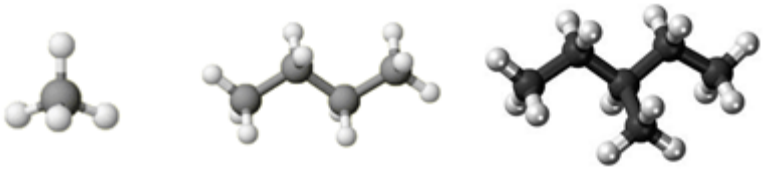
3 HYDROCARBONS - ALKANES AND CYCLOALKANES

3.1 INTRODUCTION

Alkanes are the simplest of the homologous series of organic compounds and are also the least reactive hydrocarbons. Alkanes are **saturated** hydrocarbons as they contain only C–H and C–C **single** (σ) bonds with a maximum of 4 σ bonds per carbon. All C atoms in alkanes are **sp^3 hybridised** with each C atom in a **tetrahedral** geometry. Alkanes can be classified as ***acyclic*** (aliphatic, straight and branched chains) or cyclic closed rings.

3.1.1 Acyclic (non-cyclic) Alkanes

Acyclic alkanes have the general formula $\mathbf{C_nH_{2n+2}}$ and contain zig-zag chains of **C** atoms. Acyclic alkanes can be classified as straight and/or branched chains.



methane	butane	3-methylpentane
CH_4	$CH_3CH_2CH_2CH_3$	$CH_3CH_2CH(CH_3)CH_2CH_3$
Straight chain	Straight chain	Branched chain

3.1.2 Cyclic Alkanes (closed rings alkanes)

Cyclic alkanes (cycloalkanes) have the general formula $\mathbf{C_nH_{2n}}$ (same as alkenes).

Molecular formula	Name	Skeletal formula
C_3H_6	cyclopropane	
C_4H_8	cyclobutane	
C_5H_{10}	cyclopentane	
C_6H_{12}	cyclohexane	

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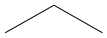
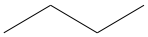
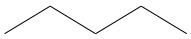
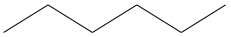
3.2 NOMENCLATURE OF BRANCHED CHAIN ISOMERS (IUPAC SYSTEM)

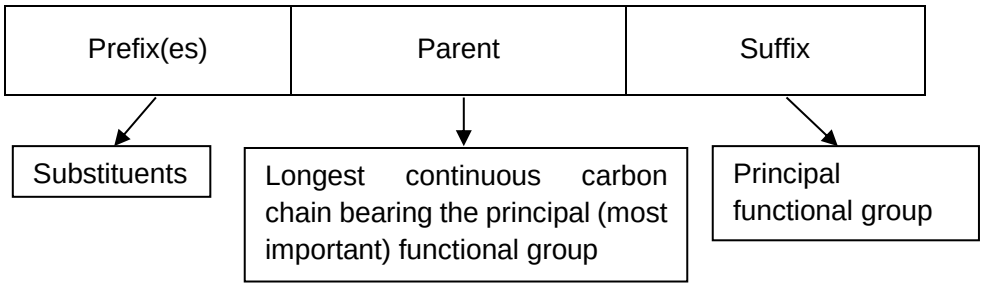
Success criteria:
• I can deduce the structure of an alkane from its given IUPAC name (and vice versa)

The names of alkanes end with the letters '*-ane*'. The following are the names for the first 6 straight-chain alkanes.

n	**Molecular formula**	**Name**	**Condensed Structural formula**	**Skeletal formula**
1	CH_4	meth**ane**	CH_4	
2	C_2H_6	eth**ane**	CH_3CH_3	
3	C_3H_8	prop**ane**	$CH_3CH_2CH_3$	
4	C_4H_{10}	but**ane**	$CH_3(CH_2)_2CH_3$	
5	C_5H_{12}	pent**ane**	$CH_3(CH_2)_3CH_3$	
6	C_6H_{14}	hex**ane**	$CH_3(CH_2)_4CH_3$	

With branching, atoms or groups of atoms that make up the side chains have to be considered a substituent.

The IUPAC name of an organic compound consists of a **parent** (or **stem**), a **suffix** and as many **prefixes** as necessary.



How to name an organic compound

1 Identify the longest continuous carbon chain for the parent name.

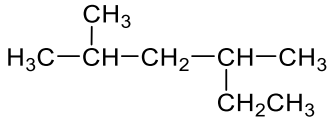
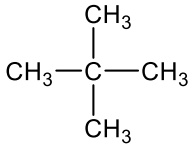
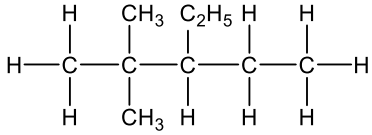
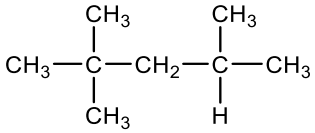
2 Numbers carbon atoms in the longest chain nearer to the first branch point

3 Identify and label numbers on the substituents. If two or more substituents are present, cite them in alphabetical order.

The number prefixes *di-*, *tri-*, *tetra-*, etc. are ignored in alphabetising.

Checkpoint 1

1 Determine if each alkane is named correctly using IUPAC nomenclature. If the naming is **incorrect**, give the correct IUPAC name.

Organic compound	Is naming correct? (Y / N)	Correct IUPAC name (if relevant)
 2-methyl-4-ethylpentane		
 2,2-methylpropane		
 4,4-dimethyl-3-ethylpentane		
 2,2,4-trimethylpentane		

2 Draw the skeletal formula of 2-ethyl-1,1-dimethylcyclohexane.

3.3 ISOMERISM

Alkanes with 4 or more carbon atoms exhibit structural isomerism due to branching of the hydrocarbon chains. Optical isomerism can also occur in higher members of the alkane series.

3.4 PHYSICAL PROPERTIES OF ALKANES

Success criteria:
• I can explain the difference in melting point and boiling point between alkanes. • I can understand the solubility of alkanes in different types of solvent.

Alkane molecules are made up of only C and H atoms which have **similar electronegativities**. The C–H bond is considered **non-polar** with a very small dipole moment. Thus, alkane molecules are held together by weak instantaneous dipole-induced dipole interactions.

3.4.1 Boiling and Melting point

Remember?
The strength of instantaneous dipole - induced dipole (id-id) interactions between molecules increases with increasing size of electron cloud.

Molecules of branched alkanes have a smaller surface area of contact between adjacent molecules than that of their straight-chain isomers, resulting in a weaker id-id interaction.

The boiling and melting points of alkanes **increase** as the number of carbon atoms in the molecules increases due to the increase in M_r and hence the increasing size of electron cloud.

Formula	**Name**	M_r	**Melting point / ºC**	**Boiling point / ºC**	**State** (at r.t.p)
CH_4	Methane	16	–182	–162	gas
C_2H_6	Ethane	30	–183	–89	gas
C_3H_8	Propane	44	–188	–42	gas
C_4H_{10}	Butane	58	–138	0	gas
C_5H_{12}	Pentane	72	–130	36	liquid
C_6H_{14}	Hexane	86	–95	69	liquid

Branched-chain alkanes usually have **lower** boiling points than their corresponding straight-chain alkanes. The greater the degree of branching, the lower the boiling point of the compound.

3.4.2 Solubility

For dissolution to take place, solute-solvent interaction should be stronger or comparable to solute-solute and solvent-solvent interaction.

Alkanes are **insoluble** in **polar** solvents (e.g. water) but **soluble** in **non-polar solvents** (e.g. CCl_4, benzene).

3.4.3 Density

Density of alkanes **increases** down the homologous series. M_r is larger and stronger instantaneous dipole-induced dipole interactions between molecules bring the alkane molecules closer to each other. Larger mass and smaller volume results in higher density. However, density of alkanes decreases with more branching in the molecules of similar M_r values due to poorer packing (branched isomers occupy bigger space than straight chain).

3.4.4 Viscosity

Viscosity is a measure of the internal resistance to the flow of a fluid which form friction between neighbouring molecules. The viscosity of liquid alkanes increases with increasing M_r as the strength of intermolecular instantaneous dipole-induced dipole interactions increases.

3.5 CHEMICAL PROPERTIES OF ALKANES

3.5.1 Reactivity

Success criteria:
• I can explain why alkanes are generally unreactive towards most reagents.

Alkanes are generally unreactive and chemically inert towards most chemical reagents such as acids, bases, oxidising and reducing agents.

Alkanes lack chemical reactivities as:
(i) the **C–H** bonds are **non-polar** (C and H have **similar electronegativities**)
(ii) C–C and C–H bonds are rather strong.

As a result, alkane do not have electron rich or electron poor centres to attract reactive charged species. This renders alkanes unreactive towards ionic and polar reagents. Instead, alkanes react with oxygen **(combustion)** and halogens involving electrically neutral free radicals **(substitution)**, the two most important reactions.

3.5.2 Combustion

Success criteria:
• I can write balanced equation for alkanes to undergo combustion. • I can deduce the identity of a hydrocarbon based on combustion data

Alkanes burn *exothermically* in excess oxygen when ignited.

(i) Limited supply of oxygen
Incomplete combustion of alkanes results in the production of CO and/or C (as black soot) and water.

e.g. $2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$
$CH_4 + O_2 \rightarrow C\ (soot) + 2H_2O$

(ii) Excess supply of oxygen
Complete combustion of alkanes results in the production of CO_2 and H_2O as the only products.
e.g. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $\Delta H = -890\ kJ\ mol^{-1}$

General equation for the combustion of hydrocarbon:

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

Many alkanes, such as methane (natural gas), propane, butane, are used as fuels due to their ease of burning which are highly exothermic.

Alkanes burn readily in the gaseous state. Hence, solid and liquid alkanes must be vapourised before they will burn. Higher members of alkanes have a lower volatility and burn less readily to give sooty flames.

Checkpoint 2

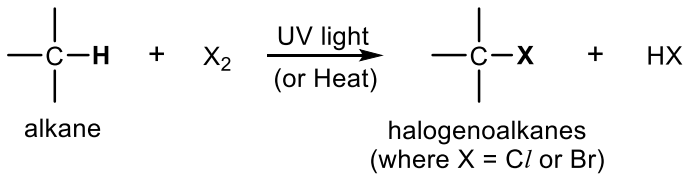
State the oxidation number of carbon in each molecule.

	CO	HCHO	CH_3CH_2OH
oxidation state of C			

3.5.3 Free radical substitution

Success criteria:
• I can describe/ outline the free radical substitution (FRS) mechanism with reference to initiation, propagation and termination reactions using equations and curly arrows (1st step only). • I can understand why FRS is an unsuitable method for many organic synthesis. • I can predict the structures of the possible products from FRS. • I can apply my understanding of FRS mechanism to a novel context.

Alkanes react with halogens such as Cl_2(g) or Br_2(*l*) in the presence of (i) **UV light at room temperature** or (ii) at **high temperatures** to produce halogenoalkanes via **free radical substitution** (involves **free radicals**).



This reaction is called **substitution** as one or more of the **hydrogen atoms** in the alkane are **replaced** (substituted) **by** the **halogen** atoms.

Video on Free Radical Substitution Mechanism

https://tinyurl.com/frsdance

Note:
Initiation: Halogen molecule produces low concentration of halogen radicals

Propagation: repeated cycle of one or more pairs of steps **(a)** and **(b)**:
(a) halogen radical produces organic radical. **(b)** regeneration of halogen radical.

Poly substitution occurs through multiple iteration of **(a)**-**(b)** pairs
Mono-substitution: 1 pair
Di-substitution: 2 pairs
Tri-substitution: 3 pairs
Refer to 3.5.3 c.

Watch a demonstration of an FRS reaction between methane and chlorine:

(i) Free-radical substitution mechanism

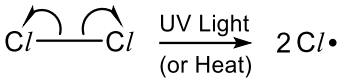
It involves 3 elementary steps:

1 Initiation

2 Propagation

3 Termination

Example: chlorination of methane: $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

Mechanism	Explanation
Initiation  	A brief exposure to **UV light** cleaves C*l*–C*l* bond **homolytically** to produce low concentration of **free C*l*• radicals** (atoms). Each half curly arrow ( ) shows the movement of **one electron**.
Propagation $Cl\bullet + CH_4 \rightarrow \bullet CH_3 + \mathbf{HCl}$ --**(a)** $\bullet CH_3 + Cl_2 \rightarrow Cl\bullet + \mathbf{CH_3Cl}$ --**(b)**	Once C*l*• radicals are formed, they go through a **chain reaction** sequence (repeated cycle of steps **(a)** and **(b)**). ***Cl*•** used and regenerated keeps the chain reaction going.
Termination $2Cl\bullet \rightarrow Cl_2$ $\bullet CH_3 + \bullet CH_3 \rightarrow CH_3CH_3$ $\bullet CH_3 + Cl\bullet \rightarrow CH_3Cl$ (any 2 equations)	This step involves **2 reactive free radicals** combining to form a stable (unreactive) product**. Free radicals** are **consumed** but **not generated**. This step occurs towards the end of the reaction where collision between radicals are more likely as effective collision between decreasing number of reactant alkane molecule become increasingly difficult.

Important points to note*

a. *Why does the C*l*–C*l* bond break preferentially during the initiation step?*

From *Data Booklet*:
BE(C*l*–C*l*) = 244 kJ mol^{-1} BE(C–H) = 410 kJ mol^{-1} BE(C–C) = 350 kJ mol^{-1}

Energy provided by the UV light is only sufficient to overcome weakest C*l*–C*l* bond but not those of C–H and C–C bonds.

b. *Are H• radicals (atoms) formed during the propagation step? Why?*

No. Consider 2 two possible propagation steps:
$CH_4 + Cl\bullet \rightarrow \bullet CH_3$ (***alkyl radical***) + HC*l* $\Delta H_{rxn\ 1}$
$CH_4 + Cl\bullet \rightarrow CH_3Cl + H\bullet$ (***hydrogen radical***) $\Delta H_{rxn\ 2}$

$\Delta H_{rxn\ 1}$ = BE(C–H) – BE(H–C*l*) = 410 – 431 = **–21** kJ mol^{-1}
$\Delta H_{rxn\ 2}$ = BE(C–H) – BE(C–C*l*) = 410 – 340 = **+70** kJ mol^{-1}

Remember?
$\Delta H_{reaction}$ = $\sum$BE (bonds broken) – $\sum$BE (bonds formed)

The above ΔH values show that it is energetically more favorable to form alkyl radicals than hydrogen radicals. Thus, **no H• radicals are formed during propagation**. Hence, hydrogen gas is never formed in such reactions.

c. *Does the propagation reaction stop at monosubstitution?*

No. CH_3**C*l*** formed by monosubstitution can **undergo further substitution** to produce **multi-substituted halogenoalkanes**, CH_2**C*l*$_2$**, CH**C*l*$_3$** and C**C*l*$_4$** as shown below.

$CH_4 + Cl_2 \rightarrow CH_3$**C*l*** + CH_2**C*l*$_2$** + CH**C*l*$_3$** + C**C*l*$_4$**
(*various degree of substitution**)***

$Cl\bullet + CH_3Cl \rightarrow \bullet CH_2Cl + HCl$
$\bullet CH_2Cl + Cl_2 \rightarrow Cl\bullet$ + **CH_2Cl_2** (dichloromethane is produced)

$Cl\bullet + CH_2Cl_2 \rightarrow \bullet CHCl_2 + HCl$
$\bullet CHCl_2 + Cl_2 \rightarrow Cl\bullet$ + **$CHCl_3$** (trichloromethane is produced)

$Cl\bullet + CHCl_3 \rightarrow \bullet CCl_3 + HCl$
$\bullet CCl_3 + Cl_2 \rightarrow Cl\bullet$ + **CCl_4** (tetrachloromethane is produced)

Hence free radical substitution **does not give a single product** but a mixture of products and has limited *synthetic utility* in the laboratory because of the multiplicity of products formed.

d. How to minimise multiple substitutions?

By modifying the conditions of the reaction, it is possible for the reaction to favour formation of one product over others. Product that is formed in a significantly greater quantity is known as the **major product** while those formed in smaller quantities are known as the **minor products**.

When **excess alkane** (or **limited C*l*$_2$**) is used, **monosubstituted** alkane, e.g. CH_3Cl, predominates since there is a higher probability for C*l*• radicals to collide with

CH_4 molecules instead of CH_3Cl molecule in the propagation step. Thus, a considerable amount of CH_3Cl will be formed.

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

When **excess Cl_2** is used, the more **highly substituted** products such as CH_2Cl_2, $CHCl_3$, CCl_4 are formed.

$$CH_4 + 2Cl_2 \rightarrow CH_2Cl_2 + 2HCl$$
$$CH_4 + 3Cl_2 \rightarrow CHCl_3 + 3HCl$$
$$CH_4 + 4Cl_2 \rightarrow CCl_4 + 4HCl$$

e. What are the conditions for free radical substitution of alkanes with different halogens of different reactivity?

Reactivity of halogens with alkanes **increases** in the order (**reverse** of the X–X bond energies):

$$I_2 < Br_2 < Cl_2 < F_2$$

F_2	:	reaction proceeds explosively even at r.t.p. (not carried out in laboratory)
Cl_2 / Br_2	:	reaction occurs at 250 – 400 °C or in UV light
I_2	:	least reactive and reaction is so slow that it is not carried out

For example:

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ **$\Delta H_{rxn\ 1}$**

$\Delta H_{rxn\ 1}$ = [BE(C–H) + BE(Cl–Cl)] – [BE(C–Cl) + BE(H–Cl)]
= (410 + 242) – (340 + 431) = **–119 kJ mol^{-1}**

$CH_4 + I_2 \rightarrow CH_3I + HI$ **$\Delta H_{rxn\ 2}$**

$\Delta H_{rxn\ 2}$ = [BE(C–H) + BE(I–I)] – [BE(C–I) + BE(H–I)]
= (410 + 151) – (240 + 299) = +**22 kJ mol^{-1}**

As $\Delta H_{rxn\ 2}$ is positive, the reaction is endothermic and it is much less likely to synthesise iodoalkanes by this method.

Important Note:

When describing/ outlining a reaction mechanism,

- *state name of the mechanism*
- *Label "initiation", "propagation" and "termination" steps and give the structural formula of the organic molecule/ radical for each equation under each step.*
- *draw a half curly arrow to show movement of an electron*
- *show lone electron, (•), of all radicals. For alkyl radical, must place the "•" next to the C atom. E.g.*

CH_3CH_2• × $CH_3\dot{C}H_2$ √

- *no need for detail descriptions / explanations*

Checkpoint 3

1. Write an overall equation for the formation of bromoethane from the reaction of ethane with bromine.

2. Describe the mechanism for the synthesis of bromoethane from ethane.

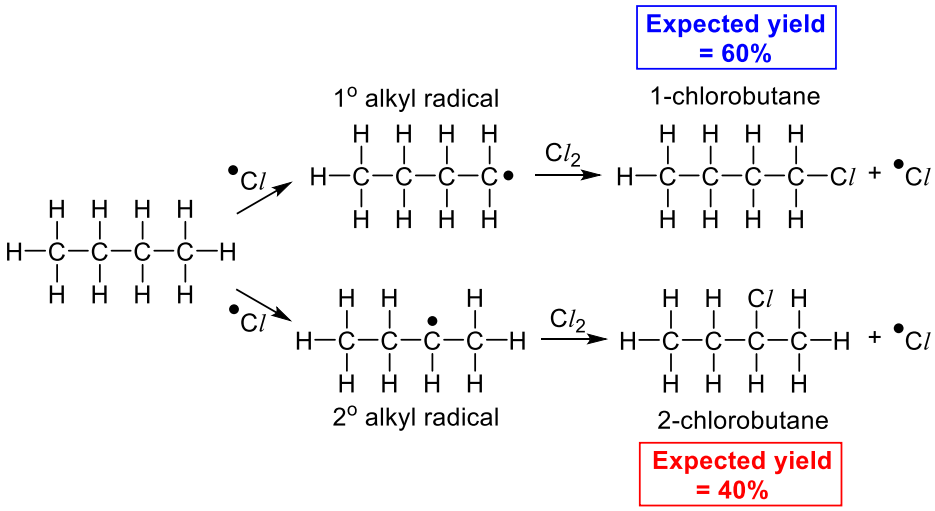
Name of Mechanism:

(ii) Expected yield for monosubstitution of alkane (Based on probability)

Success criteria:
• I can use probability to predict the expected/ theoretical relative ratio of different monosubstituted product for an alkane undergoing free radical substitution.

In higher members of alkanes, substitution of hydrogen atoms at different carbon atoms leads to different products.

e.g. Butane reacts with chlorine in the presence of UV light to form two mono-substituted products as shown below.



There are a total of 4 H that can be substituted to form 2-chlorobutane while there are a total of 6 H that can be substituted to form 1-chlorobutane.

Assuming each H has an equal chance of being substituted by C*l*, thus molar ratio of 1-chlorobutane and 2-chlorobutane formed is 60% : 40%, i.e. 3 : 2. This is the theoretical ratio.

Checkpoint 4

1. The following alkanes undergo free radical substitution with chlorine. Identify the monochlorinated products and their expected ratio.

(a) 2-methylpropane

(b) Pentane

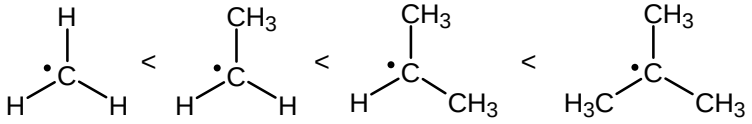
(ii) Rate of substitution at 1°, 2° & 3° carbon atoms

Success criteria:
• I can explain how electron-donating alkyl groups stabilize the alkyl radical, thus favouring substitution at a particular carbon, causing the experimental ratio to differ from theoretical ratio.

Important Note:

Greater stability in the reactive intermediate lowers the activation energy of the reaction.

Radical stability increases in the order
methyl < primary < secondary < tertiary



Least stable **Most stable**

Alkyl groups are weakly **electron-donating / releasing**. They stabilise alkyl radicals by shifting their electron density towards the **electron-deficient** carbon atom that bears the lone electron. The **more alkyl groups** bonded to this carbon, the **more stable** the radical due to a decrease in its electron deficiency.

Thus, a tertiary (3°) radical (radical C connected to 3 other alkyl groups) is the most stable of all, followed by the secondary (2°) radical, and in turn, the primary (1°) radical (radical C connected to 1 other alkyl groups).

Checkpoint 5

Based on the probability consideration, substitution of H atoms of butane would produce 1-chlorobutane and 2-chlorobutane in the expected molar ratio of **60% : 40%**. However, the experimental yields for 1-chlorobutane and 2-chlorobutane are 30% and 70% respectively.

Explain the discrepancy between the expected and experimental ratios of the monochlorinated products.

3.6 PETROLEUM AND ITS ENVIRONMENTAL CONSEQUENCES

3.6.1 Environmental pollutants

Success criteria:
• I can state the environmental pollutants and the impacts they have on the environment.

During the combustion of petrol, the following pollutants may be produced in the car exhaust emissions:

(i) Smog

As a result of incomplete combustion of fuel, unburnt hydrocarbons that escape into the atmosphere become smog under the strong sunlight and can cause lung damage.

(ii) Carbon monoxide

CO is formed from the incomplete combustion of hydrocarbon fuels.

CO binds much more strongly to haemoglobin than O_2 in red blood cells. This reduces the oxygen-carrying ability of the cells, which can be fatal.

(iii) Nitrogen oxides (NO_x, nitrox)

The combustion of fuel in car engines causes the temperature to rise so high that it can break N≡N bonds in nitrogen, which then react with oxygen to form NO and NO_2. NO and NO_2 (collectively termed **nitrox**, **NO_x**) can contribute to

- formation of smog through reaction with other air pollutants. PAN is a major component of smog which is harmful to plants and humans.

  Hydrocarbons + O_2 + NO_2 + light $\rightarrow$ peroxyacetyl nitrate (PAN)

- formation of ozone at lower atmosphere. **High concentration of ozone at lower atmosphere causes respiratory problems.**

  $NO_2 \rightarrow NO + O$

  $O + O_2 \rightarrow O_3$

Recall homogeneous catalyst from reaction kinetics

- NO_2 acts as a **catalyst for the oxidation** of SO_2 to SO_3.

  Overall Eqn: $SO_2 + ½\ O_2 \rightarrow SO_3$

  Mechanism:

  $NO_2 + SO_2 \rightarrow SO_3 + NO$

  $NO + ½\ O_2 \rightarrow NO_2$ (regenerated)

  SO_3 dissolves in rainwater to cause acid rain (H_2SO_4).

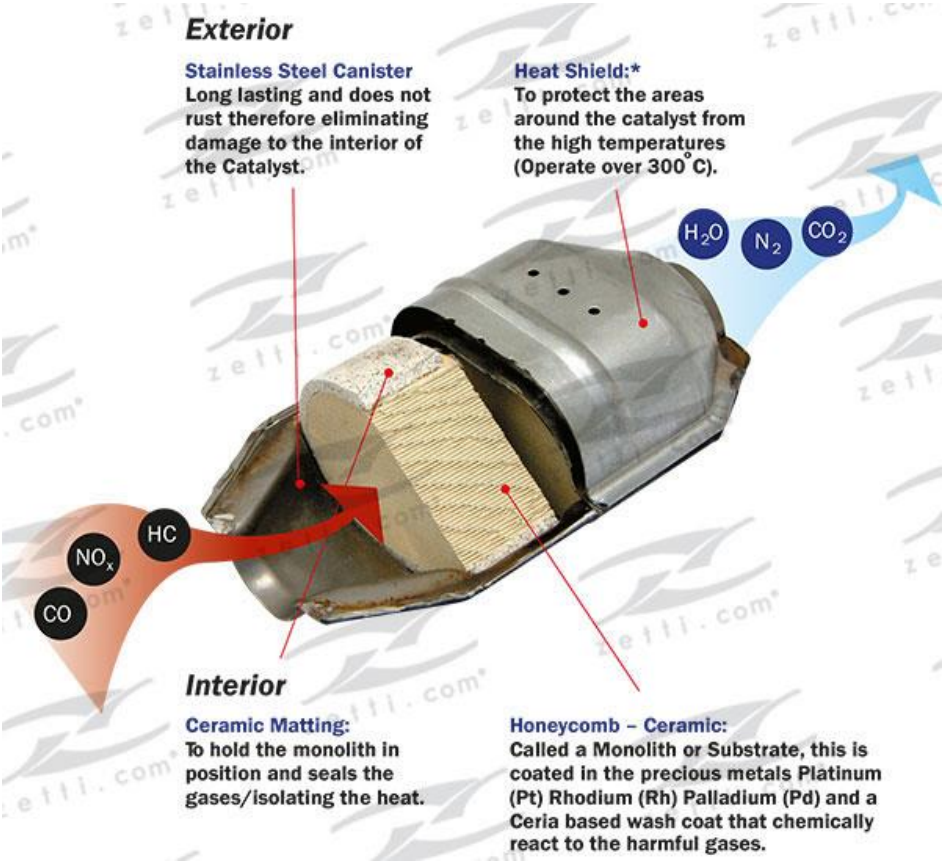
3.6.2 Use of catalytic converter

Success criteria:
• I understand the purpose of catalytic converter in motor vehicles. • I understand the reactions in the catalytic converters are redox reactions.

To reduce pollution from motor vehicles, catalyst converters containing rhodium, platinum and/or palladium are fixed onto the exhaust pipes. These catalysts convert the more harmful C, CO, NO, NO_2 and unburnt hydrocarbons to less harmful or harmless compounds of CO_2, H_2O, N_2 and O_2 shown below.

hydrocarbons + oxides of nitrogen → carbon dioxide + water + nitrogen

$2CO + 2NO \rightarrow 2CO_2 + N_2$ (CO is oxidised to CO_2, NO is reduced to N_2)
$2NO_2 + 2C \rightarrow 2CO_2 + N_2$ (C is oxidised to CO_2, NO_2 is reduced to N_2)



3.6.3 Greenhouse Gases and the Enhanced Greenhouse Effect

Many greenhouse gases occur naturally in the atmosphere, such as carbon dioxide, methane (CH_4), water vapor, and nitrous oxide (N_2O). The problem we now face is that human activities – particularly burning fossil fuels (coal, oil and natural gas), agriculture and land clearing – are increasing the concentrations of greenhouse gases.

The disruption to Earth's climate equilibrium caused by the increased concentrations of greenhouse gases has led to an increase in the global average surface temperatures. This process is called the **enhanced greenhouse effect.**

The greenhouse gases that was emitted directly in *significant* quantities are:

- **Carbon dioxide (CO_2).** Accounts for around 75% of the warming impact of current human greenhouse-gas emissions. The key source of CO_2 is the burning of fossil fuels such as coal, oil and gas, though deforestation is also a very significant contributor.

- **Methane (CH_4).** Accounts for around 14% of the impact of current human greenhouse-gas emissions. Key sources include agriculture (especially livestock and rice fields), fossil fuel extraction and the decay of organic waste in landfill sites.

Success Criteria	Relevant Tutorial questions	What do you still struggle with? Write your queries here.
1. I can deduce the structure of an alkane from its given IUPAC name (and vice versa)	DQ1,2	
2. I can explain the difference in melting point and boiling point between alkanes. 3. I can understand the solubility of alkanes in different types of solvent.	DQ3	
4. I can explain why alkanes are generally unreactive towards most reagents.	DQ7	
5. I can write balanced equation for alkanes to undergo combustion.	DQ4,6	
6. I can deduce the identity of a hydrocarbon based on combustion data.	DQ5	
7. I can describe/ outline the free radical substitution (FRS) mechanism with reference to initiation, propagation and termination reactions using equations and curly arrows (1st step only).	DQ10, DQ15(iii)	
8. I can understand why FRS is an unsuitable method for many organic synthesis.	DQ9	
9. I can predict the structures of the possible products from FRS.	DQ12, DQ15(i)-(ii)	
10. I can apply my understanding of FRS mechanism to a novel context.	DQ16	
11. I can use probability to predict the expected/ theoretical relative ratio of different monosubstituted product for an alkane undergoing free radical substitution.	DQ11,13-14	
12. I can explain how electron-donating alkyl groups stabilize the alkyl radical, thus favouring substitution at a particular carbon, causing the experimental ratio to differ from theoretical ratio.	DQ13	
13. I can state the environmental pollutants and the impacts they have on the environment.	DQ18	
14. I understand the purpose of catalytic converter in motor vehicles. 15. I understand the reactions in the catalytic converters are redox reactions.	DQ17,18(d)	

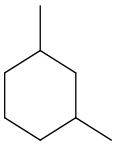
HYDROCARBONS - ALKANES AND CYCLOALKANES TUTORIAL

Structure and naming

1 Give the IUPAC name for each compound. Identify any chiral center and draw its stereoisomers, if any.

(a) $CH_3CH_2CH_2CH(CH_3)CH_2CH_2CH_3$ **(b)** $CH_3CH(CH_3)CH(CH_3)CH_2CH_3$

(c)



2 Give the structural formula of the following alkanes.

(a) 4-ethyl-3,4-dimethylheptane

(b) a saturated compound with molecular formula C_5H_{10}

Physical Properties

3 Crude oil consists mainly of alkanes. The alkanes in crude oil can be separated because they have different boiling points.

The table below shows the boiling points of some alkanes.

Alkane	Boiling point / ^oC	M_r
butane	0	58
pentane	36	72
hexane	69	86
2-methylbutane	28	72
2,2-dimethylpropane	10	72
3-methylpentane	?	86
2,3-dimethylbutane	58	86

(a) State what is meant by the term *saturated hydrocarbon*.

(b) **(i)** Explain the trend in boiling points of the straight chain alkanes.

(ii) Explain the difference in the boiling points of the three isomers with M_r = 72.

(iii) With reference to your answer in **b(ii)**, suggest a possible value for the boiling point of 3-methylpentane.

Combustion of hydrocarbon

4 What is the volume of CO_2 formed when y cm^3 of a 50:50 mixture of methane and propane is completely burnt?

A 2y cm^3 **B** $\frac{5y}{2}$ cm^3 **C** 4y cm^3 **D** 5y cm^3

5 When 15 cm^3 of a gaseous hydrocarbon **A** were burned in 100 cm^3 of oxygen, the final gaseous mixture contained 60 cm^3 of carbon dioxide and 10 cm^3 of unreacted oxygen. [All gaseous volumes measured under identical conditions.]

What is the formula of hydrocarbon **A**?

A C_3H_6 **B** C_3H_8 **C** C_4H_8 **D** C_4H_{10}

6 (2016 P3 Q1c) Carbon monoxide is a product of the incomplete combustion of hydrocarbons in internal combustion engines.
Write an equation for the incomplete combustion of octane, C_8H_{18}, giving CO_2 and CO in a 3:1 molar ratio.

Free Radical Substitution

7 (2016 P3 Q4d) Alkanes are very unreactive.
(i) Suggest two reasons why this is the case.

(ii) However, alkanes such as propane, C_3H_8, do react with oxygen and with chlorine.
For each of these reactions,
I. State the conditions under which the reaction is carried out.
II. Name the *type of reaction* which takes place,
III. Write an equation for the reaction.

8 Which explains why chlorine gas reacts readily with ethane in the presence of ultraviolet light?

A UV light breaks the C–H bonds in ethane.

B UV light increases the temperature of the mixture.

C UV light splits the chlorine molecules into chlorine atoms.

D UV light breaks up the chlorine molecules into chloride ions.

9 Which statement best explains why a high yield of 2-bromobutane is **not** usually obtained when butane and bromine react in the presence of UV light?

A Bromine reacts with butane too vigorously.

B Bromine can replace any hydrogen atom in butane.

C The second and third carbon atoms of butane are too strongly electrophilic.

D The second and third carbon atoms of butane are too strongly nucleophilic.

10 Which is a **propagation** step in the reaction between propane and bromine when they are irradiated with ultraviolet light?

A $CH_3CH_2CH_2Br + Br\bullet \rightarrow CH_3CH_2\overset{\bullet}{C}H_2 + Br_2$

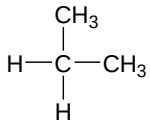
B $CH_3CH_2\overset{\bullet}{C}H_2 + Br\bullet \rightarrow CH_3CH_2CH_2Br$

C $CH_3CH_2\overset{\bullet}{C}HBr + Br_2 \rightarrow CH_3CH_2CHBr_2 + Br\bullet$

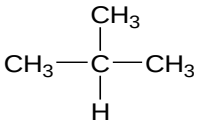
D $CH_3CH_2\overset{\bullet}{C}H_2 + Br_2 \rightarrow CH_3CH_2CHBr + HBr$

11 An alkane **J** reacts with chlorine gas under ultraviolet light to form only two monochlorinated alkanes in an approximate molar ratio of 6 : 1.
Which could be **J**?

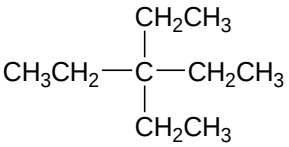
A



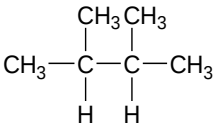
B



C



D



12 Propane reacts with chlorine gas in the presence of UV light.
Which is true about the reaction?

A The maximum number of mono-chlorinated structural isomers with formula C_3H_7Cl is 2.

B C_6H_{12} is present in a small quantity in the product.

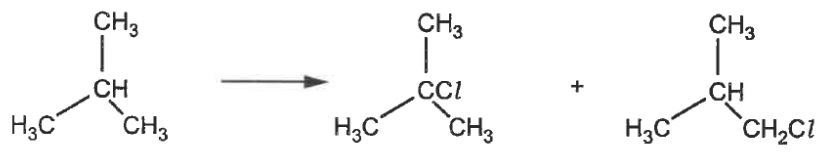
C Homolytic fission occurs only in the initiation step.

D HCl is formed in the termination step.

13 It is found by experiment that during free radical substitution, primary, secondary and tertiary hydrogen atoms are replaced by chlorine atoms at different rates, as shown in the following table.

reaction	relative rate
$RCH_3 \longrightarrow RCH_2Cl$	1
$R_2CH_2 \longrightarrow R_2CHCl$	7
$R_3CH \longrightarrow R_3CCl$	21

Predict the relative ratio of the two possible products L and M from the chlorination of 2-methylpropane, using the information in the table above, together with the number of hydrogen atoms of each type (primary, secondary or tertiary) within the molecule.
Explain your answer.



2-methylpropane L M

Application Questions

14 **A** and **B** are two structural isomers with the molecular formula C_4H_{10}.
When **A** reacts with chlorine gas in the presence of UV light, two monochlorinated alkanes **C** and **D** are formed. Only **D** contains a chiral carbon.
When **B** reacts with chlorine gas in the presence of UV light, two monochlorinated alkanes **E** and **F** are formed. Both **E** and **F** are optically inactive.

(a) Identify **A**, **B**, **C**, **D**, **E** and **F** by drawing their structural formulae.

(b) **(i)** State the type of isomerism exhibited by **A** and **B**.

(ii) State the type of isomerism exhibited by **C** and **D**.

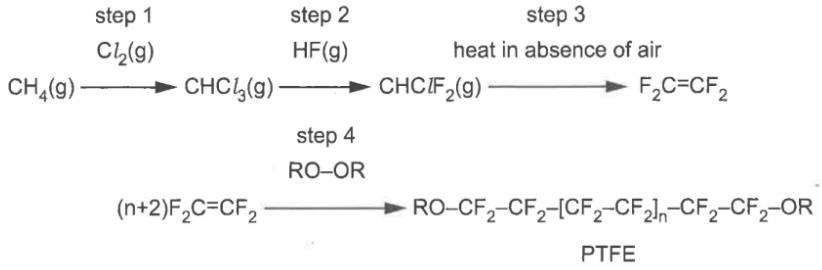
15 In an experiment, propane is added to liquid bromine in the dark. When the reaction mixture is exposed to sunlight, the reddish brown colour slowly disappears and a misty gas is given off.

(i) Identify the misty gas formed in the reaction.

(ii) Write an overall equation for the reaction of one mole of propane, C_3H_8, with two moles of bromine. Draw the structural formulae of all the possible products formed.

(iii) Outline the mechanism for the formation of 1,2-dibromopropane in **b(ii)**.
There are four steps in the propagation stage of the mechanism.

16 (2021 P2 Q4d) The term 'polymer' is given to a large molecule made up of many repeat units. Poly(tetrafluoroethane), PTFE, is a polymer made from many tetrafluorethane molecules, $F_2C{=}CF_2$. PTFE can be manufactured from methane in a series of steps.



Step 4 occurs via four separate reactions, **A** to **D**.

A Homolytic fission of RO−OR at 330K and 10-20 atm to produce two RO• radicals

B RO• reacts with one $F_2C{=}CF_2$ molecule to produce a new radical

C Repeated steps involving production of a series to produce

$$RO{-}CF_2{-}CF_2{-}[CF_2{-}CF_2]_n{-}CF_2{-}CF_2{\bullet}$$

D Two radicals combine to form $RO{-}CF_2{-}CF_2{-}[CF_2{-}CF_2]_{(2n+2)}{-}CF_2{-}CF_2{-}OR$

(i) Explain what is meant by the term homolytic fission.

(ii) Name reactions **A** to **D**.

(iii) Suggest a name for the overall mechanism of step 4.

(iv) Suggest the mechanism which occur in reactions **A** and **B** of step 4. Use curly arrows to show movements of electrons.

Petroleum and its environmental consequences

17 (2020 P1 Q20) Exhaust fumes from car engines contain the gases carbon dioxide, nitrogen oxides and unburnt hydrocarbons.

Use of a catalytic converter in the car exhaust changes the gases emitted.

Which statements are correct about the reactions occurring in the catalytic converter?

1. Carbon dioxide is removed by reduction.
2. Oxides of nitrogen are removed by reduction.
3. Unburnt hydrocarbons are removed by oxidation.

A 1 and 3 **B** 2 and 3 **C** 1 only **D** 2 only

18 Car exhausts contain a range of toxic substances that can have a serious impact on health. Once released into the air, these substances are breathed in and transported in the blood stream to all the body's major organs.
A typical composition of gases in petrol engine exhaust fumes is as follows.

Substance	%
Water vapour	9
Carbon dioxide	8
Carbon monoxide	4-6
Oxygen	4
Hydrocarbons	0.2
Oxides of nitrogen	0.3

(a) Which gases of exhaust fumes are consequences of incomplete combustion?

(b) Suggest a reason why the exhaust gases contain products of incomplete combustion.

(c) Name a pollutant in the exhaust fumes that has an adverse effect on human health and explain its impact on human health.

(d) Suggest one substance in the exhaust fumes which can convert one of the pollutants into a harmless product in a car fitted with a catalytic converter. Write a chemical equation to support your suggestion.

Ans Key for MCQ:

4) A	5) C	8) C	9) B	10) C	11) D	12) A	17) B