

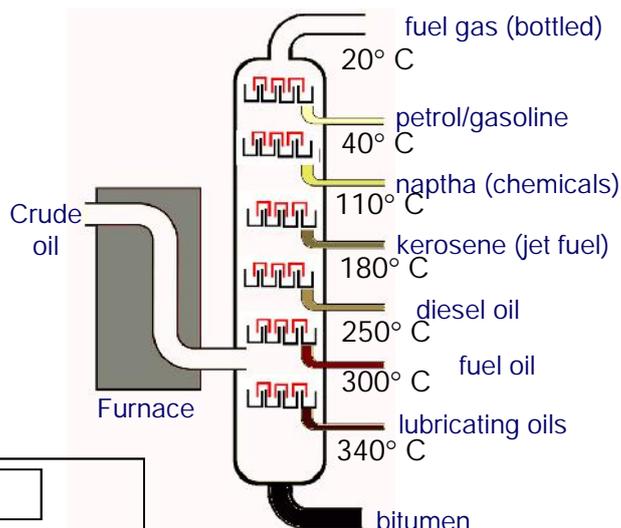
3.2 Alkanes

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.

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

Vacuum distillation unit

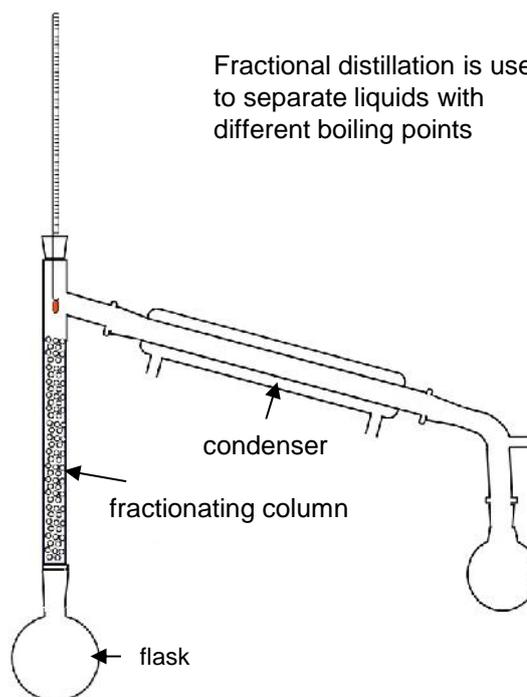
- Heavy residues from the fractionating column are distilled again under a vacuum.
- Lowering the pressure over a liquid will lower its boiling point.

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:

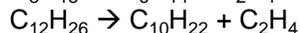
High Pressure (7000 kPa)

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



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

Catalytic Cracking

Conditions:

Slight 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

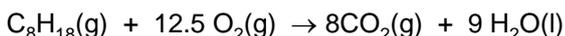
COMBUSTION

Fuel : releases heat energy when burnt

Complete Combustion

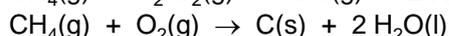
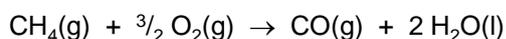
In excess oxygen alkanes will burn with complete combustion

The products of complete combustion are CO₂ and H₂O.



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)



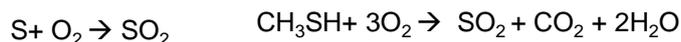
Alkanes readily burn in the presence of oxygen. This combustion of alkanes is highly exothermic, explaining their use as **fuels**.

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

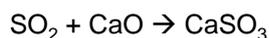
Sulphur containing impurities are found in petroleum fractions which produce SO₂ when they are burned.



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

SO₂ will dissolve in atmospheric water and can produce **acid rain**.

SO₂ can be removed from the waste gases from furnaces (e.g. coal fired power stations) by flue gas desulphurisation. The gases pass through a scrubber containing **basic** calcium oxide which reacts with the **acidic** sulphur dioxide in a **neutralisation** reaction



The calcium sulphite which is formed can be used to make calcium sulphate for plasterboard.

Nitrogen Oxides NO_x

Nitrogen oxides form from the reaction between N₂ and O₂ inside the car engine.

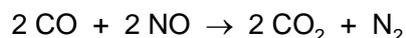
The **high temperature** and **spark** in the engine provides sufficient energy to break strong N₂ bond



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, C₈H₁₈) from the exhaust gases, turning them into 'harmless' CO₂, N₂ and H₂O.



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 (CO₂), methane (CH₄) and water vapour (H₂O) 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.

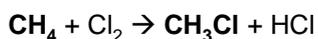
Synthesis of chloroalkanes

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



methane chloromethane

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

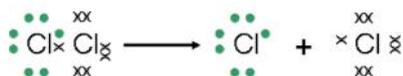
To understand this reaction fully we must look in detail at how it proceeds step by step. This is called its **mechanism**

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



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

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

each atom gets one electron from the covalent bond

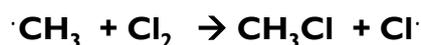
When a bond breaks by homolytic fission it forms **Free Radicals**.

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



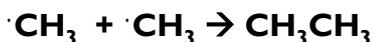
The chlorine free radicals are very reactive and remove an H from the methane leaving a methyl free radical

The methyl free radical reacts with a Cl₂ 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 don't use molecular formulae

Applying the mechanism to other alkanes

Example: Write mechanism of Br₂ and Propane

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

STEP ONE Initiation

Essential condition: UV light

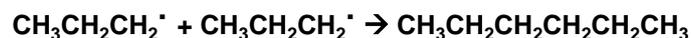


Br₂ splits in the same way as Cl₂

STEP TWO Propagation



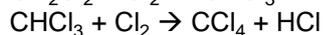
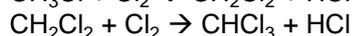
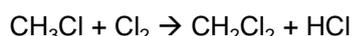
STEP THREE Termination



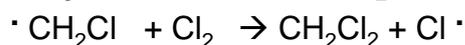
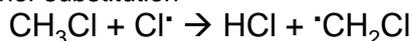
Further substitution

Excess Cl₂ present will promote further substitution and could produce **CH₂Cl₂, CHCl₃ and CCl₄**

These reactions could occur

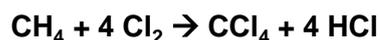


Example propagation steps that would lead to further substitution

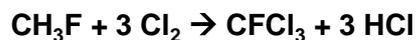


You should be able to write **overall reaction** equations for various reactions

Example 1. Write the overall reaction equation for the formation of CCl₄ from CH₄ + Cl₂



Example 2. Write the overall reaction equation for the formation of CFCI₃ from CH₃F + Cl₂



Note HCl is always the side product – never H₂