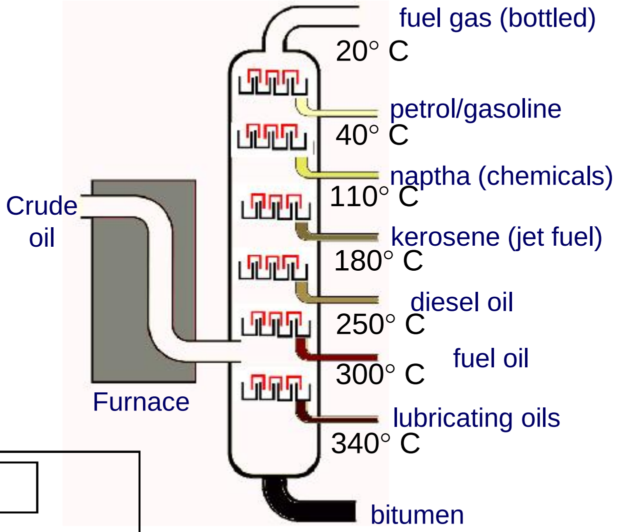
3.2 Alkanes

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 <u>column</u> 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.

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

Vacuum distillation unit

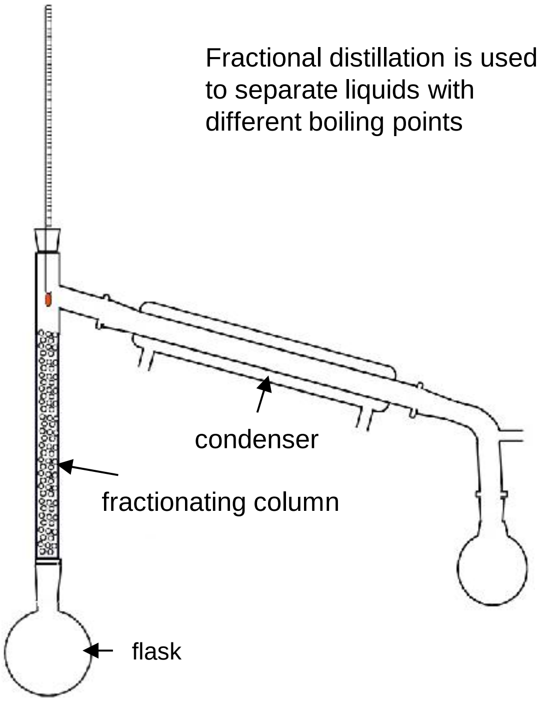
- Heavy residues from the fractionating column are distilled again under a vacuum.
- Lowering the pressure over a liquid will lower its boiling point.

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

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 different boiling points



Cracking

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

High Mr alkanes → smaller Mr 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

$C_8H_{18} \rightarrow C_6H_{14} + C_2H_4$
$C_{12}H_{26} \rightarrow C_{10}H_{22} + C_2H_4$

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

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

Complete Combustion

In excess oxygen alkanes will burn with complete combustion

The products of *complete* combustion are CO_2 and H_2O.

$C_8H_{18}(g) + 12.5\ O_2(g) \rightarrow 8CO_2(g) + 9\ H_2O(l)$

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)

$CH_4(g) + {}^3/_2\ O_2(g) \rightarrow CO(g) + 2\ H_2O(l)$
$CH_4(g) + O_2(g) \rightarrow C(s) + 2\ H_2O(l)$

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_2 when they are burned.

$S + O_2 \rightarrow SO_2$ $CH_3SH + 3O_2 \rightarrow SO_2 + CO_2 + 2H_2O$

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

SO_2 will dissolve in atmospheric water and can produce **acid rain**.

SO_2 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

$$SO_2 + CaO \rightarrow CaSO_3$$

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

Nitrogen Oxides NO_x

Nitrogen oxides form from the reaction between N_2 and O_2 inside the car engine.
The **high temperature** and **spark** in the engine provides sufficient energy to break strong N_2 bond

$N_2 + O_2 \rightarrow 2NO$ $N_2 + 2O_2 \rightarrow 2NO_2$

Pollutant	**Environmental consequence**
Nitrogen oxides (formed when N_2 in the air reacts at the **high temperatures and spark** in the engine)	NO is toxic and can form acidic gas NO_2 NO_2 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_x and unburned hydrocarbons (e.g. octane, C_8H_{18}) from the exhaust gases, turning them into 'harmless' CO_2, N_2 and H_2O.

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

$$C_8H_{18} + 25\,NO \rightarrow 8\,CO_2 + 12\tfrac{1}{2}\,N_2 + 9\,H_2O$$

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_2), methane (CH_4) and water vapour (H_2O) are all greenhouse gases. (They trap the Earth's radiated infra red energy in the atmosphere).
- Water is the main greenhouse gas (but is natural), followed by carbon dioxide and methane.

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 Halogeonalkanes

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.

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

Overall Reaction

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

methane **chloromethane**

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

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**

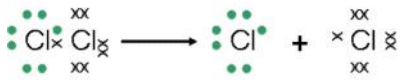
Step one: Initiation

Essential condition: UV light

$Cl_2 \rightarrow 2Cl^{\bullet}$

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

$CH_4 + Cl^{\bullet} \rightarrow HCl + {}^{\bullet}CH_3$

${}^{\bullet}CH_3 + Cl_2 \rightarrow CH_3Cl + Cl^{\bullet}$

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 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

${}^{\bullet}CH_3 + Cl^{\bullet} \rightarrow CH_3Cl$

${}^{\bullet}CH_3 + {}^{\bullet}CH_3 \rightarrow CH_3CH_3$

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_2 and propane

STEP ONE Initiation

Essential condition: UV light

$Br_2 \rightarrow 2Br^{\bullet}$

Br_2 splits in the same way as Cl_2

STEP TWO Propagation

$CH_3CH_2CH_3 + Br^{\bullet} \rightarrow HBr + CH_3CH_2CH_2^{\bullet}$ ← Remove one H from the alkane to produce a radical

$CH_3CH_2CH_2^{\bullet} + Br_2 \rightarrow CH_3CH_2CH_2Br + Br^{\bullet}$ ← To the radical produced in the previous step add a Br

STEP THREE Termination

$CH_3CH_2CH_2^{\bullet} + Br^{\bullet} \rightarrow CH_3CH_2CH_2Br$

$CH_3CH_2CH_2^{\bullet} + CH_3CH_2CH_2^{\bullet} \rightarrow CH_3CH_2CH_2CH_2CH_2CH_3$

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

$CH_3CH_2CH_3 + Br^{\bullet} \rightarrow HBr + CH_3CH^{\bullet}CH_3$

$CH_3CH^{\bullet}CH_3 + Br_2 \rightarrow CH_3CH_2BrCH_3 + Br^{\bullet}$

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_2 present will promote further substitution and could produce **CH_2Cl_2, $CHCl_3$ and CCl_4**

These reactions could occur

$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$
$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$
$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$

Example propagation steps that would lead to further substitution

$CH_3Cl + Cl^{\bullet} \rightarrow HCl + {}^{\bullet}CH_2Cl$

${}^{\bullet}CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + Cl^{\bullet}$

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_4 from $CH_4 + Cl_2$

$$CH_4 + 4\,Cl_2 \rightarrow CCl_4 + 4\,HCl$$

Example 2. Write the overall reaction equation for the formation of $CFCl_3$ from $CH_3F + Cl_2$

$$CH_3F + 3\,Cl_2 \rightarrow CFCl_3 + 3\,HCl$$

Note HCl is always the side product – never H_2