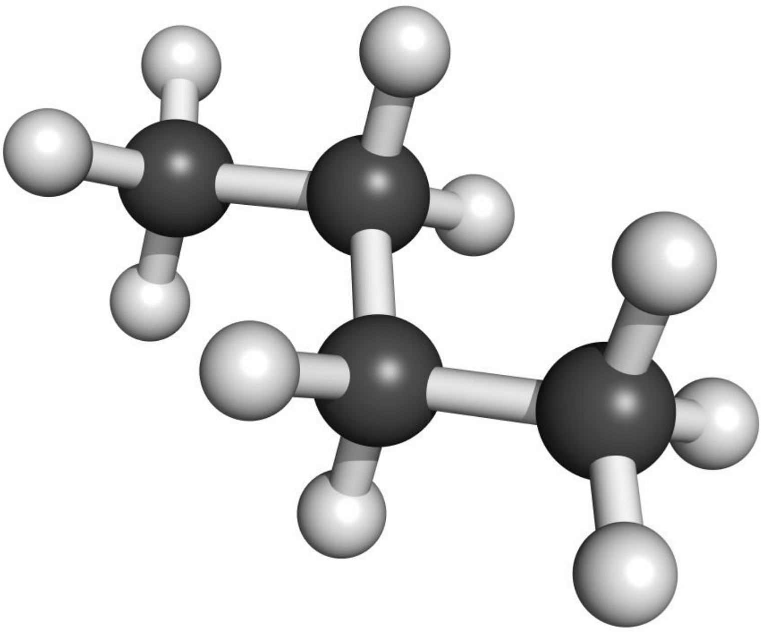
ALKANES



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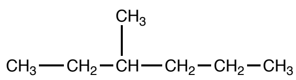
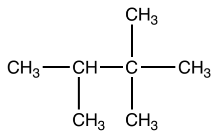
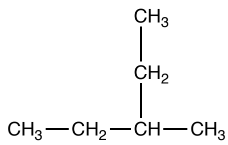
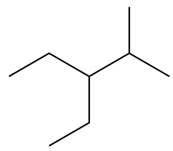
INTRODUCTION

- Alkanes are a homologous series of saturated hydrocarbons with the general formula C_nH_{2n+2}
- Alkanes are very unreactive, although they do burn and react with halogens (e.g. chlorine).

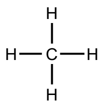
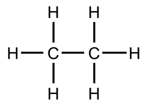
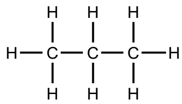
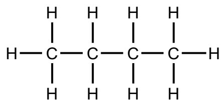
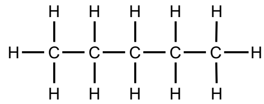
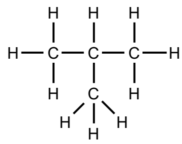
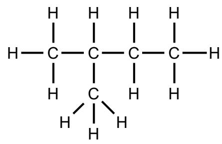
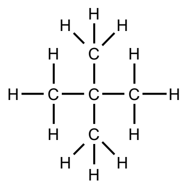
TASK 1 – Drawing and naming alkanes

structure				
name				

TASK 2 – Isomers

Draw the structural formula of and name all the alkanes with the molecular formula C_6H_{14}

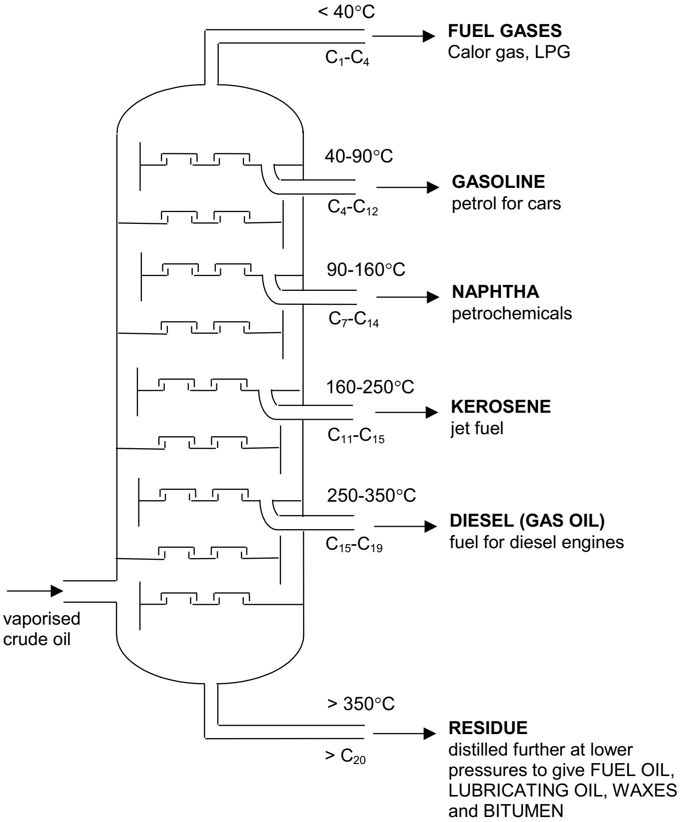
Boiling points of alkanes

CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}
 methane –162°C	 ethane –89°C	 propane –42°C	 butane –0.5°C	 pentane 36°C
			 methylpropane –12°C	 methylbutane 28°C
				 dimethylpropane 10°C

- The longer the carbon chain, the higher the boiling point of alkanes due to stronger van der Waals' forces between molecules (because there are more electrons in the molecules).
- For alkanes that are isomers, the more branched the carbon chain, the lower the boiling point due to weaker van der Waals' forces between molecules (due to molecules not being able to pack as close together).

CRUDE OIL (PETROLEUM)

- Deposits of crude oil and natural gas usually occur together and they are formed by the slow decay of marine animals and plants, over millions of years, under heat and pressure in the absence of air.
- Although the exact composition of crude oils vary around the world, all are a complex mixture consisting mainly of alkanes (including cycloalkanes, some aromatics and other compounds containing some S and O).
- Crude oil has no use in its raw form, so to provide useful products its components must be partly separated (and if necessary modified) - the separation uses the differences in the physical properties of alkanes.
- The compounds in crude oil have different boiling points and this is used to separate them by fractional distillation at an oil refinery.
- The basic idea of the separation process is:
  - that crude oil is vaporised
  - the vapour is passed into a tower which is hot at the bottom and cold at the top
  - as the vapour rises it cools
  - molecules will condense at different heights as they have different boiling points
  - the larger the molecule (with higher boiling points), the lower down the column it condenses



- This produces fractions – a fraction is a mixture of hydrocarbons with similar boiling points.
- As the C chain gets longer, the hydrocarbons:
  - become more viscous
  - harder to ignite
  - less volatile
  - have higher boiling points

- The residue from the primary distillation (first distillation) contains useful substances, such as fuel oil, lubricating oil, waxes and bitumen, that boil above 350°C at atmospheric pressure. However, they would decompose at temperatures above 350°C, so they are separated further by distillation at lower pressure (where their boiling points are lower).

CRACKING

- The petroleum fractions with shorter C-chains (e.g. petrol) are better fuels than ones with longer C-chains and so the shorter C-chain fractions are in greater demand.
- This leads to greater demand than supply for these fractions with shorter C-chains, but a greater supply than demand for those with longer C-chains.
- Cracking is done to make use of excess the fractions with longer C-chains and meet supply demand for shorter alkanes.
- Cracking is the thermal decomposition of alkanes to produce higher value shorter C-chain products.
- C-C bonds are broken in cracking.

Thermal cracking		Catalytic cracking
900°C	Temperature	450°C
70 atm	Pressure	1-2 atm
none	Catalyst	zeolites (a type of aluminosilicate catalyst)
alkenes	Products	motor fuels (cyclic alkanes, branched alkanes, aromatics)

COMBUSTION OF ALKANES

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

- The products of *complete* combustion are CO_2 and H_2O.

  e.g. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $\Delta H = -890$ kJ/mol (i.e. very exothermic)

- If there is not enough oxygen then *incomplete* combustion occurs, producing CO (which is very toxic) and/or C (soot):

  e.g. $CH_4 + {}^{3}/{}_{2}O_2 \rightarrow CO + 2H_2O$

  $CH_4 + O_2 \rightarrow C + 2H_2O$

TASK 3 – Burning alkanes

Write an equation for the complete combustion and two equations for the incomplete combustion of each of these alkanes

propane (C_3H_8) ……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

octane (C_8H_{18}) ……………………………………………………………………………………………

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PROBLEMS WITH THE USE OF ALKANES AS FUELS

- Alkanes are superb fuels but substances are produced that cause problems.

Pollutant	How it is formed	Problem it causes	Ways to reduce the problem
CO_2	complete combustion of fuels containing C	greenhouse gas	burn less fossil fuels
CO	incomplete combustion of fuels containing C	toxic	ensure a good supply of oxygen when burning fuels
C (soot)	incomplete combustion of fuels containing C	blackens buildings, can cause respiratory problems, global dimming	ensure a good supply of oxygen when burning fuels
H_2O	combustion of fuels containing H	not a problem	
SO_2	combustion of S containing compounds in fuel	acid rain	remove S from fuel before burning, flue gas desulfurisation
NO_x (NO, NO_2)	reaction of N_2 in the air with O_2 in the air at very high temperatures (in engines & furnaces)	acid rain	use catalytic converters in cars
unburned hydrocarbons	some of the fuel may not actually burn	wastes fuel	ensure engines are well-tuned and there is a good supply of oxygen

Sulfur dioxide, SO_2

- Sulfur containing impurities are found in petroleum fractions which produce SO_2 when they are burned, which lead to acid rain.
- SO_2 can be removed from the waste gases from furnaces (e.g. coal fired power stations) by **flue gas desulfurisation**.
- The gases pass through a filter containing calcium oxide or calcium carbonate which reacts with the sulfur dioxide:

$$CaO + SO_2 \rightarrow CaSO_3 \quad \text{or} \quad CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2$$

- This is an acid-base reaction as $CaCO_3$ and CaO are bases and SO_2 is an acidic oxide (non-metal oxide).
- The reaction forms calcium sulfate(IV) which is used to make plasterboard.

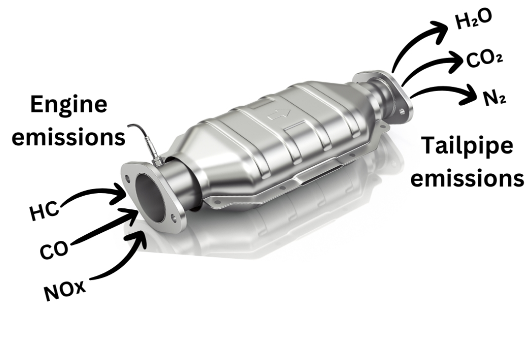
The internal combustion engine (e.g. cars)

- Petrol (gasoline fraction, which consists of liquid alkanes) is used in the internal combustion engine where the alkanes are vaporised and combusted with air.
- **Catalytic converters** remove CO, NO_x and unburned hydrocarbons (e.g. octane, C_8H_{18}) from the exhaust gases, turning them into CO_2, N_2 and H_2O.

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

$$C_8H_{18} + 25\ NO \rightarrow 8\ CO_2 + 12\tfrac{1}{2}\ N_2 + 9\ H_2O$$

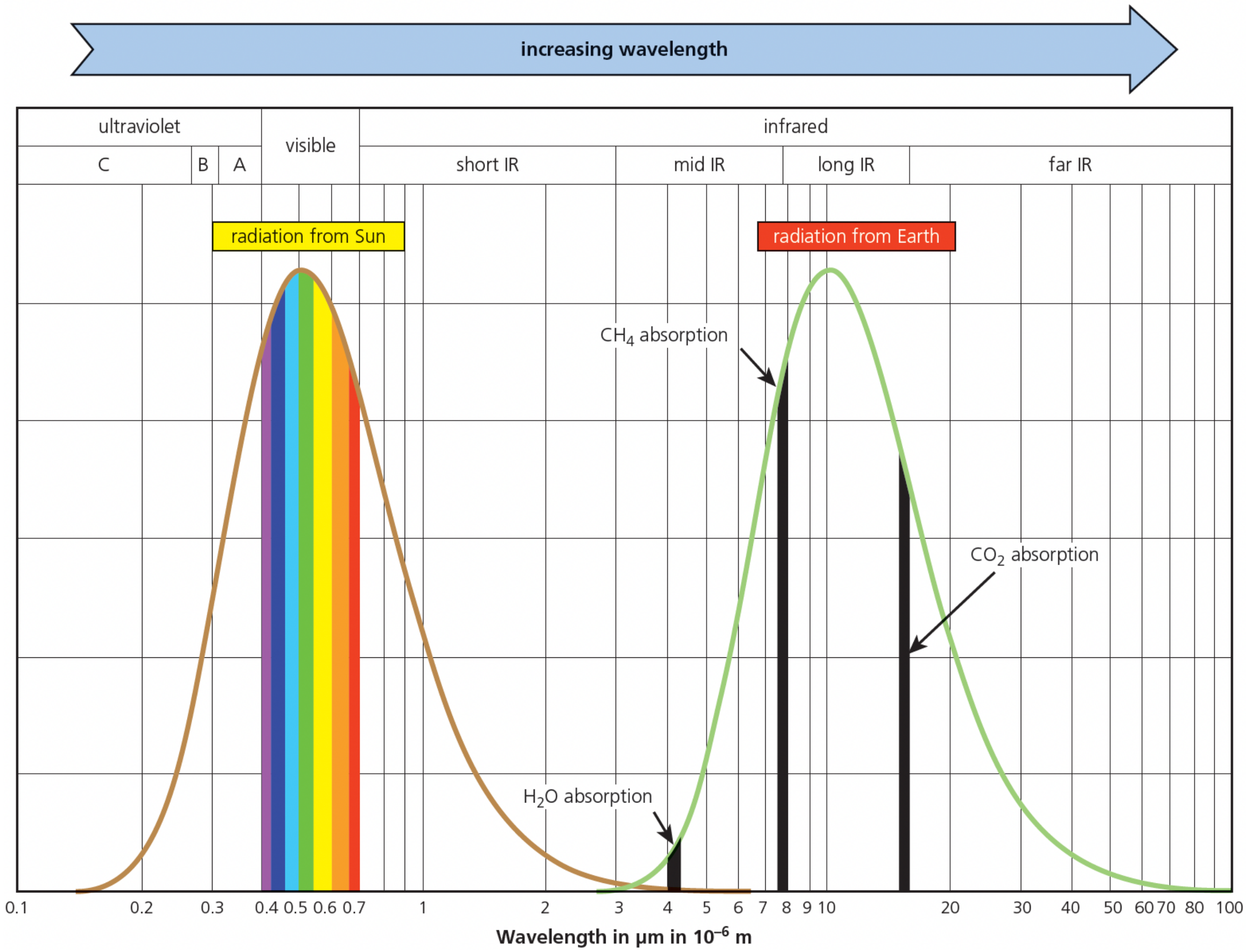
- Converters have a ceramic honeycomb coated with a thin layer of catalyst metals (Pt, Pd, Rh) – to give a large surface area.



Greenhouse gases

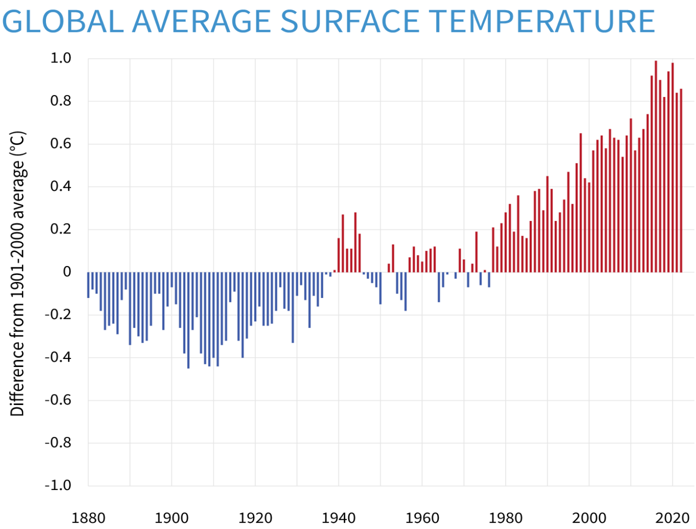
- **Greenhouse gases** are gases that absorbs the IR radiation given off by the Earth, but do not absorb the higher frequency UV/visible radiation given off by the sun.
- Molecules that contain **polar bonds** absorb IR radiation to make bonds vibrate.

Greenhouse gases	**NOT** greenhouse gases
CO_2 (the C=O bonds are polar)	N_2 (no polar bonds)
H_2O (the O-H bonds are polar)	O_2 (no polar bonds)
CH_4 (the C-H bonds are slightly polar)	Ar (no bonds at all)

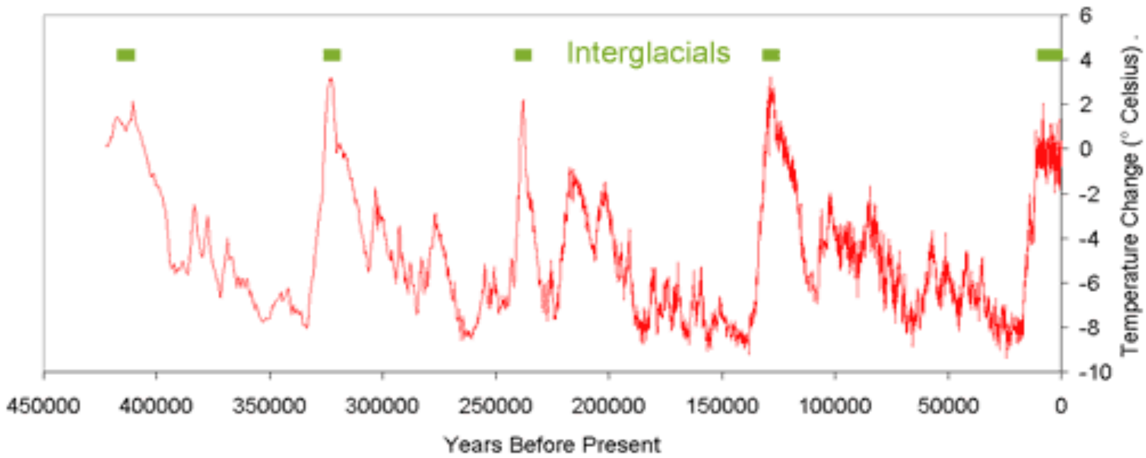


Global warming

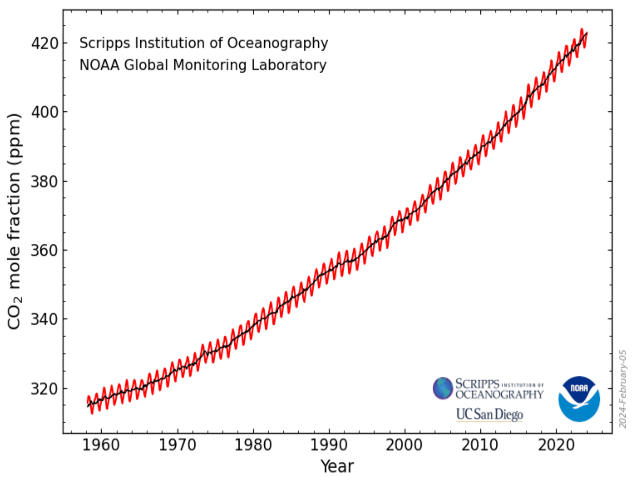
- The Earth is currently getting warmer.
- Most scientists believe it is due to increasing amounts of greenhouse gases (e.g. CO_2 and CH_4) in the atmosphere.
- However, the Earth does have natural variations in temperature over time, and some scientists think the current warming may be a natural variation.
- However, many scientists think the recent increase has been more rapid than would be expected in any natural variation.



The earth's temperature over the last 0.7 million years

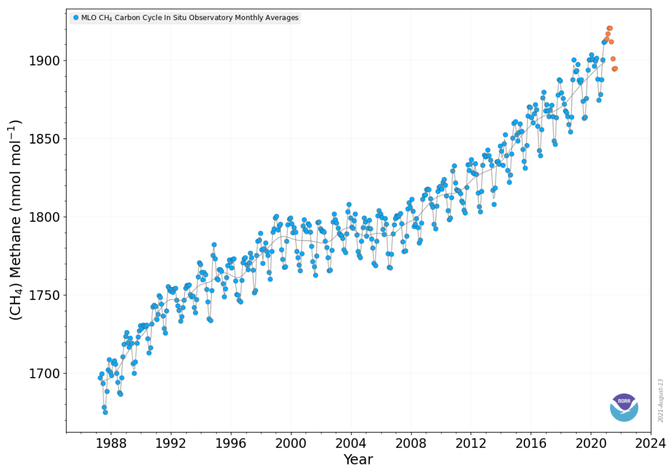


CO_2 in the atmosphere



- The burning of fossil fuels (including alkanes) releases carbon dioxide into the atmosphere.
- Carbon dioxide levels have risen significantly in recent years largely due to large scale burning of fossil fuels and deforestation.

CH_4 in the atmosphere



- Methane levels have also increased significantly largely due to the increasing world population leading to increased
  - cattle farming
  - rice production
  - landfill (methane produced from the decomposing waste)

FREE-RADICAL SUBSTIUTION REACTIONS OF ALKANES

WHAT HAPPENS	H atoms on alkanes or halogenoalkanes are replaced by halogen atoms (F / Cl / Br / I)

OVERALL EQUATION	For every H atom replaced by F / Cl / Br / I, one molecule of F_2 / Cl_2 / Br_2 / I_2 is used and one molecule of HF / HCl / HBr / HI is released. In order to replace many H atoms with F / Cl / Br / I atoms, an excess of F_2 / Cl_2 / Br_2 / I_2 is used. In order to only replace one H atom, an excess of the alkane / halogenoalkane is used.

e.g.	$CH_4 \rightarrow CH_3Cl$	$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$
e.g.	$CH_4 \rightarrow CF_4$	$CH_4 + 4F_2 \rightarrow CF_4 + 4HF$
e.g.	$CH_3\text{-}CBr_3 \rightarrow CBr_3\text{-}CBr_3$	$CH_3\text{-}CBr_3 + 3Br_2 \rightarrow CBr_3\text{-}CBr_3 + 3HBr$
e.g.	$CH_2Cl_2 \rightarrow CCl_4$	…………………………………………………………………………………………
e.g.	$CH_3\text{-}CH_3 \rightarrow CF_3\text{-}CF_3$	…………………………………………………………………………………………
e.g.	$CHF_2\text{-}CH_3 \rightarrow CBrF_2\text{-}CBr_3$	…………………………………………………………………………………………
e.g.	$CF_3\text{-}CH_3 \rightarrow CF_3\text{-}CCl_3$	…………………………………………………………………………………………

INITIATION	When exposed to ultraviolet light, a molecule of a halogen F_2 / Cl_2 / Br_2 / I_2 breaks apart into two halogen atom free radicals F● / Cl● / Br● / I●. The ultraviolet light provides the energy to break the covalent bond between the two halogen atoms. (Free radicals are species with an odd number of electrons – they are very reactive – the atom with the odd number of electrons is shown with a ●) fluorine: $F_2 \rightarrow 2F$● bromine: $Br_2 \rightarrow 2Br$● chlorine: $Cl_2 \rightarrow 2Cl$ ● iodine: $I_2 \rightarrow 2I$●

PROPAGATION	(molecule + radical → molecule + radical) For every H that is replaced, there is one pair of propagation reactions. Step 1 the alkane / halogenoalkane reacts with the F● / Cl● / Br● / I● – this removes an H atom from the alkane / halogenoalkane – this produces HF / HCl / HBr / HI and a C based free radical. Step 2 the C based radical from step 1 reacts with F_2 / Cl_2 / Br_2 / I_2 to put an atom of F / Cl / Br / I onto the C based radical – this also produces another halogen free radical (F● / Cl● / Br● / I●) to continue the chain reaction in another step 1.

e.g. $CH_4 \rightarrow CH_3Cl$	(1)	$CH_4 + Cl\bullet \rightarrow \bullet CH_3 + HCl$
	(2)	$\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$
e.g. $CHBr_2\text{-}CH_3 \rightarrow CBr_3\text{-}CH_3$	(1)	$CHBr_2\text{-}CH_3 + Br\bullet \rightarrow \bullet CBr_2\text{-}CH_3 + HBr$
	(2)	$\bullet CBr_2\text{-}CH_3 + Br_2 \rightarrow CBr_3\text{-}CH_3 + Br\bullet$
e.g. $CH_3Cl \rightarrow CH_2Cl_2$	(1)	…………………………………………………………………………………
	(2)	…………………………………………………………………………………
e.g. $CHCl_3 \rightarrow CCl_4$	(1)	…………………………………………………………………………………
	(2)	…………………………………………………………………………………
e.g. $CHF_2\text{-}CH_3 \rightarrow CF_3\text{-}CH_3$	(1)	…………………………………………………………………………………
	(2)	…………………………………………………………………………………
e.g. $CHF_2\text{-}CH_3 \rightarrow CHF_2\text{-}CH_2F$	(1)	…………………………………………………………………………………
	(2)	…………………………………………………………………………………
e.g. $CH_3\text{-}CH_2\text{-}CF_3 \rightarrow CH_3\text{-}CHBr\text{-}CF_3$	(1)	…………………………………………………………………………………
	(2)	…………………………………………………………………………………

TERMINATION	(2 radicals → molecule) If two free radicals collide, they will form a molecule and stop the chain reaction. Any two free radicals involved in the mechanism could collide in this way.

Write an equation to show how each of the molecules shown could be formed by a termination step in the reactions shown.

e.g.	$CH_3\text{-}CH_3$ in $CH_4 \rightarrow CH_3Cl$	$2\ \bullet CH_3 \rightarrow CH_3\text{-}CH_3$
e.g.	$CCl_3\text{-}CCl_3$ in $CH_4 \rightarrow CCl_4$	$2\ \bullet CCl_3 \rightarrow CCl_3\text{-}CCl_3$
e.g.	$CH_2Cl\text{-}CCl_3$ in $CH_4 \rightarrow CCl_4$	$\bullet CH_2Cl + \bullet CCl_3 \rightarrow CH_2Cl\text{-}CCl_3$
e.g.	$CF_3\text{-}CH_2F$ in $CH_4 \rightarrow CF_4$	…………………………………………………………………
e.g.	butane in $CH_3\text{-}CH_3 \rightarrow CH_3\text{-}CH_2F$	…………………………………………………………………
e.g.	$CBr_3\text{-}CBr_3$ in $CH_4 \rightarrow CBr_4$	…………………………………………………………………
e.g.	1,3-dibromobutane in $CH_3\text{-}CH_3 \rightarrow CBr_3\text{-}CBr_3$	…………………………………………………………………

TASK 4 – Free radical substitution problems

1) For the conversion of ethane to 1,1-dibromoethane.

a) Give the overall equation.

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b) Give the pair of propagation steps to form bromoethane from ethane.

....

....

c) Give the pair of propagation steps to form 1,1-dibromoethane from bromoethane.

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d) Give the termination step that forms butane.

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2) For the conversion of methane to tetrachloromethane.

a) Give the overall equation.

....

b) Give the pair of propagation steps to form chloromethane from methane.

....

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c) Give the pair of propagation steps to form tetrachloromethane from trichloromethane.

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d) Give the termination step that forms a substance with the empirical formula CCl_3.

....

3) For the conversion of 2-iodopropane to 1,2-diiodopropane.

a) Give the overall equation.

....

b) Give the pair of propagation steps to form 1,2-diiodopropane from 2-iodopropane.

....

....

c) Give the termination step that forms a substance with empirical formula C_3H_6I.

....

4) For the conversion of 1,1,1-tribromoethane to 1,1,1-tribromo-2,2,2-trichloroethane.

a) Give the overall equation.

....

b) Give the pair of propagation steps to form 1,1,1-tribromo-2-chloroethane from 1,1,1-tribromoethane.

....

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c) Give the pair of propagation steps to form 1,1,1-tribromo-2,2,2-trichloroethane from 1,1,1-tribromo-2,2-diichloroethane.

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d) Give the termination step that forms a bromoalkane.

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