



Higher Chemistry

HSN12000
Unit 2 – All Topics

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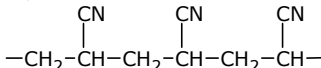
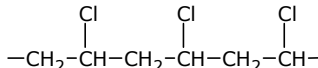
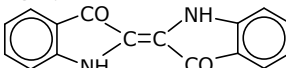
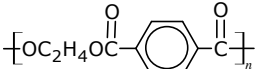
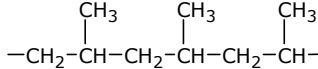
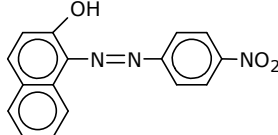

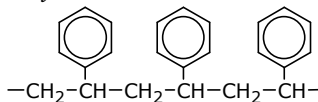
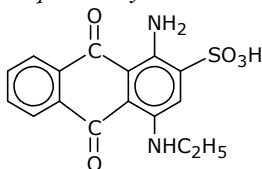
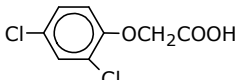
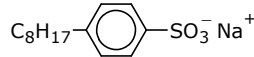
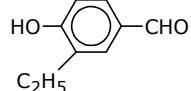
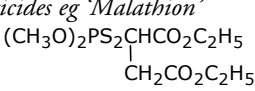
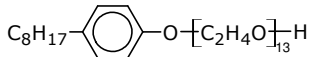
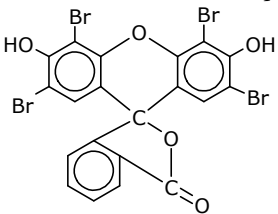
Topic 1 – Fuels, Homologous Series and Naming

Fuels and Feedstocks

This topic assumes you know and understand the work done in Standard Grade on Fuels and Hydrocarbons. Coal, oil and natural gas are finite resources – they are not renewable. From these resources we get carbon compounds that can be used as fuels or feedstocks. A feedstock is simply a chemical from which other chemicals can be manufactured. Sometimes one chemical can be used both as a fuel or a feedstock.

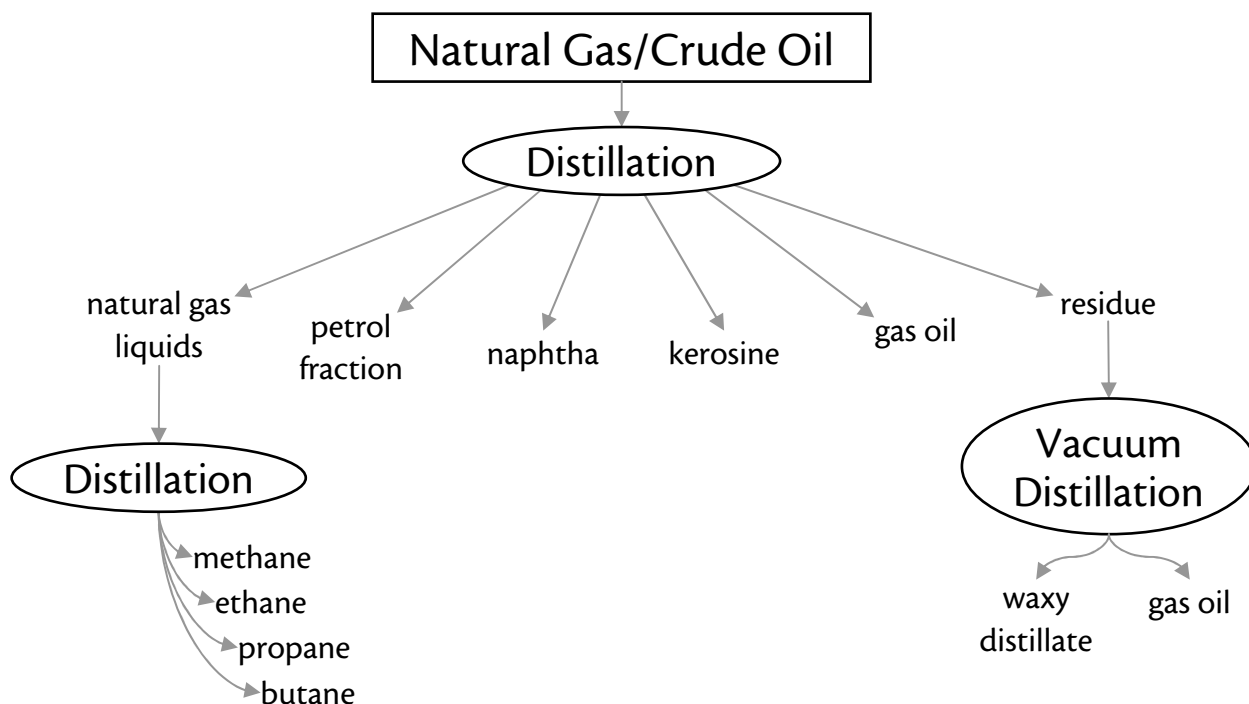
eg. the naphtha fraction from crude oil distillation can produce petrol (a fuel) or it can be used as a feedstock to produce ethene and then polythene.

The table below shows some of the vast range of consumer products containing carbon compounds.

Textiles	Plastics	Dyes
a) <i>Acrylic</i> 	a) <i>PVC</i> 	a) <i>Indigo (for blue denim)</i> 
b) <i>Polyester</i> 	b) <i>Polypropene</i> 	b) <i>Azodyes eg 'Para Red'</i> 
c) <i>Nylon</i> 	c) <i>Polystyrene</i> 	c) <i>Anthraquinone dyes</i> 
Agricultural Chemicals	Detergents	Cosmetics
a) <i>Herbicides eg '2,4-D'</i> 	These contain a) <i>Anionic surfactants</i> 	a) <i>Perfumes may include ethyl vanillin</i> 
b) <i>Pesticides eg 'Malathion'</i> 	b) <i>Non-ionic surfactants</i> 	b) <i>Lipsticks include coloured compounds</i> 

These large complex molecules have been synthesised (built up) from small reactive molecules.

In this country, crude oil is our main source of these compounds. Crude oil undergoes an initial separation by fractional distillation as shown in the flow diagram on the next page.



Some of these fractions are used to make fuels (petrol, diesel etc) and some of the fractions are used to make a whole range of other chemicals. Let us consider the important facts and features of the fuels first – dealing mainly with petrol.

Petrol

The petrol fraction produced by distillation of crude oil is still not ready to use as a car fuel. There are two problems with it:

- it is a low quality fuel.
- there is not enough of it to satisfy market demand for petrol.

The petrol fraction contains mostly straight chain hydrocarbons and this makes a poor quality petrol. When ignited in the combustion chamber of the engine, straight chain hydrocarbons tend to explode rather than burn smoothly. These explosions are called ‘auto-ignition’ or ‘knocking’ and can damage the engine. Petrol burns more smoothly if it contains branched, cyclic and aromatic hydrocarbons. Leaded petrol contains the additive lead tetra-ethyl, $\text{Pb}(\text{C}_2\text{H}_5)_4$. This is an antiknock agent and helps poor quality petrol to burn smoothly. Petrol also contains dibromoethane. This combines with the lead which then leaves the exhaust as volatile lead (II) bromide. Lead is poisonous and pressure was put on the oil companies to produce unleaded petrol. To make it burn smoothly unleaded petrol must have an even greater amount of branched and aromatic hydrocarbons.

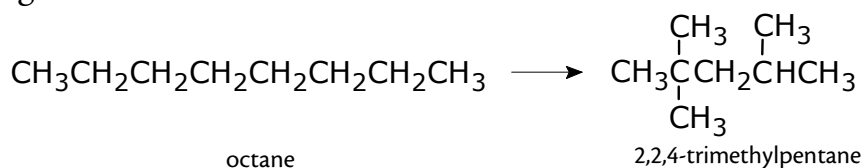
The quantity of the petrol fraction is increased by using the naphtha fraction and waxy distillate but first their quality must be improved. This is done as follows:

The naphtha fraction is mostly straight chain C_5 to C_{10} hydrocarbons. This is the correct size of molecules for petrol.

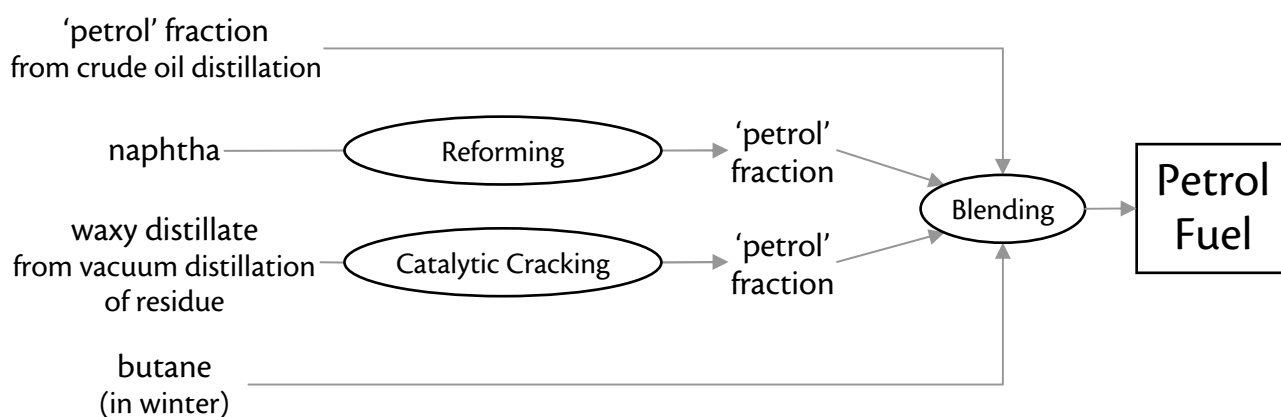
The waxy distillate consists of C_{20} to C_{40} hydrocarbons. These are first cracked to reduce the chain length. We now have molecules which are the correct size for petrol but they are still straight chained.

Reforming is a chemical reaction which changes the structure of molecules without changing their size. Reforming of the naphtha fraction and the products of cracking gives aromatics, cycloalkanes and branched chain products as well as some straight chain compounds.

eg the reforming of octane



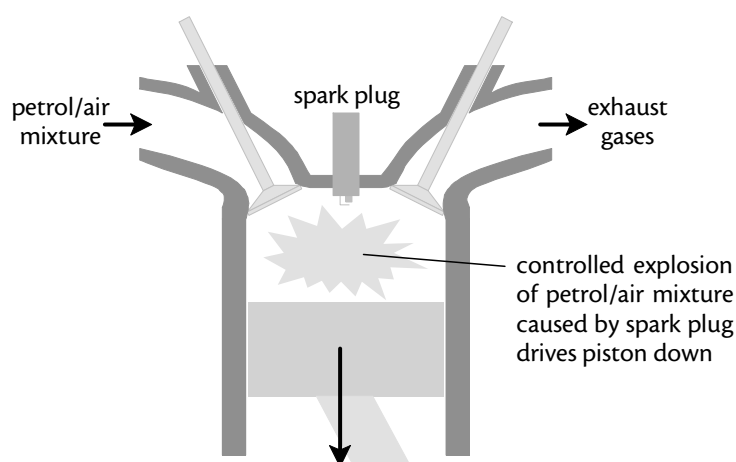
These are blended with the original petrol fraction to increase both the quality and the amount. The flow diagram shows these processes:



This better quality fuel can be burned much more smoothly in a petrol engine without lead compounds and is therefore referred to as 'unleaded' petrol. As we will see in the next section, petrol is drawn in to an engine as a vapour so it is important to have the correct mix of volatile compounds and this actually depends on the time of year – in winter more volatile compounds are added (eg butane and pentane) and in summer, the blend has a larger proportion of slightly larger hydrocarbons.

Petrol Engines

Petrol contains small (C_5 to C_{10}) volatile hydrocarbon molecules. They are drawn into the engine as a petrol vapour/air mixture. They are ignited by an electric spark from the spark plug. We have seen the importance of branched and aromatic molecules in providing a smooth combustion. The following diagram shows part of the workings in a petrol engine.



Pollution due to burning Fuels

This has been studied at Standard Grade but is an important issue so is worth a brief reminder at this point:

The burning of fossil fuels yields products that can harm the environment.

- **Carbon dioxide** contributes to the green house effect.
- **Carbon monoxide** produced by incomplete combustion is toxic.
- **Sulphur dioxide:** Sulphur is a common impurity in fuels and, unless it is removed, it produces sulphur dioxide when the fuel is burned. Sulphur dioxide is a major contributor to acid rain.
- **Nitrogen oxides:** The spark in a car engine, as well as igniting the petrol, produces nitrogen oxides (NO_x) from the nitrogen and oxygen of the air. They cause respiratory problems and also dissolve in water and add to the “acid rain” problem.
- **Lead compounds** resulting from leaded petrol are poisonous. Evidence suggests that accumulations of lead in the body can cause brain damage especially in young children.

Alternatives to petrol

We know that, one day, the sources of crude oil will run out – fossil fuels are finite resources. There are some alternative liquid fuels such as ethanol and methanol. These belong to a homologous series called alkanols which we will study later. We have already met ethanol at Standard Grade as the alcohol which is formed when sugar (glucose) ferments. In countries where sugar cane can be grown in great quantities (eg Brazil), ethanol is produced and mixed with petrol. It is also possible to manufacture methanol on an industrial scale; this can be used as a fuel directly or mixed with petrol. Methanol burns according to the following equation:



Advantages and disadvantages of using methanol are outlined below:

Advantages

- The burning of methanol is complete so reducing the carbon monoxide in the air.
- Petrol contains benzene and other aromatic hydrocarbons which are carcinogenic; methanol does not contain these compounds.
- Methanol is relatively quite cheap and renewable.
- Methanol is less volatile and less likely to be an explosion risk.

Disadvantages

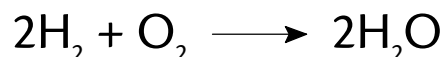
- Methanol is toxic and can cause blindness/brain damage
- Methanol produces less energy than petrol (for equivalent volumes)
- Methanol absorbs water – this gives a corrosive mixture
- Methanol and petrol are quite immiscible (don't mix readily)

The industrial preparation of methanol is an important chemical process and it is discussed in more detail on page 17.

The Hydrogen Economy

Hydrogen has for a long time now been recognised as potentially a very useful fuel for a number of good reasons:

Internal combustion engines could be designed to use hydrogen burning instead of petrol. This would be very efficient and reduce the amount of carbon dioxide in the atmosphere.



If we compare the burning of hydrogen with the burning of petrol then, weight for weight, hydrogen produces far more energy than petrol. However, hydrogen is the lightest and least easily liquefied gas. Volume for volume, hydrogen is less energy efficient than petrol. Much research is being done to overcome this problem.

Hydrogen can be used to make electricity from a hydrogen/oxygen fuel cell, which would involve allowing the hydrogen and oxygen to react in two separate parts of the cell and making electricity instead of heat – this can be fairly easily done.

Hydrogen could be stored and distributed like natural gas and used for heating in houses. This could be cheaper than using electricity.

Using hydrogen in these ways as our main fuel source is known as a ‘hydrogen economy’ and could be very efficient compared with our present use of fossil fuels if only we did not need fossil fuels to make the hydrogen in the first place (electricity is required to make the hydrogen and this electricity is still made largely by burning fossil fuels). However, the use of solar energy to ‘split’ water into hydrogen and oxygen would be a perfect solution to this problem and is being investigated as a long term possibility.

Biogas

Biomass is a general term for plant material. When waste plant material (e.g. manure, straw, vegetables) decays in the absence of air, bacteria produce biogas. The process is called anaerobic (without air) fermentation. Biogas is a mixture consisting mainly of methane (60%) and carbon dioxide.

The Chemistry of Carbon

Fuels are important uses of hydrocarbon compounds but the chemistry of carbon extends far beyond what has been covered so far. There are over 15,000,000 different carbon compounds (containing not only C and H atoms but often O, N and many other types of atom). This arises from carbon's ability to join in straight chains, branched chains and rings as well as its ability to form strong bonds with many types of atom. The chemistry of carbon compounds is made simpler because the compounds are studied in families called homologous series. Members of a homologous series are called homologues. A homologous series has the following features:

- there is a gradual change in physical properties from one member to the next. The most common example of this is the increasing melting and boiling points as we go up a series. The reason of course is the increasing van der Waals forces as the molecules get larger.
- members have similar chemical properties and methods of preparation.
- the formula increases by CH_2 from one member to the next up the series.
- the series has a general formula.
- all members possess the same functional group. It is the functional group that gives the series its characteristic reactions.

We have met two important series of hydrocarbons – the alkanes and the alkenes.

Alkanes

The alkanes are a series of hydrocarbons with the general formula $\text{C}_n\text{H}_{2n+2}$. The table below shows the names, molecular formulae and structural formulae of the first few members.

Name	Molecular Formula	Structural Formula
methane	CH_4	<pre> H H-C-H H </pre>
ethane	C_2H_6	<pre> H H H-C-C-H H H </pre>
propane	C_3H_8	<pre> H H H H-C-C-C-H H H H </pre>
butane	C_4H_{12}	<pre> H H H H H-C-C-C-C-H H H H H </pre>

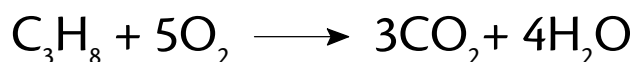
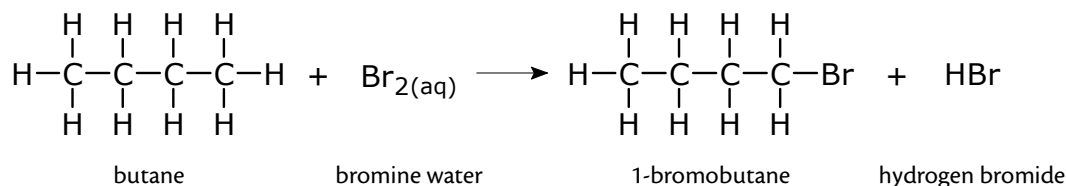
They are called saturated hydrocarbons because all the carbon atoms have formed the maximum number of single covalent bonds (4).

Chemical Reactions of Alkanes

This is revision of Standard Grade work. Alkanes can undergo two main types of reaction – combustion and substitution.

Combustion

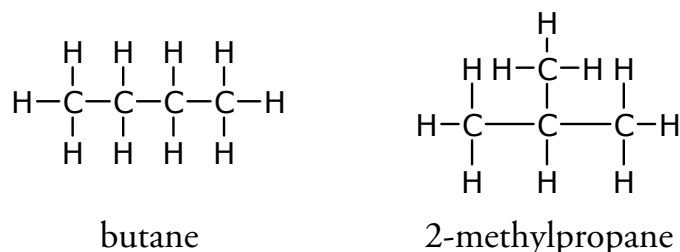
Alkanes burn in plenty oxygen to form carbon dioxide and water

*Substitution*

Substitution reactions of alkanes are slow. In this reaction with butane, the brown colour of the bromine disappears slowly. Note that all halogens (chlorine, fluorine and iodine also) can react with alkanes in this way.

Isomers and Systematic Nomenclature (names)

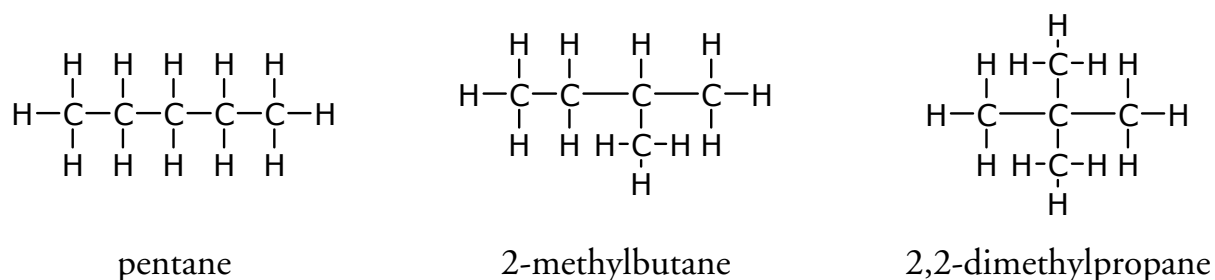
Isomers are molecules with the same molecular formula but different structural formulae. For the first three members of the alkanes only one structure is possible but butane, C_4H_{10} , has two isomers, shown below with their systematic names.



The rules for naming are:

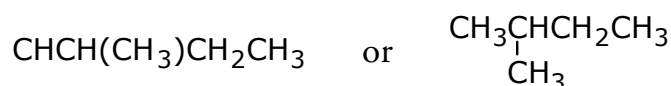
1. Find the longest carbon chain in the molecule – the name is based on the alkane with this number of carbon atoms.
2. Number the chain to give any branches the lowest possible number.
3. Name the branches: methyl ($-\text{CH}_3$), ethyl ($-\text{C}_2\text{H}_5$) etc.

We can see how this works by naming the three isomers of pentane (C_5H_{12}):



As well as the full structural formulae we have used to show the different isomers of pentane, you should also be able to represent organic compounds in the form of shortened structural formulae.

eg 2-methylbutane as shown earlier can also be drawn:



Try writing other shortened structural formulae for practice.

Alkenes

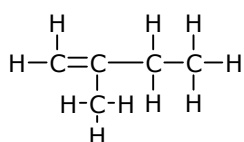
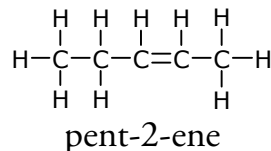
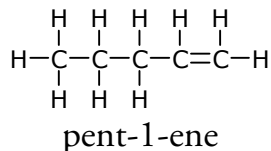
The alkenes are a homologous series of hydrocarbons with the general formula C_nH_{2n} . The table below has the names, molecular formulae and structural formulae of the first few members.

Name	Molecular Formula	Structural Formula
ethene	C_2H_4	<pre> H H C=C H H </pre>
propene	C_3H_6	<pre> H H H H-C-C=C-H H </pre>
butene	C_4H_8	<pre> H H H H H-C-C-C=C-H H H </pre>

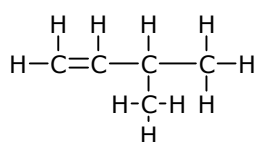
They are unsaturated because each member has a C=C bond. This feature is the functional group in the alkenes and gives the alkenes their characteristic reactions.

Isomers and Naming

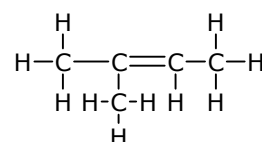
Isomers arise both by branching the chain and by varying the position of the double bond. Naming is similar to the alkanes but the main chain (the longest chain) must contain the double bond, whose position is indicated by a number. The chain is numbered to make this number as small as possible. The isomers of pentene and their names are given below.



2-methylbut-1-ene



3-methylbut-1-ene



2-methylbut-2-ene

Industrial Source of Alkenes

Ethene and propene are made by cracking of either ethane or naphtha (check where these feedstocks come from on the previous flow diagram). This involves heating the feedstock to a very high temperature (800°C). Both feedstocks give the same products but the proportions are different:

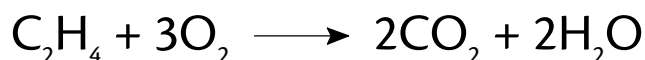
Product	Approximate percentage obtained from cracking	
	Ethane	Naphtha
Ethene	80	30
Fuel Gases (CH_4 , H_2)	10	25
Propene	5	15
Gasoline	5	30

As we can see ethane provides a much higher percentage of ethene but naphtha gives other valuable by products. Note that if propane is cracked the main product is propene.

Chemical reactions of alkenes

Combustion

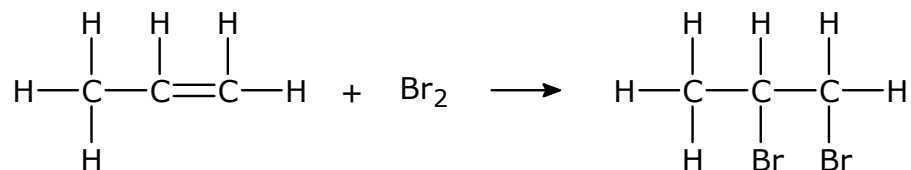
In common with all hydrocarbons, the alkenes burn in plenty oxygen to form carbon dioxide and water.



Addition

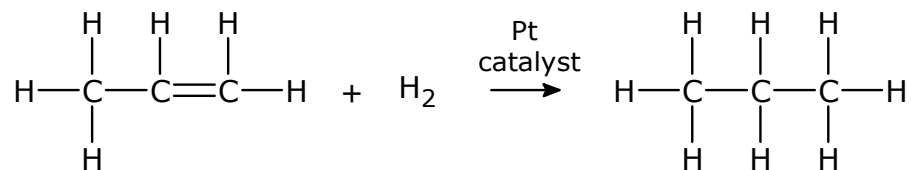
The characteristic reaction of alkenes are addition reactions – in these a molecule adds across the double bond.

a) with bromine water – bromination



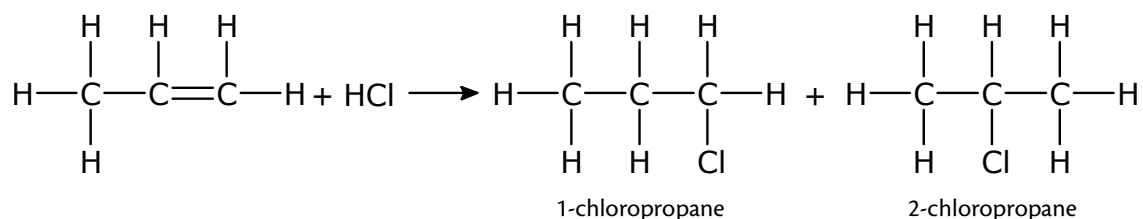
In this reaction the bromine loses its brown colour very quickly. This reaction is used as a test for unsaturation. Contrast it with the slow substitution reaction with bromine given by the saturated alkanes.

b) with hydrogen – hydrogenation



This addition of hydrogen across a double bond happens only in the presence of a catalyst – usually platinum is used in the lab reaction. This process converts an alkene into an alkane.

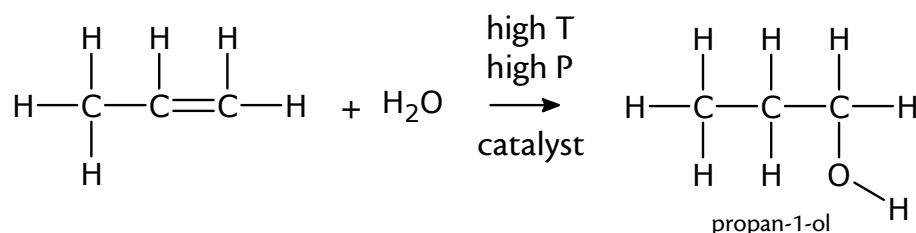
c) with hydrogen halides



Note the possibility of isomeric products in this case.

In this reaction we end up with a substituted alkane – a haloalkane.

d) with water – hydration



In all of the above addition reactions, an unsaturated compound becomes fully saturated.

Alkynes

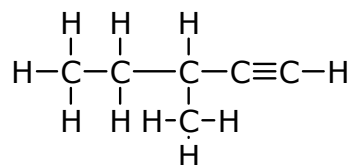
The alkynes are another homologous series, which you have not met before. The important functional group of these is the $C\equiv C$ 'triple bond'. These molecules are obviously even more unsaturated than alkenes. The naming of the alkyne isomers is exactly similar to the naming of alkenes apart from the ending being 'yne' rather than 'ene'. The general formula of the alkynes is C_nH_{2n-2} and the table below has the names, molecular formulae and structural formulae of the first few members.

Name	Molecular Formula	Structural Formula
ethyne	C_2H_2	$H-C\equiv C-H$
propyne	C_3H_4	$\begin{array}{c} H \\ \\ H-C-C\equiv C-H \\ \\ H \end{array}$
butyne	C_4H_6	$\begin{array}{c} H & H \\ & \\ H-C & -C-C\equiv C-H \\ & \\ H & H \end{array}$

Isomerism and Naming

The naming of the isomers of alkynes is exactly similar with the naming of alkenes, except that the ending -yne is used instead of -ene.

The isomer 3-methylpent-1-yne is shown below:

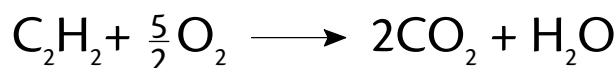


Try to write structural formulae for as many other isomers of the above and give the systematic names.

Chemical reactions of alkynes

Combustion

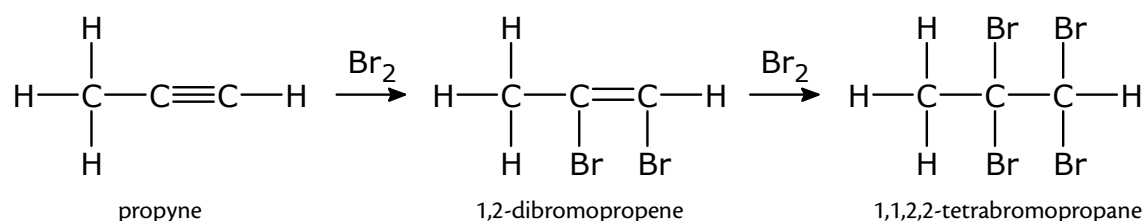
This is as expected for the combustion of a hydrocarbon



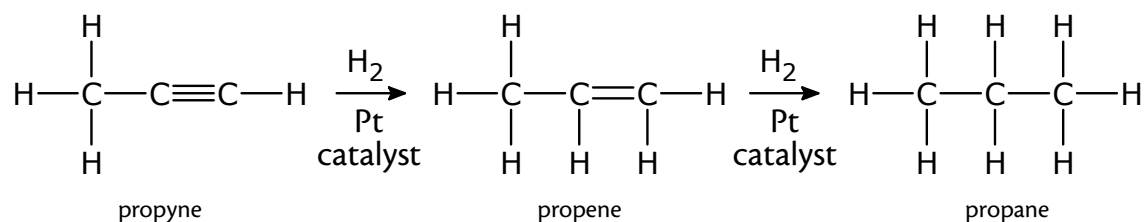
Addition

As the alkynes are unsaturated we might expect that they will undergo addition reactions like the alkenes. This is indeed the case but the reaction can happen in two stages and, with care, can be stopped after the first stage.

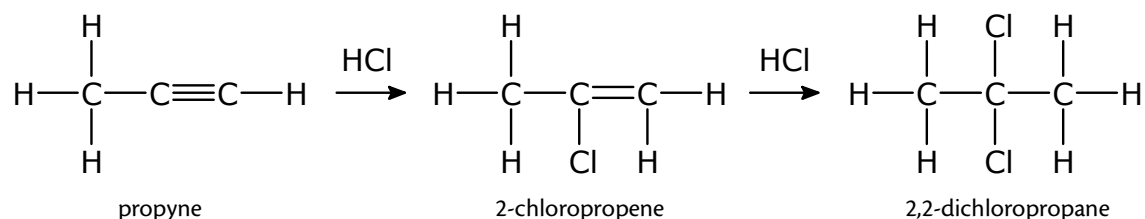
a) **with halogens** – to make dihaloalkenes, then tetrahaloalkanes.



b) **with hydrogen** – to make alkenes and then alkanes.



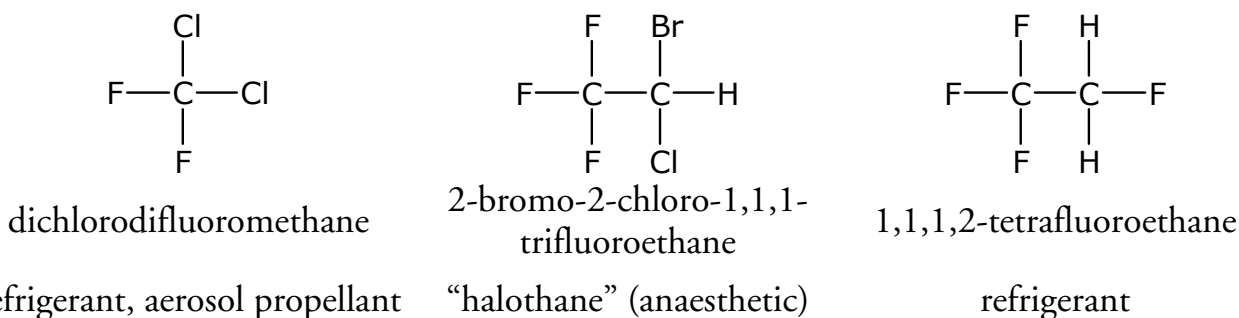
c) **with hydrogen halides** – to make haloalkenes and then dihaloalkanes.



A number of the reactions of alkanes, alkenes and alkynes have produced products containing halogen atoms. We need to look at the uses of haloalkanes.

Halogenoalkanes and their Uses

As the name might suggest, the halogenoalkanes are alkane molecules where halogen atoms have replaced at least one hydrogen atom. The most widely heard about haloalkanes are the CFCs – chlorofluorocarbons, which contain chlorine and fluorine in their molecules, and halons which contain carbon, chlorine, fluorine and bromine atoms. Examples of these are shown below:



These molecules are very unreactive, have low flammability and generally low toxicity. These properties make them very useful for certain situations:

Aerosol propellants

When the valve of an aerosol can is pushed, the pressure inside drops and that allows the CFC inside to vaporise. This then acts as the propellant, carrying the contents of the can into the atmosphere. Because of the environmental hazards, CFCs have been replaced by butane in aerosol cans.

Refrigerants

The low boiling point and lack of reactivity/corrosiveness makes CFCs useful in fridges and air conditioning units.

Blowing agents

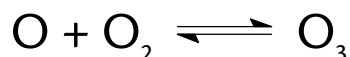
If a volatile CFC is included in the formation of a plastic, the heat generated in the polymerisation vaporises the CFC and this creates tiny bubbles in the plastic, making foam – eg expanded polystyrene. This process must involve the release of much CFC into the atmosphere.

Cleaning solvents

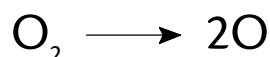
CFCs are very good solvents for grease and are used as dry cleaning solvents and for cleaning electric circuits. Again, some of the solvent ends up in the atmosphere.

The release of CFCs into the atmosphere has become a huge environmental issue in the last few years and steps have been taken to control the use and the release of these chemicals into the atmosphere because of its effect on the 'ozone layer' in the upper atmosphere.

Ozone, O₃, is a vital natural sunscreen gas which protects us from very harmful UV radiation by absorbing it. It is formed between oxygen atoms and oxygen molecules and breaks back down to oxygen molecules and atoms by absorption of UV light:



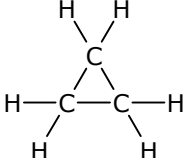
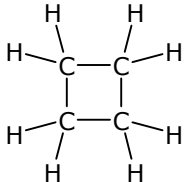
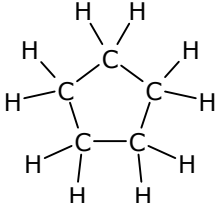
The oxygen atoms are produced by oxygen molecules, also by absorbing some UV radiation.



The ozone is constantly being formed and destroyed through the absorption of UV light and the balance of these processes is important in shielding us from too much UV radiation. It is widely accepted that certain CFCs in the atmosphere can destroy the ozone layer and this would allow more UV radiation to reach the earth. This would result in more incidents of skin cancer, eye cataracts and could have many other wide ranging effects on the environment of the earth.

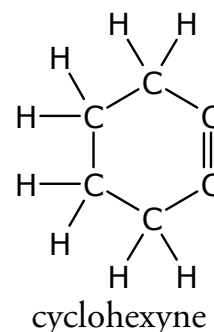
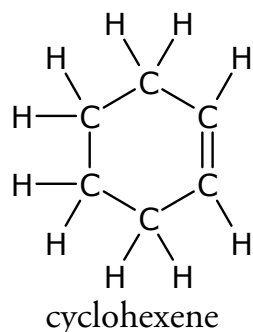
Ring Compounds

All the hydrocarbon compounds mentioned so far have been straight chain or branched compounds. We also know that one of the reasons that there are so many carbon compounds is that ring compounds can also easily be formed cyclic compounds. There are homologous series of these and we have already met one at Standard Grade – the cycloalkanes (general formula C_nH_{2n}). The smallest cycloalkane is cyclopropane (3 is the smallest number of carbons that can join to form a ring!). The structure of this is shown below as well as the next few members of the series:

Name	Molecular Formula	Structural Formula
cyclopropane	C_3H_6	
cyclobutane	C_4H_8	
cyclopentane	C_5H_{10}	

Note that cycloalkanes have the same molecular formula as the alkene with the same carbon number – they are isomeric.

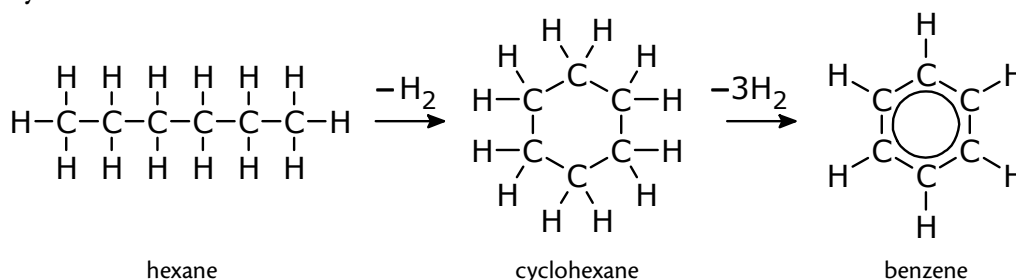
Cycloalkanes react in exactly the same way as the alkanes – combustion and substitution. Cycloalkenes and cycloalkynes are other possible homologous series of cyclic compounds. They react respectively like the alkenes and alkynes. The structures of the 6 carbon members of these series are shown.



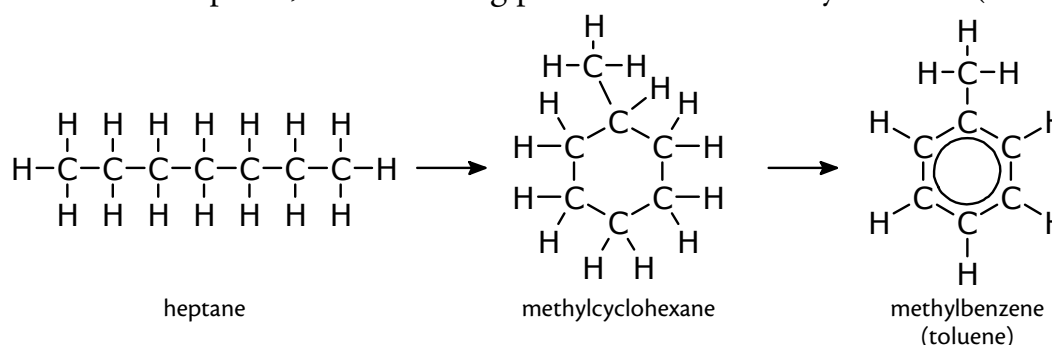
Note that cycloalkenes are isomeric with alkynes.

Aromatic Hydrocarbons

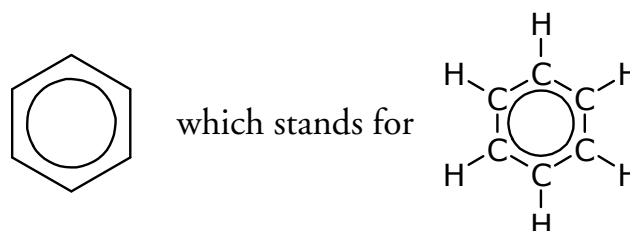
Naphtha, from the distillation of crude oil, can be used for the production of a very important group of compounds called aromatic hydrocarbons. Straight chain alkanes in naphtha undergo cyclisation to form cycloalkanes which then lose hydrogen to form aromatic hydrocarbons, like benzene.



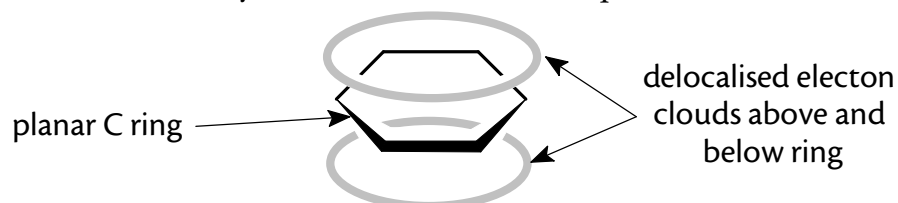
The process is called reforming – the structure of the molecules alters without any change in their size. With heptane, the reforming process leads to methylbenzene (toluene).



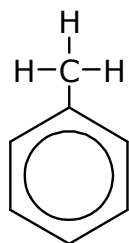
In practice the process of reforming gives a mixture of aromatic compounds that must be carefully separated. Benzene, C_6H_6 , is the simplest aromatic compound. It has a ring structure usually drawn as shown:



At each corner there is a carbon with a hydrogen attached. Although this formula seems very unsaturated, the benzene ring is very resistant to addition reactions – there is no fast reaction with bromine water. The structure can be thought of as a ring of six carbon atoms, each with a hydrogen atom. This takes up three of the four bonding electrons from each carbon atom. The fourth electron can be imagined as being shared over the whole ring, above and below as shown in the diagram below. The electrons are said to be delocalised and it is thought that this delocalisation of the electrons gives the benzene ring great stability. It is therefore very resistant to attack and quite unreactive.



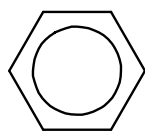
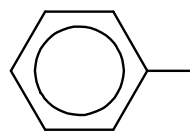
There is an enormous range of aromatic molecules but all are based on the benzene unit. Several of the important groups of molecules shown on the first page are aromatic.



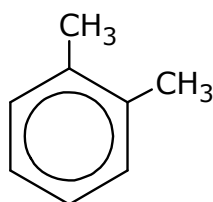
In the molecule methylbenzene (toluene), $C_6H_5CH_3$, one of the hydrogens in benzene has been replaced with a methyl group ($-CH_3$).

Another way of looking at this molecule is to regard the methane molecule as having a hydrogen replaced with the aromatic part $-C_6H_5$. The $-C_6H_5$ group is called the phenyl group.

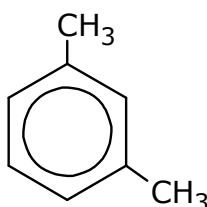
Below we summarise the relationship between benzene and the phenyl group:

benzene, C_6H_6 phenyl group, C_6H_5

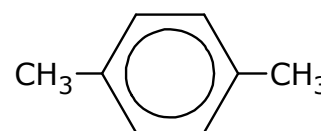
If two hydrogen atoms in benzene are replaced with methyl groups, then three isomeric dimethylbenzenes are possible:



1,2-dimethylbenzene



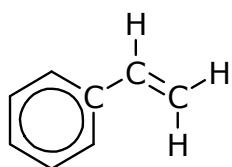
1,3-dimethylbenzene



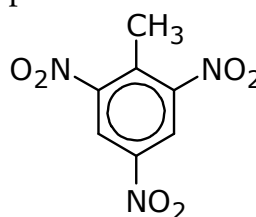
1,4-dimethylbenzene

These three molecules are also called xylenes. They are used in the manufacture of paints, fibres and dyes.

Benzene is a very important feedstock. Most of the benzene made is reacted with ethene to form phenylethene (styrene). This, as we know, is used to make the polymer, poly(phenylethene), more commonly known as polystyrene. Methylbenzene (toluene) is used to make TNT (trinitrotoluene) which is an explosive:

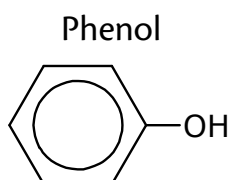


phenylethene (styrene)

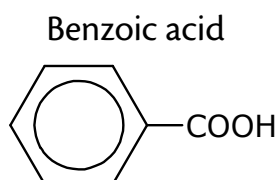


trinitrotoluene

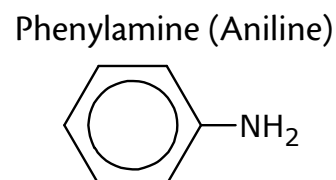
Other examples of derivatives of benzene are:

 C_6H_5OH

- Used in the manufacture of
- bakelite
 - nylon monomers
 - drugs (eg Aspirin) and dyes
 - germicides (eg Dettol)

 C_6H_5COOH

Used as a food additive
(E210)

 $C_6H_5NH_2$

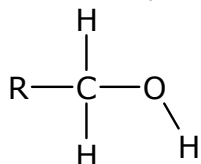
Used in the manufacture of
dyes and drugs

Alkanols

Alcohols are molecules that contain the hydroxyl (-OH) functional group. The alkanols are a homologous series of alcohols with the general formula $C_nH_{2n+1}OH$. They can be thought of as derived from the parent alkanes by substituting a hydrogen atom with an -OH group.

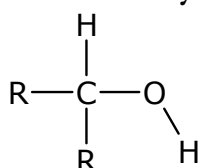
Alkanols can be classified in three groups:

1. Primary alkanols



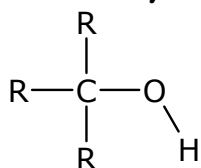
The carbon bearing the -OH group is directly bonded to only one alkyl group.

2. Secondary alkanols



The carbon bearing the -OH group is directly bonded to two alkyl groups.

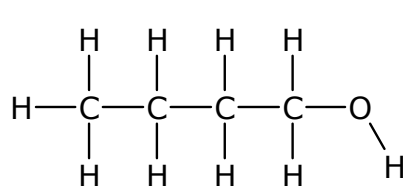
3. Tertiary alkanols



The carbon bearing the -OH group is directly bonded to three alkyl groups.

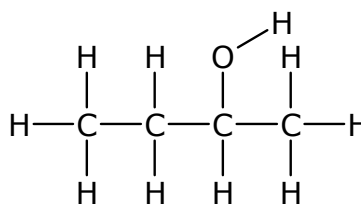
Isomers and names

Isomers can result from both chain branching and varying the position of the -OH group. In naming, the main chain must contain the -OH group, whose position is indicated by a number. We can see this by looking at the four isomers of butanol, C_4H_9OH :



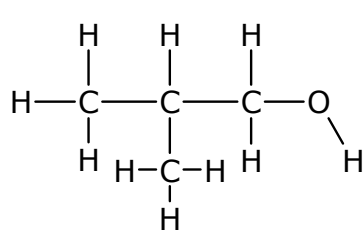
butan-1-ol

(primary)



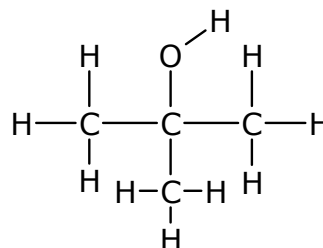
butan-2-ol

(secondary)



2-methylpropan-1-ol

(primary)



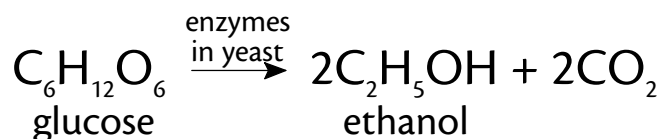
2-methylpropan-2-ol

(tertiary)

Industrial preparation of ethanol

1. Fermentation

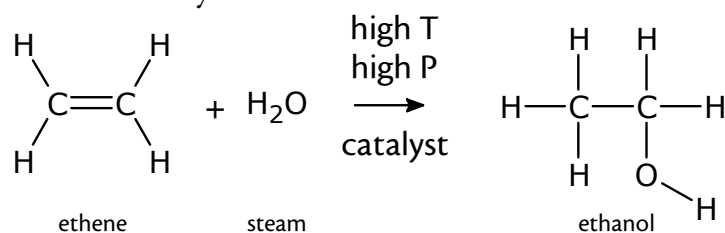
From earlier work you know that ethanol can be produced from carbohydrates by fermentation catalysed by enzymes present in yeast.



This method produces the ethanol in alcoholic drinks, but in order to meet market demand for ethanol for industrial uses other methods have been developed.

2. Hydration of alkenes

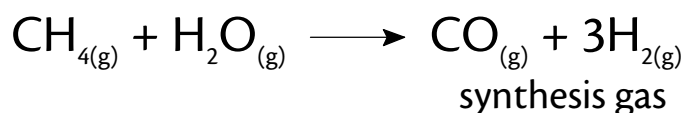
Ethanol is prepared industrially by reacting ethene with steam at high temperature, high pressure in the presence of a catalyst



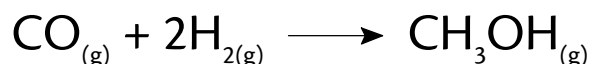
This reaction, in which the water adds across the double bond, is also called catalytic hydration. The reaction can be extended to make other alcohols: hydration of propene gives propanol; hydration of butene gives butanol. In some cases the products are isomeric (where the positioning of the double bond in the alkene is asymmetrical).

Industrial preparation of methanol

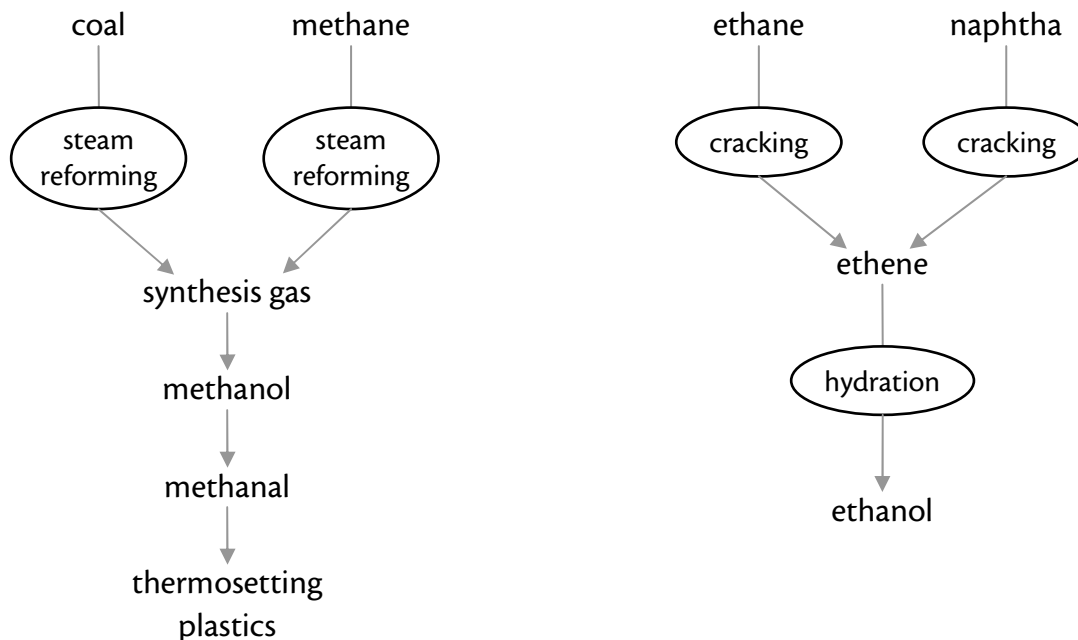
Methanol has only one carbon and so cannot be prepared by hydration of the C=C bond of an alkene. Industrially, methanol is prepared from synthesis gas which is a mixture of carbon monoxide and hydrogen. Synthesis gas is prepared by passing methane and steam at very high temperature over a catalyst.



This process is called the steam reforming of methane. Synthesis gas can also be made by the steam reforming of coal but in this case a little oxygen must be added to the coal/steam reactant mixture. Once the hydrogen content of the synthesis gas has been adjusted, the carbon monoxide/hydrogen mixture is passed over another catalyst and methanol is formed.



Methanol is a very important feedstock in industry – it is converted to methanal and then to thermosetting plastics as we will see later. Note also that synthesis gas provides the hydrogen for the Haber process for ammonia production. The processes we have just met are summarised on the flow diagram:

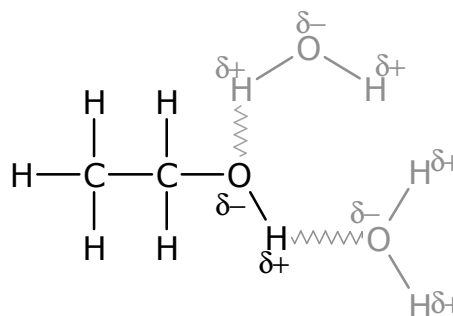


Thermosetting plastics will be dealt with later, in the section on polymers.

Physical Properties of Alkanols

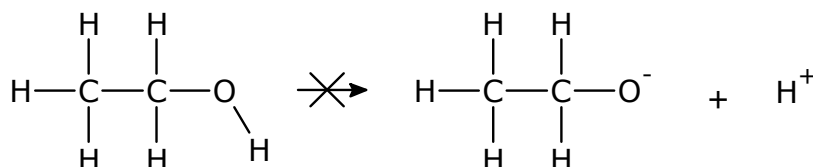
1. Solubility in water

The first three alkanols are miscible with water because the polar hydroxyl group can hydrogen bond with water molecules.



2. Acidity

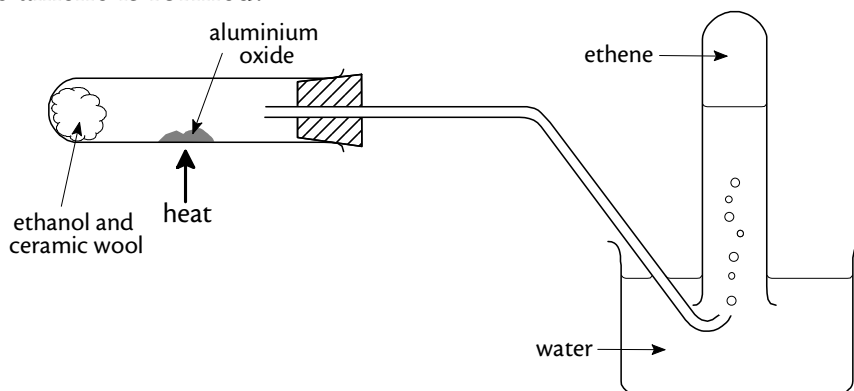
Alkanols are not acidic in water and so do not give any of the usual acid reactions.



Chemical Reactions of Alkanols

1. Dehydration to alkenes

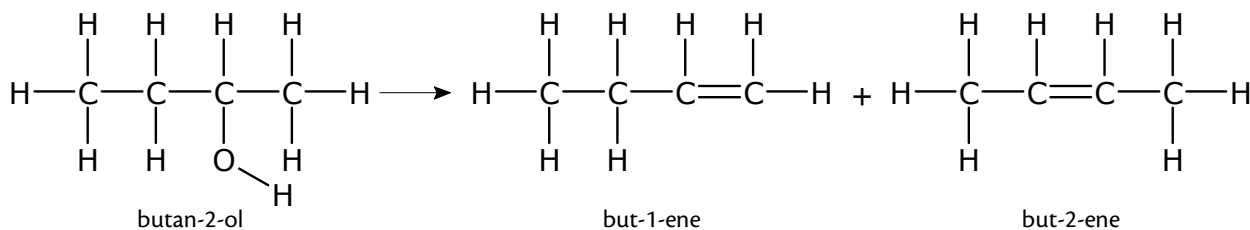
If an alcohol is passed over hot aluminium oxide as catalyst, water is removed from the alcohol and the alkene is formed.



eg



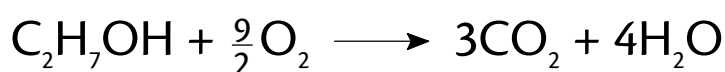
Concentrated sulphuric acid, which has a strong attraction for water, can also be used as the catalyst for this dehydration. Note that with larger alkanols, when dehydration is performed, the -OH and -H from adjacent carbon atoms are removed to form the double bond. This can sometimes result in different isomers being possible:



2. Oxidation

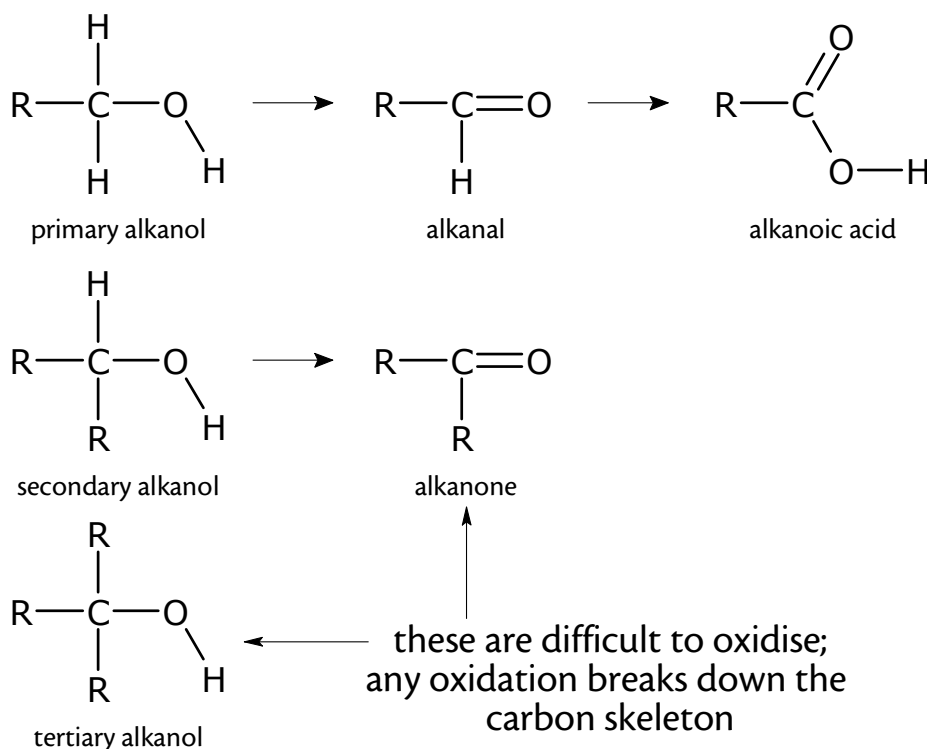
a) Complete oxidation

Combustion Alcohols burn and in excess oxygen the products are carbon dioxide and water.



b) Partial Oxidation

The products of the oxidation of alcohols depend on whether the alcohol is primary, secondary or tertiary. The equations below show this:

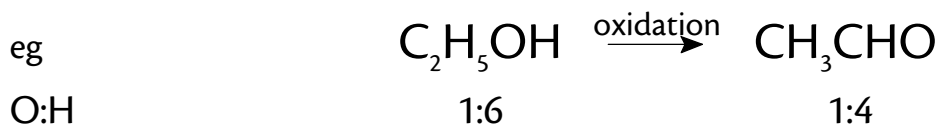


The Oxidising Agent for these reactions can be:

- acidified potassium permanganate solution (KMnO_4). During the reaction the purple permanganate (MnO_4^-) ion is reduced to colourless Mn^{2+} ions.
- acidified potassium dichromate solution ($\text{K}_2\text{Cr}_2\text{O}_7$). During the reaction the orange dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) is reduced to green Cr^{3+} ions
- copper (II) oxide and heat. The black oxide is reduced to reddish copper metal during the reaction.

Oxidation and reduction – a new definition

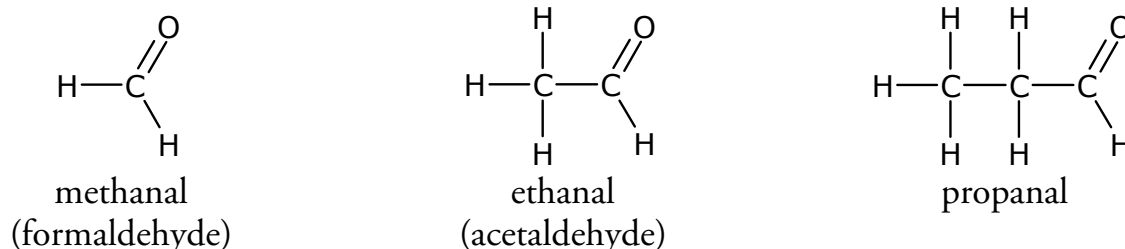
In carbon chemistry, oxidation is defined as increasing the O:H ratio and reduction is defined as decreasing the O:H ratio. These are different definitions from those met previously and only apply in carbon chemistry.



Oxidation of ethanol to ethanal has increased the O:H ratio. Ethanal can also be reduced back to ethanol and this would be a decrease of the ratio.

Alkanals

Alkanals have the functional group -CHO. Clearly this group must be at the end of a chain. They are named by replacing the -ol of the alkanol with -al. The first three members are:



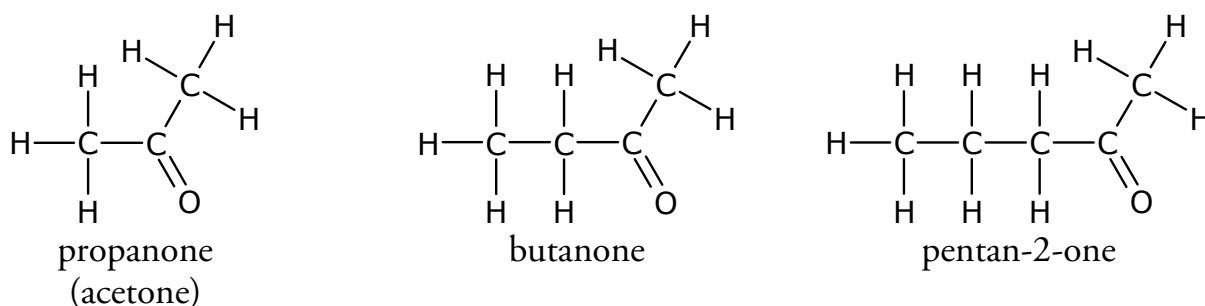
Note that the C=O group is called the carbonyl group. Any compound containing the -CHO group is called an aldehyde. The alkanals which are derivatives of alkanes are a sub-group of aldehydes.

Preparation and uses

Alkanals are made by oxidising primary alkanols. The main industrial use is in the making of thermosetting plastics eg phenol/methanal resins and urea/methanal resins (more on this later). Methanal (formaldehyde) is also used in the preservation of bodies of dead animals.

Alkanones

Alkanones also have the functional group C=O, the carbonyl group. This group must be within a chain. Names are formed by replacing the -ol of the alkanol with -one. A number usually has to be used to indicate the position of the carbonyl group. The first three members are:



Alkanones are a subset of the more general ketones.

Preparation

Alkanones are made by oxidising secondary alkanols.

Uses of ketones

Mainly as solvents for varnishes and plastics.

eg Propanone is the solvent in nail varnish remover.

Distinguishing aldehydes and ketones

In many reactions, aldehydes and ketones behave similarly because they both contain the carbonyl group, C=O. However aldehydes can be oxidised to carboxylic acids whereas ketones cannot be oxidised. This provides a method of distinguishing them. The table below lists the oxidising agents that can be used and the results of the tests:

Oxidising Agent	Observation and reason
Benedict's or Fehling's solution	Blue solution \longrightarrow Orange-red precipitate Cu ²⁺ ions reduced to Cu ₂ O ie copper (I) oxide
Tollen's reagent ie AgNO _{3(aq)} + NH _{3(aq)}	A 'silver mirror' is formed Ag ⁺ ions reduced to Ag atoms
Acidified potassium dichromate solution	Orange solution \longrightarrow Blue-green solution Cr ₂ O ₇ ²⁻ reduced to Cr ³⁺

Note that glucose, fructose etc. give positive tests with Benedicts solution because they contain the aldehyde group -CHO.

Alkanoic acids

Compounds whose molecules contain the carboxyl functional group (-COOH) are generally called carboxylic acids. A homologous series based on the parent alkanes exists, and is called the alkanoic acids. The names, molecular and structural formulae of the first few members are given below.

Name	Molecular Formula	Structural Formula
Methanoic acid	HCOOH	
Ethanoic acid	CH ₃ COOH	
Propanoic acid	C ₂ H ₅ COOH	
Butanoic acid	C ₃ H ₇ COOH	

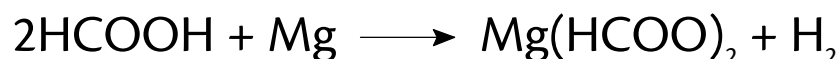
The carboxyl group in alkanoic acids is able to release a hydrogen ion when in water and this gives rise to acid reactions.



The negative ion above is called the ethanoate ion. Generally, the ion produced from alkanoic acids when they ionise is called an alkanoate ion.

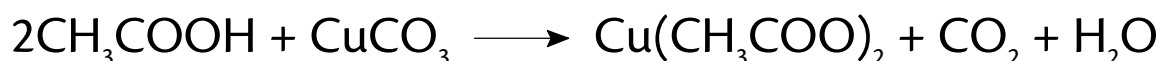
These organic acids react in the same way as the other acids that we have met in the past: With MAZIT metals; with metal oxides/hydroxides; with metal carbonates.

eg The reaction of methanoic acid with magnesium



The salt formed in this case is magnesium methanoate.

eg The reaction of ethanoic acid with copper(II) carbonate

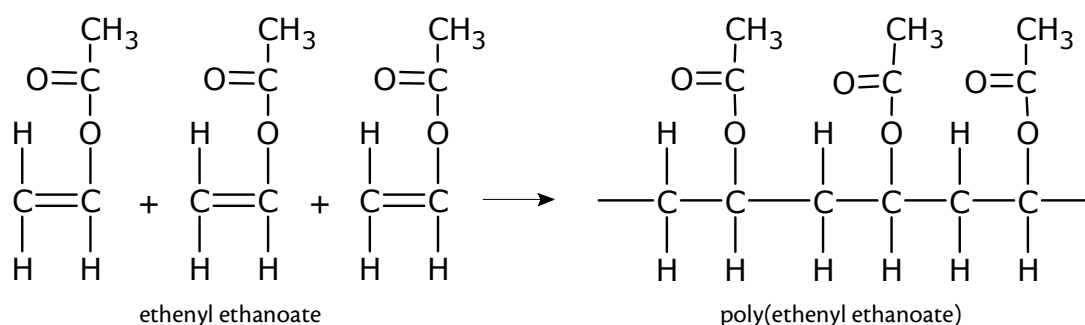


The salt formed in this case is called copper(II) ethanoate.

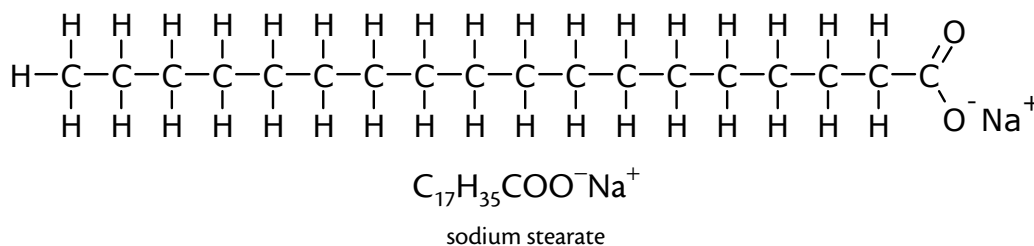
The Industrial uses of Carboxylic Acids

Ethanoic acid is also known as acetic acid, and when in a fairly dilute solution it is used as vinegar.

Ethanoic acid is used as a feedstock for the production of ethenyl ethanoate (an unsaturated ester) and this can be used to make a polymer poly(ethenyl ethanoate), which is used extensively in paints. This polymer is mentioned later.



Soaps are made from carboxylic acids which have fairly long chains – eg stearic acid can be easily reacted to make sodium stearate, a common compound in soap.

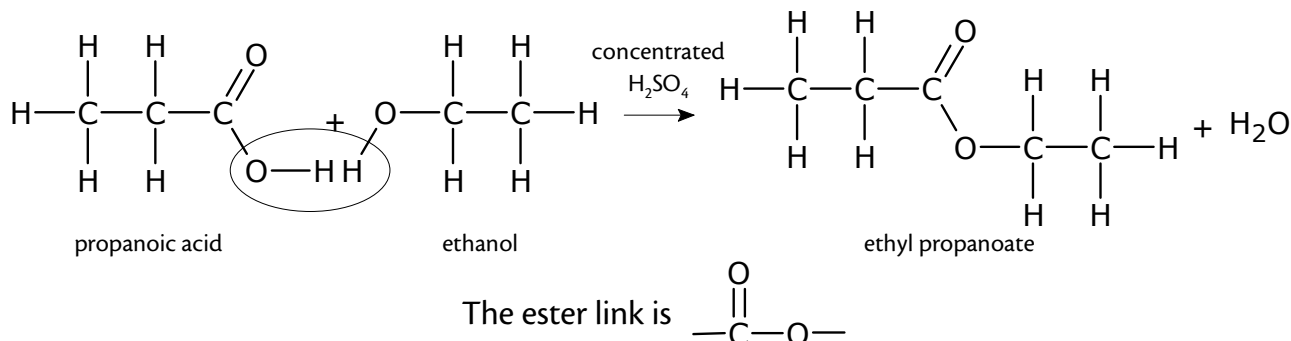


We will also see later that molecules with two carboxyl groups on their molecules (dicarboxylic acids) can be used to make the polymers 'Terylene' and nylon-6,6.

Ester Formation

There is a PPA on this.

Esters are compounds formed by a condensation reaction between alcohols and carboxylic acids. In a condensation reaction two molecules join and a small molecule (often water) is removed.

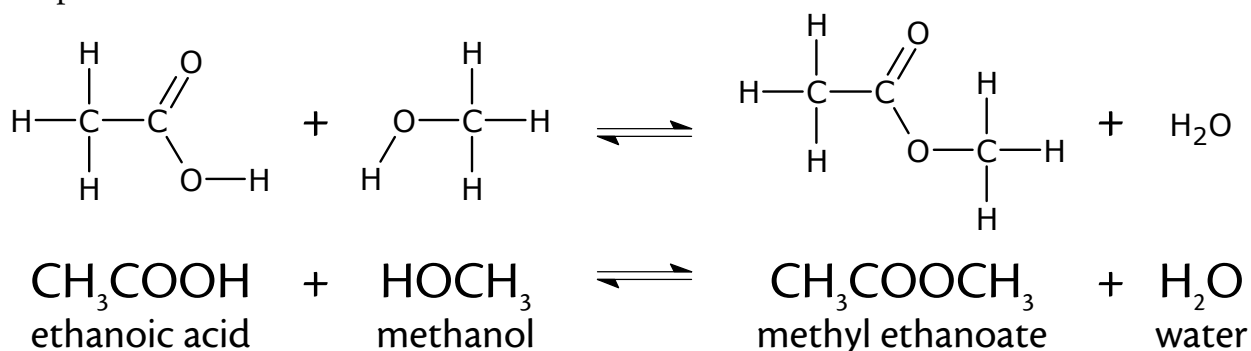


Naming Esters

The name of an ester indicates the alkanol and acid which go into making it. The first name is derived from the alkanol: -anol becomes -yl. The second name is derived from the alkanic acid: -oic becomes -oate.

Reactions of Esters

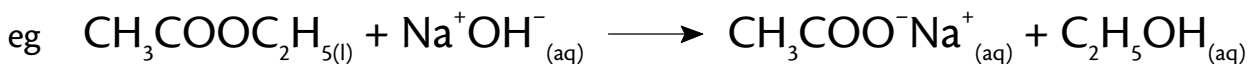
The main reaction of esters is the reaction given by all compounds formed from condensation reactions – hydrolysis, which is the reverse of condensation. Esters are formed as a result of the loss of water molecule between an alkanol and alkanic acid. It is possible, under the right conditions, to react the ester with a water molecule. This would reform the original acid and alkanol. So the formation and hydrolysis of an ester is an example of a reversible reaction.



We will study reversible reactions in detail in Unit 3.

The formation of the ester is favoured by removing the other product, water. Concentrated sulphuric acid is a powerful dehydrating agent; this means that it absorbs water. If the alkanol/alkanoic acid mixture is heated with a few drops of concentrated sulphuric acid it is possible to get a good quantity of ester. The ester can be separated from the rest by pouring it into a solution of sodium carbonate – this neutralises the acid and the oily ester layer forms on top.

To reverse the formation of ester (ie hydrolyse it) we need to react the ester with water. However in practice the ester is heated in the apparatus below with either dilute acid or dilute alkali. The ester is said to be heated under “reflux”. When sodium hydroxide solution is used the ester is ‘split up’ into the alkanol and the sodium salt of the acid. The alkanol can be removed by distillation and the alkanoic acid can be regenerated by reacting the sodium alkanoate with dilute hydrochloric acid. The equations for these reactions are also shown below.

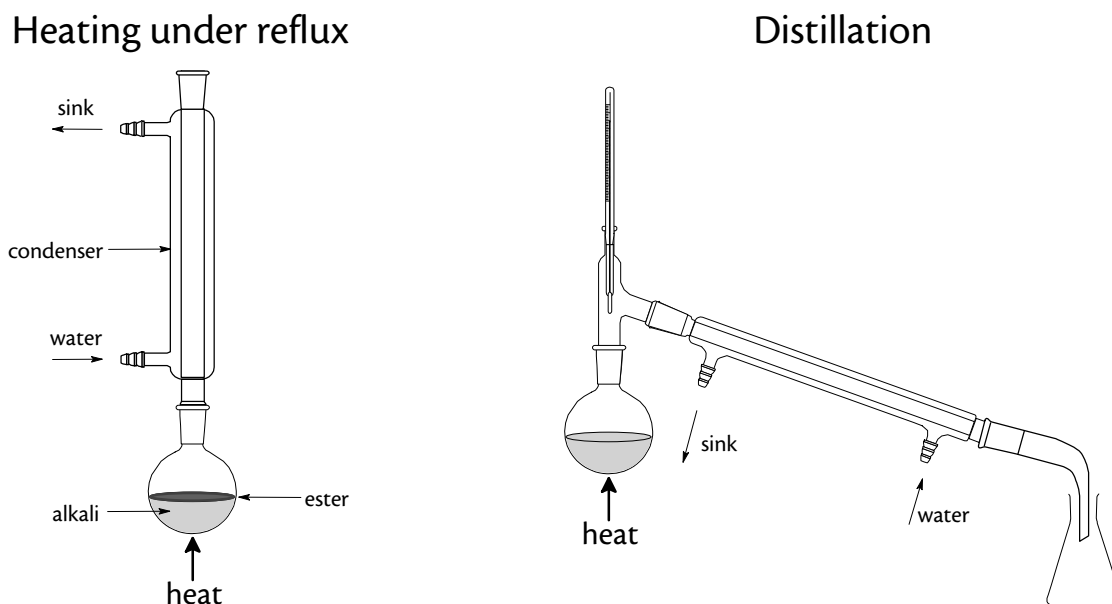


then,



Apparatus for Hydrolysis

The apparatus usually used is shown:



Properties and Uses of Esters

Esters are generally very pleasant smelling compounds and have a range of uses. Some of the smaller ones are quite volatile and are used as solvents in adhesives, inks and paints – pentyl ethanoate is used in nail varnish for example. Many esters are used as flavourings and in perfumes. Natural fruit flavours contain subtle blends of some of the esters in the table below:

Name	Shortened Structural Formula	Odour/Flavour
Pentyl Ethanoate	$\text{CH}_3\text{COO}(\text{CH}_2)_4\text{CH}_3$	Banana
Octyl Ethanoate	$\text{CH}_3\text{COO}(\text{CH}_2)_7\text{CH}_3$	Orange
Methyl Butanoate	$\text{CH}_3(\text{CH}_2)_2\text{COOCH}_3$	Pineapple
3-Methylbutyl Butanoate	$\text{CH}_3(\text{CH}_2)_2\text{COO}(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2$	Apple

Percentage Yields

In organic chemical reactions we very rarely (if ever) get the total quantity of product that we can calculate from the chemical equation. The reasons for this can be:

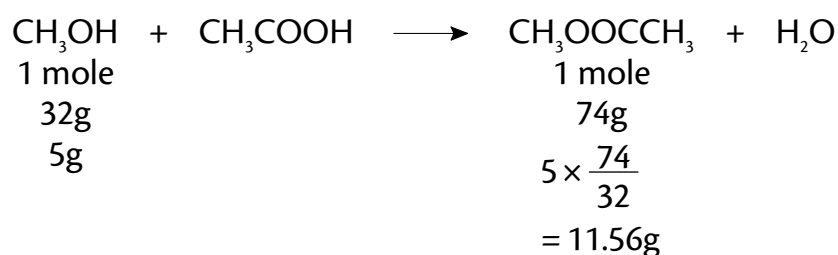
- at the end of the reaction there may be reactant left unconverted to product
- some reactant may be converted into a by-product
- the isolation of the product may be difficult

Organic chemists sometimes like to know the percentage yield of product from their reactions and this is calculated as follows:

$$\text{Percentage Yield} = \frac{\text{Actual quantity obtained}}{\text{Theoretical quantity from equation}} \times 100$$

An example illustrates the point:

When 5g of methanol reacts with excess ethanoic acid 9.6g of methyl ethanoate is produced. What is the percentage yield in this reaction?



Theoretical yield = 11.56g

Actual yield = 9.6g

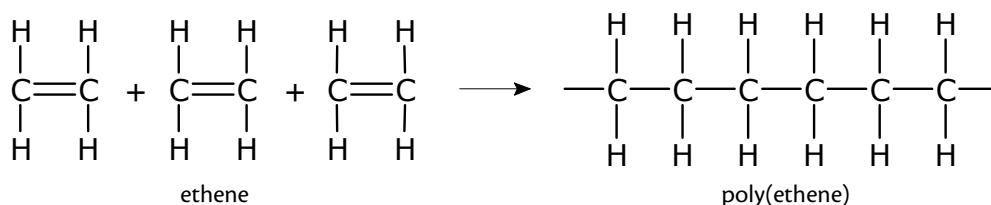
$$\begin{aligned} \text{Percentage yield} &= \frac{9.6}{11.56} \times 100 \\ &= 83\% \end{aligned}$$

Polymers and Polymerisation

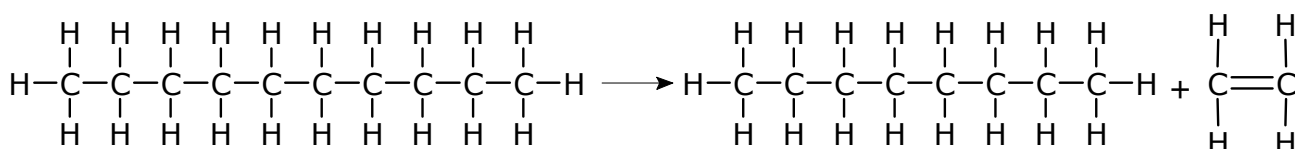
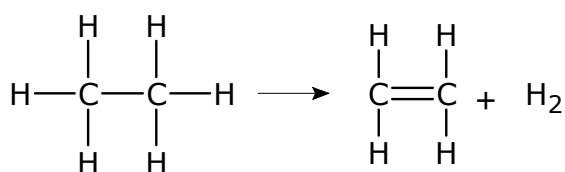
This aspect of the chemical industry has become extremely important over the last few decades and a huge range of polymers have been developed – eg the ordinary ‘polythene’ for plastic basins, polystyrene foams, nylon and other synthetic fibres and the special plastic needed for CDs and microchip circuit boards. We have already studied polymerisation at Standard Grade but it is worth looking at the important features again.

Polymers are large molecules made by joining many smaller molecules (monomers) together thousands of times. There are two main types of reaction which allows molecules to be polymerised – addition and condensation. We will deal with addition polymerisation first.

Addition Polymerisation

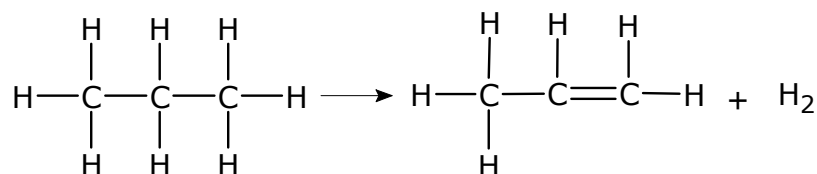


The above example used ethene, which is obtained by cracking of the ethane from the gas fraction from crude oil or by cracking the naphtha fraction. (Note that ethene is a feedstock of very major importance in the chemicals industry). Equations to show the cracking process of ethane and naphtha are shown:

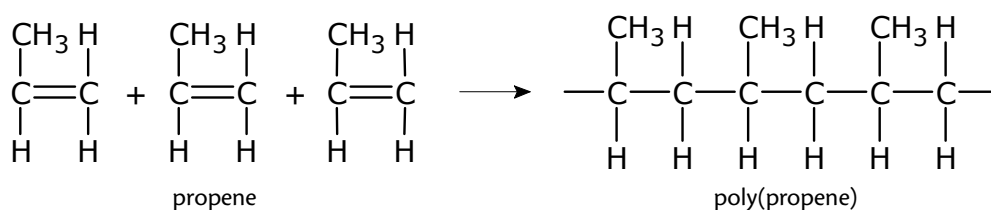


A similar polymerisation can be done using propene, which is obtained from the cracking of propane, or again from the cracking of the naphtha fraction.

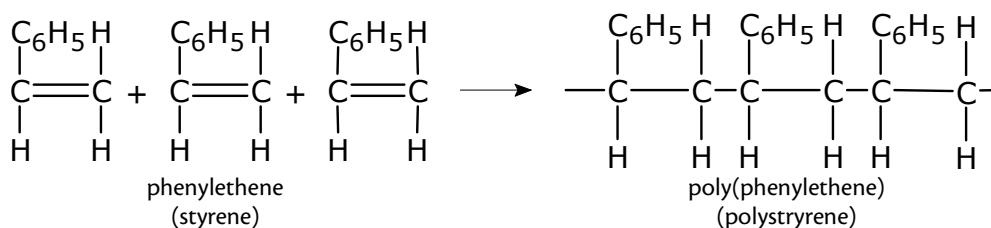
eg cracking propane produces propene and hydrogen:



The polymerisation reaction of propene is shown below. (Note that it is important to draw the propene structure in such a way that the C=C bonds can ‘get at’ each other edge to edge.)

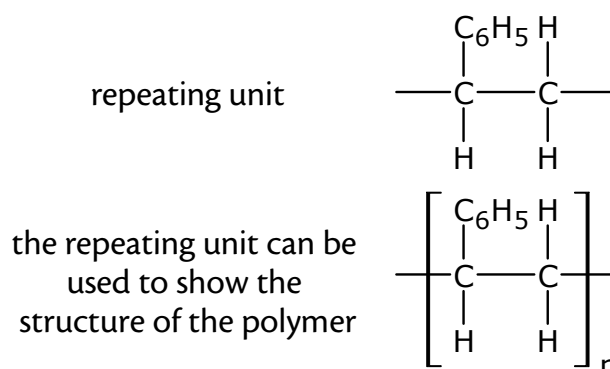


Phenylethene (styrene) has already been mentioned as important in the making of poly(phenylethene), or polystyrene as it is more commonly known, and the reaction scheme is also shown below:



Please refer to your Standard Grade notes (topic 6) for other examples.

All of these polymerisations involve using the addition reaction of the C=C double bond thousands of times. Another feature worth pointing out in the examples is that the small molecules (monomers) were of the same type, and this allows us to identify a small 'repeating unit' which can be enclosed in square brackets to denote the formula of the polymer:

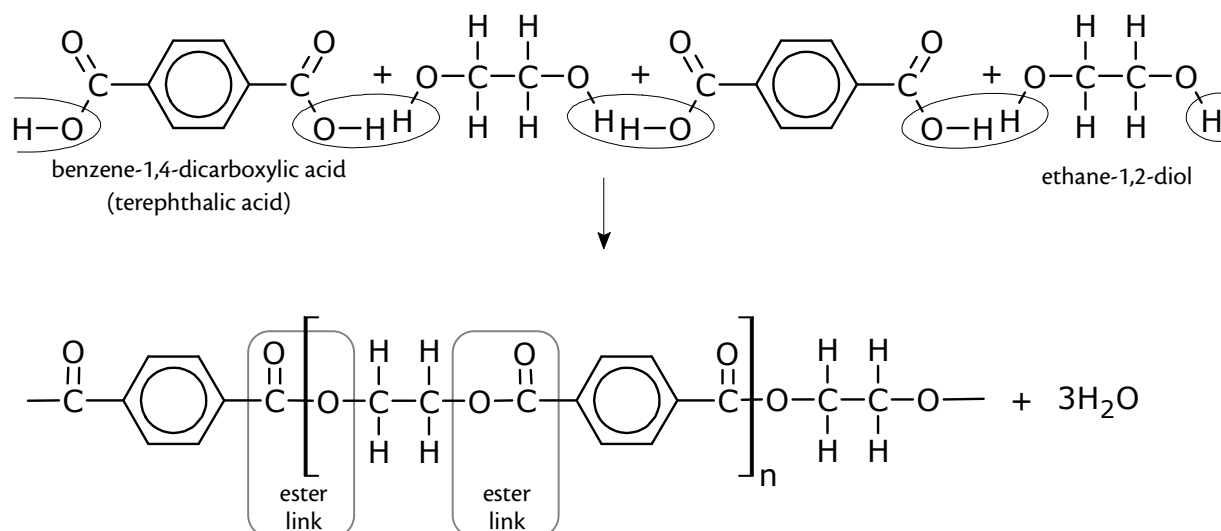


Condensation Polymerisation

The other reaction which can be used to make polymers involves condensation; where a small molecule (often water) is lost from between the two joining molecules. We have already seen an example of this in making esters.

Polyester Formation

If we use a small molecule with two acid groups and another small molecule with two hydroxyl groups it is possible to make thousands of ester links and form long chains.

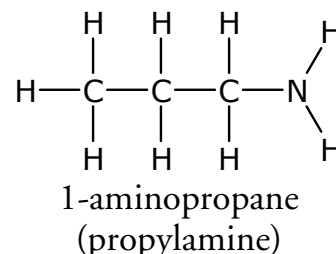
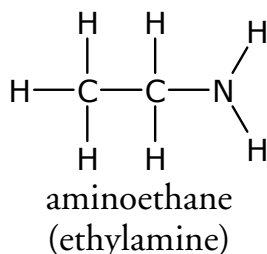
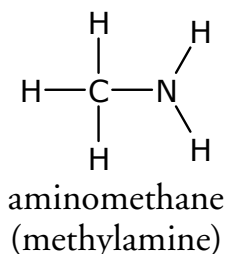


This polymer (terylene) is a linear polymer (a fibre). The fibres can be spun together to give a strong, flexible product used in clothing. This polymer can also be used in making photographic films and recording tapes.

It is also possible to get resins made from polyesters. Here, the di-carboxylic acid has C=C double bonds (ie is unsaturated) so the fibres can 'cross link', giving a three dimensional network. These resins, unlike the polyester fibres, are thermosetting. They are commonly used in conjunction with glass fibre to form glass reinforced plastic (GRP), which is light, inexpensive and hard wearing. It is used in boats, car bodies and in building.

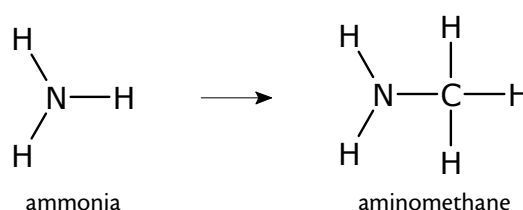
Another example of condensation polymerisation can be seen with molecules having an amine (or amino) functional group. This group has not been met before so we need to introduce it here. Molecules with this type of group give rise to a new homologous series called the **amines**.

The first few members with their names are given:



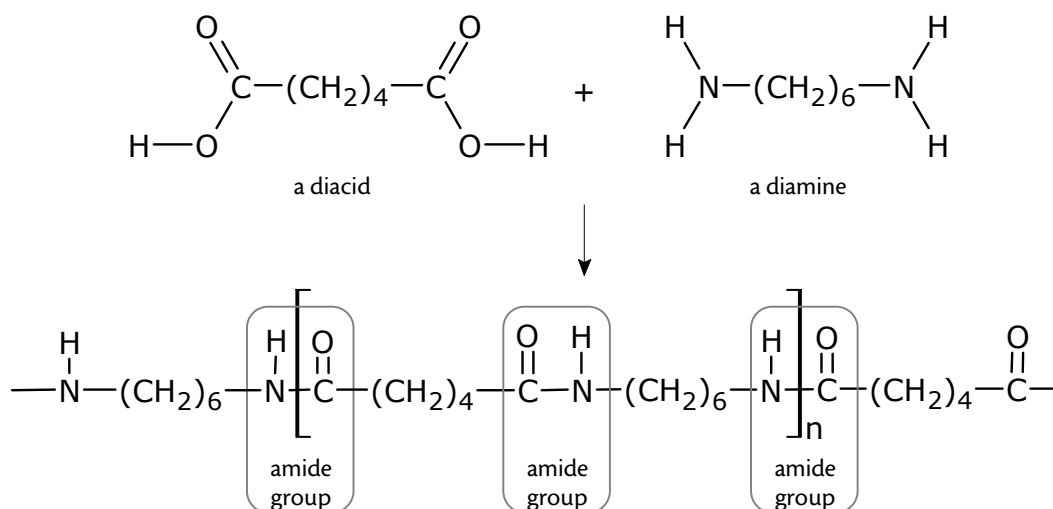
Amines can be thought of as arising from ammonia by replacing a hydrogen with an alkyl group.

The similarity between amines and ammonia is shown by their reaction with copper (II) sulphate solution. Both amines and ammonia give a deep blue solution.



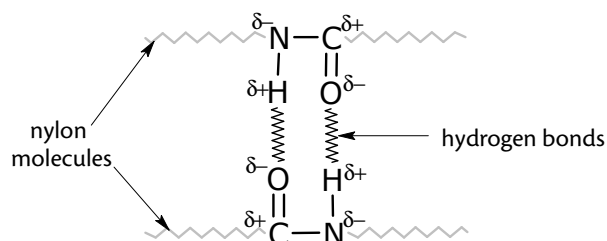
Polyamide Formation

In this, a di-amine condenses with a di-acid.



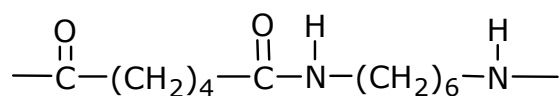
(Note: This is called 'nylon-6,6' because each monomer has six carbon atoms.)

The link formed is an amide link, hence the name polyamide. The best known polyamide has the trade name Nylon. Again, since condensation is the 'joining' reaction, polyamides are classed as condensation polymers. Note that nylon is an extremely important engineering polymer with great strength for its weight. This strength for such a light material is due to strong hydrogen bonding between the chains and along the length of the polymer chains. The $\text{O}^{\delta-}$ of the polar $\text{C}=\text{O}$ groups are strongly attracted to the $\text{H}^{\delta+}$ of the polar $\text{N}-\text{H}$ groups on adjacent chains.

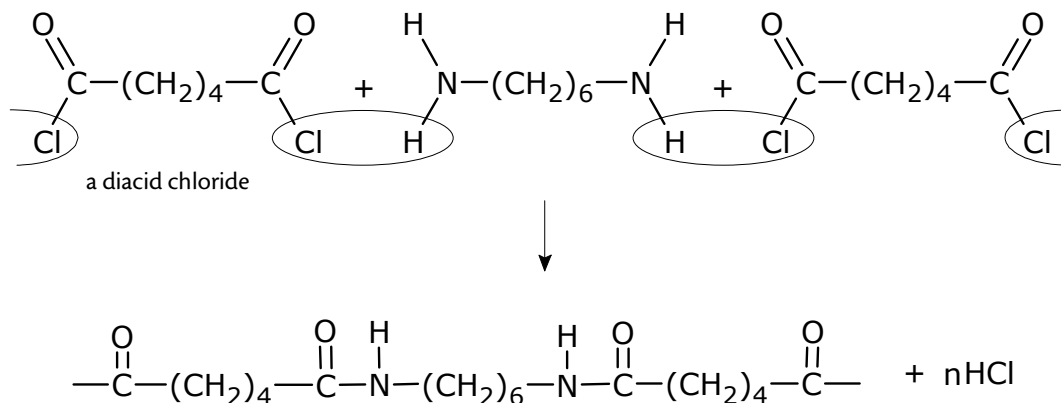


When we are dealing with condensation polymers, the monomers must both have two functional groups. Also, the 'repeating unit' is not as simple as with the addition polymers. The repeating unit must indicate the structures of both the monomers used.

eg The repeating unit for nylon 6,6:



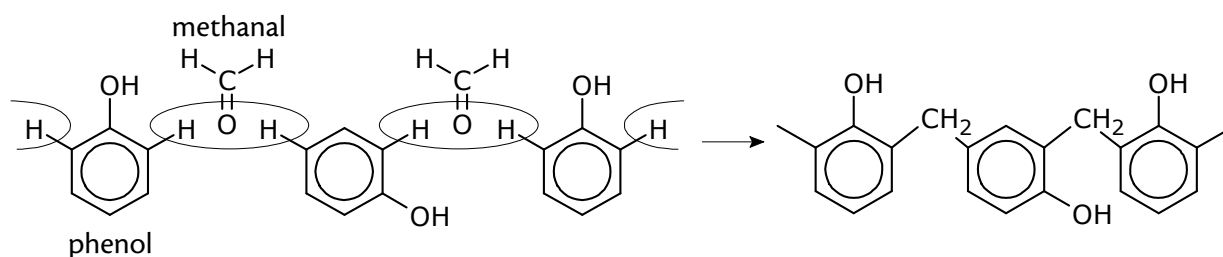
Nylon can also be made using a di-acid chloride instead of a di-acid:



Thermosetting Plastics

The polymers we have met so far have been thermoplastic.

Methanal and phenol react together to form bakelite, a thermosetting plastic. The reaction is another example of condensation polymerisation – as the monomers join, molecules of water are formed as shown:



The reaction goes further than shown. The chains cross link to give a 3-dimensional covalent network. This is a very strong structure which does not soften on heating – in other words a thermosetting plastic.

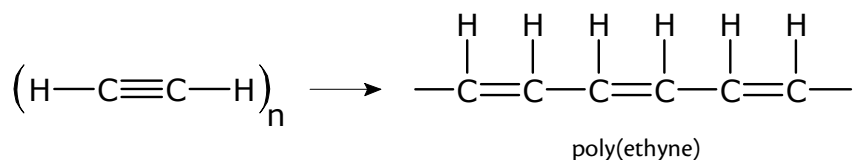
Methanal and urea also react by a condensation polymerisation to produce urea methanal resin, another thermosetting plastic. These plastics are found in pot handles, light fittings, formica work tops and other situations where thermoplastics would soften or melt.

Recent Polymers

A great deal of research has gone into polymer chemistry and some very interesting new materials have been made as a result, such as water soluble polymers and conducting polymers. Here are some examples of recent developments:

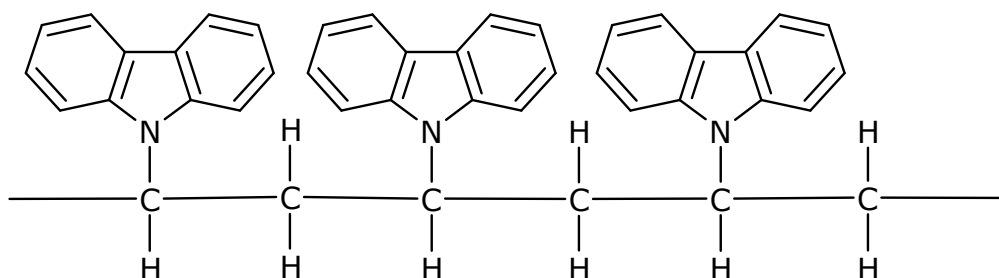
A Conducting Polymer

If ethyne is used to make an addition polymer, we still have a chain which is very unsaturated – with alternating single and double bonds along the chain – poly(ethyne):



The structure is able to allow ‘delocalised’ electrons to pass along the chain (recall the delocalised electrons in benzene). With the correct treatment, poly(ethyne) can be used to make conducting membranes for high performance loudspeakers.

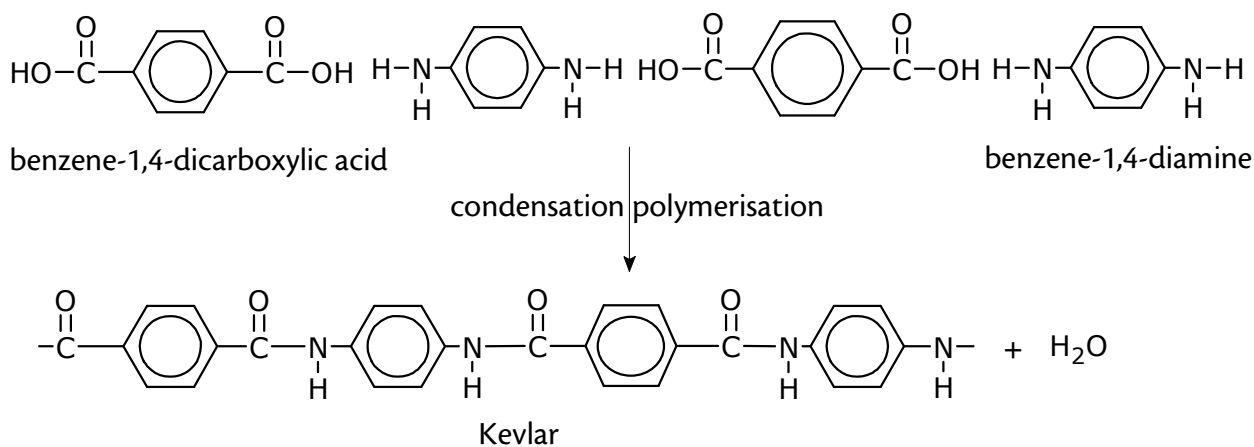
Poly(vinyl carbazole) has the special property of photoconductivity – it can conduct better when light is shone on it. This is used in photocopying machines. It is an addition polymer with the following structure:



Try drawing the repeating unit and the monomer structure for this.

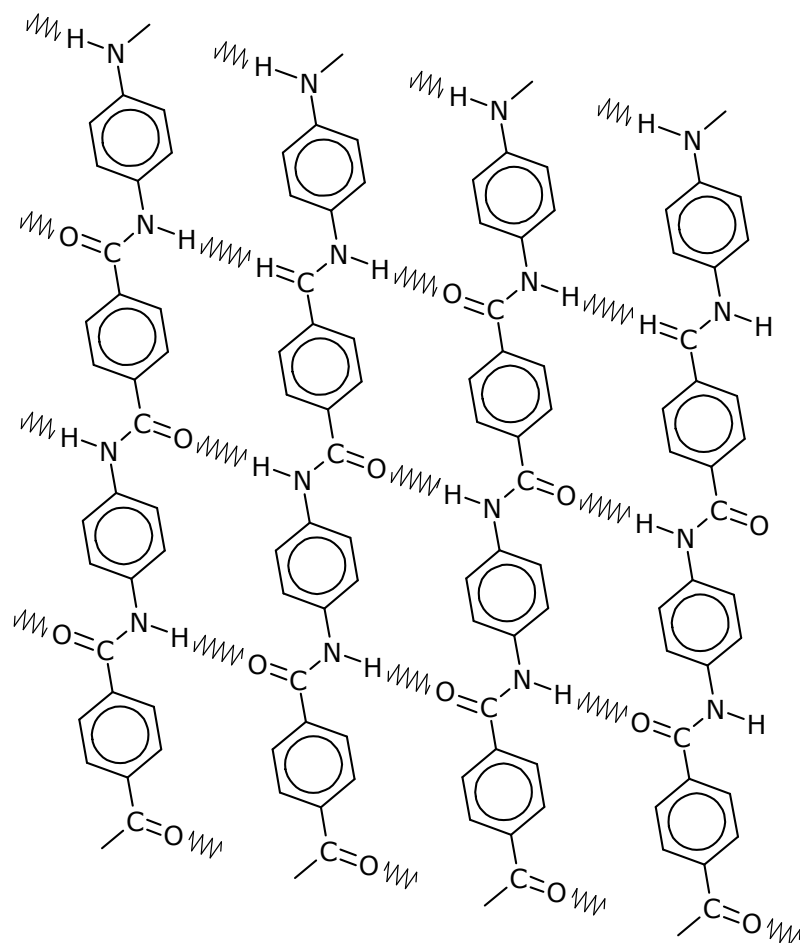
A Bulletproof Polymer

The following two structures are able to make a very special polyamide – Kevlar



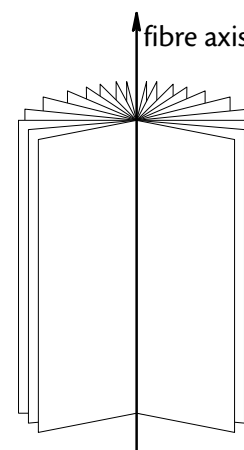
This polymer is special in that the chains of alternating aromatic rings align themselves in a flat formation which makes it possible to hydrogen bond in a very regular and closely packed formation as shown:

Hydrogen-bonded molecular sheet



~~~~~ represents hydrogen bonding

## Stacked sheets



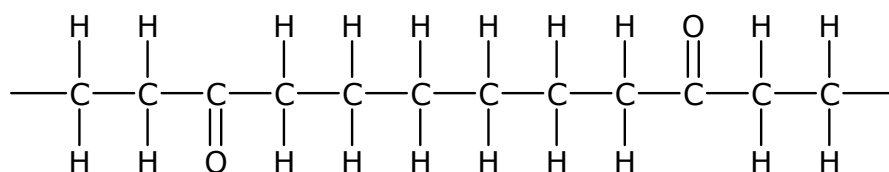
The sheets of molecules can then pack around the axis along their length so we have a material which has great strength due to the extensive bonding. Kevlar is used to make very strong ropes and cords for car tyres – it is much stronger than steel yet considerably lighter. When stiffened, it can be used to make wings on aircraft and it is also used to make bulletproof vests, safety jackets for fencers, and body protectors for motorcyclists and horse riders.

## Degradable Polymers

The polymers already mentioned are all very stable and pose a huge environmental problem – they do not break down and are therefore a big disposal problem. If simply dumped in landfill sites in large quantities, they will just stay there without breaking down. Natural materials like wood and paper do break down and become part of the natural processes again. A great deal of research has been necessary to try to combat this increasing problem, including methods of recycling plastics and also the production of 'degradable polymers', which do break down and are less likely to cause environmental damage.

### A Photodegradable Polymer

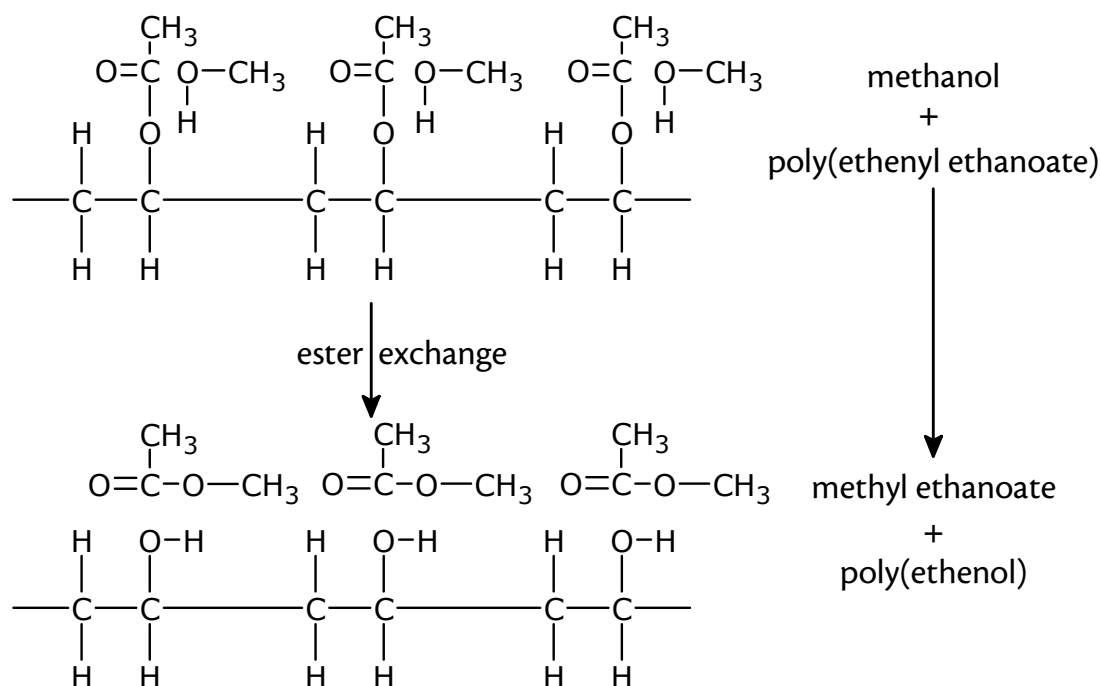
If poly(ethene) is made in such a way that carbonyl groups can be introduced into the chain, we have a polymer which can break down on exposure to light.



The presence of the carbonyl groups in these chains allows the absorption of strong sunlight. The energy trapped by this is able to be used to break carbon-carbon bonds near the carbonyl group and this eventually breaks the molecules into smaller chunks which can 'biodegrade'. This type of material is already being used as the can rings around six pack drinks and is likely to become more used in carrier bags, packaging material and as protective films around young plants.

### A Water Soluble Polymer

The polymer poly(ethenyl ethanoate) was mentioned earlier. This polymer can be reacted with methanol in a reaction called 'ester exchange', in which the ester groups along the chain are replaced as can be seen in the reaction scheme:



The poly(ethenol) produced from this is water soluble if the number of -OH groups along the chain is controlled. The following table shows how the solubility is altered by controlling the number of ester groups which are exchanged:

| % -OH Groups | Solubility in water  |
|--------------|----------------------|
| 100-99       | insoluble            |
| 99-97        | soluble (hot water)  |
| 96-90        | soluble (warm water) |

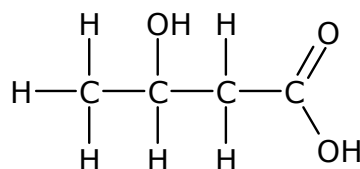
Pure poly(ethenol) is insoluble in water because the -OH groups are involved in a great deal of internal hydrogen bonding so water is unable to interfere with the structure. If,

however, the internal hydrogen bonding is broken up by having the ester groups at regular sites along the chain, then water is able to break in to the structure and dissolve it.

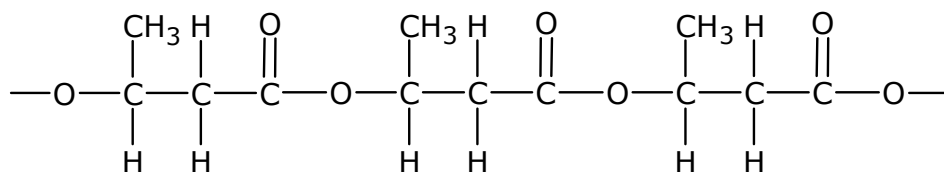
This polymer is used to make laundry bags for hospitals – the laundry is put in to the washing machines enclosed in the bags and the bag quickly dissolves away, exposing the laundry to the washing liquid. It is also used for soluble stitches in surgery, and to make protective coatings for cars, which can be hosed off.

### Biodegradeable polymers (biopol)

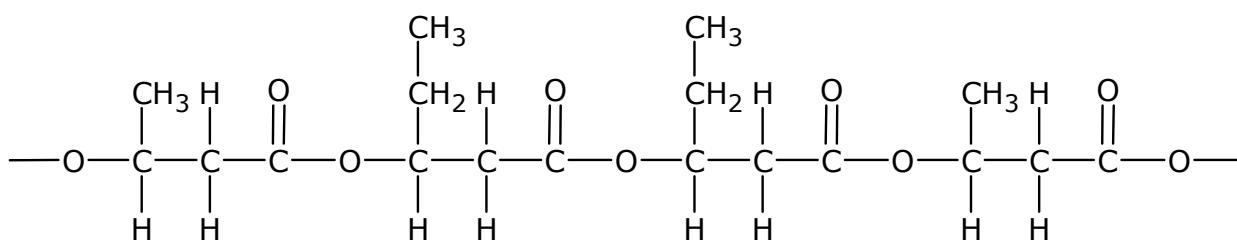
Biodegradeable polymers are a group of natural condensation polymers which can be broken down by micro-organisms in the environment. The trade name biopol is one such polymer. The structure is based on the polymerisation of 3-hydroxybutanoic acid to make poly(3-hydroxybutanoate) or PHB for short. This polymer was in fact discovered about 70 years ago when it was discovered that certain bacteria actually synthesise it and use it as an energy store. It is made commercially by using bacteria in a fermenting mixture. The basic monomer has the following structure:



The linking of the monomers is through the carboxyl group and the hydroxyl group to make ester linkages so it is a polyester.



A modified form of this is actually made to suit the commercial requirements, where propanoic acid is added to the fermenting mixture and some side reactions result in monomers which polymerise to make the following structure:



It was hoped that Biopol could be used in medical fields (surgical stitches and for holding broken bones while they healed) as well as a few other applications. However, high production costs have halted the commercial production in the meantime.

## Topic 2 – Natural Products

### Organic Chemistry

In the last two topics of this unit, the impression that carbon chemistry deals with synthetic or man-made substances might have been suggested. Nothing could be further from the truth. The traditional name for carbon chemistry is ‘Organic Chemistry’ and this was derived from the chemistry dealing with molecules found in living things – molecules found in nature. Another name for such molecules is biomolecules, and most organic chemistry still deals with these – the man made organic chemistry has only really developed during the 20th century.

In this topic we will meet some of the carbon molecules which are found in living systems; fats/oils and proteins.

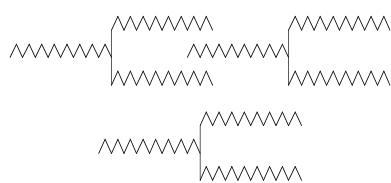
### Fats and Oils

Fats and oils may be obtained from plants and animals and some examples are shown in the table. Note that the fats are mainly obtained from land animals and oils from plants and marine animals.

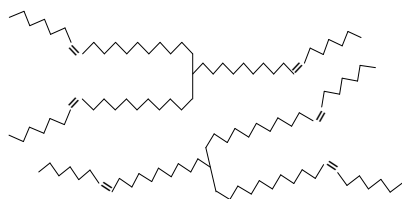
| Vegetable origin | Animal origin  |
|------------------|----------------|
| Soyabean oil     | Whale oil      |
| Palm oil         | Cod liver oil  |
| Olive oil        | Pork fat: Lard |
| Castor oil       | Mutton fat     |
| Linseed oil      | Beef fat       |

The main obvious difference between fats and oils is that fats are solid at room temperature and oils are liquids. There must be some difference between the two types of molecule that affects the melting points (melting points are lower for oils). The main ‘chemical’ difference which ties in with this is the higher level of unsaturation in oils – oil molecules contain many more C=C double bonds. This can be shown by shaking oils with bromine water – the brown colour disappears quite readily. If fats, dissolved in a suitable saturated solvent, are tested with bromine water the brown colour remains.

The diagrams and explanations below show how the presence of even just one C=C double bond can drastically alter the shape of the molecules and change the properties of the compound.



Diagrammatic representation of the structure of fat molecules



An exaggerated picture of oil molecules

The shape of both oil and fat molecules is roughly that of a tuning fork. The absence of a double bond allows the molecules to be more regularly tuning fork shaped and consequently the molecules can fit into one another. If a double bond is present then the molecules ‘zigzag’; chains become distorted and cannot fit into one another.

Molecules which can pack closely together due to their regular structure have stronger Van der Waals forces between the molecules and thus higher melting points. So fats have higher melting points than oils – fats are solid at room temperature.

Marine animals that live in cold oceans often have oils because fats would be solid and could not be transported round the body.

## Hardening of oils

It is possible to ‘harden’ oils into fats simply by reacting the double bonds with hydrogen. This is an addition reaction and changes unsaturated compounds into saturated ones. This is similar to the catalytic addition of hydrogen across the double bond in an alkene.

Margarines are made by partial hydrogenation of oils using a nickel catalyst. The degree of hydrogenation, along with different forms of refinement and blending can produce margarines with different properties.

## Additives in margarines

Various ingredients are added to margarines to improve taste, appearance, saleability and health. These include:

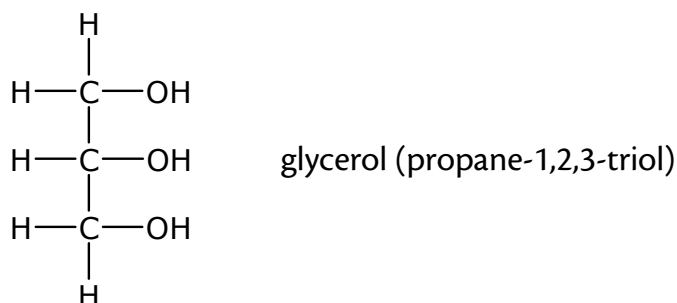
- Vitamins A and D. These are vitamins which are mainly obtained from oils and fats and which people obtained from butter. They must now be added to the butter substitutes.
- Colouring materials.
- Emulsifiers. Margarine is actually a water/oil emulsion and to keep the emulsion stable it is necessary to add emulsifying agents such as lecithin.
- Flavouring agents. These are added to enhance the ‘butter’ flavour of the margarines.

## Fats in the body

The main dietary function of fats and oils is to provide energy. Weight for weight, they release about twice the amount of energy of carbohydrates. The difference between fats/oils in the body and carbohydrates is that fats/oils release their energy much more slowly – sugars etc. are quick burning sources of energy. Fats and oils also provide the body with some vitamins such as A, D, E and K, as these vitamins are soluble in fats/oils. In fact, margarine manufacturers are required to add some of these vitamins to their products to prevent certain vitamin deficiency problems.

## The Structure of Fats and Oils

Fats and oils are actually special forms of esters where the alcohol, glycerol (propane-1,2,3-triol) has three hydroxyl groups. Because of this, glycerol is termed a ‘trihydric alcohol’.



Each of the hydroxyl groups forms an ester linkage with a long chain carboxylic acid – these are called ‘fatty acids’. The ratio of combining of glycerol molecules with fatty acid molecules is therefore 1:3.

It is in the acid chain that we find the absence or presence of the double bond – if there is a double bond the acid is called an alkenoic acid. Some examples of these acids are given below:

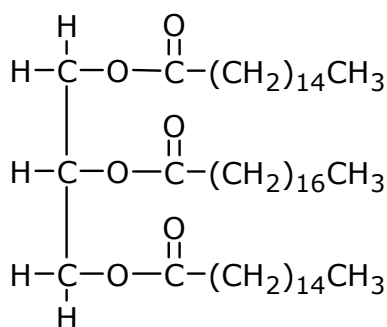
Palmitic acid  $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$

Stearic acid  $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$

Oleic acid  $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$

Linoleic acid  $\text{CH}_3(\text{CH}_2)_3(\text{CH}_2\text{CH}=\text{CH}_2)_2(\text{CH}_2)_7\text{COOH}$

Note that fatty acids are saturated or unsaturated straight chain carboxylic acids with even numbers of C atoms ranging from  $\text{C}_4$  to  $\text{C}_{24}$ , but mainly  $\text{C}_{16}$  to  $\text{C}_{18}$ . A typical fat molecule is shown below:



The fat or oil molecule is called a triglyceride. When a fat or oil is formed, the glycerol molecule can react with three different fatty acid molecules.

Any particular fat, such as beef fat, is made of a mixture of different triglycerides. So no fat or oil is a pure triglyceride.

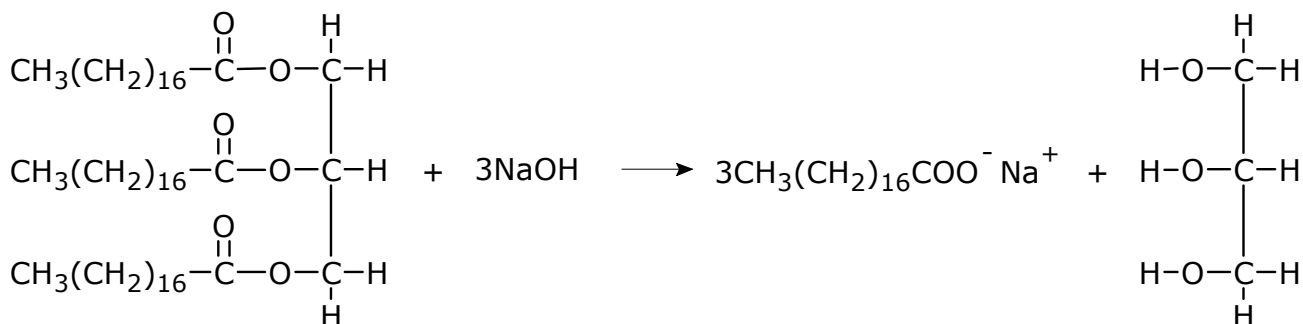
## Hydrolysis

We have already seen that ester groups can undergo a hydrolysis reaction where a water molecule can be ‘reinserted’ into the ester link. This results in the alcohol and the carboxylic acid being formed.

It is possible to break up fat and oil molecules into the glycerol (the alcohol part) and the fatty acids by hydrolysis. This can simply be done by treatment with superheated steam. In the lab, this hydrolysis is normally done using aqueous acid or alkali. A very important example of the hydrolysis of fats and oils is in the production of soaps.

## Soaps

Soaps are made from fats and oils by hydrolysing them using solutions of sodium hydroxide or potassium hydroxide. The fatty acid is formed as the sodium or potassium salts. These salts are 'salted out' of the reaction mixture by adding a great excess of sodium chloride and the soap can then be filtered off.

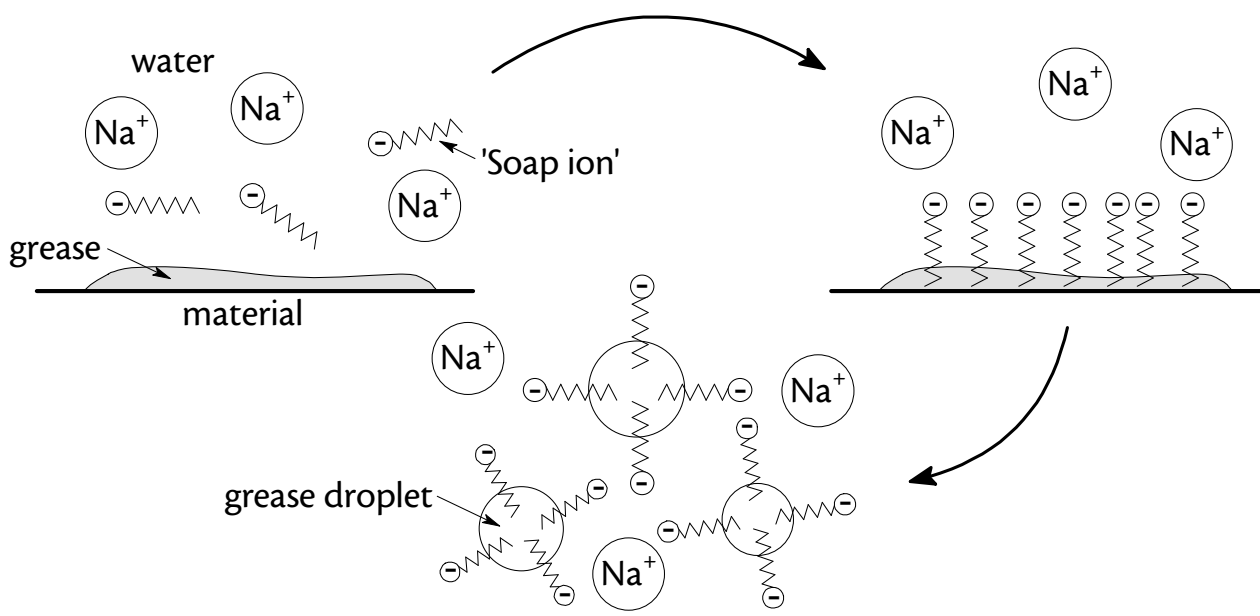


## The Cleaning Action of Soaps and Detergents

Soaps and detergents are 'emulsifying reagents'. These are simply chemicals which can make oil and water become permanently mixed to produce a stable emulsion. As most of the grime and dirt on skin, clothes and dishes tends to be trapped in oils and greases, water alone cannot rinse away the muck. If the oils/greases can be made to mix with water then it becomes easy to wash off, along with the grime. Soaps and detergents do this job in a clever way, due to the structure of the molecules:

Sodium or potassium salts of long chain fatty acids really have two quite separate parts in terms of their bonding types – a long hydrocarbon chain which is non polar and an ionic 'head'.

Recall that non polar molecules are very insoluble in water but are soluble in non polar solvents such as oil. Ionic compounds (particularly those of the alkali metals) are generally soluble in water but not in non polar solvents. Soap molecules have two sets of solubility properties in different parts of their structure and it is this that makes soaps and detergents good emulsifying agents. The following set of diagrams show how this works.

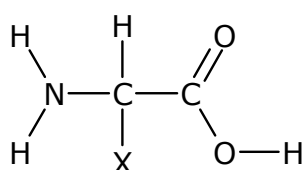


## Proteins

At Standard Grade, we learned that the element nitrogen was essential in the food chain (you may wish to revise the nitrogen cycle) and its place in the food cycle is in the formation of proteins.

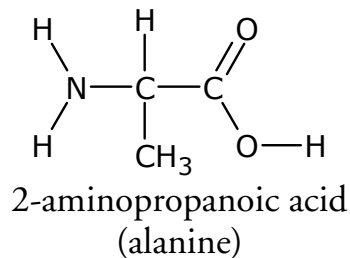
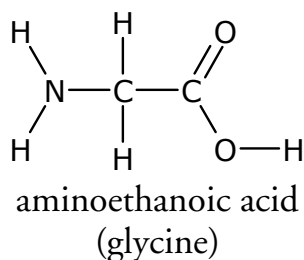
Proteins are the molecules which make up our muscle fibres, hair, nails, skin, enzymes etc. They are generally very large molecules which are made up from smaller molecules called amino acids – ie they are natural polymers.

The smaller molecules (monomers) contain two functional groups which have been met before; the amine group  $\text{-NH}_2$  and the carboxyl group  $\text{-COOH}$ . The amino acids contain both these groups on the same molecule, and it is possible to get many isomers by altering the relative positions of the two groups on a molecule, but natural amino acids must have the two groups bonded to the same carbon atom. They are called  $\alpha$ -amino acids



X can be H, or an alkyl group, or sometimes even groups with S, P, or other N atoms.

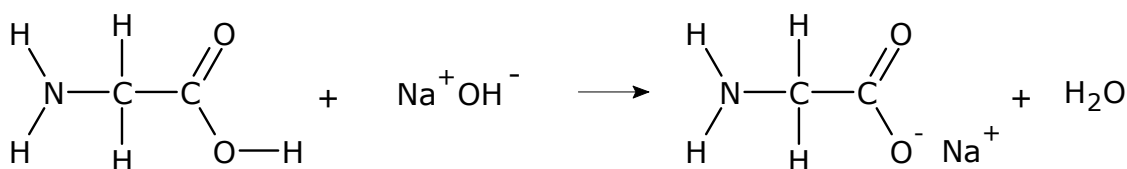
There are about 20 naturally occurring  $\alpha$ -amino acids; the simplest two are glycine and alanine. Their structures and systematic names are:



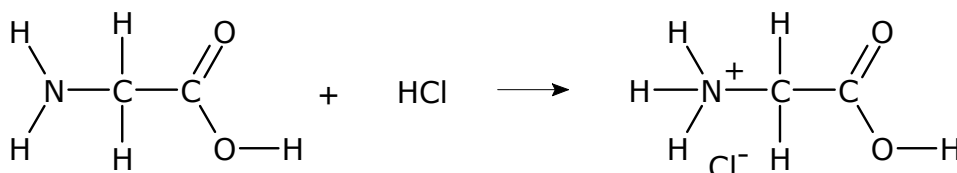
## Reactions of amino acids

Amino acids have two functional groups on their molecules – the carboxyl group and the amino group, both of which have been met before. Amino acids can therefore react as acids and as bases, using either of these groups:

eg as an acid



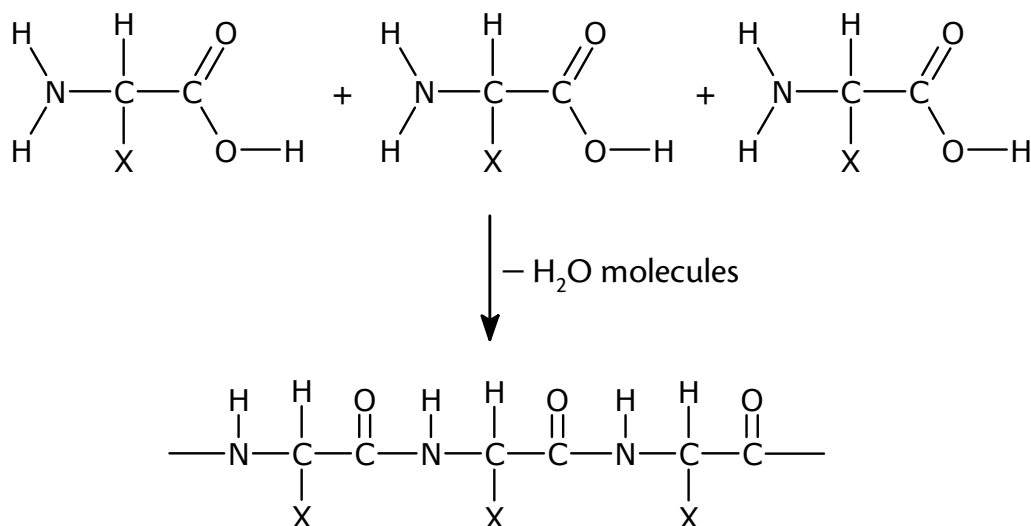
eg as a base



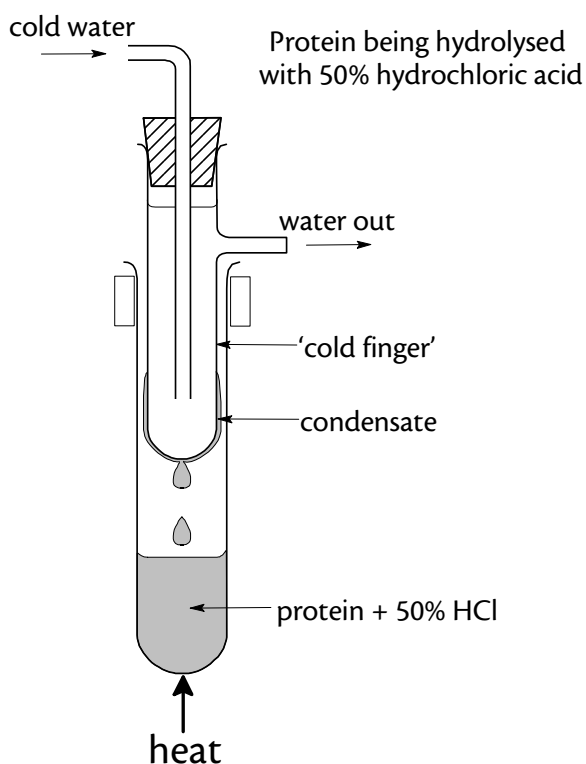


Proteins are made by the condensation of amino acid molecules to give a long string-like molecule. Proteins are therefore condensation polymers of amino acids. The link formed between the amino acids is called a peptide link (we have met the same link before in nylon and kevlar but it was referred to as the 'amide' link. In biological molecules, the term peptide has become preferred). The actual structure of a particular protein depends on the amino acids present.

The scheme below shows that the links are formed between the amino group of one molecule and the carboxyl group of an adjacent molecule.

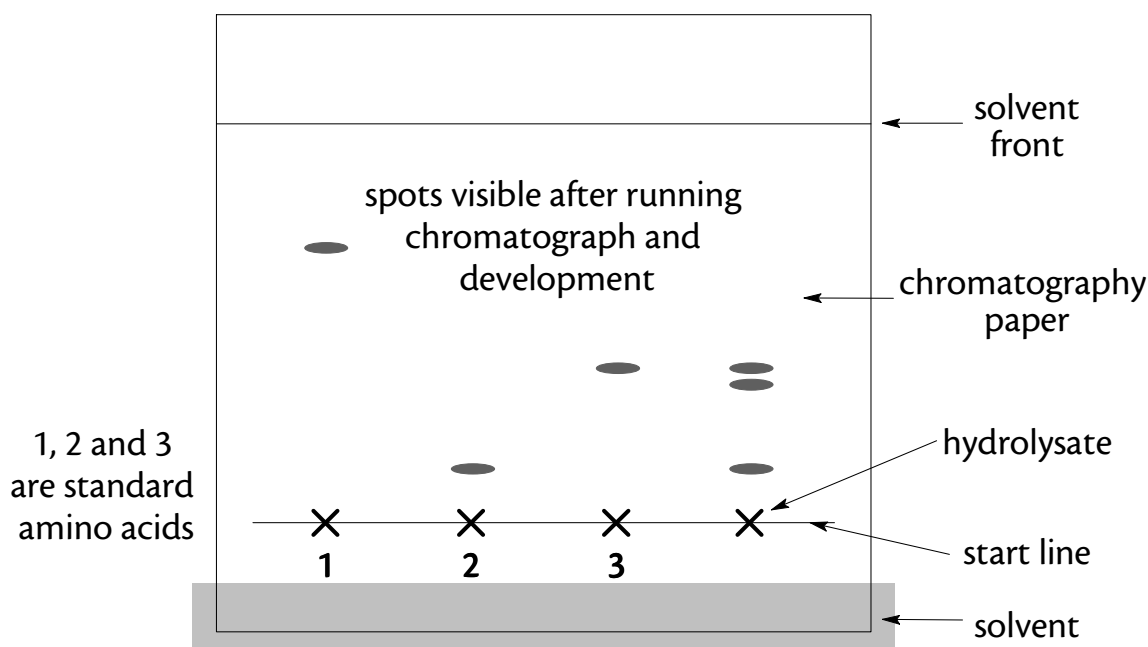


Proteins have very large molecular mass due to their being made from several thousand amino acid molecules. They can be broken back down to their constituent amino acids by hydrolysis (just as all condensation polymers can!) In the lab, this can be done by 'refluxing' the protein with fairly concentrated hydrochloric acid. The apparatus below shows how this can be done simply. In the stomach, enzymes more efficiently hydrolyse the proteins into the amino acids.



## Chromatography

The amino acids produced by the breakdown of proteins can be identified by using the technique of chromatography. This has been studied at Standard Grade level. The diagram below shows the result of running a simple chromatogram of a hydrolysed protein. Note that, unlike the pigments in inks, amino acids are colourless and invisible so the spots on the paper must be 'developed' using a special solution.



## Other Reactions of Proteins

Proteins are nitrogen containing compounds and this can be shown by heating the protein with a strong alkali. Soda lime is normally used for this and if the protein is ground up with soda lime and gently heated in a test tube alkaline gases are given off – this can be shown using damp pH paper, which turns blue. Note that this test does not confirm that a substance is a protein, only that it contains nitrogen!

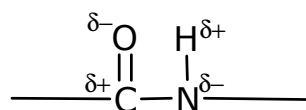
## Amino Acids in Nature

The number of possible amino acid structures is very great, but nature only uses 26 different structures. Protein molecules normally consist of several thousand amino acids condensed together so the permutations are endless! (Hence the huge variety of protein structures.) The bodies of living things cleverly build up proteins specific to the bodies' needs from the supply of amino acids in the diet. Some amino acids can actually be made in the body given the correct materials. Some, however, must be present in our diet and these are called 'essential amino acids'. The absence of even one of these essential amino acids from our diet can cause serious dietary deficiencies – remember it takes only the lack of one amino acid to prevent the formation of a protein which it contains! If the body cannot produce it and it is not present in our diet then the protein can't be made. In many Asian and African countries, the people live on a highly restricted vegetarian diet and the availability of all the essential amino acids is limited – protein deficiency diseases such as kwashiorkor affect many people as a result.

## Types of Protein

Proteins in the body perform a vast range of jobs. As a result of this, they can exist in a range of sizes and shapes.

We have seen that the amino acids are joined by peptide links:

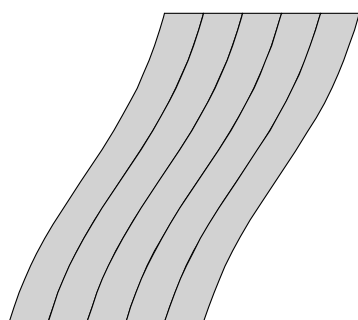


These polar peptide links can hydrogen bond (an intermolecular force) with each other in the same chain to produce a helix structure or in different chains to produce a sheet structure. These helices or sheets can then be folded to give fibrous or globular proteins.

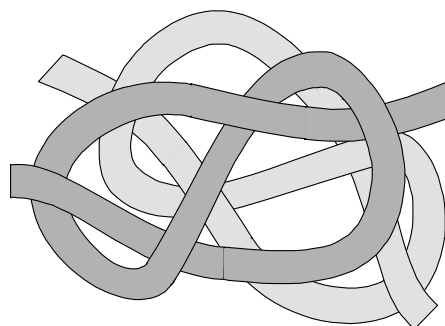
Fibrous proteins are the ones which form the structural materials in animal tissues – eg skin, muscle, hair, nails.

Globular proteins tend to have spiral chains folded and twisted round into more compact units and are generally the ones which are involved in the chemistry of metabolic regulation within the living systems. For example, enzymes (more of which later), hormones (eg insulin for the control of blood sugar levels) and haemoglobin for the transport of oxygen within the bloodstream are globular proteins.

The following diagram shows examples of these two types of protein.



fibrous protein



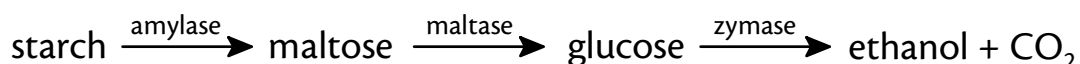
globular protein

## Enzymes

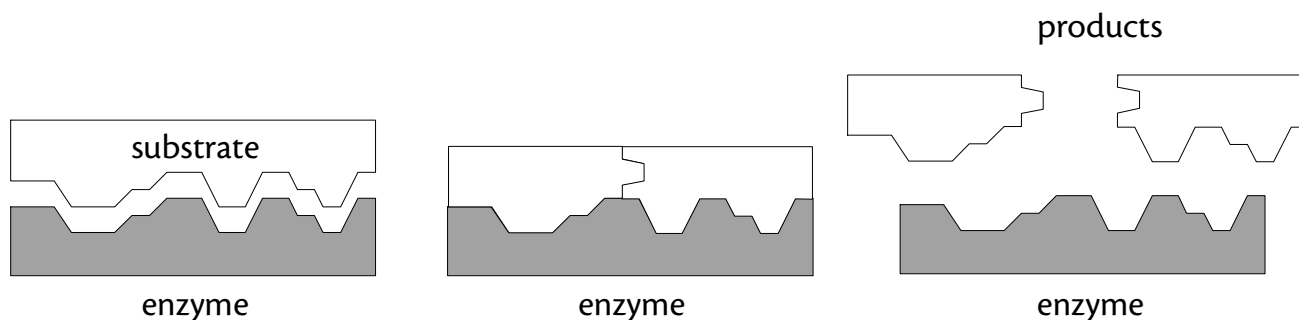
Enzymes are proteins. They are important natural substances in the bodies of all living things. Enzymes are natural catalysts and without them, the biochemical reactions which happen in all living things would not take place. All enzymes are totally protein in their structure but some need another part (called a co-enzyme) before they can function.

Enzymes are said to be specific. This means that each enzyme only catalyses one reaction – the enzyme diastase can only break down molecules of starch to glucose in the mouth and stomach but can have nothing to do with the breakdown of proteins for example.

Some chemical processes involve a sequence of reactions each stage of which requires a different enzyme. The production of ethanol from starch in fermentation for example:



The scheme below shows how enzymes are thought to work; the ‘lock and key’ principle.



The specificity of enzymes is therefore due to their molecular shapes. Different proteins can have different shapes so can interact with different molecules. The 3D shapes of the molecules are influenced by the presence of hydrogen bonds between the chains. Enzymes are most active within certain narrow temperature and pH ranges. The protein structure of the enzyme is permanently altered at high temperature or low pH conditions as the hydrogen bonds are broken. This is called ‘denaturing’ the protein – eg. cooking an egg – once the egg is cooked it can never become ‘uncooked’. How easily the protein is denatured depends on how susceptible the enzyme is to pH and temperature. Note that in denaturing, that covalent bonds are not broken.