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### **ORGANIC CHEMISTRY**



### OIL and its many useful PRODUCTS



### The origin of oil

- **Crude oil** is **formed** from organic material of the remains of plant and animal organisms that lived millions of years ago. These remains form sediments eg at the bottom of seas, and become **buried** under layers of sedimentary rock. They decay, **without air (oxygen)**, under the action of **heat and pressure** to form crude oil over millions of years.
- It is a **fossil fuel** because it is formed from once living organisms and the Sun is the original source of energy. It is a **non-renewable** and **finite (limited reserves) energy** resource because it takes millions of years to form and we burn it faster than its is formed! It is also known as a **finite energy resource** because it will eventually run out! We do not have unlimited oil reserves!
- **Coal** and **natural gas** (mainly methane CH<sub>4</sub> and often found with oil) are **also non-renewable fossil fuels** formed from the remains of plants or animals.
- When the **fossil fuels are burned** the 'carbon', as **carbon dioxide**, is returned to the living environment, gets used up in **photosynthesis**, the plant material decays or is eaten by animals, so completing the **carbon cycle**.



#### The SEPARATION of the crude oil mixture into fractions and the USES of these fractions

A **fraction** is a mixture of a restricted boiling point range of molecules, they have a similar number of carbon atoms and physical properties. The uses of the fractions depend on their physical and chemical properties.



### Н Н Н Н H-C-C-C-C-H H Н Н Н

- Hydrocarbon molecules are only made of a chemical combination of carbon and hydrogen atoms.
- They are compounds because they consist of atoms of atleast two different elements.

 Crude oil is a complex mixture of mainly hydrocarbon compound molecules. A mixture consists of two or more elements or compounds which are not chemically combined. The chemical properties of each substance in the mixture is unchanged.

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- This means crude oil can be separated by physical methods, in this case **fractional distillation**, because they have **different boiling and condensation points**.
- The most volatile fraction, ie with the lowest boiling point, boils or evaporates off first and goes to the top of the column.
- The rest separate out according to their boiling point so that the highest boiling fraction, ie the **less volatile with higher boiling points**, tend to **condense more easily** lower down the column.
- The bigger the molecule, the greater the intermolecular forces, so the higher the boiling point. Chemical bonds are not broken in the process, only the intermolecular force of attraction.

THE FRACTIONAL DISTILLATION OF CRUDE OIL		names of fractions	C atoms in the molecule	boiling range in °C	USES of the fraction
fractionating column to separate		Fuel Gas, LPG, Refinery Gas	1 to 4	-160 to 20°C	methane gas fuel, C <sub>3-4</sub> easily liquefied, portable energy source bottled gas for cooking (butane), higher pressure cylinders (propane)
the components in crude oil decrease in • boiling point • viscosity • carbon atoms in molecule increase in • volatility • ease of ignition		Gasoline, Petrol	5 to 11	20 to 60°C	easily vaporised, highly flammable, easily ignited, car fuel
		Naphtha	7 to 13	60 to 180°C	no good as a fuel, but valuable source of organic molecules to make other things, cracked to make more petrol and alkenes
	╼╼╴	Paraffin, Kerosene	10 to 16	120 to 240°C	less flammable than petrol, domestic heater fuel, jet fuel
		Diesel oil, Gas oil	15 to 25	220 to 250°C	Car and larger vehicle fuel
		Fuel and lubricating Oils and Waxes	20 to 70		not so easily evaporated, not as flammable, safe to store for central heating oil, quite viscous (sticky) and can also be used for lubricating oils, clear waxes and polishes
		Bitumen	over 70	over 350°C	forms a thick, black, tough and resistant adhesive on cooling, used as waterproofing material and to sticks rock chips on roofs or road surfaces





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#### More on examples of relating the physical properties of the fractions to their uses and dangers

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the list the molecule gets bigger, more viscous, higher boiling and less flammable

- The refinery gas fractions, under pressure, are conveniently pumped to burner systems, but are easily ignited and explosive.
- Vehicle fuels must be liquid for compact and convenient storage but they must be easily vapourised to mix with air in the engine prior to ignition. The ease of vaporisation does however make them flammable!
- Paraffin and kerosine are less flammable and safer, but not as easily ignited.
- Fuel oil is not too viscous to pump to a central heating burner, and it is not very volatile and so not as flammable and dangerous as petrol or diesel etc. for domestic use.
- Lubricating oil must be quite viscous to stick onto surfaces. Smaller molecules might be more runny but they would evaporate away! It is also water repellent and helps reduce corrosion on moving machine parts.
- Candle wax is very convenient as a solid for humble lamp (especially in power cuts!), but via a wick, the heat from the flame is sufficient to vaporise the hydrocarbons to burn them.
- Bitumen is a water repellent solid at room temperature but is readily melted (sometimes too easily in hot weather). Used as base for a road chipping top surface or sometimes directly. It is also used to waterproof roofing felt.





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### TABLE 25.1 First Several Members of the Straight-Chain Alkane Series

Molecular Formula	Condensed Structural Formula	Name	Boiling Point (°C)
CH4	CH4	Methane	-161
C <sub>2</sub> H <sub>6</sub>	CH <sub>3</sub> CH <sub>3</sub>	Ethane	-89
C <sub>3</sub> H <sub>8</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	Propane	-44
$C_{4}H_{10}$	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Butane	-0.5
C <sub>5</sub> H <sub>12</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Pentane	36
C <sub>6</sub> H <sub>14</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Hexane	68
C7H16	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Heptane	98
C <sub>8</sub> H <sub>18</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Octane	125
C <sub>9</sub> H <sub>20</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> CH <sub>3</sub>	Nonane	151
C <sub>10</sub> H <sub>22</sub>	CH <sub>3</sub> CH <sub>2</sub>	Decane	174

TABLE 25.2 Condensed Structural Formulas and Common Names for Several Alkyl Groups					
Group	Name				
CH <sub>3</sub> -	Methyl				
CH <sub>3</sub> CH <sub>2</sub> —	Ethyl				
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> —	Propane				
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -	Butyl				
с́н <sub>3</sub> нс— сн <sub>3</sub>	Isopropyl				
сн <sub>3</sub> сн <sub>2</sub> —с— сн <sub>3</sub>	≁-Butyl				



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#### The Incomplete Combustion of hydrocarbons

- If there is **not enough oxygen** present to completely burn the fuel to carbon dioxide and water other products may form causing **pollution and fuel inefficiency**.
- The most common partially burned products are likely to be **carbon C (soot)** and deadly **carbon monoxide CO**.
- It would appear that the hydrogen in the fuel molecules is more easily burned and usually forms water.
- There is also less heat released compared to complete combustion.
  - eg  $CH_{4(q)} + O_{2(q)} = > C_{(s)} + 2H_2O_{(l)}$
  - o or  $2CH_{4(q)} + 3O_{2(q)} = > 2CO_{(q)} + 4H_2O_{(1)}$
- Therefore it is extremely important that any combustion system is as efficient as possible eg gas heaters, furnaces etc. must all have excellent ventilation for complete combustion to harmless water and carbon dioxide.
- If there is any smell of gas, make sure (i) all appliances are turned off, (ii) all sources of ignition are absent, and (iii) ring the gas board!
- Faulty gas appliances have led to tragic deaths. **Carbon monoxide** is **colourless** and **odourless** and even **low concentrations** in the air can be **fatal**.
- Carbon monoxide is unfortunately emitted by all car exhausts, though **catalytic converters** help reduce this by converting nitrogen monoxide (another pollutant) and carbon monoxide into harmless nitrogen and carbon dioxide.
  - $\circ$  2NO<sub>(g)</sub> + 2CO<sub>(g)</sub> => N<sub>2(s)</sub> + 2CO<sub>2(l)</sub>

#### What makes a good fossil fuel?

#### Factors that should be taken into consideration

- Energy value: eg kJ of heat energy released per kg;
- Availability: Geographical convenience, oil production levels;
- Storage: Health and safety issues eg coal very safe, natural gas more dangerous
- **Cost**: Extraction, transport, market price
- **Toxicity** and **Pollution**: Greenhouse effect (which produces the least or most CO<sub>2</sub>/energy released?); sulphur content of fuel (most removed before fuel used to minimise sulphur dioxide and acid rain formation); efficiency of combustion eg minimum carbon monoxide and soot levels
- Ease of use:
- •



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#### The ALKENE hydrocarbons series

**Alkenes** are hydrocarbons containing a **double bond** as well as single bonds. These are called **unsaturated molecules** because two atoms can join onto the bond when it opens up. The first two in the series are shown below. They are extremely reactive and important compounds in the chemical industry and are converted into very useful compounds eg plastics. They are made from <u>cracking</u> processes (see below)

**1)** is the **molecular formula**: a **summary** of the totals **of** each **atoms** of each element in one molecule; **(2)** is a **'shorthand'** version of the structural or displayed formula (3); **(3)** is called the **structural or displayed formula**: it shows how all the atoms are linked with the covalent bonds **-**





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#### Three problems associated with using Polymers or Plastics

- Polymers or plastics cannot be easily broken down by microorganisms ie they are **not** biodegradable. This leads to waste disposal problems and 'non-rotting' litter around the environment and land-fill sites are getting full!
- When plastic materials burn they can produce highly toxic gases such as carbon monoxide, hydrogen cyanide and hydrogen chloride (particularly from PVC and other plastics containing chlorine and nitrogen). This has caused deaths in house fires and controversial problems with alleged inefficient waste incinerators and they will generally cause environmental problems if burning on waste tips etc.
- It is **difficult to recycle plastics** because of separation into the various sorts. It would be beneficial to prolong the life of the finite crude oil reserves AND reduce pollution and space in land-fill sites.
- New plastics are being developed which are more biodegradable or can be recycled, so will the paper bag and cardboard package make a comeback? (in Eire you have to bring your own bag or buy one, and not necessarily a plastic one!).



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- It is a non-polluting clean fuel since the only combustion product is water and so its use 0 would not lead to all environmental problems associated with burning fossil fuels.
- It would be ideal if it could be manufactured by electrolysis of water eq using solar cells. 0

A<sup>l</sup><sup>4</sup>EVE

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Hydrogen can be used to power **fuel cells** on the "Extra Electrochemistry" page. 0





Isopentane





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Some organic compounds are used as fuels. Other organic compounds, including plastics, are burned as waste. Burning these organic compounds releases gases into the atmosphere.

- All organic compounds consist partly of carbon atoms. Coal, crude oil, natural gas (methane) and wood contain organic compounds
  - o all are used as fuels, either directly like coal or natural gas,
  - o or indirectly as coke from coal or petrol from crude oil etc.,
  - o and apart from wood, they are finite (limited reserve) fossil (from decayed organic material) fuels.
  - Many hydrocarbons are fuels ie a substance burned to release heat energy.
- When organic compounds are burned in a plentiful supply of air the carbon is oxidised to carbon dioxide and the hydrogen is oxidised to water.
- In a limited supply of air **incomplete combustion** occurs forming carbon monoxide and/ or carbon. Carbon monoxide is poisonous because it reduces the capacity of blood to carry oxygen.
- Combustion equations and tests for combustion products are all on the <u>Oil Notes</u> web page.
- Each fossil fuel has a different cost, efficiency and cleanliness on burning. Generally speaking in 'cleanliness' the order is methane (natural gas) > alkanes in petrol > heavy oil and from left to right there is also an increase in C/H atom ratio in the molecule so more CO<sub>2</sub> produced too. Some <u>notes on other fuels</u> (but they are designed for more advanced level courses) and a <u>fossil fuel survey</u> on Oil Products Notes page
- **The combustion of plastics** (and other organic compounds) which contain chlorine and nitrogen produce poisonous fumes when burnt eg choking hydrogen chloride HCl and toxic hydrogen cyanide HCN respectively. Especially where there is a limited supply of air. The combustion products of carbon (toxic CO and CO<sub>2</sub>) and hydrogen (H<sub>2</sub>O) are also formed.
- Hydrogen gas can be used as fuel.
  - It burns with a pale blue flame in air reacting with oxygen to be oxidised to form water.
  - hydrogen + oxygen ==> water or  $2H_{2(g)} + O_{2(g)} ==> 2H_2O_{(1)}$
  - It is a non-polluting clean fuel since the only combustion product is water and so its use would not lead to all environmental problems associated with burning fossil fuels.
  - It would be ideal if it could be manufactured by electrolysis of water eg using solar cells.
  - Hydrogen can be used to power <u>fuel cells</u> on the "Extra Electrochemistry" page.





#### 2a INTRODUCTION

Organic compounds belong to different families. The compounds in each family have a similar chemical structure and a similar chemical formula. Each family of organic compounds forms what is called a **homologous series**. Different families arise because carbon atoms readily join together in chains (catenation) and strongly bond with other atoms such as hydrogen, oxygen and nitrogen. The result is a huge variety of 'organic compounds'. The name comes from the fact that most of the original organic compounds studied by chemists came from plants or animals.

- A homologous series is a family of compounds which have a general formula\* and have similar chemical properties • because they have the same functional group of atoms (eq C=C alkene, C-OH alcohol or -COOH carboxylic acid). \* Match the general formula pattern with the alkane and alkene examples shown below. 0
- members of a homologous series have similar physical properties such as appearance, melting/boiling points, solubility etc. but show trends in them eg steady increase in melting/boiling point with increase in carbon number or molecular mass.
- The **molecular formula** represents a summary of all the atoms in the molecule (see examples below).
- The structural or displayed formula shows the full structure of the molecule with all the individual bonds and atoms shown (though there are different 'sub-styles' of varying detail, see below).

#### **2b ALKANES**

- These are obtained directly from crude oil by fractional distillation (see oil notes).
- The saturated hydrocarbons form an homologous series called alkanes with a general formula C<sub>n</sub>H<sub>2n+2</sub>
- Saturated means the molecule has no C=C double bonds, only carbon-carbon single bonds, and so has combined with the maximum number of atoms is no atoms can add to it. The alkanes don't really have a functional group and have quite a limited chemistry BUT they are still a clearly defined homologous series.
- **Alkane examples**: The gases: methane  $C_{44}$ , ethane  $C_{2}H_{67}$ , propane  $C_{3}H_{87}$ , butane  $C_{4}H_{107}$ , liquids: pentane  $C_{5}H_{127}$ , hexane  $C_{6}H_{147}$ etc. The first four alkane structures are shown on the oil notes page. Names end in ...ane
- Carbon always forms 4 bonds with other atoms and hydrogen 1 bond with other atoms eq **Propane**: molecular formula  $C_3H_8$ , structural and displayed formula styles include ...

 $CH_{3}CH_{2}CH_{3} CH_{3} - CH_{2} - CH_{3} Or H H H$ 

Isomerism occurs when two or more compounds have the same chemical formula but have different structures. eg for the molecular formula C<sub>4</sub>H<sub>10</sub> there are two possibilities - one 'linear' and one with carbon chain 'branching' ...







- (a) as the chain length increases the surface-surface contact must increase per molecule,
- o (b) for isomers, with more branching, the chain length decreases and the molecule is more 'compact' reducing the surface-surface contact per molecule.
- For example ...
  - (a) from methane ==> ethane ==> propane ==> petrol ===> oils ==> grease ==> waxes etc. the boiling point rises and so does the viscosity (stickiness!) as the carbon chain length increases (trend also indicated by gases ==> liquids ==> solids).
  - (b) 'linear' butane has a higher boiling point than 'branched' methylpropane (diagrams above).
- Alkanes and alkenes undergo combustion reactions (see Oil).
- They are not very reactive unless burned! BUT they will react with strong oxidising chemicals like chlorine when heated or subjected to uv light (you need something to initiate the reaction).
  - A **substitution** reaction occurs and a chloro-alkane is formed eq
  - a hydrogen is swapped for a chlorine and the hydrogen combines with a chlorine atom
  - ethane + chlorine ==> chloroethane + hydrogen chloride
  - $\circ$  C<sub>2</sub>H<sub>6</sub> + Cl<sub>2</sub> ==> C<sub>2</sub>H<sub>5</sub>Cl + HCl



- **2c ALKENES**
- These cannot be obtained directly from crude oil and must be made by cracking (see oil notes).
- The unsaturated hydrocarbons form an homologous series called alkenes with a general formula C<sub>n</sub>H<sub>2n</sub> Unsaturated means the molecule has a C=C double bond to which atoms or groups can add.
- Alkene examples: Names end in ...ene



- The alkenes are more reactive than alkanes because of the presence of the carbon=carbon double bond. The alkenes undergo addition reactions in which one of the carbon=carbon double bonds breaks allowing each carbon atom to form a covalent bond with another atom such as hydrogen or bromine.
- Examples of addition reactions are: with hydrogen under pressure and in the presence of a nickel catalyst to form an





- Alkenes react by 'addition' with bromine and decolourises the orange bromine water because the organic product is colourless, and this is a simple test to distinguish an alkene from an alkane.
  - 0 see Oil Notes for equations for ethene and propene
- Vegetable oils contain unsaturated fats and can be hardened to form margarine by adding hydrogen on to some of the carbon=carbon double bonds using a nickel catalyst.
- Alkenes can add to themselves by addition polymerisation to form 'plastic' or polymeric materials (see below or oil notes)
- Alkenes are isomeric with cycloalkanes eg  $C_6H_{12}$  can be hexene or cyclohexane



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#### hexene CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub> or cyclohexane 0

- and note that .... 0
  - hexene is an unsaturated hydrocarbon with a double bond,
  - the isomeric cyclohexane does not have a double bond and is a saturated hydrocarbon,
    - so a simple bromine test could distinguish the two similar colourless liquids,
      - because only the hexene would decolorise the bromine water test reagent.

#### 3. What is ethanol and how can we make it?

What we call alcohol in everyday life is a substance whose chemical name is ethanol. Ethanol is just one member of a family of substances called **alcohols** which have a C-OH functional group in their structure.



- Ethanol is used as a solvent, as a fuel (can be mixed with petrol), and used to make 'ethyl esters' (see below) as well as
  - $_{\odot}$   $\,$  The % alcohol in wines, spirits and beer varies from 1-40%  $\,$
  - There are health and social issues about the medical and behavioral aspects of alcohol consumption. 0
  - Methylated spirit is mainly ethanol but poisonous and nasty tasting chemicals like methanol are added so it is not 0 used as a beverage!
- Ethanol can be produced by fermentation of sugars. The raw materials are mixed with water and yeast at just above room temperature. The yeast contains enzymes which are biological catalysts. The sugars react to form ethanol and carbon dioxide. The carbon dioxide is allowed to escape and air is prevented from entering the reaction vessel to stop oxidation of ethanol to ethanoic acid ('acetic acid' or vinegar!). When the reaction is over the ethanol is separated from the reaction mixture by fractional distillation.
  - eg glucose ==enzyme==> ethanol + carbon dioxide 0

- $\circ \quad C_{6}H_{12}O_{6(aq)} = = > 2C_{2}H_{5}OH_{(aq)} + 2CO_{2(q)}$
- Ethanol, from a solution made from fermented sugar cane, can be concentrated by fractional distillation. In Brazil it is 0 blended with petrol to give an alternative motor vehicle fuel.

• 
$$C_2H_5OH_{(1)} + 3O_{2(q)} = = > 2CO_{2(q)} + 3H_2O_{(1)}$$

- The alcohols form an homologous series with the functional group C-OH. It is the presence of this functional group that gives alcohols their characteristic properties. The simplest homologous series of alcohols have the **general formula** C<sub>n</sub>H<sub>2n+1</sub>OH eg
- Ethanol is shown above and the simplest, lowest carbon number one, is **methanol** (shown below) ы

CH<sub>3</sub>OH or CH<sub>3</sub>-O 0

- All the alcohols are flammable colourless liquids with a not un-pleasant odour? 0
- They all behave chemically in the same way but the boiling point steadily rises with increase in molecule 0 size.
- The next two are called propanol and butanol, the names end in ...ol

$$\begin{array}{c} H H H H \\ H - C - C - C - OH \\ H - C - C - C - OH \\ H - C - C - C - OH \\ H H H \\ \end{array}$$

- Alcohols react, reversibly, with carboxylic acids to form esters and water. Ethyl ethanoate is formed by the reaction of ethanoic acid with ethanol eq

its an equilibrium, 2/3rds conversion, and catalysed by a few drops of concentrated sulphuric acid 0

#### Alcohols react with sodium to form hydrogen.

0

- o normal fizzing is observed and the salt product is soluble in the alcohol itself.
- $\circ$  eg ethanol + sodium ==> sodium ethoxide + hydrogen
- $\circ$  2C<sub>2</sub>H<sub>5</sub>OH + 2Na ==> 2C<sub>2</sub>H<sub>5</sub>O<sup>-</sup>Na<sup>+</sup> + H<sub>2</sub>
- Ethanol can be produced by the reaction of steam and ethene in the presence of a strong acid catalyst (Phosphoric acid). The reversible reaction is carried out at a moderately high temperature (eq  $300^{\circ}$ C) and a high pressure (eq  $60 \times$ atmospheric pressure). The higher temperature and catalyst speed up the reaction and increasing pressure moves the equilibrium to the right (side least gaseous molecules at 300°C)



- Advantages and disadvantages of the two methods of making ethanol:
  - advantages of fermentation: cheap and renewable resource like sugar cane (Brazil), sugar beet
  - disadvantages of fermentation: slow reaction and made by an inefficient batch process, poor quality product eq low aqueous concentration, other organic chemicals formed to and yeast cell residues to remove .
  - advantages of ethene route: fast and efficient continuous process, relatively pure product, country may have local 0 oil supply (eg North Sea for UK, Middle East countries)
  - disadvantages of ethene route: using a non-renewable finite resource (crude oil/cracking)
- Ethanol can be oxidised to form ethanoic acid which is a useful organic chemical. BUT it is this oxidation of ethanol that results in alcoholic drinks turning sour (eg cider, wine) when exposed to air. Ethanoic acid (old name 'acetic acid') is the basis of vinegar and is also used in making esters (eg pear drop essence, or .



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- This oxidation can also be done by heating the ethanol with a mixture of sulphuric acid and potassium dichromate(VI) solution. The mixture turns from orange to green.
- $\circ$   $\;$  When burned, ethanol, like any alcohol, forms carbon dioxide and water  $\;$
- $CH_3CH_2OH + 2O_2 = = > 2CO_2 + 3H_2O$
- Ethanol can be dehydrated to ethene by passing the alcohol vapour over heated aluminium oxide catalyst.



- This reaction is potentially an important source of organic chemicals eg plastics from a renewable resource since the ethanol can be made by fermentation of carbohydrates etc.
- Alcohols from propanol upwards, ie from carbon number 3 or greater, will form isomers.
  - You will find plenty of examples on the **advanced organic chemistry page for alcohols**.
- The steroid, **cholesterol**, **contains the alcohol group -OH**. Cholesterol is an essential steroid to humans but if too much is produced it can cause heart disease.
- <u>http://webbook.nist.gov/cgi/cbook.cgi?Name=cholesterol&Units=SI</u> gives the skeletal formula structure of cholesterol (this structure representation is only dealt with at advanced level). All the lines in the structure represent bonds between carbon atoms except the 'dash' for the -OH alcohol group in the bottom right of the molecule. Also note the 'alkene' double bond functional group to the right of the -OH group.

#### 4. What other families of organic compounds are there?

4a. The acids that we find in fruits and in vinegar belong to a homologous series called **carboxylic acids** and many fragrances and food additives are **esters**.

4b. **Polymers** do not form a homologous series but they are all organic compounds having very long molecules.

#### 4a. CARBOXYLIC ACIDS and ESTERS

- Carboxylic acids form another homologous series and have the functional group -COOH.
- The structures of the first three members are given below: Names end in ...oic acid.



- Ethanoic acid is used in the manufacture of the fibre, acetate rayon.
- Oranges, lemons and many soft drinks contain a carboxylic acid eg citric acid.
- Aspirin is a carboxylic acid. Aspirin is a drug used for pain relief and is taken regularly by those at risk from heart attacks.
- Ascorbic acid (vitamin C) is another carboxylic acid and is present in fresh fruit and vegetables.
- Carboxylic acids are weak acids, typically solutions are around pH3 (yellow-orange-pink with universal indicator).



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- [theory on Extra Aqueous Chemistry page look for keywords]
- **They react and are neutralised by** ... with examples ...
  - **metals** to form salts and hydrogen
    - ethanoic acid + magnesium ==> magnesium ethanoate + hydrogen
    - 2CH<sub>3</sub>COOH + Mg ==> (CH<sub>3</sub>COO)<sub>2</sub>Mg + H<sub>2</sub>
    - alkali bases to form a carboxylic acid salt and water eg ...
      - eg ethanoic acid + potassium hydroxide ==> potassium ethanoate + water
        - $CH_3COOH + KOH = = > CH_3COOK + H_2O$
  - carbonate and hydrogencarbonate bases to produce a carboxylic acid salt, water and carbon dioxide eg ...
    - eg ethanoic acid + sodium hydrogen carbonate ==> sodium ethanoate + water + carbon dioxide
    - $CH_3COOH + NaHCO_3 = > CH_3COONa + H_2O + CO_2$
    - OR propanoic acid + sodium carbonate ==> sodium propanoate + water + carbon dioxide
    - $2CH_3CH_2COOH + Na_2CO_3 = > 2CH_3CH_2COONa + H_2O + CO_2$
- Carboxylic acids react with alcohols to form members of another homologous series called esters. Concentrated sulphuric acid acts as a catalyst in this reaction. See the <u>formation of ethyl ethanoate</u> above in section 3. above.



- show the structures of other esters made from ethanoic acid: namely methyl ethanoate using methanol, and propyl ethanoate from propyl alcohol
- o and what would the structure of their original alcohols be and what would the structure of butyl ethanoate be?
- Esters are usually sweet smelling and widely used as fragrances (eg perfumes) and food flavourings.

#### 4b. POLYMERS - synthetic macromolecules

- Some basic notes on polymers and plastics in the <u>Oil Products Notes</u>.
- Some important structure, strength and 1D to 3D dimension concepts) in the "Chemical Bonding" notes.
- Most polymers (plastics) are made from alkene compounds containing the -C=C- bond by addition polymerisation.
- Poly(chloroethene) is made from chloroethene (old name 'vinyl chloride), CH<sub>2</sub>=CHCl but the polymer is generally called polyvinylchloride, PVC. The general equation and the formation of poly(ethene) and poly(propene) are shown on the <u>Oil notes</u> page. The formation of PVC is shown below.



- **Polymers (plastics) consist of a tangled mass of very long molecules** in which the atoms are joined by strong covalent bonds to form long chains, but there are much weaker intermolecular forces holding the material together.
- In **thermosoftening plastics** like poly(ethene), poly(propene) or poly(chloroethene) PVC, because the inter-molecular attractive forces between the chains are weak, the plastic softens when heated and hardens again when cooled. It also means the polymer molecules can slide over each other. This means they can be easily stretched or moulded into any desired shape.



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- However it is possible to manufacture and process plastics in which the polymer chains are made to line up. This greatly increases the intermolecular forces between the 'aligned' polymer molecules and strong **fibre** strands of the plastic can be made.
- Examples: The addition polymer **poly(propene)** and the condensation polymers **nylon** and **Terylene**
- When a **thermosetting plastic** is first heated covalent bonds are formed between adjacent chains of the polymers. These strong covalent cross-linkages give the material a high melting point and greatly increased strength and rigidity. They also prevent thermosetting plastics from being softened with heat and therefore from being stretched or re-shaped. However it does make a much stronger material and not as flammable. On heating strongly they do NOT melt, but tend to char, gradually giving off gases.



- **Melamine** (used in furniture) and many glues are examples of thermosetting polymers.
- **Problems with using plastics** are on the **<u>Oil Products Notes</u>** page.
- Some important structure, strength and 1D to 3D dimension concepts) in the "<u>Chemical Bonding</u>" notes.

#### 4c. Other Synthetic Polymers - macromolecules

- **Condensation polymerisation** involves linking lots of small monomer molecules together by eliminating a small molecule. This is often water from two different monomers, a H from one monomer, and an OH from the other, the 'spare bonds' then link up to form the polymer chain.
- **Nylon (a polyamide)** is formed by **condensation polymerisation**, the structure of nylon represented as ... (the rectangles represent the rest of the carbon chains in each unit)



- This is the same linkage (-CO-NH-) that is found in linked amino acids in naturally occurring macromolecules called proteins, where it is called the 'peptide' linkage.
- Terylene (a polyester) is formed by condensation polymerisation and the structure of Terylene represented as



- This is the same kind of 'ester linkage' (-COOC-) found in fats which are combination of long chain fatty carboxylic acids and glycerol (alcohol with 3 -OH groups, a 'triol').
- **Terylene and nylon are good for making 'artificial' or 'man-made' fibres** used in the clothing and rope industries. In the manufacturing process the polymer chains are made to line up. This greatly increases the intermolecular forces between the 'aligned' polymer molecules and strong **fibre** strands of the plastic can be made.
- Some important structure, strength and 1D to 3D dimension concepts in "Chemical Bonding" notes.



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- **Carbohydrates** are a whole series naturally occurring molecules based on the elements carbon, hydrogen and oxygen.
- Historically the name 'carbohydrate' comes from the fact that all their formulae seemed to be based on  $C_x(H_2O)_v$  (see key above) BUT this is not the way to think of their formula.
- They range from relatively **small molecules** called **monosaccharide** (means one basic unit), or **disaccharide** (two basic units combined) to **very large natural polymers or macromolecules** called **polysaccharides** (many units combined). A summary of them is shown in the **key diagram above** along with some **familiar names** from biology.





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- The formation of complex carbohydrates:
  - These are made of smaller carbon, hydrogen and oxygen based molecules combining together eg starch and cellulose are formed from glucose, molecular formula C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>.
- Their formation can be described in terms of a large number of sugar units joined together by condensation polymerisation
  - eg the 'box' diagram below shows 4 units of a natural carbohydrate polymer being formed
  - Note: Condensation polymerisation means the joining together of many small 'monomer' molecules by eliminating an even smaller molecule between them to form the linkage.
    - eg HO-XXXXX-OH + HO-XXXXX-O-XXXXX-OH + H<sub>2</sub>O etc.
  - $n C_6 H_{12}O_6 = = > (C_5 H_{10}O_5)_n + n H_2O$  (where n is a very large number to form the natural polymer)
- The XXXXX or the [rectangles] below, represent the rest of the carbon chains in each unit (more detail in the 3rd diagram below).



This **diagram of starch or cellulose** is in 'skeletal formula' style and both are polymers of glucose - can you see the connection between each 'unit' and the structure of glucose itself?

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- The resulting **natural polymer** is called a **polysaccharide**.
  - Acid hydrolysis of complex carbohydrates (eg. starch) gives simple sugars.
    - This can be brought about by eg warming starch with hydrochloric acid solution to form glucose.
    - $\circ \quad (C_5H_{10}O_5)_n + nH_2O ==> n C_6H_{12}O_6 \text{ (where n is a very large number)}$



• The hydrolysis products from polysaccharides can be analysed with paper chromatography.



• **Amino acids** are carboxylic acids (like ethanoic acid) but one of the hydrogen atoms of the 2nd carbon atom is substituted with an **amino group** (a nitrogen + two hydrogens gives -NH<sub>2</sub>). Another hydrogen on the same 2nd carbon can be substituted with other groups of atoms (R) to give a variety of amino acids.

• 
$$H_2N - CH_2 - C_{OH_{or}}^{O} H_2NCH_2COOH_{The simplest is aminoethanoic acid or 'Glycine'
•  $CH_3 - CH - C_{OH_{oH_{oh}}}^{O}$  is another amino acid called **2-aminopropanoic acid** or '**Alanine**'.$$

- All amino acids have the general structure H<sub>2</sub>N-CH(R)-COOH.
  - **R** can vary, think of it as the '**Rest of the molecule**!
    - R = H for Glycine,  $R = CH_3$  for Alanine.
- They polymerise together, by condensation polymerisation, forming proteins or polypeptides.
  - The peptide linkage is formed by elimination of water between two amino acids.
  - HNH-CH(R)-COOH + HNH-CH(R)-COOH ==>  $H_2N$ -CH(R)-CO-HN-CH(R)-COOH +  $H_2O$  etc. so ...
  - $\circ$  n H<sub>2</sub>N-CH(R)-COOH ==> -NH-CO-CH(R)-NH-CO-CH(R)-NH-CO-CH(R)-NH-CO-CH(R)- etc. n units long
    - So proteins are condensation polymers of amino acids.
    - Proteins have the same (amide) linkages as nylon but with different units.
- Proteins are an important component of tissue structure and enzymes are protein molecules.
- When proteins are heated with aqueous hydrochloric acid or sodium hydroxide solution they are hydrolysed to amino acids.
  - see **<u>chromatography</u>** below, about how amino acids are identified in proteins.

#### 5c. Fats, Oils and Margarine

- Oils and Fats are an important way of storing chemical energy in living systems and are also a source of essential longchain fatty acids.
- Most of them are **esters of** the tri-alcohol ('triol') **glycerol** (systematic name propane-1,2,3-triol, but that can wait until AS-A2 level!).
- The carboxylic acids which combine with the glycerol are described as 'long-chain fatty acids'.
- The resulting ester is called a 'triester' or 'triglyceride'.
- The 'long-chain fatty acids' can be saturated, with **no** C=C double bonds, and so forming **saturated oils or fats** (1st diagram below of the triglyceride formed from **palmitic acid**).





• The 'long-chain fatty acids' can be **unsaturated**, with **one or more C=C double bonds**, and so forming **unsaturated oils or fats** (2nd diagram below of the triglyceride formed from oleic acid).



- Some sub-notes on Oil and Fat Structure: (health issues dealt with further down)
  - They have the same linkages as Terylene but with different units.
  - They are not as big as polymer molecules, but a lot bigger than a single petrol or sugar molecule.
  - There can be **1 to 3 different saturated or unsaturated fatty acid components**, so lots of variation possible in structure of the oil or fat. The diagrams just assume three molecules of the same 'fatty' acid.
  - Monounsaturated fats have one C=C double bond in them, polyunsaturated fats usually have at least three C=C bonds in their molecular structure.
  - For the same molecular size in terms of carbon number, unsaturated fats have slightly lower intermolecular forces because the C=C double bond produces a kink in the carbon chain and they can't pack as closely together as the saturated molecules.
    - This gives unsaturated fats a lower melting point and so they tend to occur as eg vegetable oils rather than saturated low melting solids from meat and dairy products.
  - However, this means these unsaturated oils are not as conveniently 'spreadable' as 'butter'.
    - To overcome this problem, '**margarine**' was invented. The vegetable oils are reacted with hydrogen using the gas and a nickel catalyst.
    - This reaction adds hydrogen atoms to the double bonds making a more saturated and more 'spreadable' solid fat we call 'margarine'.
    - The reaction for any double bond is: >CH=CH< + H<sub>2</sub> == Ni ==> -CH<sub>2</sub>-CH<sub>2</sub>-
    - BUT it does mean that it is more like animal fat now but various blendes have been developed to suit your dietary needs or desires!



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- 'Traditional' soap is a product of the hydrolysis of fats.
  - 'Soapy' soaps (not modern detergents) are the sodium salts of long chain fatty acids formed by heating fatty oils with sodium or potassium hydroxide to hydrolyse them.
  - This reaction breaks the fat molecule down into one glycerol molecule (triol alcohol) and three sodium salts of the long chain carboxylic fatty acids.
- Since fats and oils are important to our diet, there is the ever present danger of over-consumption (speaking as someone who loves chips and spicy crisps!). So there are health and social, as well as 'molecular' issues to address!
  - We need oils and fats as sources of important essential fatty acids.
  - We need both saturated and unsaturated fats or oils.
    - The main sources of saturated fats are from meat and dairy products eg 'dripping' and butter.
    - The main sources of unsaturated fats are plant oils eg olive oil.
  - o It is recommended that we do not overdo the fat intake but we do need both saturated and unsaturated fats.
    - However, too much saturated fat raises cholesterol levels and is not too good for the heart.
- If you wish to know more about fats and oils there is plenty on the web! eg ....
  - http://www.healthnet.org.uk/diet/fatoil.htm
  - o <u>http://biology.clc.uc.edu/courses/bio104/lipids.htm</u>
  - <u>http://www.nutristrategy.com/fatsoils.htm</u>

#### 5d. Chromatography

- Hydrolysis means breaking down a molecule with water to form two or more products.
  - Hydrolysis is accelerated if the substance is heated with acid or alkali solutions.
- When proteins are heated with aqueous acid they are hydrolysed to amino acids.
- Acid hydrolysis of complex carbohydrates (eg. starch) gives simple sugars.
- Chromatography is useful in separating and identifying the products of hydrolysis of carbohydrates and proteins.
  - $\circ$  The hydrolysis can be done by boiling the carbohydrate or protein with hydrochloric acid.
    - The hydrolysed mixture is then 'spotted' onto the pencil base line of the chromatography paper.
      - Known sugars or amino acids are also spotted onto the base line too.
      - The prepared paper is then placed vertically in a suitable solvent, which rises up the paper.
  - Since the products are colourless, the dried chromatogram is treated with another chemical to produce a coloured compound.
    - Ninhydrin produces purple spots with amino acids
    - and resorcinol makes coloured spots with sugars.
    - You can then tell which amino acids made up the protein or the sugars from which the carbohydrate was formed.
      - The number of different spots tells you how many different amino acids or sugars made up the natural macromolecule.
      - Spots which horizontally match the standard known molecule spots confirm identity.
        - Starch gives one spot because only glucose is formed on hydrolysis.
          - $(C_5H_{10}O_5)_n + nH_2O = > n C_6H_{12}O_6$  (where n is a very large number)
  - More details on <u>chromatography</u>.

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#### 6. Vitamins, Drugs and Food Additives (NOT FINISHED)

#### Vitamins are particular essential molecules with particular roles in living systems which are

**NOT** proteins, carbohydrates, fats or mineral salts.

- One of the most important ones in any diet is **Vitamin C** or **Ascorbic Acid**. Its structure is related to 'simple' sugars but humans are one of the few mammals that are unable to synthesise vitamin C.
  - It is essential for healthy tissue and one of its functions is the removal of dangerously reactive chemical species called **free radicals** (see further on).
  - Vitamin C is present in fruit and vegetables but the amount is reduced by prolonged storage and cooking..
  - $\circ$  250 years ago, as many as  $^{2}/_{3}$  of a ship's crew died from vitamin C deficiency causing scurvy. In 1747 it was decided to give sailors citrus fruits to recover from scurvy but wasn't until 200 years later that vitamin C was recognised.
  - In contrast to the other water-soluble vitamins, vitamin C has no clear cut role as a catalyst or part of an enzyme. It does, however, have a range of other important functions:
    - Collagen formation. Vitamin C in collagen formation which is found wherever tissues require strengthening, especially in tissues with a protective, connective, or structural function. Collagen is critical to the maintenance of bone and blood vessels and is essential in wound healing.
    - Antioxidant activity. Ascorbic acid can act as an antioxidant by donating electrons and hydrogen ions, and reacting with reactive oxygen species or free radicals.
    - Iron absorption. Vitamin C is important for the effective absorption of iron and reduces iron(III) Fe<sup>3+</sup> to iron(I) Fe<sup>2+</sup>.
    - It helps in the synthesis of vital cell compounds. During times of physical and emotional stress, as well as during infection, there is increased production of oxygen radicals. Therefore there is increased reliance on vitamin C's activity as an antioxidant.
    - Vitamin C is vital for the function of the immune system, but the effectiveness of large doses of vitamin C in preventing and alleviating the symptoms of the common cold is still a matter of debate.
  - Two of the earliest signs of deficiency (prevention of collagen synthesis) relate to its roles in maintaining the integrity of blood vessels. The gums around the teeth bleed more easily, and the capillaries under the skin break spontaneously producing tiny haemorrhages. If you are short of vitamin C for say 20 days, scurvy can develop and is characterised by further haemorrhaging, muscles depletion, rough-brown-dry-scaly skin, deep bruising. Wounds fail to heal properly and bone fails to rebuild properly too and you are further likely to suffer from anaemia and infections.
  - SO EAT yer fruit and veg 'guys' (as well as a few crisps!) AND keep yer health and still pass those dreaded exams!!!!
- **Drugs** can be defined as an externally administered substances which modifies or affects chemical reactions in the body, usually for the bodies greater well-being. Poisons can be defined in the same way, but hopefully not intentionally and have undesired effects!
  - An **analgesic** is a drug used to reduce pain and is type of anti-inflammatory agent.
  - The molecular structure of three well known analgesics are shown in the diagram below.
  - All are used for 'headache' treatment, and hopefully using this website and others will help minimise their use!



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The central hexagonal ring of 6 carbon atoms is called a 'benzene' or 'aromatic' ring. The 4th outer electron of carbon (group 4) is delocalised, so the expected 4th bond per C atom forms part of a 'communal' system (more on this at advanced level, but the covalence rule of 4 for carbon is not broken!, you have seen this situation before, check out graphite. You can show a benzene ring as a simple hexagon with a circle in it

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- The modern pharmaceutical industry has its origins in herbal and other traditional medicine.
- eg An extract of willow herb extract can be made from the leaves, bark and seeds of the willow tree. Amongst other ailments it was given to help curing feverish headaches and relief of pain in childbirth. When ingested the body hydrolyses and oxidises the naturally occurring 'precursor' molecule to form salicylic acid\* which is the 'active' molecule in the body. in the 1890's the German chemist Hoffmann experimented with various chemical modifications of salicylic acid and found the best and chemically stable form was 'aspirin' (shown below). He tried the variations on his own father! who survived to provide valuable 'clinical trials' hardly acceptable these days! \* 'Oil of winter green' from certain plants is the methyl ester of salicylic acid and has similar 'medicinal effects'.
- Aspirin (and the others shown) are not very soluble in water. **Soluble aspirin** is made by neutralising the carboxylic acid with the alkali sodium hydroxide to make the **much more soluble sodium salt of the acid**. The reaction, using skeletal formula, is shown in the diagram below the three analgesic drug structures.
- New drugs and testing them:
- It costs a lot of money to develop a new medicine so the price charged by the pharmaceutical company must cover the cost of research, production and marketing.
  - Patents are taken out to protect the company's commercial interests in the new medicine.
  - There can be a range of formulations of a particular medicine when you buy it over the counter eg tablet of 100% aspirin, soluble aspirin (via Na<sup>+</sup> salt of the acid from neutralisation) and aspirin might form part of a mixture including substances that have other beneficial effects.
  - The main point here is that aspirin, like many drugs, can have multi-functional effects, hopefully all beneficial.
  - BUT this, sadly, is not always the case, because with any new drug there is always the danger of unknown side-effects.
  - Therefore there is a tremendous responsibility on pharmaceutical companies to ensure the development of safe and effective drugs.
  - Lots of time and money spent on discovering and developing new drugs and there are lots of factors to consider:
    - From the discovery of a potentially useful molecule, sometimes called the 'lead molecule', which can be from natural source or produced in some other project etc.
    - o Is there room in the commercial market place for it?
    - Do research to see if its safe, otherwise further development is a waste of time and money or if not safe, can its molecular structure be modified?
    - Can the modification be safe? and more effective?
    - In what form, can it be/needs to be, administered in? for clinical trials.
    - Carefully clinical trials in various phases, noting particularly if any side-effects which may be harmful.

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- Do you test new drugs on animals? an emotive issue, can non-animal testing always 0 allow the safe development of new products? Do you test new drugs on patients in a life threatening situation, give them a last chance 0 at some risk? Patient health and safety issues versus very big drug company commercial interests are a 0 matter of public concern. Any new drug must finally pass all the tests before legally licensed for patient consumption ... 0 sadly, the 'drug companies' and the 'powers to be' do not always get it right (eg phthalidomide), but do not the benefits outweigh the occasional tragedy which we should do our best to avoid? Food additives are chemicals added to food to give particular effects eq colourings, flavourings, preservation and sweetening. **Colourings** to make food more attractive, to fit in with the consumers perception of what it should look like. 0 Flavourings to make food more 'tasty', less 'bland', and to fit in with the consumers perception of what it should taste 0 like. Preservatives are to increase the 'shelf-life' of packaged food, decrease risk of food poisoning. Sweeteners counter bitterness or pander to our taste! E-numbers are reference numbers used by the European Union to help identification of food additives. • All food additives used in the European Union are identified by an E-number. The "E" stands for "Europe" or "European Union". 0 Normally each food additive is assigned a unique number, though occasionally, related additives are given an extension 0 (eq a,b,i or ii etc.) to another E-number. The Commission of the European Union assigns E-numbers after the additive is cleared by the Scientific 0 **Committee on Food (SCF)**, the body responsible for the **safety evaluation of food additives** in the European Union. A summary is given below. E100-199 food colours E200-299 preservatives E300-399 anti-oxidants, phosphates, and complexing agents E400-499 thickeners, gelling agents, phosphates, emulsifiers E500-599 salts and related compounds E600-699 flavourings E700-899 not used for food additives (used for animal feed additives!) E900-999 surface coating agents, gases, sweeteners E1000-1399 miscellaneous additives E1400starch derivatives
  - E-numbers are only used for substances added directly to food products, so contaminants, enzymes and processing aids, which may be classified as additives in the USA, are not included in the E-number system.
  - There is an EU directive on food labeling which requires food additives to be listed in the product ingredients whenever they are added for technological purposes.
    - This includes colouring, sweetening and favor enhancement as well as for preservation, thickening, emulsifying and the like.
    - Ingredients must be listed in descending order of weight, which means that are generally found close to the end of the list of ingredients.
    - However, substances used in the protection of plants and plant products, flavorings and substances added as nutrients (e.g., minerals, trace elements or vitamins) do not need to be included in the ingredient list.
    - Because of this, some substances that are regulated as food additives in other countries may be exempt from



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the food additive definition in the EU.

#### 7. CFC's and Free Radicals (NOT FINISHED)

- If enough energy is supplied by heat or by visible/uv electromagnetic radiation, or the is weak enough, a covalent bond can break in two ways. This illustrated with the molecule chloromethane CH<sub>3</sub>Cl.
  - **Unevenly** where the electron bond pair can stick with one fragment and a positive and negative ion form.
    - eg  $CH_3Cl ==> CH_3^+ + Cl^-$  (at AS-A2 level this is called **heterolytic bond fission**)



shows what happens to the molecule

- or evenly, where the bonding pair of electrons are equally divided between two highly reactive fragments called free radicals.
  - Free radicals are characterised by having **an unpaired electron** not involved in a chemical bond.
  - The 'means the 'lone' electron on the free radical, which is not part of a bond anymore, and wants to pair up with another electron to form a stable bond - that's why free radicals are so reactive!
  - eg  $CH_3Cl = = > CH_3 + Cl$  (at AS-A2 level this is called **homolytic bond fission**)



shows what happens to the molecule

- In the stratosphere small amounts of unstable **ozone O<sub>3</sub> (trioxygen)** are formed by free radical reactions.
- The chemistry of free radicals is important in the current environmental issue of ozone layer depletion.
  - **Chlorofluorocarbons** (**CFC**'s for shorthand) are organic molecules containing carbon, fluorine and chlorine
    - $\circ \quad \text{eg}\;\; \text{dichlorodifluoromethane}\; \text{has the formula } \text{CCl}_2\text{F}_2$
    - They are very useful low boiling organic liquids or gases, until recently, extensively used in **refrigerators** and **aerosol sprays** eg repellents.
  - They are **relatively unreactive**, **non-toxic and have low flammability**, so in many ways they are 'ideal' for the job they do.
  - However it is their chemical stability in the environment that eventually causes the ozone problem but first we need to look at **how ozone is formed and destroyed** in a '**natural cycle**'. This presumably has been in balance for millions of years and explains the uv ozone protection in the upper atmosphere.
  - $\circ$   $\,$  Ozone is formed in the stratosphere by free radical reactions.
    - 'ordinary' stable **oxygen O<sub>2</sub>** (**dioxygen**) is split (dissociates) into two by high energy **ultraviolet radiation** (**uv photon energy 'wave packets**) into two oxygen atoms (which are themselves radicals) and then a 'free' oxygen atom combines with an oxygen molecule to form ozone.
      - O<sub>2</sub> + uv ==> 20<sup>•</sup> then 0<sup>•</sup> + O<sub>2</sub> ==> O<sub>3</sub>
    - The ozone is a highly reactive and unstable molecule and decomposes into dioxygen when hit by other uv light photons. The oxygen atom radical can do several things including help forming O<sub>3</sub>, and O<sub>2</sub>.

$$0_3 + uv = > 0_2 + 0$$

- This last reaction is the main uv screening effect of the upper atmosphere and the ozone absorbs a lot of the harmful incoming uv radiation from the Sun.
- If the ozone levels are reduced more harmful uv radiation reaches the Earth's surface and can lead to medical problems such as increased risk of sunburn and skin cancer and it also accelerates skin aging processes.
- There is strong evidence to show there are 'holes' in the ozone layer with potentially harmful





#### effects, so back to the CFC problem!

- The chemically very stable CFCs diffuse up into the stratosphere and decompose when hit by ultraviolet light (uv) to produce free radicals, including free chlorine atoms, which themselves are highly reactive free radicals.
   eg CCl<sub>2</sub>CF<sub>2</sub> ==> CClF<sub>2</sub> + Cl (note the C-Cl bond is weaker than the C-F bond)
- The formation of chlorine atom radicals is the root of the problem because they readily react with ozone and change it back to much more stable ordinary oxygen.
  - $O_3 + CI^{\circ} = > O_2 + CIO^{\circ}$  by by ozone! and no uv removed in the process!
- Therefore **many countries are banning the use of CFCs**, but not all despite the fact that scientists predict it will take many years for the depleted ozone layer to return to its 'original' O<sub>3</sub> concentration.

