

## 3.2 Alkanes

### Refining crude oil

#### Fractional Distillation: Industrially

Petroleum is a mixture consisting mainly of alkane hydrocarbons

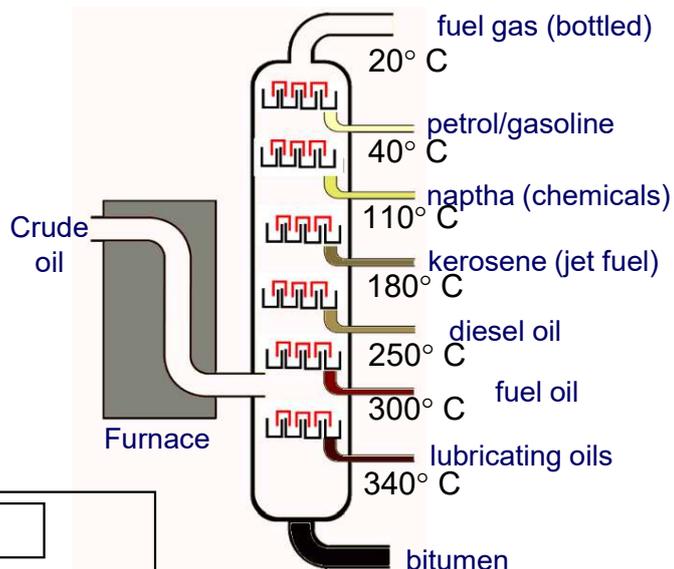
**Petroleum fraction:** mixture of hydrocarbons with a similar chain length and boiling point range

- Key points to learn
- Oil is pre-heated
  - then passed into column.
  - The fractions condense at different heights
  - The temperature of column decreases upwards
  - The separation depends on boiling point.
  - Boiling point depends on size of molecules.
  - The larger the molecule the larger the van der waals forces
  - Similar molecules (size, bp, mass) condense together
  - Small molecules condense at the top at lower temperatures and big molecules condense at the bottom at higher temperatures.

#### Vacuum distillation unit

- Heavy residues from the fractionating column are distilled again under a vacuum.
- Lowering the pressure over a liquid will lower its boiling point.

Vacuum distillation allows heavier fractions to be further separated without high temperatures which could break them down.

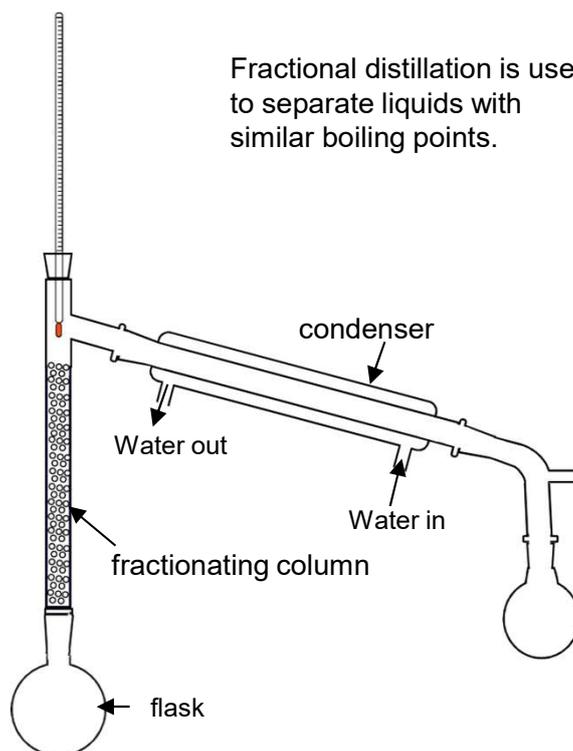


This is a physical process involving the splitting of weak van der waals forces between molecules.

#### Fractional distillation: In the laboratory

- Heat the flask, with a Bunsen burner or electric mantle
- This causes vapours of all the components in the mixture to be produced.
- Vapours pass up the fractionating column.
- The vapour of the substance with the lower boiling point reaches the top of the fractionating column first.
- The thermometer should be at or below the boiling point of the most volatile substance.
- The vapours with higher boiling points condense back into the flask.
- Only the most volatile vapour passes into the condenser.
- The condenser cools the vapours and condenses to a liquid and is collected.

Fractional distillation is used to separate liquids with similar boiling points.



## Cracking

**Cracking:** conversion of large hydrocarbons to smaller hydrocarbon molecules by breakage of C-C bonds

High  $M_r$  alkanes  $\rightarrow$  smaller  $M_r$  alkanes + alkenes + (hydrogen)

### Economic reasons for cracking

- The petroleum fractions with shorter C chains (e.g. petrol and naphtha) are in **more demand** than larger fractions.
- To make use of excess larger hydrocarbons and to supply demand for shorter ones, longer hydrocarbons are cracked.
- The products of cracking are **more valuable** than the starting materials (e.g. ethene used to make poly(ethene), branched alkanes for motor fuels, etc.)

This is a chemical process involving the splitting of strong covalent bonds so requires high temperatures.

There are two main types of cracking: **thermal** and **catalytic**. They need different conditions and are used to produce different products

### Thermal cracking

#### Conditions:

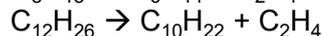
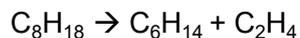
**High pressure** (7000 kPa)

**High temperature** (400°C to 900°C)

**Produces mostly alkenes** e.g. ethene used for making polymers and ethanol

**Sometimes produces hydrogen** used in the Haber process and in margarine manufacture.

#### Example equations



Bonds can be broken anywhere in the molecule by C-C bond fission and C-H bond fission.

### Catalytic cracking

#### Conditions:

**Slight or moderate pressure**

**High temperature (450°C)**

**Zeolite catalyst**

**Produces branched and cyclic alkanes and aromatic hydrocarbons**

Used for making motor fuels

Branched and cyclic hydrocarbons burn more cleanly and are used to give fuels a higher octane number.

Cheaper than thermal cracking because it saves energy as lower temperatures and pressures are used.

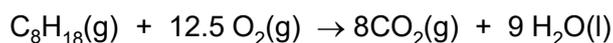
## Combustion

**Fuel** : releases heat energy when burnt

### Complete combustion

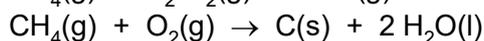
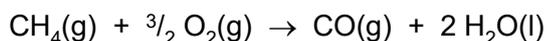
In **excess** oxygen alkanes will burn with complete combustion.

The products of **complete** combustion are  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .



### Incomplete combustion

If there is a **limited amount of oxygen** then incomplete combustion occurs, producing CO (which is very toxic) and/or C (producing a sooty flame)



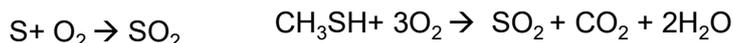
**Alkanes** readily burn in the presence of oxygen. This combustion of alkanes is highly exothermic, explaining their use as **fuels**.

Incomplete combustion produces less energy per mole than complete combustion.

Carbon (soot) can cause global dimming- reflection of the sun's light.

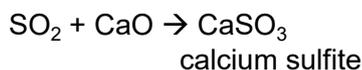
## Pollution from combustion

Sulfur containing impurities are found in petroleum fractions which produce SO<sub>2</sub> when they are burned.



SO<sub>2</sub> will dissolve in atmospheric water and can produce **acid rain**.

SO<sub>2</sub> can be removed from the waste gases from furnaces (e.g. coal fired power stations) by flue gas desulfurisation. The gases pass through a scrubber containing **basic** calcium oxide which reacts with the **acidic** sulfur dioxide in a **neutralisation** reaction.



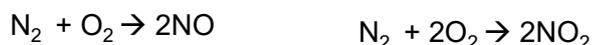
Coal is high in sulfur content, and large amounts of sulfur dioxide are emitted from power stations.

The calcium sulfite which is formed can be used to make calcium sulfate for plasterboard.

## Nitrogen oxides NO<sub>x</sub>

Nitrogen oxides form from the reaction between N<sub>2</sub> and O<sub>2</sub> inside the car engine.

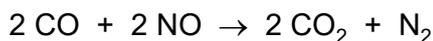
The **high temperature** and **spark** in the engine provides sufficient energy to break the strong N<sub>2</sub> bond.



Pollutant	Environmental consequence
Nitrogen oxides (formed when N <sub>2</sub> in the air reacts at the <b>high temperatures and spark</b> in the engine)	NO is toxic and can form acidic gas NO <sub>2</sub> NO <sub>2</sub> is toxic and acidic and forms acid rain
Carbon monoxide	Toxic
Carbon dioxide	Contributes towards global warming
Unburnt hydrocarbons (not all fuel burns in the engine)	Contributes towards formation of smog
soot	Global dimming and respiratory problems

## Catalytic converters

These remove CO, NO<sub>x</sub> and unburned hydrocarbons (e.g. octane, C<sub>8</sub>H<sub>18</sub>) from the exhaust gases, turning them into 'harmless' CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O.



Converters have a ceramic honeycomb coated with a thin layer of catalyst metals **platinum, palladium, rhodium** – to give a large surface area.

## Global warming

- Carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>) and water vapour (H<sub>2</sub>O) are all greenhouse gases.
- Water is the main greenhouse gas (but is natural), followed by carbon dioxide and methane.

### Mechanism of greenhouse effect

**UV wavelength** radiation passes through the atmosphere to the Earth's surface and heats up Earth's surface. The Earth radiates out infrared **long wavelength** radiation. The C=O Bonds in CO<sub>2</sub> absorb infrared radiation so the IR radiation does not escape from the atmosphere. This energy is transferred to other molecules in the atmosphere by collisions so the atmosphere is warmed.

Carbon dioxide levels have risen significantly in recent years due to increasing burning of fossil fuels. Carbon dioxide is a particularly effective greenhouse gas and its increase is thought to be largely responsible for global warming.

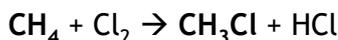
The Earth is thought to be getting warmer, and many scientists believe it is due to increasing amounts of greenhouse gases in the atmosphere.

# Synthesis of Halogenoalkanes

## Reaction of alkanes with bromine / chlorine in UV light

In the presence of **UV light** alkanes react with chlorine to form a mixture of products with the halogens substituting hydrogen atoms.

### Overall reaction



methane      chloromethane

This is the overall reaction, but a more complex mixture of products is actually formed.

In general, alkanes do not react with many reagents. This is because the C-C bond and the C-H bond are relatively strong

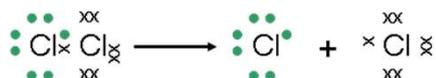
To understand this reaction fully we must look in detail at how it proceeds step by step. This is called its **mechanism**

The **mechanism** for this reaction is called a **free radical substitution**

It proceeds via a series of steps:  
Step one: **initiation**  
Step two: **propagation**  
Step three: **termination**

### Step one: Initiation

Essential condition: UV light



The UV light supplies the energy to break the Cl-Cl bond. It is broken in preference to the others because it is the weakest.

The bond has broken in a process called **homolytic fission**.

**each** atom gets **one** electron from the covalent bond

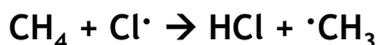
When a bond breaks by homolytic fission it forms **free radicals**.

**Free radicals** do not have a charge and are represented by a ●

### DEFINITION

A **free radical** is a reactive species which possess an **unpaired electron**.

### Step two: Propagation



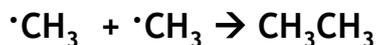
The chlorine free radicals are very reactive and remove an H from the methane leaving a methyl free radical

The methyl free radical reacts with a  $\text{Cl}_2$  molecule to produce the main product and another Cl free radical

All propagation steps have a **free radical** in the **reactants** and in the **products**.

As the Cl free radical is regenerated, it can react with several more alkane molecules in a **chain reaction**.

### Step three: Termination



Collision of two free radicals does not generate further free radicals: the chain is **terminated**.

Minor step leading to impurities of ethane in product. **Write this step using structural formulae** and do not use molecular formulae.

## Applying the mechanism to other alkanes

The same mechanism is used: Learn the patterns in the mechanism

Example: Write mechanism of Br<sub>2</sub> and propane

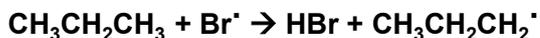
### Step one: Initiation

Essential condition: UV light

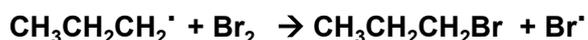


Br<sub>2</sub> splits in the same way as Cl<sub>2</sub>

### Step two: Propagation

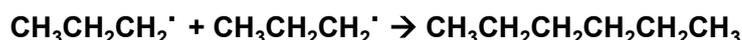


← Remove one H from the alkane to produce a radical



← To the radical produced in the previous step add a Br

### Step three: Termination



## Propagation steps for substituting a halogen on a 'middle' carbon



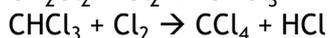
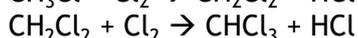
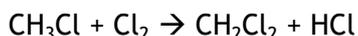
If the question asks for the halogen to be substituted onto a middle carbon in the chain, it is important to put the free radical 'dot' on the correct carbon in the propagation stages.



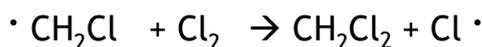
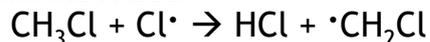
## Further substitution reactions

Excess Cl<sub>2</sub> present will promote further substitution and could produce CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and CCl<sub>4</sub>

These reactions could occur



Example propagation steps that would lead to further substitution



## Overall reaction equations

You should be able to write overall reaction equations for various reactions.

Example 1. Write the overall reaction equation for the formation of CCl<sub>4</sub> from CH<sub>4</sub> + Cl<sub>2</sub>



Example 2. Write the overall reaction equation for the formation of CFCl<sub>3</sub> from CH<sub>3</sub>F + Cl<sub>2</sub>



Note HCl is always the side product – never H<sub>2</sub>