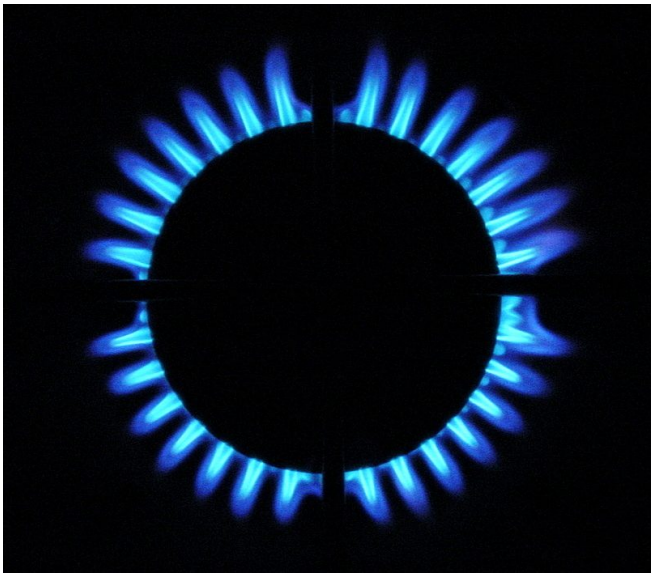
Hydrocarbons

A-Level Chemistry

Alkanes



Natural gas — mainly methane, the simplest alkane — burns on a stove.

Alkanes 烷烃 are saturated hydrocarbons (general formula C_nH_{2n+2}).

Making alkanes

- **hydrogenation** 氢化: add hydrogen to an **alkene** 烯烃, using a Pt or Ni catalyst and heat.
- **cracking** 裂化: break a long-chain alkane into shorter ones by heating with Al_2O_3.

Combustion

In **combustion** 燃烧 an alkane burns in oxygen:

$$\text{complete: alkane} + O_2 \rightarrow CO_2 + H_2O$$

$$\text{incomplete: alkane} + \text{less } O_2 \rightarrow CO + \text{soot} + H_2O$$

Complete combustion gives CO2 and water; incomplete also gives CO and soot

- **complete combustion** 完全燃烧 (plenty of oxygen) gives carbon dioxide and water.
- **incomplete combustion** 不完全燃烧 (not enough oxygen) gives water plus toxic **carbon monoxide** 一氧化碳 (CO) and soot (carbon).

You are often asked to **write the balanced equation**. Balance it in a fixed order - **carbon first, then hydrogen, and oxygen last** - because oxygen is the only element left on just one side:

$$C_6H_{14} + 9\tfrac{1}{2}\,O_2 \rightarrow 6\,CO_2 + 7\,H_2O$$

The 6 carbons fix $6\,CO_2$; the 14 hydrogens fix $7\,H_2O$; counting the oxygens on the right gives $12+7=19$, so the left needs $19 \div 2 = 9\frac{1}{2}$. A **half** of O_2 is perfectly acceptable in this equation - and if the question asks for whole numbers, simply double everything ($2\,C_6H_{14} + 19\,O_2 \rightarrow 12\,CO_2 + 14\,H_2O$).

Free-radical substitution

Alkanes react with chlorine or bromine by **free-radical substitution** 自由基取代, in **ultraviolet light** 紫外线. For ethane and chlorine the mechanism has three steps:

- **initiation** 引发 — UV light splits the halogen into two **free radicals** 自由基: $Cl_2 \rightarrow 2\,Cl\cdot$ This kind of break is **homolytic fission** 均裂: the bond splits **evenly**, one electron going to each atom, which is what makes two radicals. (The opposite, **heterolytic fission** 异裂, sends **both** electrons to one atom and makes a pair of **ions** - that is what happens in the polar mechanisms such as electrophilic addition.) Examiners ask for this word by name, so use it.
- **propagation** 增长 — radicals react and make new radicals:

$$Cl\cdot + C_2H_6 \rightarrow C_2H_5\cdot + HCl \qquad C_2H_5\cdot + Cl_2 \rightarrow C_2H_5Cl + Cl\cdot$$

- **termination** 终止 — two radicals join, ending the chain: $Cl\cdot + C_2H_5\cdot \rightarrow C_2H_5Cl$

1. initiation

$$Cl_2 \xrightarrow{UV} 2\,Cl^{\bullet}$$

UV light splits Cl–Cl into two radicals

2. propagation

$$Cl^{\bullet} + C_2H_6 \longrightarrow C_2H_5^{\bullet} + HCl$$

$$C_2H_5^{\bullet} + Cl_2 \longrightarrow C_2H_5Cl + Cl^{\bullet}$$

each radical makes a new radical, so the chain continues

3. termination

$$Cl^{\bullet} + C_2H_5^{\bullet} \longrightarrow C_2H_5Cl$$

two radicals join, ending the chain

Free-radical substitution in three steps: initiation makes radicals, propagation carries the chain, and termination ends it

Why cracking is useful, and why alkanes are unreactive

Cracking turns heavy fractions of **crude oil** 原油 into more useful, lower-M_r alkanes and alkenes. (A **fraction** 馏分 is a group of molecules with a similar boiling-point range.)

Alkanes are generally unreactive, especially towards polar reagents. This is because the C–H and C–C bonds are strong and have little **polarity** 极性, so there is no charge to attract an attacking species.

Environmental effects

Burning alkanes in an internal combustion engine gives off carbon monoxide, oxides of nitrogen and unburnt hydrocarbons. A catalytic converter removes these by turning them into harmless gases.

Alkenes

Cracking heavy fractions at a refinery produces alkenes for plastics and fuels.

Alkenes have a C=C double bond (general formula C_nH_{2n}). The double bond is the functional group, so alkenes are reactive.

Making alkenes

- **elimination** 消去 of HX from a **halogenoalkane** 卤代烷, using NaOH dissolved in ethanol, with heat.
- **dehydration** 脱水 of an **alcohol** 醇, using a hot Al_2O_3 catalyst or concentrated sulfuric acid.
- cracking of a longer-chain alkane.

Reactions of alkenes

Most reactions are **electrophilic addition** 亲电加成 across the double bond:

Reagent and conditions	Product
H_2, Pt/Ni catalyst, heat	alkane
steam 水蒸气 (H_2O), H_3PO_4 catalyst	alcohol
a **hydrogen halide** 卤化氢 (HX), room temperature	halogenoalkane
a halogen X_2	a di-substituted alkane

There are also two oxidation reactions with acidified $KMnO_4$:

- **cold, dilute** $KMnO_4$ adds two –OH groups to give a **diol** 二醇.
- **hot, concentrated** $KMnO_4$ breaks the C=C bond right apart, and what each half turns into tells you exactly where the double bond used to be.

That second reaction is worth learning properly, because it is how the exam asks you to **locate a double bond in a large molecule**. Oxidation is written with [O], meaning "an oxygen atom from the oxidising agent". Cut the molecule at the C=C, then look at **what each of the two carbons was carrying**:

The C=C carbon carries	It becomes
two alkyl groups (=CR_2)	a **ketone** 酮, $R_2C{=}O$
one alkyl and one H (=CHR)	a **carboxylic acid** 羧酸, RCOOH
two hydrogens (=CH_2)	CO_2 and water

The pattern is simply how many hydrogens that carbon had: none stops at a ketone, one is pushed on to an acid, and two are oxidised all the way to CO_2.

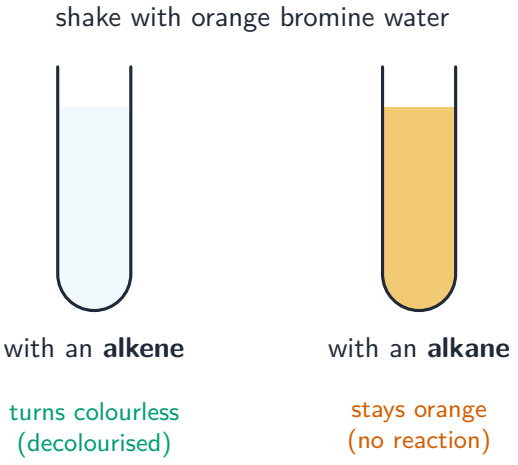
Worked example. Give the products when $(CH_3)_2C{=}CHCH_3$ is heated with hot concentrated acidified $KMnO_4$. Cut at the C=C and take each carbon separately. The **left** carbon carries **two methyl groups** and no hydrogen, so it stops at a **ketone**: $(CH_3)_2C{=}O$, which is propanone. The **right** carbon carries **one methyl and one H**, so it goes on to a **carboxylic acid**: CH_3COOH, ethanoic acid. So:

$$(CH_3)_2C{=}CHCH_3 + 3[O] \rightarrow CH_3COCH_3 + CH_3COOH$$

Now run it **backwards**, which is the way the question is usually set. Given the products, rebuild the alkene by putting the two carbonyl carbons back together as a C=C: a ketone means that carbon had **two alkyl groups**, an acid means **one alkyl and one H**, and CO_2 means the chain **ended** in $=CH_2$. Getting CO_2 is the strongest clue of all - it can only come from a **terminal** double bond.

Test for a C=C bond

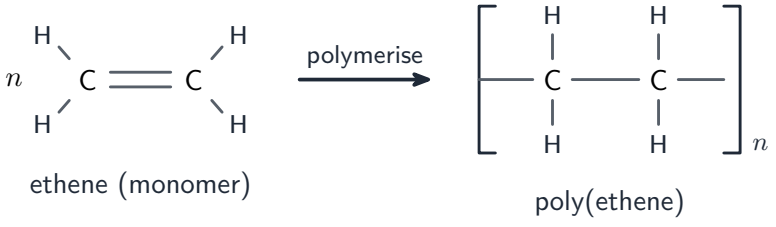
Shake the compound with orange **bromine water** 溴水. An alkene **decolourises** it (turns it colourless) by electrophilic addition. An alkane does not.



The bromine-water test: an alkene decolourises the orange bromine water, while an alkane leaves it orange

Addition polymerisation

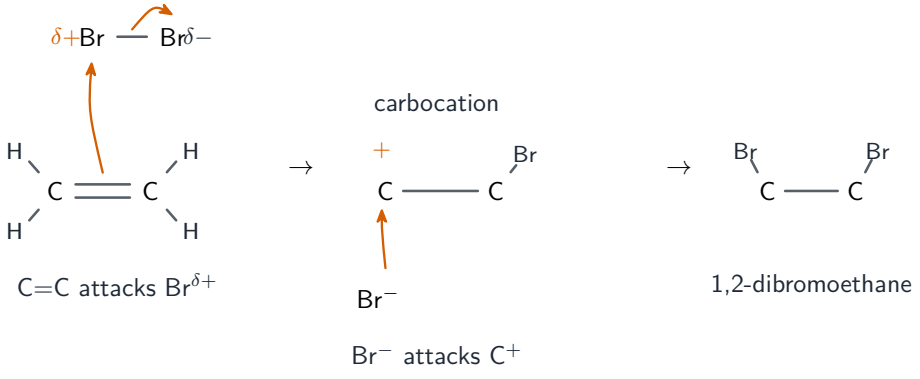
In **addition polymerisation** 加成聚合, many alkene molecules join into one long chain, with no other product. Ethene gives poly(ethene). The long-chain product is a **polymer** 聚合物.



Addition polymerisation: many ethene molecules open their double bonds and join into the long chain of poly(ethene)

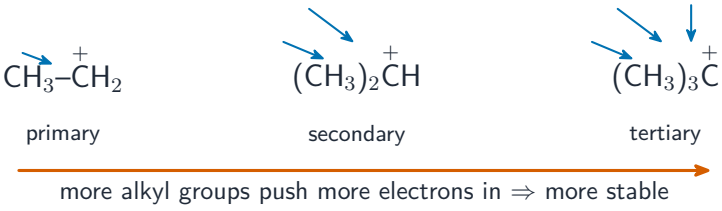
The mechanism and Markovnikov's rule

In electrophilic addition (for example bromine with ethene), the electron-rich C=C attracts the electrophile. This forms a positive intermediate called a **carbocation** 碳正离子, which the negative part then attacks.



Electrophilic addition of bromine to ethene: the C=C attacks $Br^{\delta+}$, a carbocation forms, then Br^- attacks it

Alkyl groups push electrons towards the positive carbon — this is the **inductive effect** 诱导效应. So a carbocation with more alkyl groups is more stable: tertiary is more stable than secondary, which is more stable than primary. When HBr adds to propene, the more stable carbocation forms, so hydrogen adds to the carbon that already has more hydrogens. This pattern is **Markovnikov's rule** 马氏规则.



Markovnikov: HBr adds so the *more stable* carbocation forms

Carbocation stability rises from primary to tertiary as more alkyl groups push electrons in — the basis of Markovnikov's rule

Worked example. Predict the major product when HBr adds to propene, $CH_3CH{=}CH_2$. The H^+ adds first, and it adds in whichever way makes the **more stable carbocation**. Adding the H to the **end** carbon puts the positive charge on the middle carbon, giving a **secondary** carbocation, which is stabilised by electron-releasing alkyl groups on **two** sides. Adding it to the middle carbon would leave a less stable **primary** carbocation. The bromide ion then attacks the secondary

carbocation, so the major product is **2-bromopropane**. That is Markovnikov's rule - but quote the **reason** (carbocation stability: tertiary > secondary > primary), because the rule on its own is not the explanation.

Exam tips

- **Alkanes**: free-radical substitution needs **UV light** — show initiation, propagation and termination with the radical dots.
- **Alkenes**: electrophilic addition via a **carbocation**; draw curly arrows from the C = C.
- **Markovnikov**: H adds to the carbon with more H's, via the **more stable carbocation** (alkyl groups are electron-releasing).
- Test for C = C: **bromine water decolourises** (orange → colourless) — state the observation.