2022 JC1 H2 CHEMISTRY (9729)
ORGANIC CHEMISTRY
Topic 2: HYDROCARBONS – ALKANES

Name: ____ Civics Group: _________

Students should be able to:

(a) Explain the general unreactivity of alkanes, including towards polar reagents.

(b) Describe the chemistry of alkanes as exemplified by the following reactions of ethane:

  (i) Combustion

  (ii) Free-radical substitution by chlorine and by bromine

(c) Describe the mechanism of free-radical substitution with particular reference to the initiation, propagation and termination reactions.

(d) Recognise the environmental consequences of:

  (i) carbon monoxide, oxides of nitrogen and unburnt hydrocarbons arising from the internal combustion engine and their catalytic removal.

  (ii) gases that contribute to enhanced greenhouse effect

(e) Recognise that petroleum, a chemical feedstock, is a finite resource and the importance of recycling

LECTURE CONTENT

REFERENCES:

1. **Chemistry for Advanced Level**, Peter Cann, 2002
2. **Chemistry, The Molecular nature of Matter and Change**, Silberberg, 2003
3. **Chemistry (2nd edition)**, Chris Conoley and Phil Hill
4. **Chemistry in Context**, Hill & Holman
5. **Understanding Chemistry for Advanced Level**, Ted Lister, Janet Renshaw

1 Introduction

1.1 Hydrocarbons

- Hydrocarbons are compounds containing **only hydrogen and carbon** (e.g. alkanes, alkenes, arenes, alkynes) and are obtained from crude oil, a fossil fuel.

(Recap from 'O' Levels) **Fractional distillation** separates the components of crude oil (which is mainly made up of alkanes) based on their **different boiling points**.

Major fractions of crude oil and their uses:

fraction	boiling point range / °C	length of carbon chain	uses
refinery gas	< 20	C_1 to C_4	fuels and feedstock (starting reactants) for petrochemicals.
gasoline/ naphtha	20–120	C_5 to C_{12}	petrol for transport and as a feedstock for petrochemicals
kerosene	120–220	C_{10} to C_{16}	jet fuel, paraffin
diesel	220–350	C_{15} to C_{25}	fuel for transport, power plants and heating
residue	> 350	> C_{25}	oil-fired power stations, polishing waxes, lubricating oils and bitumen on roads

LO (e) Recognise that petroleum, a chemical feedstock, is a finite resource and the importance of recycling

- Petroleum is used to produce things such as plastics. Since **petroleum is a finite resource** thus **recycling is important to reduce the amount of waste** sent to landfills and incinerators, as well as the **conservation of natural resources**. It also helps sustain the environment for future generations.

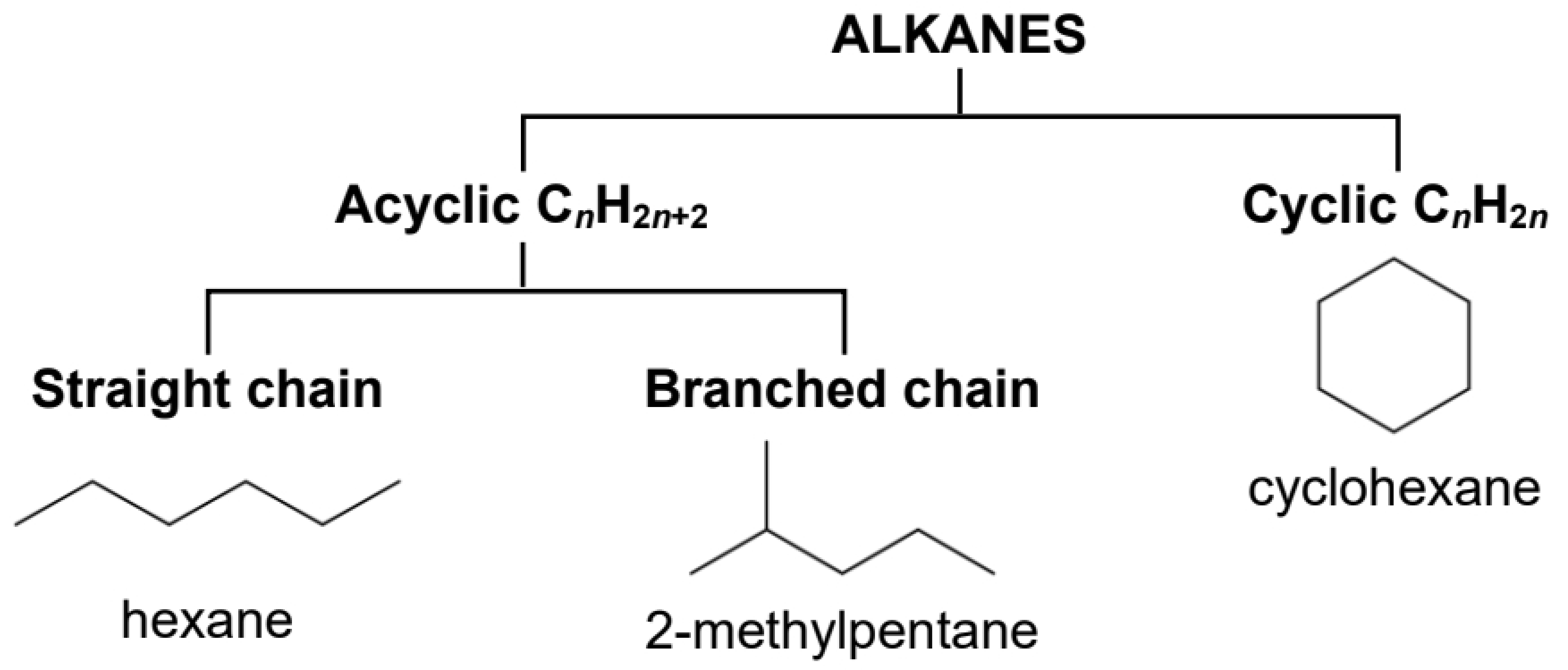
1.2 Alkanes

- Alkanes are **saturated** hydrocarbons **(only have single bonds, *e.g.* C–C, C–H)**.

- Each C atom is **sp^3** hybridised, **tetrahedrally** surrounded by H and other C atoms with bond angle of **109.5°**.

- Alkanes can exist as straight chains, branched chains, and rings (these are known as cycloalkanes).

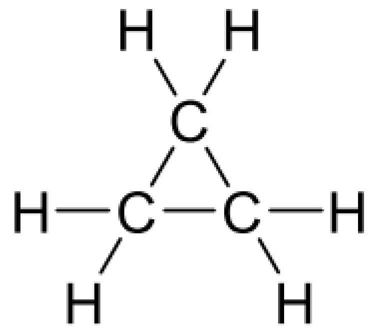
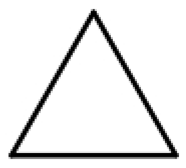
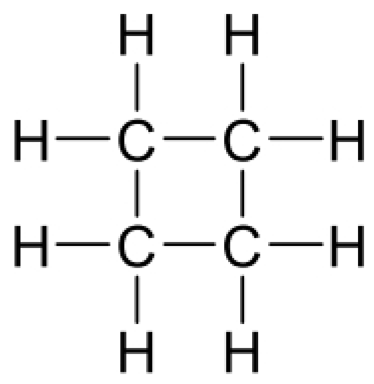
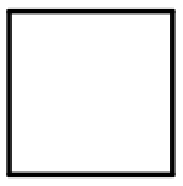
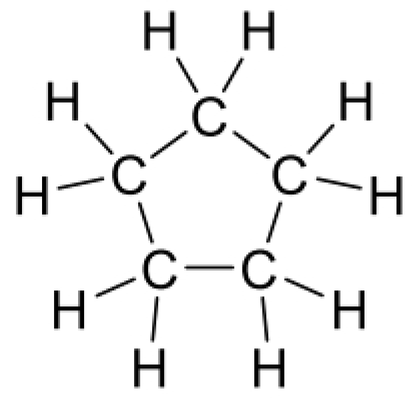
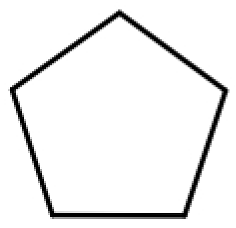
- General formula:
  - ❐ for all straight chain and branched chain alkanes: $\mathbf{C_nH_{2n+2}}$,
  - ❐ for cycloalkanes: $\mathbf{C_nH_{2n}}$, where *n* equals the number of carbon atoms (the difference of 2 H atoms is equivalent to a ring structure).



1.2.1 Examples of straight chain alkanes

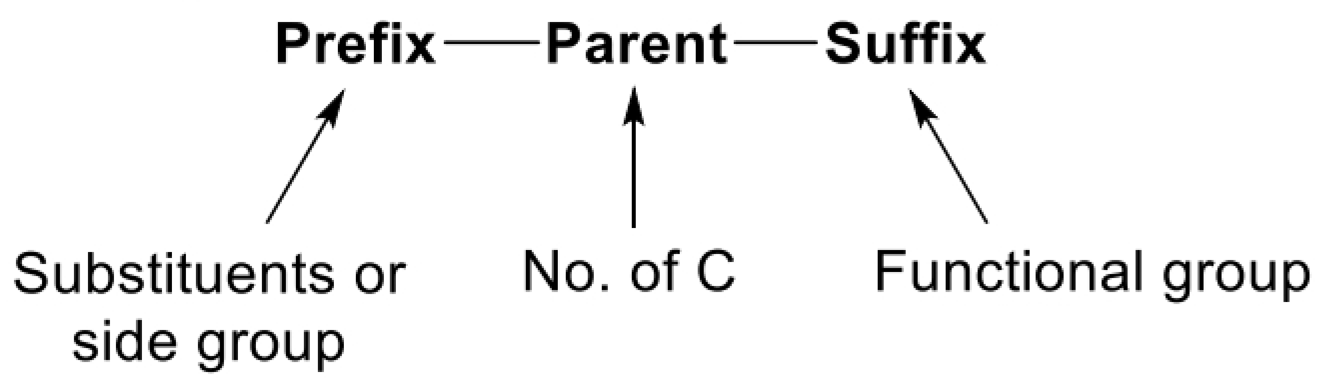
alkane	structural formula	m.p. / ºC	b.p. / ºC
methane	CH_4	–183	–162
ethane	CH_3CH_3	–172	–89
propane	$CH_3CH_2CH_3$	–188	–42
butane	$CH_3CH_2CH_2CH_3$	–135	–0.5
pentane	$CH_3CH_2CH_2CH_2CH_3$	–130	36
hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	–95	69
heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	–91	98
octane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	–57	126
nonane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	–54	151
decane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	–30	174

1.2.2 Examples of cycloalkanes (isomeric with alkenes)

n	**molecular formula**	**name**	**displayed formula**	**skeletal formula**
3	C_3H_6	**cyclopropane**		
4	C_4H_8	**cyclobutane**		
5	C_5H_{10}	**cyclopentane**		

2 Nomenclature (using the IUPAC system)

The IUPAC system is the most common method used for naming most organic compounds. In the IUPAC nomenclature, every name consists:



Steps in naming alkanes:

a) Name the parent chain

- Determine the *longest continuous carbon chain* present as the parent chain.
- If there are two different chains of equal length, choose the one with the *larger number* of branched groups.
- Alkanes are named with the suffix –***ane***.

no. of C atoms	**1**	**2**	**3**	**4**	**5**
parent chain	methane	ethane	propane	butane	pentane
no. of C atoms	**6**	**7**	**8**	**9**	**10**
parent chain	hexane	heptane	octane	nonane	decane

b) Name every ***side group*** (that branches off from the parent chain)

CH_3–	CH_3CH_2–	$CH_3CH_2CH_2$–
methyl	ethyl	propyl

c) Assign a number to side group according to its *position* on the chain

- Ensure that each of these carbon atoms has the ***smallest*** *number* possible.

d) Write the name as a single word

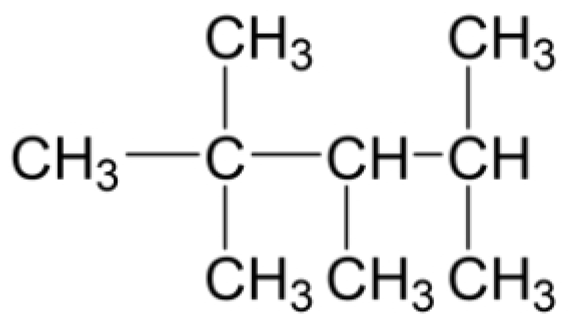
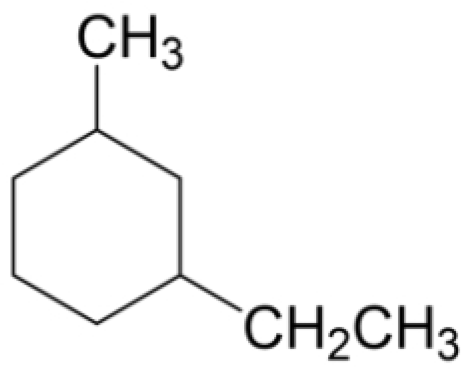
- Name each side group attached to the parent chain by placing the position of substituents in front and separating the name by a hyphen. (*e.g.* 3-methyl)
- If two or more *different* substituents are present, cite them in ***alphabetical* order**. (*e.g.* ethylmethyl)
- If two or more *identical* substituents are present, use one of the multiplier prefixes:

di = 2
tri = 3
tetra = 4
penta = 5
hexa = 6
hepta = 7
octa = 8
nona = 9
deca = 10

- Ignore the above prefixes when establishing the alphabetical order. *E.g.* ethyl before dimethyl.
- Use hyphens to separate the different prefixes, and use commas to separate numbers.

Example 2A

Write the IUPAC names of the following compounds.

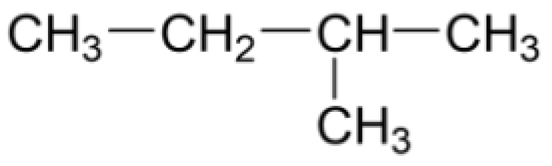
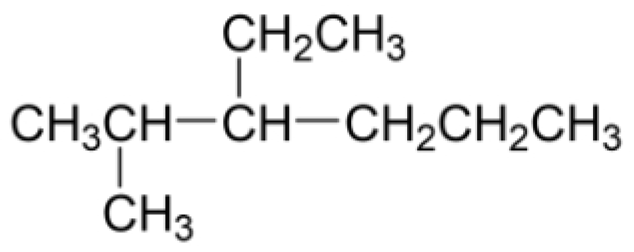
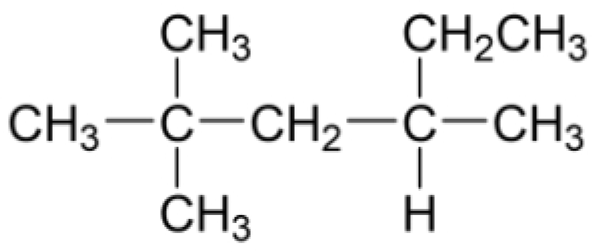
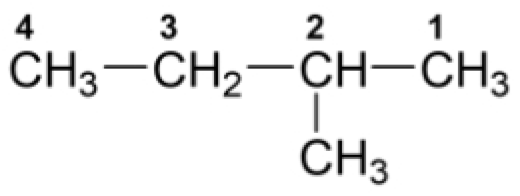
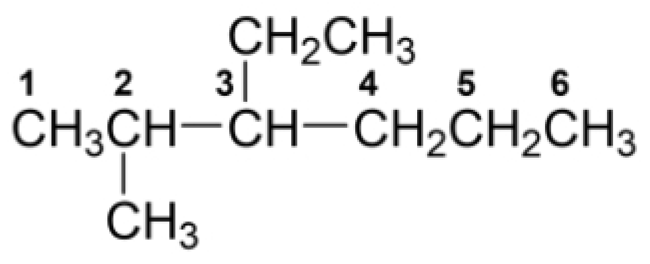
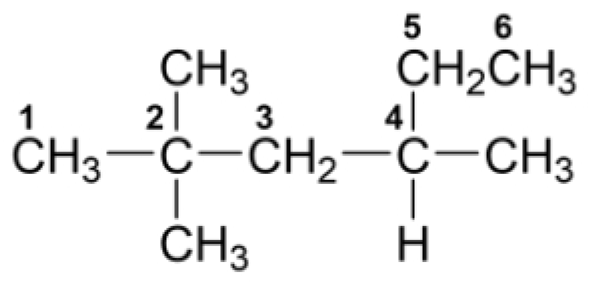
 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{CH_3}{CH}-\overset{CH_3}{\underset{CH_3}{CH}}$		$CH_3CHBrCHClCH_2CH_3$

Example 2B

Draw the full structural formula and skeletal formula for each of the following compounds.

compound	2,2-dimethylpentane	5-ethyl-2,2-dimethylheptane
full structural formula		
skeletal formula		

Self Check 2A

alkane molecule	 $CH_3-CH_2-\underset{CH_3}{CH}-CH_3$	 $CH_3\underset{CH_3}{CH}-\overset{CH_2CH_3}{CH}-CH_2CH_2CH_3$	 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_2CH_3}{\underset{H}{C}}-CH_3$
step 1: parent chain			
step 2: side groups			
step 3: assign numbers to side groups	 $\overset{4}{CH_3}-\overset{3}{CH_2}-\underset{CH_3}{\overset{2}{CH}}-\overset{1}{CH_3}$	 $\overset{1}{CH_3}\underset{CH_3}{\overset{2}{CH}}-\overset{CH_2CH_3}{\overset{3}{CH}}-\overset{4}{CH_2}\overset{5}{CH_2}\overset{6}{CH_3}$	 $\overset{1}{CH_3}-\underset{CH_3}{\overset{CH_3}{\overset{2}{C}}}-\overset{3}{CH_2}-\underset{H}{\overset{\overset{5}{CH_2}\overset{6}{CH_3}}{\overset{4}{C}}}-CH_3$
name			

3 Physical Properties

All alkane molecules are **non-polar molecules** (as C–C bond is non-polar and C–H bonds are effectively non-polar due to the very small difference in electronegativity between C and H atoms).

3.1 Boiling Point / Volatility

Alkanes have relatively low boiling points (or high volatility or high vapour pressure) as they have weaker instantaneous dipole–induced dipole interactions.

Recall from Chemical Bonding that the strength of such electrostatic forces of attraction is affected by:

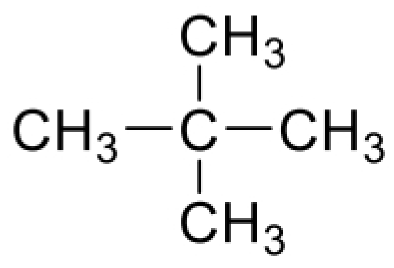
(1) Number of electrons in the molecule

If we look at the melting and boiling points of the alkanes on page 3, they generally increase from one member of the homologous series to the next member. This is due to the additional $-CH_2-$ group which leads to a **greater number of electrons** in the molecule, thus **greater polarisation of electron cloud** in the molecule, and **stronger instantaneous dipole – induced dipole interactions**. Hence, more energy is needed to overcome these electrostatic forces of attraction, leading to higher melting/boiling point and lower volatility or higher enthalpy change of vapourisation.

(2) Shape of the molecule

$CH_3CH_2CH_2CH_2CH_3$

pentane (36 ºC)



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3$$

2,2-dimethylpropane (10 ºC)

Straight chain alkanes (*e.g.* pentane) have higher boiling point (or lower volatility) than their corresponding branched chain alkanes (*e.g.* 2,2-dimethylpropane). This is because **straight chain molecules have larger surface area of contact between them** and thus have **more extensive instantaneous dipole–induced dipole interactions** which need more energy to overcome.

Example 3A

Arrange the following alkanes in order of increasing boiling points. Explain your answer.

- 2,3-dimethylbutane
- hexane
- propane

Among the 3 alkanes, **propane has least number of electrons.** Hence, **strength of instantaneous dipole–induced dipole interactions is weakest for propane.** Comparing hexane and 2,3-dimethylbutane, hexane is a ______________ chain alkane and 2,3-dimethylbutane is a ______________ chain alkane. Therefore, **hexane has greater surface area of contact than 2,3-dimethylbutane**. **Hexane has more extensive instantaneous dipole–induced dipole interaction compared to 2,3-dimethylbutane.**

Thus in order of increasing boiling point: ____

3.2 Solubility

Alkanes are soluble in non-polar solvents such as benzene but are insoluble in water and other (highly) polar solvents.

Reason:

<u>Between alkane and non-polar solvent:</u>

The energy released in forming the **instantaneous dipole−induced dipole (i.d.–i.d.)** interactions between the alkane molecules and non-polar solvent molecules is sufficient to overcome the **i.d.–i.d. interactions between the alkane molecules** and the **i.d.–i.d. interactions between the non-polar solvent molecules**.

<u>Between alkane and water/polar solvent:</u>

The energy released in forming the **permanent dipole−induced dipole (p.d.–i.d.)** interactions between the alkane molecules and water molecules / polar solvent molecules is insufficient to overcome the **i.d.–i.d. interactions between the alkane molecules** and the **hydrogen bonds / permanent dipole-permanent dipole (p.d.–p.d.) interactions between the water molecules / polar solvent molecules**.

3.3 Density

Generally, **<u>alkanes are less dense than water</u>**. The **<u>density of alkanes increases with size of the molecule</u>** $\left(\text{density} = \dfrac{\text{mass}}{\text{volume}}\right)$ due to the **higher relative molecular mass and stronger instantaneous dipole–induced dipole interactions** that make the molecules come closer to each other.

4 Chemical Reactivity of Alkanes

LO (a) Explain the general unreactivity of alkanes, including towards polar reagents.

Alkanes are generally unreactive. They are inert towards most bases, acids, oxidising and reducing agents. Alkanes also do not react with polar reactants and ions.

Reasons:

- **C–C bond and C–H bond are strong covalent bonds** which are difficult to break under ordinary conditions.

  (In comparison, in the next topic "Alkenes", we will see that alkenes undergo many reactions due to the weak π bond being relatively easier to break).

- Furthermore, since there are only single bonds in alkane molecules, there are **no regions of high electron density to attract electrophiles (electron pair acceptors/Lewis acids)** since **C–C bond and C–H bond can be considered as non-polar bonds** (because carbon and hydrogen are very similar in electronegativity). There are also **no electron-deficient carbon atoms to attract nucleophiles (electron pair donors/Lewis bases)**.

  (In comparison, over the next few topics, we will see many reactions that involve electrophiles and nucleophiles reacting with various functional groups).

Checkpoints for Section 1–4

- To understand hydrocarbons are compounds containing only hydrogen and carbon.
- To recognise that petroleum, a chemical feedstock, is a finite resource and the importance of recycling.
- To understand alkanes are saturated hydrocarbons, with the general formula $\mathbf{C_nH_{2n+2}}$ (straight chain alkanes) and $\mathbf{C_nH_{2n}}$ (cycloalkanes).
- To be able to write IUPAC names of simple alkane molecules given the structural formula.
- To be able to draw the structural formula, especially full structural formula and skeletal formula, of alkanes given the IUPAC names.
- To understand the physical properties of alkanes such as the boiling points and solubility, and the factors affecting them (refer to Chemical Bonding).
- To understand and recognise that alkanes are generally unreactive towards polar reagents.

5 Reactions of Alkanes

LO (b) Describe the chemistry of alkanes as exemplified by the following reactions of ethane:
- (i) Combustion
- (ii) Free-radical substitution by chlorine and by bromine

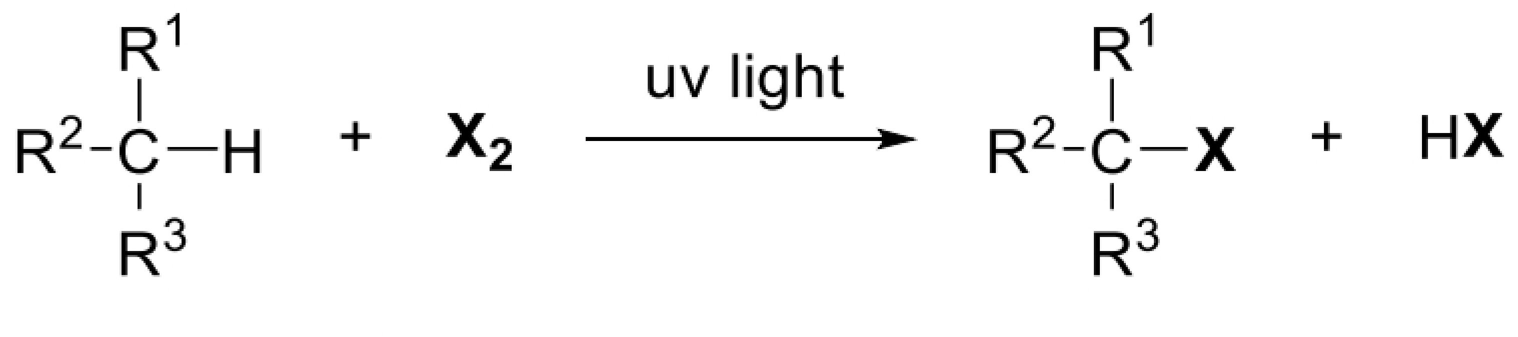
5.1 Combustion

- The complete combustion of alkanes is a highly exothermic process, making alkanes an important fuel. Solid and liquid alkanes must be **converted to the gaseous state** before they burn. Examples of this include the combustion of petrol in motorcars, bottled gas (butane) for cooking food, and oil in electricity-generating stations.

Complete Combustion	**Incomplete Combustion**
• occurs in **excess** oxygen or normal air (Note: For normal air, complete combustion is possible only if there is much more air than fuel)	• occurs in a **limited** supply of oxygen
• general equation: $C_nH_{2n+2} + \frac{3n+1}{2}O_2 \rightarrow nCO_2 + (n+1)H_2O$	• no general equation
e.g. complete combustion of methane $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$	*e.g.* incomplete combustion of methane Soot is produced: $CH_4(g) + O_2(g) \rightarrow C(s) + 2H_2O(l)$ Soot is not produced: $CH_4(g) + \frac{3}{2}O_2(g) \rightarrow CO(g) + 2H_2O(l)$

5.2 Free Radical Substitution (Halogenation)

- Alkanes react with halogens such as $Cl_2(g)$ or $Br_2(l)$ to give halogenoalkanes.
- The hydrogen atom(s) in the alkane can be substituted by the halogen atom(s).



$$R^2R^1R^3C{-}H + \mathbf{X_2} \xrightarrow{\text{uv light}} R^2R^1R^3C{-}\mathbf{X} + H\mathbf{X}$$

where R^1, R^2 and R^3 are either H atoms or alkyl group

Reagents and conditions: $Cl_2(g)$ or $Br_2(l)$, in the presence of UV light or heat

- The type of reaction is known as **free radical substitution**.

[Recall: A free radical is an atom or group of atoms that has one unpaired electron in its valence shell, *e.g.* $\bullet Cl$, $\bullet CH_3$. **Free radicals are usually very reactive (as it is considered electron-deficient)** as the unpaired electron pairs up with another unpaired electron to form an electron pair readily.]

5.2.1 Free Radical Substitution Mechanism
(using methane as an example)

Not in H1 Syllabus

LO (c) Describe the mechanism of free-radical substitution with particular reference to the initiation, propagation and termination reactions.

In Reaction Kinetics, we discussed about mechanisms and how they show us details such as how many steps does the reaction involve, which bonds are broken/formed and the order in which they do so, as well as the relative rates of the different steps within the reaction. Here, we will look into the first mechanism – free radical substitution.

The mechanism involves three stages – initiation, propagation and termination.

Using the reaction between methane and chlorine as an example, the overall equation for the reaction is:

$$CH_4 + Cl_2 \xrightarrow{\text{uv light}} CH_3Cl + HCl$$

Stage 1: Initiation

- Under ultraviolet light or heat, the **homolytic fission of Cl–Cl bond** takes place and **chlorine free radicals, •Cl**, are formed.

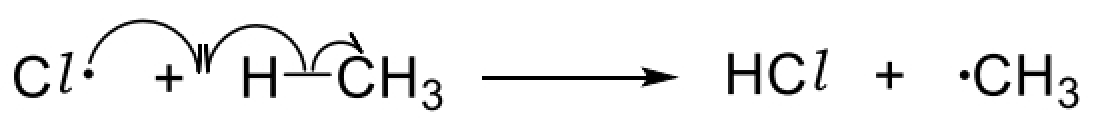
$$Cl{-}Cl \xrightarrow{\text{uv light}} Cl\cdot + \cdot Cl$$

Note: The uv light used (*e.g.* sunlight consisting of UV-A of wavelength 315–400 nm, corresponding to energy of 380–299 kJ mol^{-1}) only provides enough energy to break the weaker Cl–Cl bond (244 kJ mol^{-1}) and not the stronger C–H bond (410 kJ mol^{-1}).

Stage 2: Propagation

- The **highly reactive chlorine free radical**, on colliding with alkanes such as methane, abstracts a hydrogen atom to produce HCl and a **methyl radical, •CH$_3$**.

(a)



$$Cl\cdot + H{-}CH_3 \longrightarrow HCl + \cdot CH_3$$

- The methyl radical **reacts further** with another chlorine molecule to form the product (**chloromethane, CH$_3$Cl**) and a **chlorine free radical is regenerated**.

(b)

$$H_3C\cdot + Cl{-}Cl \longrightarrow H_3C{-}Cl + \cdot Cl$$

- This step leads to a chain reaction [**(a)**, **(b)**, **(a)**, **(b)**, …] since the chlorine free radical formed can react in the same way as shown in the first propagation step.

Note: The **reaction only requires a flash of ultraviolet light rather than prolonged radiation**. Since the •Cl radical is **regenerated** in the propagation stage, the **generation of •Cl radical by using ultraviolet light** is only required in the initiation stage to start the chain reaction.

Stage 3: Termination

- ❒ When any two free radicals collide, the unpaired electrons pair up to form a stable product. This terminates the chain reaction.
- ❒ Possible termination steps:

$$Cl\cdot + \cdot CH_3 \longrightarrow CH_3Cl$$
$$2\,Cl\cdot \longrightarrow Cl_2$$
$$2\,\cdot CH_3 \longrightarrow C_2H_6$$

- ❒ **Termination reactions are exothermic** as they involve bond forming only. The **energy released can help speed up the reaction**.

- ❒ **Trace amount of ethane** is formed as a by-product.

5.2.2 Formation of Multi-Substituted Products

The chloromethane formed from the earlier reaction in Section 5.2.1 can undergo **further substitution** via the same mechanism to give **multi-substituted** halogenoalkanes in the **propagation** step. The equations for the further substitution to form dichloromethane and trichloromethane are shown below:

$$CH_3Cl + \cdot Cl \longrightarrow \cdot CH_2Cl + HCl$$
$$\cdot CH_2Cl + Cl_2 \longrightarrow CH_2Cl_2 + \cdot Cl \quad \text{(dichloromethane)}$$

$$CH_2Cl_2 + \cdot Cl \longrightarrow \cdot CHCl_2 + HCl$$
$$\cdot CHCl_2 + Cl_2 \longrightarrow CHCl_3 + \cdot Cl \quad \text{(trichloromethane)}$$

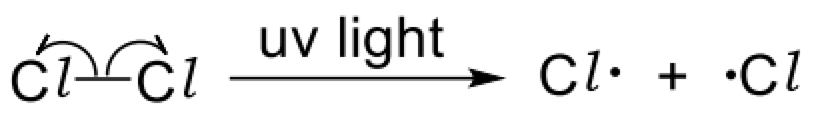
Note:

- Generally, **free radical substitution is not a good method to prepare halogenoalkanes**, as a mixture containing **many different halogen-substituted alkanes** is produced (*i.e.* other than the desired product, many other products are formed).

- **To obtain the monosubstituted product (*e.g.* CH_3Cl) as the major product, limited amount of halogen / large excess of the alkane is used**. This decreases the probability that the chlorine radical will collide with a monosubstituted alkane molecule, which will lead to formation of the multi-substituted product.

Summary of mechanism for the chlorination of methane

Free Radical Substitution98

Initiation	 $Cl{-}Cl \xrightarrow{\text{uv light}} Cl\cdot + \cdot Cl$
Propagation **(half arrows not required for this stage)**	$Cl\cdot + H{-}CH_3 \longrightarrow HCl + \cdot CH_3$ $H_3C\cdot + Cl{-}Cl \longrightarrow H_3C{-}Cl + \cdot Cl$
Termination **(half arrows not required for this stage)**	$Cl\cdot + \cdot CH_3 \longrightarrow CH_3Cl$ $2\ Cl\cdot \longrightarrow Cl_2$ $2\ \cdot CH_3 \longrightarrow CH_3CH_3$

The mechanism above only shows the formation of CH_3Cl only. For the formation of CH_2Cl_2, it will be a different free-radical subsitution mechanism with a different propagation and termination stages involving $\cdot CH_2Cl$ instead of $\cdot CH_3$.

Note:
In drawing the mechanism of the free radical substitution reaction, please note the following:

- the type of reaction, free radical substitution, and names of the 3 stages must be given
- half arrows are **only required** for **Initiation Stage**
- for Termination Stage, it is sufficient to show any **two** steps
- description of each step is **not** required

Checkpoints for Section 5.2.1 and 5.2.2

- To understand and describe the chemistry of alkanes in the following reactions:
  1. Combustion
  2. Free radical substitution by chlorine and bromine
- To be able to describe the mechanism of free-radical substitution using the initiation, propagation and termination reactions.
- To recognise that free radical substitution is not a good method to prepare halogenoalkanes as a mixture with different halogen-substituted alkanes is produced.

5.2.3 Reactivity of Halogens with Alkanes

Generally, down the group **from fluorine to iodine**, there is a **decrease in reactivity between halogens and alkanes**.

halogen	reaction with alkanes
$F_2(g)$	reacts **explosively** with alkanes
$Cl_2(g)$ $Br_2(l)$ (*both reagents can be dissolved in inert solvents like* CCl_4)	react with alkanes in the presence of **UV light or heat**. Br_2 reacts less readily than chlorine. both have **no reaction** with alkanes in dark conditions or at room temperature.
I_2	**no reaction** with alkanes

Reactivity trend: **$F_2 > Cl_2 > Br_2 > I_2$**

In particular, the lack of reactivity involving iodine means that iodoalkanes are **not** prepared using free radical substitution reaction. The reason behind the lack of reactivity involves energetics – during the **first step of the propagation stage, the reaction is highly endothermic**.

In the first propagation stage of the reaction between a halogen and an alkane, the **C–H bond is broken and the H–X bond is formed**.

$$X\cdot + H{-}R \longrightarrow X{-}H + \cdot R \qquad \Delta H_r^{\ominus}$$

The enthalpy change of reaction for the first propagation stage, $\Delta H_r^{\ominus}$, for the different halogens can be calculated by considering bond energy values:

$$\begin{aligned}\Delta H_r^{\ominus} &= \sum \text{B.E.(bonds broken)} - \sum \text{B.E.(bonds formed)} \\ &= \text{B.E.(C–H)} - \text{B.E.(H–X)}\end{aligned}$$

X	B.E.(C–H)/kJ mol^{-1}	B.E.(H–X)/kJ mol^{-1}	$\Delta H_r^{\ominus}$/kJ mol^{-1}
F	410	562	–152
Cl	410	431	–21
Br	410	366	+44
I	410	299	+111

The $\Delta H_r^{\ominus}$ of the first propagation step is highly endothermic (**+111 kJ mol^{-1}**) in the case of I.

Reasons:

As the **size of the halogen atom increases** down the group, orbital becomes more **diffuse** and **overlap between the H and X atom is less effective**. Hence, $\Delta H_r^{\ominus}$ **becomes more endothermic down the group**.

Example 5A

Propane and chlorine react when irradiated with ultraviolet light to form 2-chloropropane as one of the products.

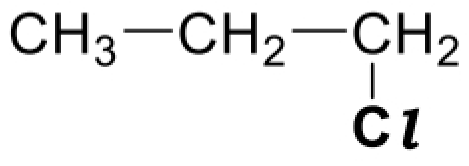
(i) Write two equations for the propagation stage for this reaction.

(ii) A compound with molecular formula C_6H_{14} was formed in this reaction. Suggest the structural formula of this alkane.

5.2.4 Predicting ratio of monosubstituted products of free radical substitution

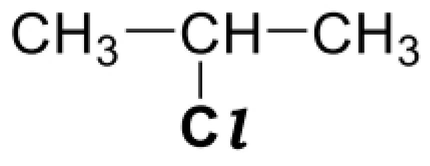
As seen in section 5.2.1, when methane undergoes free radical substitution with chlorine, chloromethane can be formed.

However, when propane undergoes free radical substitution with chlorine, 1-chloropropane and 2-chloropropane can be formed.



$\mathrm{CH_3{-}CH_2{-}}\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH_2}}}$

1-chloropropane



$\mathrm{CH_3{-}}\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}\mathrm{{-}CH_3}$

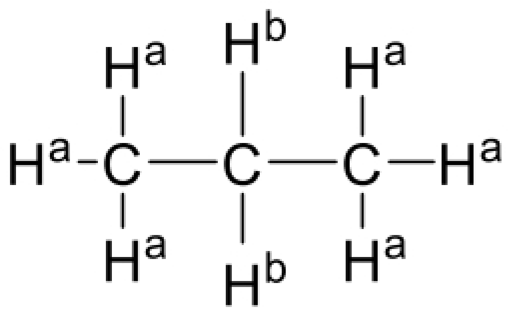
2-chloropropane

What would be the expected ratio of the two products formed? This requires us to consider two aspects:

(1) the **number and type of H atoms** that can undergo free radical substitution, and
(2) the **stability of the alkyl radicals** formed.

5.2.4.1 Number and types of H atoms that can undergo free radical substitution

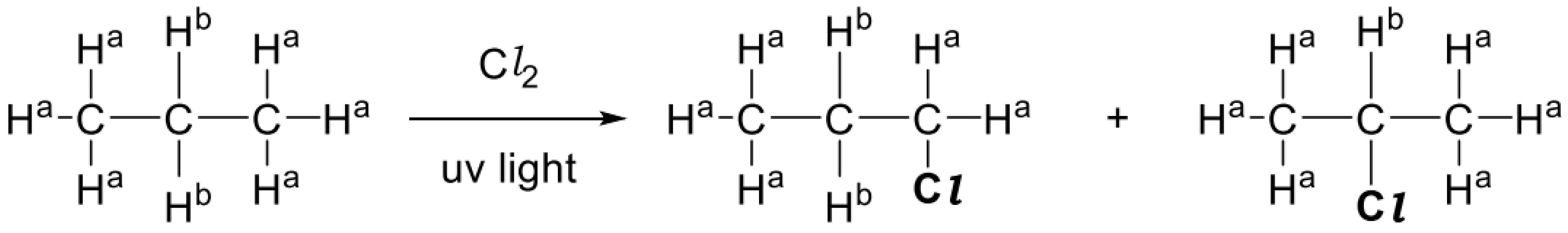
In propane, there are two types of H atoms, H^a and H^b. H^a is a primary hydrogen as it a hydrogen atom residing on a carbon which is directly attached to ONE other carbon atom. H^b is a secondary hydrogen atom as it is a hydrogen atom residing on a carbon which is directly attached to TWO other carbon atoms.



propane

From the above structural formula, we can deduce that the ratio of types of H atoms, **H^a : H^b**, is 6 : 2 = **3 : 1**.

Assuming **equal stability** of the alkyl radical formed, ratio of **1-chloropropane : 2-chloropropane** formed **should** also be **3 : 1**.



propane 1-chloropropane 2-chloropropane

	1-chloropropane	2-chloropropane
statistical	**75%**	**25%**
actual	**45%**	**55%**

However, from the above data, it can be seen that the actual percentage of 1-chloropropane (45%) formed is lower than that of 2-chloropropane (55%). Therefore, in the chlorination of propane, we also have to consider the rate of abstraction of different types of hydrogen atoms on different carbon atoms.

5.2.4.2 Stability of the alkyl radicals formed

In the chlorination of propane, the rate of abstraction of different types of hydrogen atoms on different carbon atoms is different. We observe selectivity in that primary hydrogen are abstracted much slower than secondary hydrogen.

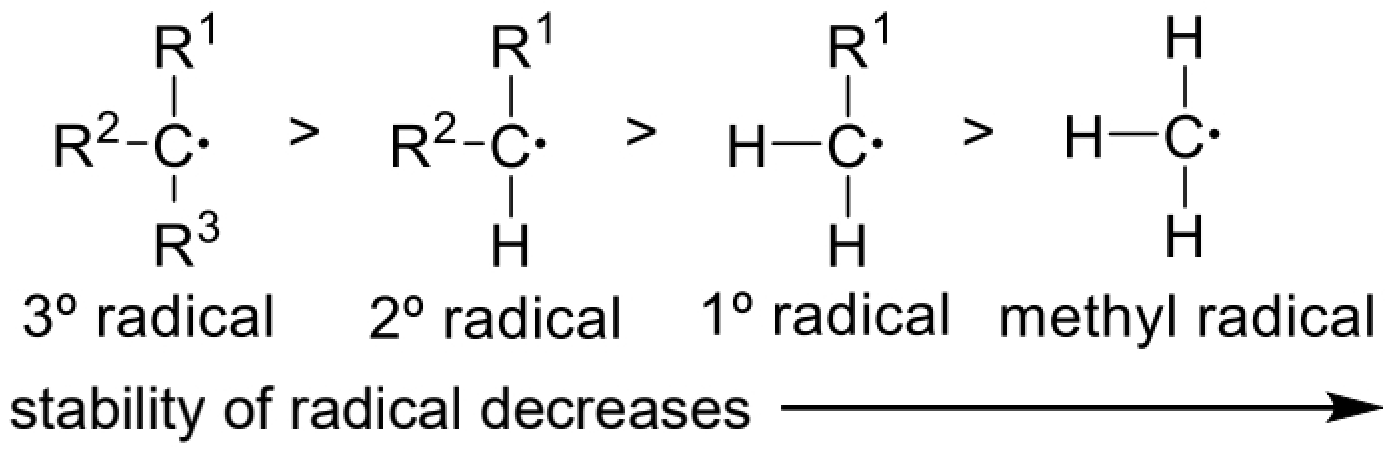
This is attributed to the stability of the resultant radical formed:

$$CH_3-\underset{\bullet}{C}H-CH_3 \quad > \quad CH_3-CH_2-\underset{\bullet}{C}H_2$$

2° 2-propyl radical 1° 1-propyl radical

The more stable the resultant radical, the faster the hydrogen can be abstracted.

Order of stability of alkyl radicals:



Reason:

- ❒ Alkyl groups are **electron-releasing/-donating**, they help to **increase the electron density** in the electron deficient carbon of the alkyl radical, thus stabilising it.
- ❒ Therefore, the more highly substituted alkyl radical has greater stability, and more products will be formed from it.

Example 5B

Pentane was reacted with limited chlorine in the presence of uv light. Assuming that only mono-chlorination takes place and the reaction occurs at the same rate at all carbon atoms, predict the ratio of the products obtained.

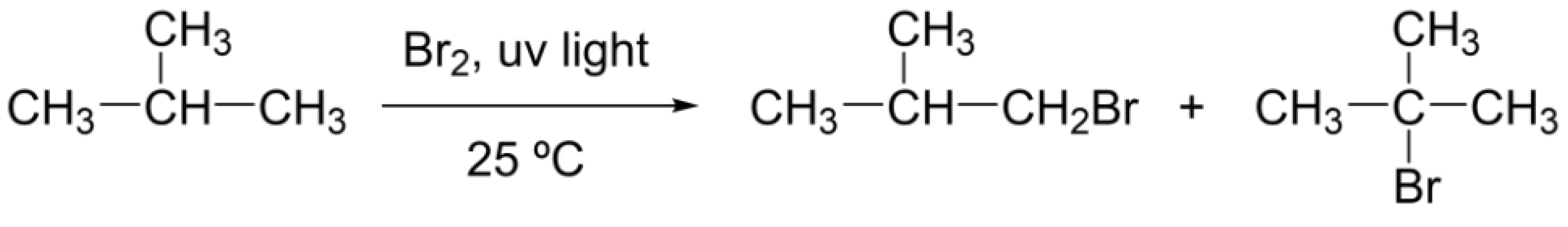
	1-chloropentane	:	2-chloropentane	:	3-chloropentane
A	3	:	2	:	1
B	1	:	2	:	3
C	1	:	3	:	2
D	3	:	1	:	2

Assuming equal stability of the alkyl radical formed,

$CH_3—CH_2—CH_2—CH_2—CH_3$

Example 5C

It was observed that methylpropane reacts with bromine to form a mixture of two monobrominated alkanes, **A** and **B**, as shown below.



A **B**

Given that the rate of abstraction of primary, secondary and tertiary hydrogen is 1 : 4 : 6 respectively, what is the expected ratio of the mono–substituted products **A** : **B** formed?

A 1 : 2 **B** 2 : 1 **C** 2 : 3 **D** 3 : 2

Assuming equal probability of substitution,
Ratio of **A : B** =

However since a tertiary H is substituted 6 times faster than a primary H,
Ratio of **A : B**

Checkpoints for Section 5.2.3 and 5.2.4

- To understand the reactivity trend of halogens with alkanes, and to be able to describe the observations of the reactions.
- To be able to explain the reactivity trend by calculating the $\Delta H_r^\ominus$ of the first propagation step.
- To be able identify the number and types of H atoms in an alkane.
- To recognise that the stability of alkyl radicals is in the following order:

  3° radical > 2° radical > 1° radical > methyl radical
- To understand that the order of stability of alkyl radicals is due to the electron-donating effect of the alkyl groups.
- To understand that the more highly substituted the alkyl radical, the greater the stability, and more products will be formed from it.
- To understand that the ratio of products formed in free radical substitution depends on both the factors

  (1) the **number and type of H atoms** that can undergo free radical substitution, and

  (2) the **stability of the alkyl radicals** formed.

6 Environmental Consequences of Using Alkanes as Fuels

LO (d) Recognise the environmental consequences of:
- (i) carbon monoxide, oxides of nitrogen and unburnt hydrocarbons arising from the internal combustion engine and their catalytic removal.
- (ii) gases that contribute to enhanced greenhouse effect

6.1 Pollutants arising from internal combustion engines

pollutants	causes of emission	detrimental effects
carbon monoxide	• incomplete combustion of hydrocarbons in petrol in car engines	• combines with haemoglobin in the blood to form stable carboxyhaemoglobin, which **prevents transportation of O_2** to all parts of the body; causes **dizziness, fatigue and even death**
unburnt hydrocarbons	• incomplete combustion of fuel	• becomes **photochemical smog** in strong sunlight; causes **respiratory problems**
lead bromide vapour	• addition of tetraethyllead (TEL), $(CH_3CH_2)_4Pb$, to petrol	• **lead poisoning**; accumulation causes general mental depression, slowness in reaction times & **brain damage**
oxides of nitrogen	• burning of the fuel after ignition by the spark is sudden and intense • reaction of N_2 with O_2 takes place at high temperature (~2800 °C) of car engine $N_2(g) + O_2(g) \rightarrow 2NO(g)$ • NO gas is readily oxidised in oxygen to form NO_2 gas $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$	• forms **acid rain** that causes corrosion of buildings, destroy crops and marine life • NO_2 is a brown pungent acidic gas which contributes to acid rain $2NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq)$ • NO_2 can also catalyse the formation of SO_3 from SO_2. SO_3 then reacts with water to form H_2SO_4 (aq) $SO_2(g) + NO_2(g) \rightarrow SO_3(g) + NO(g)$ $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$ • oxides of nitrogen can also cause **respiratory problems** in humans and interfere with nitrogen metabolism in plants • also contributes to **photochemical smog**
sulfur dioxide	• combustion of traces of sulfur or sulfur compounds in petrol	• acidic gas which forms **acid rain** that causes corrosion of buildings, destroy crops and marine life.

6.2 Gases contributing to enhanced greenhouse effect

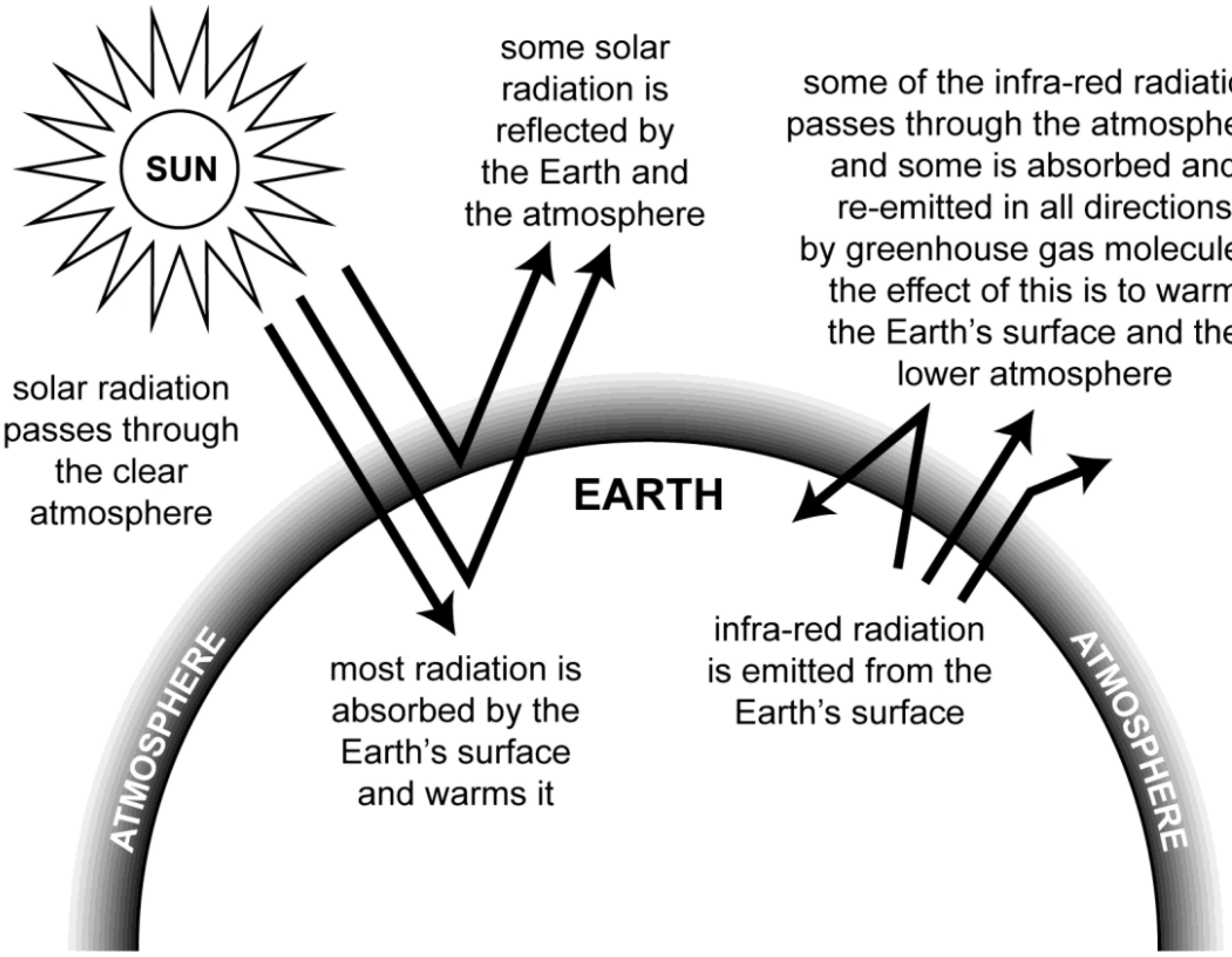
- Greenhouse gases are gases in the atmosphere that absorb and emit radiation within the infrared (IR) range. They trap infrared heat energy trying to escape back to space, thereby causing a rise in temperature. This warming process is called natural greenhouse effect, which keeps the Earth at a suitable temperature.

  - ❒ **Carbon dioxide, CO_2:** A major greenhouse gas. It is produced from burning of fossil fuels for heating, transport and generating electricity.

  - ❒ **Methane, CH_4**: Produced from more intensive agricultural activity, *e.g.* cattle-rearing.

  - ❒ **Water vapour, H_2O**: If global warming increases, the warmer atmosphere absorbs more water vapour, which in turn leads to a greater greenhouse effect, increasing the global warming even more.

- Environmental effect of excessive greenhouse gases:
  An increase in global temperature will cause sea levels to rise and will change the amount and pattern of precipitation (e.g. rain and snow). Other likely effects include increase in the intensity of extreme weather events, species extinctions, and changes in agricultural yields.



THE GREENHOUSE EFFECT

7 Measures to Reduce Pollution

7.1 Catalytic Converters

(Refer to Kinetics lecture notes)

Vehicles are fitted with catalytic converters to convert harmful emissions to harmless products**.** Exhaust gases are passed through heated solid platinum, rhodium or palladium catalyst.

The three harmful compounds that can be converted are:

- **Hydrocarbons** (in the form of unburned gasoline)
- **Carbon monoxide** (formed by the incomplete combustion of gasoline)
- **Oxides of nitrogen or NO_x** (created when high temperatures in the engine promote reaction between the nitrogen and oxygen present in the air)

These pollutants are converted into CO_2, N_2 and water vapour.

- **Unburnt hydrocarbons are oxidised to CO_2 and H_2O.**
- **CO is oxidised to CO_2**
- **NO_x is converted to N_2**

Examples of equations for these conversions (not exhaustive) are given below:

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

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ (Pt/ Pd catalyst)

$2CO(g) + NO(g) \rightarrow 2CO_2(g) + N_2(g)$ (Rh catalyst)

Checkpoints for Section 6 and 7

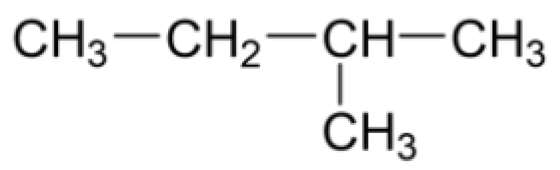
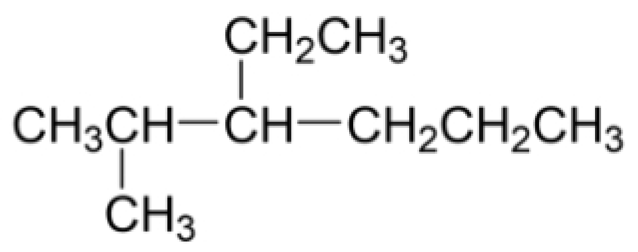
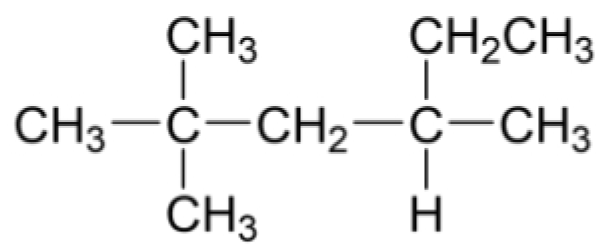
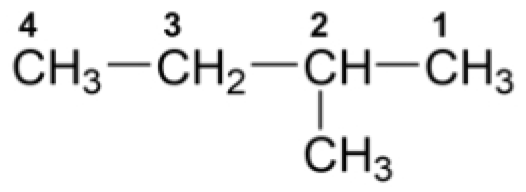
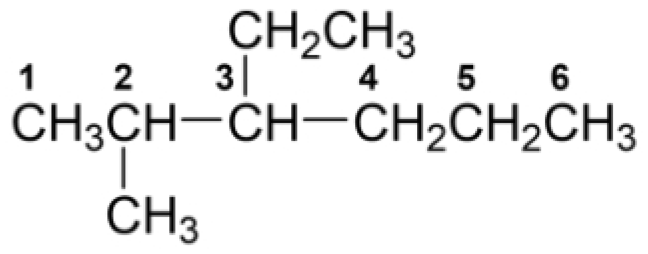
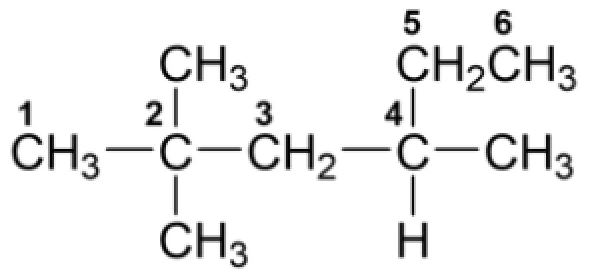
– To recognise the environmental consequences of:

  1. carbon monoxide, oxides of nitrogen and unburnt hydrocarbons arising from the internal combustion engine and their catalytic removal.
  2. gases that contribute to enhanced greenhouse effect.

– To describe how catalytic converters can convert harmful C_xH_y, CO and NO_x into harmless products with the aid of equations.

Solutions:

Self Check 2A

alkane molecule	 $CH_3-CH_2-\underset{CH_3}{\underset{\mid}{CH}}-CH_3$	 $CH_3\underset{CH_3}{\underset{\mid}{CH}}-\overset{\overset{CH_2CH_3}{\mid}}{CH}-CH_2CH_2CH_3$	 $CH_3-\underset{CH_3}{\underset{\mid}{\overset{\overset{CH_3}{\mid}}{C}}}-CH_2-\underset{H}{\underset{\mid}{\overset{\overset{CH_2CH_3}{\mid}}{C}}}-CH_3$
step 1: parent chain	4 carbons ⇒ butane	6 carbons ⇒ hexane	6 carbons ⇒ hexane
step 2: side groups	methyl group (×1)	methyl group (×1) ethyl group (×1)	methyl group (×3)
step 3: assign numbers to side groups	 $\overset{4}{CH_3}-\overset{3}{CH_2}-\underset{CH_3}{\underset{\mid}{\overset{2}{CH}}}-\overset{1}{CH_3}$	 $\overset{1}{CH_3}\underset{CH_3}{\underset{\mid}{\overset{2}{CH}}}-\overset{\overset{CH_2CH_3}{3\mid}}{CH}-\overset{4}{CH_2}\overset{5}{CH_2}\overset{6}{CH_3}$	 $\overset{1}{CH_3}-\underset{CH_3}{\underset{\mid}{\overset{\overset{CH_3}{2\mid}}{C}}}-\overset{3}{CH_2}-\underset{H}{\underset{\mid}{\overset{\overset{\overset{5}{CH_2}\overset{6}{CH_3}}{4\mid}}{C}}}-CH_3$
name	2-methylbutane	3-ethyl-2-methylhexane	2,2,4-trimethylhexane