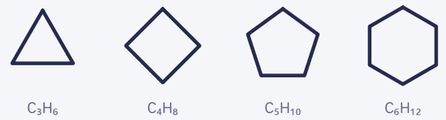
11.2 Alkanes



1 Structure and Naming

1.1 The alkane homologous series

- **Alkanes**: _____ hydrocarbons, C_nH_{2n+2}. Every C is _____, tetrahedral, 109.5°.
- **Cycloalkanes**: closed rings, C_nH_{2n} (same general formula as alkenes)

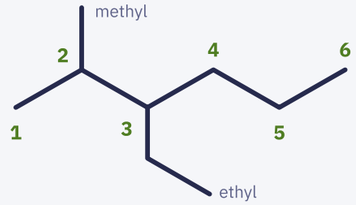


n	Name	Structural formula	n	Name	Structural formula
1	methane	CH_4	4	butane	$CH_3(CH_2)_2CH_3$
2	ethane	CH_3CH_3	5	pentane	$CH_3(CH_2)_3CH_3$
3	propane	$CH_3CH_2CH_3$	6	hexane	$CH_3(CH_2)_4CH_3$

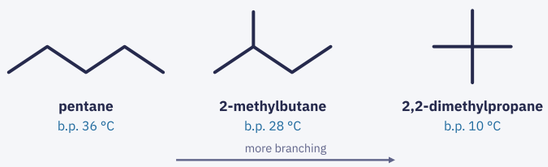
1.2 Naming a branched alkane

1. Find the _____ continuous carbon chain (parent name)
2. Number from the end _____ the first branch
3. Name substituents with locants, in _____ order (ignore di-, tri-)

3-ethyl-2-methylhexane: 6-carbon main chain, numbered from the left so the branches get the lowest locants. "Ethyl" comes before "methyl".



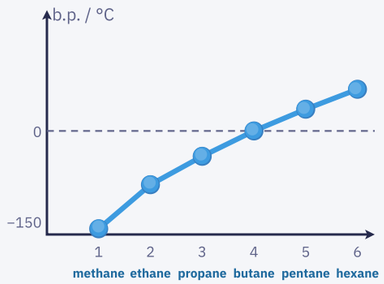
1.3 Structural isomers of C_5H_{12}



Same molecular formula, different structural formula. Alkanes with 4 or more C show branching isomerism.

2 Physical Properties

C–H bonds are essentially _____ → molecules held by weak _____ interactions.



1. b.p. increases with the number of C atoms

1. No. of electrons ↑ → larger, more _____ electron cloud
2. → stronger id–id → more energy needed to overcome them

2. Branched isomers have lower b.p.

1. More branching → more spherical, smaller _____
2. → weaker id–id → less energy needed to overcome them

pentane 36 °C > 2-methylbutane 28 °C > 2,2-dimethylpropane 10 °C

2 Physical Properties (continued)

2.1 Solubility

Soluble in non-polar solvents (e.g. CCl_4). **Insoluble in water**:

1. Energy released from forming _____ interactions between alkane and water
2. is _____ to overcome the id–id between alkane molecules and the _____ between water molecules

2.2 Density and viscosity

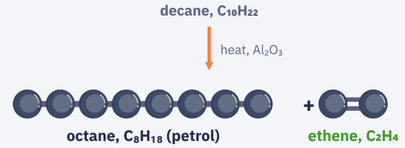
Less dense than water

1. Molecules are held by weaker _____ than the hydrogen bonds between water molecules
2. → molecules are _____

- Density and viscosity ↑ with M_r: stronger id–id draws molecules closer
- More branching → poorer packing → lower density

3 Cracking

DEFINITION **Cracking**: the breaking down of _____ alkanes into shorter-chain alkanes and _____, using heat and a catalyst.



- Conditions: high temperature, Al_2O_3 or SiO_2 catalyst (catalytic cracking)
- Meets demand for petrol and gives alkenes for making polymers

4 Reactivity and Combustion

Why are alkanes unreactive?

1. C–H bonds are _____: no electron-rich or electron-poor sites to attract nucleophiles or electrophiles
2. C–C and C–H bonds are _____

They react only with O_2 (combustion) and halogens (free radical substitution).

- **Complete** (excess O_2): $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$, $\Delta H = -890$ kJ mol^{-1}
- **Incomplete** (limited O_2): $2CH_4 + 3O_2 \rightarrow$ _____ $+ 4H_2O$, or C (soot)
- Alkanes burn as **gases**, higher alkanes are less volatile and burn with **sooty** flames

4.1 Identify a hydrocarbon from combustion data

WORKED EXAMPLE 15 cm³ of a gaseous hydrocarbon is burnt completely in 100 cm³ of O_2. 60 cm³ of CO_2 forms and 10 cm³ of O_2 is left over (same conditions). Find its formula.

$$C_xH_y(g) + (x + \frac{y}{4})O_2(g) \rightarrow xCO_2(g) + \frac{y}{2}H_2O(l)$$

1. 1 mol C_xH_y gives x mol CO_2:
$x = \frac{60}{15} =$ ____

2. O_2 used = 100 − 10 = 90 cm³:
$x + \frac{y}{4} = \frac{90}{15} = 6$

3. $4 + \frac{y}{4} = 6 \rightarrow y =$ _____
∴ _____

5 Free Radical Substitution

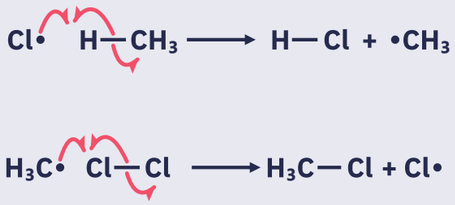
$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ Cl_2 or Br_2, _____ or heat (250–400 °C)

Step 1: Initiation



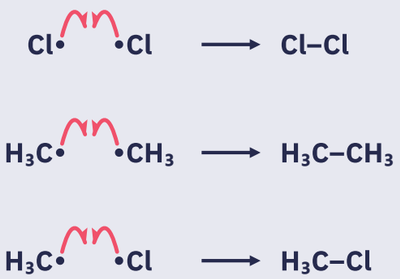
UV breaks Cl–Cl _____ to give a low concentration of Cl•. Use half arrows.

Step 2: Propagation



Cl• is _____, so the reaction is a chain reaction

Step 3: Termination



Two radicals combine, so radicals are _____ and not regenerated

EXAM TIP Write at least **two** termination steps. Show the • on the radical carbon (CH_3CH_2•).

5.1 Common explanations for FRS

- **Why does Cl–Cl break, not C–H?** BE(Cl–Cl) = 244 kJ mol^{-1} is the _____ bond, UV light does not supply enough energy to break C–H (410 kJ mol^{-1})
- **Why is no H• formed?** Cl• + CH_4 → •CH_3 + HCl has ΔH = _____ kJ mol^{-1}, but Cl• + CH_4 → CH_3Cl + H• has ΔH = +70 kJ mol^{-1}, so it is _____
- **Why does the reaction continue after the UV light is removed?** Each propagation step _____ a radical, so the chain continues until termination uses up the radicals

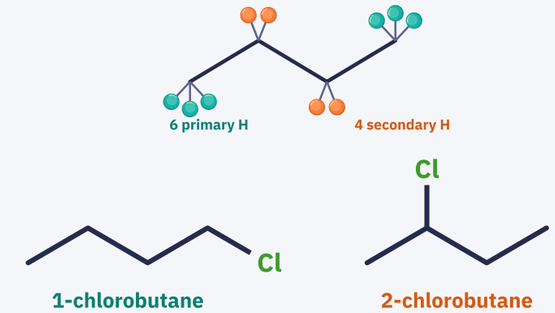
5.2 Different conditions for FRS

- **Limited Cl_2** (excess alkane): mainly _____ substitution, as Cl• is more likely to collide with CH_4
- **Excess Cl_2**: _____ substitution: CH_2Cl_2, $CHCl_3$, CCl_4
- A mixture of products forms → poor for synthesis

F_2	Cl_2, Br_2	I_2
_____	UV light or heat	_____ (ΔH = +22)

6 Ratio of Products

6.1 Statistical ratio



If every H atom were _____ to be replaced by Cl, the ratio of products would equal the ratio of the numbers of H atoms that give each product.

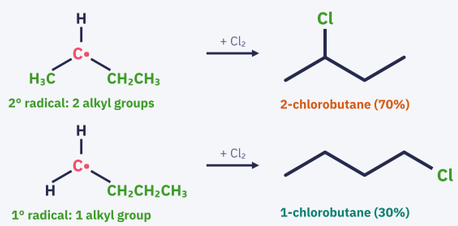
1. Butane has 6 primary H (on the two CH_3) and 4 secondary H (on the two CH_2)
2. Replacing a primary H gives 1-chlorobutane, replacing a secondary H gives 2-chlorobutane
3. ∴ statistical ratio 1-chlorobutane : 2-chlorobutane = 6 : 4 = _____

Propane: 6 primary : 2 secondary H = 3 : 1 for 1- : 2-chloropropane. 2-methylpropane: 9 primary : 1 tertiary H = 9 : 1.

6.2 Experimental ratio

Experimentally **30 : 70**: more 2-chlorobutane forms than the statistical ratio predicts. Why?

1. The intermediate that forms 2-chlorobutane is a _____: the electron-deficient radical is stabilised by _____ electron-donating alkyl groups
2. The intermediate that forms 1-chlorobutane is a primary radical, which is less stable, as it is stabilised by only 1 electron-donating alkyl group
3. ∴ formation of 2-chlorobutane is favoured due to the more _____



Radical stability: methyl < 1° < 2° < 3°. The more electron-donating alkyl groups on the radical carbon, the more stable the radical.

7 Pollution from Combustion

- **CO**: binds _____ more strongly than O_2 → less O_2 carried
- **Unburnt hydrocarbons**: form photochemical smog
- **NO_x**: high engine temperature breaks N≡N, N_2 + O_2 → 2NO. Causes smog, low-level O_3, and acid rain via NO_2 + SO_2 → SO_3 + NO
- **CO_2, CH_4**: greenhouse gases → enhanced greenhouse effect

Catalytic converter: Pt, Pd, Rh (redox)

Removing CO and NO

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

CO is _____ to CO_2, NO is _____ to N_2.

Removing unburnt hydrocarbons

hydrocarbons + NO_x → CO_2 + H_2O + N_2