion of alkanes.
The other concerns are:

- the depletion of natural resources
- global warming and climate change.

Recently, there have been attempts to produce new fuels as alternatives to fossil fuels. Most of these fuels can be described as biofuels, which means that they are obtained from living matter that has died recently, rather than having died many millions of years ago. A wide definition of biofuels would include wood, which has been used as a fuel for many centuries and is still important in some countries today.

CARBON NEUTRALITY

Fuels can be considered in terms of their carbon neutrality. Ideally, a fuel should be completely carbon neutral, although few are. The closer a fuel is to being carbon neutral, the better.

WHAT DOES CARBON NEUTRAL MEAN?

'Carbon neutral' is a term used to represent the idea of carbon dioxide neutrality. For example, when a tree grows, it absorbs carbon dioxide from the atmosphere, and the carbon atoms become part of the structure of the tree. If the tree is cut down and the wood is burned, then carbon dioxide is formed during its combustion. If the amount of carbon dioxide formed in the combustion is the same as the amount absorbed during the tree's growth, then the wood used is described as carbon neutral. This is because, over the time period between the tree starting to grow and the use of its wood as a fuel, the amount of carbon dioxide in the atmosphere has not been altered by its combustion.

BIOALCOHOLS

You might think that bioalcohols are carbon neutral fuels because they are made from recently-grown plants that have absorbed carbon dioxide from the atmosphere. However, this does not recognise the fact that the plants have to be harvested, transported to a factory and processed in the factory, and the products transported to a point of sale.

BIOETHANOL

Currently, the commonest bioalcohol is bioethanol. Remember that bioethanol and ethanol are not different compounds. Bioethanol is identical to ethanol. The 'bio' part of the name only refers to the method of production. For centuries, ethanol has been produced by the fermentation of sugars. This involves the use of yeasts that contain enzymes, but there is an upper limit to the concentration of the ethanol in the solution. The ethanol has to be separated from the much larger amount of water before it can be used as a fuel, and this separation requires energy.

COMPARING FUELS

BIOFUELS

The choice of alternative fuels is continually changing, as new sources of starting material and new processing methods are investigated. There are many factors to consider in any comparison, but for biofuels such as bioethanol these include the following.

• Land use - how much land is used to grow the crop? Should the land be used for other purposes, especially to grow food to feed people?
• Yield - how much of a crop can be grown on a given piece of land, and how quickly does it grow? What percentage of the carbon and hydrogen atoms in the crop ends up in the fuel?
• Manufacture and transport - how much energy is used in growing (including any fertilisers), processing and transporting the crop?
• Carbon neutrality - how close is the fuel to being carbon neutral?

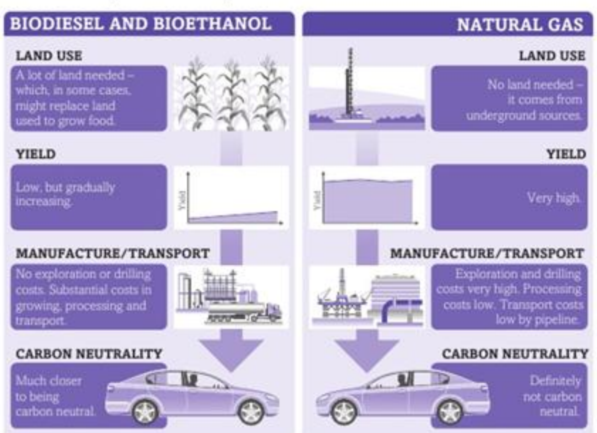
HYDROGEN

For a long time, hydrogen has been considered an ideal alternative fuel, although it is not a biofuel. There are two main ways in which hydrogen can be used as a fuel in cars:
• it can be burned instead of a fossil fuel such as petrol or natural gas
• it can be used in a fuel cell to generate electricity that powers an electric motor.

Using a hydrogen fuel cell or burning hydrogen instead of a hydrocarbon in a car seems promising. No carbon dioxide is produced, which suggests no increase in the greenhouse effect. Hydrogen is very common, and is much more abundant than carbon in the Earth's crust. However, nearly all hydrogen is present in the water molecules in the oceans.

FOSSIL FUELS AND BIOFUELS

You should also be able to compare fossil fuels with biofuels. Here is one example of a comparison between such fuels.



▲ **fig C** Comparing bioethanol with natural gas as fuels for cars.

SUBJECT VOCABULARY

biofuel fuel obtained from living matter that has died recently
bioalcohol fuel made from plant matter, often using enzymes or bacteria
carbon neutral a considered net zero effect on the amount of carbon dioxide in the atmosphere

4B – 4 Substitution reactions of alkanes

WHAT IS A SUBSTITUTION REACTION?

You already know that the most common use of alkanes is as fuels. Combustion reactions are very important in producing energy, but are not very interesting from a chemist's point of view. This topic will give you a chance to increase your understanding of other reactions in organic chemistry.

There is a type of reaction that alkanes undergo, called a substitution reaction, which we will now look at in detail. Here is the equation for a reaction of the simplest alkane, methane:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

MECHANISMS

A mechanism tries to explain the actual changes that occur during a reaction, especially in the bonding between the atoms. A mechanism is a sequence of two or more steps, each one represented by an equation, that shows how a reaction takes place.

THE CHLORINATION OF METHANE

When methane is only mixed with chlorine, no reaction occurs. If the temperature is increased, a reaction eventually occurs. However, the reaction will occur at room temperature if the mixture is exposed to ultraviolet radiation (or sunlight). We know that alkanes are not affected by ultraviolet radiation, but that ultraviolet radiation can affect chlorine.

STEP 1

Ultraviolet radiation breaks the chlorine molecule into chlorine atoms. As the bond in the chlorine molecule consists of a shared pair of electrons, which are equally shared between the two atoms, then each chlorine atom takes one electron from the shared pair. This kind of bond breaking is called **homolytic fission**, a type of reaction you met in **Topic 4A.6**.

Step 1 can be represented in an equation:

$$Cl_2 \rightarrow Cl\bullet + Cl\bullet$$

However, it is better to use a different type of equation that shows clearly what happens to the electrons in the Cl–Cl bond.

$$Cl{:}Cl \rightarrow Cl^{\bullet} + {}_{\bullet}Cl$$

The dots on the products each represent an unpaired electron. The formula Cl• does not represent an ion or a molecule; the term **free radical** (sometimes just radical) is used for it. A free radical is a species with an unpaired electron.

This equation above shows the original shared pair of electrons in the Cl–Cl bond. Each curly half-arrow shows what happens to the electrons. The upper arrow shows that one electron stays with the left-hand chlorine. The lower arrow shows that the other electron stays with the right-hand chlorine. Notice that the equation involves one molecule forming two free radicals. This type of reaction is called **initiation**, which means it starts the sequence of steps that forms the overall reaction.

STEP 2

Chlorine free radicals are very reactive species and when they collide with methane molecules they react by removing a hydrogen atom. An equation for this process is:

$$Cl\bullet + CH_4 \rightarrow HCl + CH_3\bullet$$

Notice that $CH_3\bullet$ is formed. This is a methyl free radical and, like $Cl\bullet$, it is also very reactive. It can then react with chlorine molecules as follows:

$$CH_3\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet$$

In this reaction, the methyl free radical removes a chlorine atom from a chlorine molecule, forming chloromethane and a chlorine free radical.

Notice that these two equations both involve one free radical reacting with one molecule, and that the products are also one free radical and one molecule. This type of reaction is called **propagation**, which means that the two steps considered together result in the conversion of CH_4 into the product CH_3Cl.

STEP 3

With all these free radicals being formed, it is likely that two of them will collide with each other. When this happens, they react to form a molecule, as the two unpaired electrons are shared to form a covalent bond. As there are two different free radicals available, this means that there are three possibilities:

$$Cl\bullet + Cl\bullet \rightarrow Cl_2$$

$$Cl\bullet + CH_3\bullet \rightarrow CH_3Cl$$

$$CH_3\bullet + CH_3\bullet \rightarrow C_2H_6$$

These three equations all involve two free radicals reacting with each other to form one molecule. This type of reaction is called termination. This means that the sequence of reactions comes to an end because two reactive species are converted into unreactive species.

FURTHER SUBSTITUTION REACTIONS

You now know that a hydrogen atom in methane can be replaced by a chlorine atom in a substitution reaction. You can also see that the product chloromethane (CH3Cl) still contains hydrogen atoms. These three hydrogen atoms can also be replaced, one by one, by chlorine atoms in similar substitution reactions.

It is not easy to prevent these further substitution reactions from occurring. As well as the formation of chloromethane, these other reactions occur and other products are formed:

the formation of dichloromethane
$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$

the formation of trichloromethane
$$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$$

the formation of tetrachloromethane
$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$$

SUBJECT VOCABULARY

substitution reaction reaction in which an atom or group is replaced by another atom or group

mechanism the sequence of steps in an overall reaction; each step shows what happens to the electrons involved in bond breaking or bond formation

homolytic fission the breaking of a covalent bond where each of the bonding electrons leaves with one species, forming a free radical

free radical a species that contains an unpaired electron

initiation first step that starts the reaction, involving the formation of free radicals, usually as a result of bond breaking caused by ultraviolet radiation

propagation the two steps that, when repeated many times, convert the starting materials into the products of a reaction

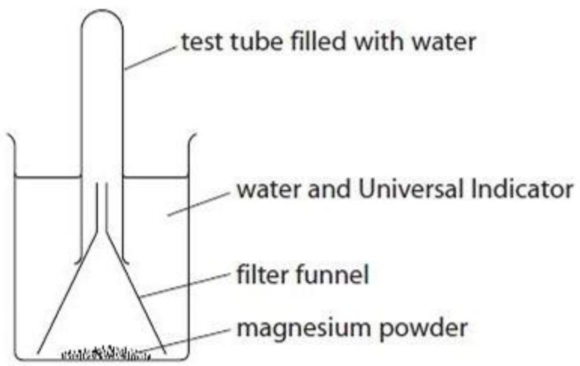
termination final step that involves the formation of a molecule from two free radicals, halting the reaction

Revision questions

1. A white solid was thought to be barium carbonate. A student suggested that the presence of the carbonate ion could be tested for by adding a small amount of sulfuric acid. Explain whether or not this suggestion is valid.

2. This question is about the elements in Group 2 of the Periodic Table. Explain how the trend in the reactivity of the Group 2 elements is determined by their electronic configurations.

3. This question is about the elements in Group 2 of the Periodic Table. Magnesium powder is added to a beaker of water containing a few drops of Universal Indicator. The apparatus is set up as shown and allowed to stand for a few days.



State two changes that will be seen after a few days.

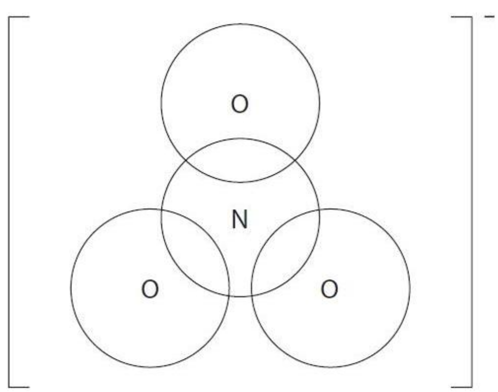
4. Explain whether magnesium carbonate is more or less thermally stable than barium carbonate.

5. This question is about s-block elements and some of their compounds.

The s-block nitrates undergo thermal decomposition.

(i) Draw a dot-and-cross diagram for the nitrate(V) ion, NO_3^-, showing outer electrons only.

(1)



(ii) Write an equation for the thermal decomposition of lithium nitrate.
State symbols are **not** required.

(1)

6. This question is about s-block elements and some of their compounds. A textbook states, 'The thermal stability of Group 1 carbonates is generally higher than the thermal stability of Group 2 carbonates in the same period'. Explain why Group 1 carbonates are more thermally stable than Group 2 carbonates.

7. This question is about trends within Group 2 of the Periodic Table. Describe, with the aid of a labelled diagram, how you would compare the thermal stability of two different Group 2 nitrates using simple laboratory equipment. Your answer must include one safety precaution (excluding the use of gloves, laboratory coat and eye protection).

8. A solid, white, water-soluble compound was thought to be magnesium bromide. A student carried out tests to confirm the identity of both ions present. A flame test was carried out to test for the cation.

(i) Describe how a flame test is carried out.

(ii) Explain the origin of flame test colours.

(iii) Give a reason why the magnesium ion does not produce a flame colour.

(iv) Give a reason why the lack of a flame colour is not a positive test for the magnesium ion.