14.1 ALKANES

Learning outcomes

Candidates should be able to:

1. recall the reactions (reagents and conditions) by which alkanes can be produced:
   (a) addition of hydrogen to an alkene in a hydrogenation reaction, $H_2(g)$ and Pt/Ni catalyst and heat
   (b) cracking of a longer chain alkane, heat with Al_2O_3
2. describe:
   (a) the complete and incomplete combustion of alkanes
   (b) the free-radical substitution of alkanes by Cl_2 or Br_2 in the presence of ultraviolet light, as exemplified by the reactions of ethane
3. describe the mechanism of free-radical substitution with reference to the initiation, propagation and termination steps
4. suggest how cracking can be used to obtain more useful alkanes and alkenes of lower M_r from heavier crude oil fractions
5. understand the general unreactivity of alkanes, including towards polar reagents in terms of the strength of the C–H bonds and their relative lack of polarity
6. recognise the environmental consequences of carbon monoxide, oxides of nitrogen and unburnt hydrocarbons arising from the combustion of alkanes in the internal combustion engine and of their catalytic removal

Initial assessment

1. Here are four types of hybridisation of carbon atomic orbitals:

only sp only sp^2 only sp^3 sp^2 and sp^3

Which do you find in the following molecules?

a ethane **b** ethene **c** propene.

2 Give the names of:

a. $CH_3CH_2CH(CH_3)CH_3$

b. $CH_3CH_2CH_2CH{=}CH_2$

c. $(C_2H_5)_3CH$

d. $(CH_3)_2CH\text{-}C(CH_3)_2\text{-}CH(CH_3)_2$.

Give the structural and skeletal formulae of:

A 2,3-dimethylhexane **b** pent-2-ene.

c. **2,2,3,3-tetramethylpentane**

d. **3,3-diethylhexane.**

Alkanes constitute the major part of crude oil, and so are the starting point of virtually every other organic compound made industrially.

1. Hexane, C_6H_{14}, has four structural isomers.
   Fig. 3.1 shows hexane and two of its structural isomers.

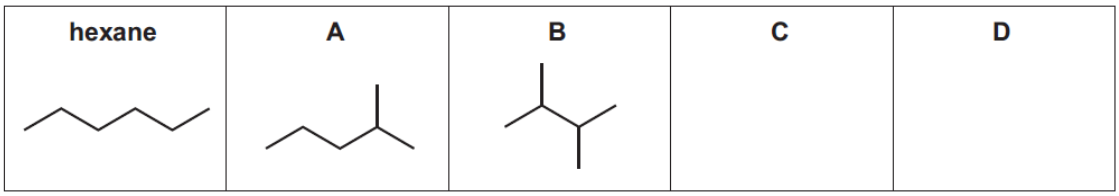


Fig. 3.1

(ii) A, B and hexane have different boiling points.
Arrange A, B and hexane in order of increasing boiling point.
Explain your answer.

lowest ..... < ..... < ..... highest

.....

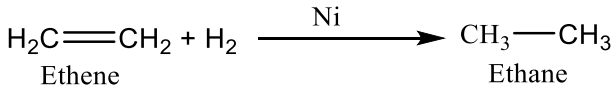
.....

..... [3]

Preparations

Hydrogenation

When hydrogen gas and an alkene are heated and passed over a finely divided platinum/nickel catalyst, the addition reaction produces an alkane:

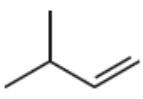


The addition reaction of alkenes with hydrogen is called **hydrogenation** and is used in the manufacture of margarine.

Unsaturated oils, such as sunflower oil, contain hydrocarbon chains with several carbon–carbon double bonds. These oils become partially saturated by reacting them with hydrogen, straightening their hydrocarbon chains. This raises the melting points of the oils, changing them from liquids to soft solids that can be spread easily.

2. Give the structural formula of the compound formed when **D** reacts with $H_2(g)$ in the presence of a Pt catalyst.[1]

D



3. Hydrated rhodium(III) chloride, $RhCl_3 \cdot xH_2O$, catalyses the conversion of ethene to but-2-ene.
Explain how the conversion of ethene to but-2-ene can be described as an addition reaction.

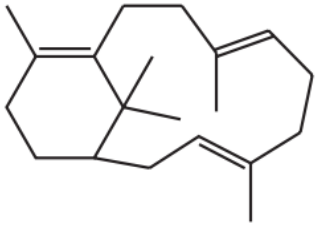
.....

.....

..... [1]

1. Compound P is treated with an excess of hydrogen gas in the presence of a nickel catalyst. The product Q is fully saturated.

compound P



What is the number of chiral carbon atoms in the product Q?

A 4 **B** 5 **C** 6 **D** 7

4. Hexane can be converted into compounds E and F at high temperature and pressure. Fig. 3.2 shows the reaction scheme involving hexane, E and F.

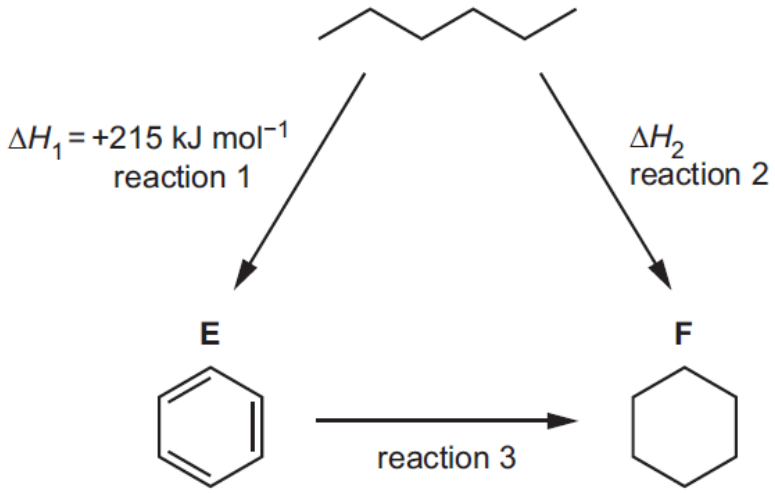


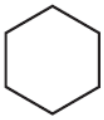
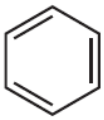
Fig. 3.2

(i) Identify a suitable reagent for reaction 3.

..... [1]

(ii) Use the data in Fig. 3.2 and in Table 3.1 to calculate the enthalpy change of reaction 2, ΔH_2.
Table 3.1

Table 3.1

compound	enthalpy change of formation, ΔH_f / kJ mol^{-1}
	−156
	+48

ΔH_2 = ... kJ mol–1 [2]

(iii) Write an equation for the complete combustion of hexane.

..... [1]

Cracking

Thermal cracking involves heating the alkane mixture to about 800°C and at moderate pressure, in the absence of air but in the presence of steam. After only a fraction of a second at this temperature, the mixture is rapidly cooled. By this means dodecane might typically be broken into hexane (boiling point 69°C) and ethene:

$$CH_3(CH_2)_{10}CH_3 \xrightarrow{\text{heat with steam at } 800^0C} CH_3(CH_2)_4CH_3 + 3\ CH_2{=}CH_2$$

The hexane is required for fuel but the ethene by-product is not wasted, as it is a key feedstock for the plastics, fibres and solvents industries; the conditions for thermal cracking are often chosen so as to optimise ethene production.

Catalytic cracking involves heating the alkane mixture to a temperature of about 500°C and passing it under slight pressure over a catalyst made from a porous mixture of aluminium and silicon oxides (called zeolites). The catalyst causes the carbon chains to undergo internal rearrangements before forming the final products.
A typical set of products from catalytic cracking is shown in the following equation:

$$2CH_3(CH_2)_{10}CH_3 \rightarrow (CH_3)_2CHCH_2CH_2CH_3 + (CH_3)_2CHCH(CH_3)_2 + 6CH_2{=}CH_2$$

The branched-chain alkanes produced by catalytic cracking are useful components of high-octane petrol.

5. Naphtha is a mixture which contains only hydrocarbon molecules.
(i) What is meant by the term *hydrocarbon*? [1]

(ii) Name the raw material that is used to produce a sample of naphtha. [1]

(b) Compound **V** is found in naphtha. It has a molecular formula $C_{10}H_{22}$.

When **V** is heated at high pressure in the absence of air, an equal number of moles of ethene, propene and W are made. W is a compound made of straight chain, saturated molecules.
(i) Name the process that describes this reaction. [1]

(ii) Deduce the structure of **W**. Draw its structure below. [1]

2. The hydrocarbon $C_{17}H_{36}$ can be cracked.
Which compound is the **least** likely to be produced in this reaction?

A C_3H_8 **B** C_4H_8 **C** C_8H_{16} **D** $C_{16}H_{34}$

6. The alkanes are a homologous series of organic molecules. Alkanes are generally unreactive and are commonly used as fuels.

Alkanes with low relative molecular mass, Mr, are more useful than those found in heavier crude oil fractions. Name the process that is used to obtain alkanes with low Mr from heavier crude oil fractions.

..... [1]

Properties

General unreactivity of alkanes

7. The alkanes are a homologous series of organic molecules. Alkanes are generally unreactive and are commonly used as fuels.
(b) Give two reasons to explain the general unreactivity of alkanes.

1 .....

2 ..... [2]

Combustion

$C_6H_{12} + 9O_2 \rightarrow 6H_2O(l) + 6CO_2(g)$ $\Delta H^{\ominus} = -4160 \text{ kJ mol}^{-1}$

$C_6H_{12} + 6O_2 \rightarrow 6H_2O(l) + 6CO(g)$ $\Delta H^{\ominus} = -2470 \text{ kJ mol}^{-1}$

$C_6H_{12} + 3O_2 \rightarrow 6H_2O(l) + 6C(g)$ $\Delta H^{\ominus} = -1800 \text{ kJ mol}^{-1}$

8. Molecule **M** is present in petrol, a fuel used in cars. M is a saturated, non-cyclic hydrocarbon.
M contains eight carbon atoms.
(i) Construct an equation for the complete combustion of **M**. [2]

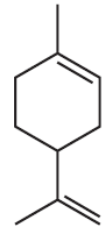
(ii) Describe how the composition of products differs when incomplete combustion of **M** occurs. [2]

3. Mixture R consists of one mole of C_3H_6 and one mole of C_4H_6.
What is the minimum number of moles of oxygen molecules needed for complete combustion of mixture R?

A 6.5 **B** 7 **C** 10 **D** 20

4. The structure of limonene is shown.

limonene



What are the number of moles of carbon dioxide and water produced when a sample of limonene is completely combusted in oxygen?

	number of moles of carbon dioxide	number of moles of water
A	4	3
B	5	4
C	5	8
D	9	7

The free-radical substitution of alkanes by Cl_2 or Br_2

Initiation step

homolytic fission

free radical

In the initiation step, we start with a molecule and get two free radicals formed.

Propagation steps

In each propagation step, we start with a molecule and a free radical and get a different molecule and a different free radical formed.

Termination steps

In the termination steps, we start with two free radicals and end up with a molecule and no free radicals.

Free radical

- ***a species with one or more unpaired electrons; e.g., Cl atom***

The word species refers to different particles such as atoms, ions, molecules, free radicals or electrons when we want to write in general terms or about more than one type of particle.

9. Cl(g) can be made from Cl_2(g).
(i) Describe the conditions required for this process.

..... [1]

(ii) Name this process.

..... [1]

5. The reaction of chlorine with methane is carried out in the presence of light.
What is the function of the light?

A to break the C–H bonds in methane
B to break the chlorine molecules into atoms
C to break the chlorine molecules into ions
D to heat the mixture

6. Which equation represents a reaction that proceeds through initiation, propagation and termination steps?
A $C_4H_{10} + Cl_2 \rightarrow C_4H_9Cl + HCl$
B $C_5H_{11}Br + NaOH \rightarrow C_5H_{11}OH + NaBr$
C $C_6H_{12} + H_2O \rightarrow C_6H_{13}OH$
D $C_6H_{13}CHO + HCN \rightarrow C_6H_{13}CH(OH)CN$

7. Ethane reacts with an excess of chlorine in the presence of ultraviolet light to form a mixture of products.
How many of these products contain two carbon atoms and one or more chlorine atoms?

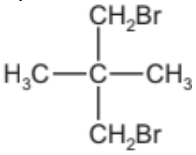
A 6 **B** 7 **C** 8 **D** 9

8. A mixture of ethane and an excess of chlorine is exposed to UV light.
How many different products, each containing only two carbon atoms and at least one chlorine atom per molecule, can be formed?

A 8 **B** 9 **C** 10 **D** 12

9. Which reaction occurs when ethane and chlorine are mixed in diffused sunlight?
A a free-radical substitution with hydrogen given off
B a free-radical substitution with hydrogen chloride given off
C a free-radical substitution with no gas given off
D a nucleophilic substitution with hydrogen chloride given off

10. The diagram shows the structure of a bromo compound that may be formed by the reaction of bromine with a hydrocarbon.



Which row is correct?

	type of reaction	mechanism
A	addition	electrophilic
B	addition	nucleophilic
C	substitution	nucleophilic
D	substitution	free-radical

11. Bromomethane, CH_3Br, decomposes in the stratosphere forming methyl free radicals and bromine free radicals. Which row correctly describes this decomposition?

	type of bond fission	number of electrons in a bromine free radical
A	homolytic	35
B	heterolytic	35
C	homolytic	36
D	heterolytic	36

10. Dichloromethane, CH_2Cl_2, is widely used as an organic solvent.

CH_2Cl_2 can be prepared by reacting CH_3Cl and Cl_2 at room temperature.
The reaction proceeds via several steps, as shown.

$$Cl_2 \xrightarrow{\text{initiation}} 2Cl^{\bullet}$$

$$Cl^{\bullet} + CH_3Cl \xrightarrow{\text{propagation 1}} HCl + {}^{\bullet}CH_2Cl$$

$$Cl_2 + {}^{\bullet}CH_2Cl \xrightarrow{\text{propagation 2}} \text{products}$$

$$Cl^{\bullet} + {}^{\bullet}CH_2Cl \xrightarrow{\text{final step}} CH_2Cl_2$$

Give the name of the mechanism of this reaction. [1]

(ii) State the essential condition required for the initiation step to take place. [1]

(iii) Give the electronic configuration of $Cl^{\bullet}$. [1]

(iv) Identify the products of the step labelled propagation 2. [1]

(v) Name the type of reaction shown in the final step. [1]

(vi) Suggest the identity of another organic molecule that is a product of the reaction of CH_3Cl and Cl_2 under the same conditions. [1]

11. Fig. 4.1 shows how propane, C_3H8, can be converted to propanoic acid, CH_3CH_2COOH.

$$C_3H_8 \xrightarrow{\text{reaction 1}} CH_3CH_2CH_2Cl \xrightarrow{\text{reaction 2}} CH_3CH_2CH_2OH \xrightarrow{\text{reaction 3}} CH_3CH_2COOH$$

Fig. 4.1

(a) Reaction 1 in Fig. 4.1 takes place in the presence of sunlight.
$C_3H8 + Cl_2$ $CH_3CH_2CH_2Cl + HCl$
The reaction takes place via initiation, propagation and termination steps.
(i) Name the mechanism shown by reaction 1.

..... [1]

(ii) Complete the mechanism for reaction 1.
Construct equations to describe the steps of the mechanism.
initiation $Cl_2 \rightarrow 2Cl^{\bullet}$

propagation 1 .....

propagation 2 .....

termination ..... $CH_3CH_2CH_2Cl$ [3]

(iii) Reaction 1 is initiated by the bond fission of Cl_2.
State the type of bond fission shown in the initiation step.

..... [1]

12. Chlorine reacts with methane in a series of reactions to produce chloroalkanes.
(i) State the conditions required for chlorine to react with methane. [1]

(ii) One of the products of the reaction is CH_2Cl_2 which reacts further to produce $CHCl_3$.
Complete the following table to show details of the mechanism that forms $CHCl_3$ from CH_2Cl_2. [3]

name of step	equation
initiation	.....
propagation	$CH_2Cl_2 + Cl\bullet \rightarrow$ .....
termination	..... $\rightarrow CHCl_3$

(iii) $CHCl_3$ and HF are used to form $CHClF_2$ in a substitution reaction.
Construct an equation for this reaction. [1]

13. The halogenoalkane CH_3CH_2Cl forms when chlorine reacts with C_2H_6 via a free-radical substitution mechanism.

(i) State the essential condition for chlorine to react with C_2H_6 at room temperature.

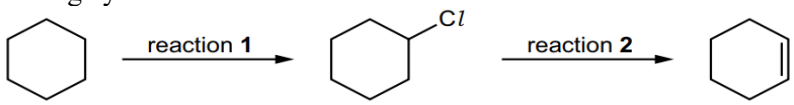
..... [1]

(ii) Write two equations to show the propagation steps in this reaction.

1 .....

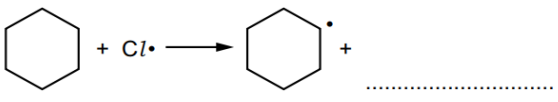
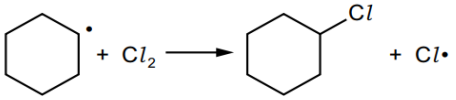
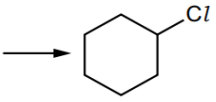
2 ..... [2]

14. A reaction scheme involving cyclohexane is shown in



Reaction **1** involves a free radical substitution mechanism.
(a) State the essential condition required for reaction **1** to occur. [1]

(b) Complete Table 4.1 to give details of the mechanism in reaction **1**. Include curly arrows to show the movement of electrons occurring in the termination step. [5]

name of step	equation
.....	$Cl_2 \longrightarrow 2Cl\bullet$
propagation	 + ...
.....	
termination	..... 

(c) Deduce the type of reaction that occurs in reaction **2**.

[1]

15. Cyclopentane reacts with Cl_2 in the presence of ultraviolet light to form C5H9Cl.

(i) The reaction is initiated by the bond fission of Cl_2.
State the type of bond fission shown in the initiation step.

..... [1]

(ii) Complete the equations to show the two propagation steps that follow the initiation step. [2]

propagation 1 C_5H_{10} + ... → C_5H_9• + ...

propagation 2 C_5H_9• + ... → .....

(iii) The final step is shown.

$$C_5H_9\bullet + Cl\bullet \rightarrow C_5H_9Cl$$

Give the name for this step in the reaction.

..... [1]

12. The free-radical substitution reaction between methane and chlorine involves initiation, propagation and termination stages.
Which row is correct?

	involved in initiation stage	radical produced in a propagation stage
A	Homolytic fission	H•
B	Homolytic fission	CH_3•
C	heterolytic fission	H•
D	heterolytic fission	CH_3•

13. Which equation represents a valid propagation step in the chlorination of ethane?

A $C_2H_5Cl + Cl\bullet \rightarrow C_2H_4Cl\bullet + HCl$
B $C_2H_6 + Cl\bullet \rightarrow C_2H_5Cl + H\bullet$
C $C_2H_5Cl + H\bullet \rightarrow C_2H_5\bullet + HCl$
D $C_2H_5\bullet + Cl\bullet \rightarrow C_2H_5Cl$

14. Hexane, C_6H_{14}, is a colourless liquid.
Two test-tubes contain equal amounts of hexane. 1cm^3 of bromine, Br_2(aq), is added to both test-tubes. One test-tube is kept in the dark and the other is exposed to sunlight.
The table describes the appearance of each test-tube after one hour.

test-tube conditions	observations
in the dark	no change, mixture remains orange
in sunlight	colour of mixture fades to pale yellow

(a) The test-tube in the dark is kept cool and is not exposed to ultraviolet light.
Explain the observations for the test-tube kept in the dark.

.....

..... [2]

(b) In sunlight, bromine reacts with hexane by a mechanism which occurs via a series of steps.
(i) State the name of the mechanism of the reaction that occurs.

..... [1]

(ii) Give an equation which shows a propagation step in this reaction in which hexane produces •C_6H_{13}.

..... [1]

(iii) Give an equation which shows a propagation step in this reaction that produces 1-bromohexane.

..... [1]

(iv) Give an equation which shows a termination step in this reaction that produces 1-bromohexane.

..... [1]

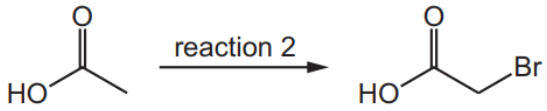
15. Which list contains a compound that is not made during the free radical substitution of methane with chlorine?

A CH_3Cl , CCl_4, C_2H_6
B Cl_2, CH_2Cl_2, CCl_4
C CH_3Cl , CH_2Cl_2, $CHCl_3$
D CH_3Cl , $CHCl_3$, $C_2H_2Cl_2$

16. Below is a list of species which can react with organic compounds.
CN^- HC*l* C*l* H_2O CO_3^{2-}
From the list, identify a species which can react with ethane.

..... [1]

17. Suggest the type of reaction that occurs in reaction 2. [1]



16. Methane and bromine react by free radical substitution.
P and Q are involved in the reaction mechanism.
P and Q:
- are **both** involved in propagation steps as reactants
- are **both** involved in termination steps as reactants.

What could be P and Q?

A Br and H **B** Br and CH_3 **C** Br and C_2H_6 **D** CH_3 and CH_3

17. The alkane $CH_3CH_2CH(CH_3)_2$ undergoes free radical substitution with chlorine. No C–C bonds are broken in this reaction.
How many isomeric products, including positional and optical isomers, of molecular formula $C_5H_{11}Cl$ can be formed?

A 4 B 5 C 6 D 7

Environmental consequences of carbon monoxide, oxides of nitrogen and unburnt hydrocarbons

When the petrol or diesel is mixed with air inside a car engine, there is only a limited supply of oxygen. Under these conditions, not all the carbon in the hydrocarbon fuel is fully oxidised to carbon dioxide. Some of the carbon is only partially oxidised to form carbon monoxide (CO) gas. This is called *incomplete combustion*.

Carbon monoxide is a toxic gas that bonds with the haemoglobin in your blood. The haemoglobin molecules can then no longer bond to oxygen and so cannot transport oxygen around your body. Victims of carbon monoxide poisoning will feel dizzy, then lose consciousness. If not removed from the toxic gas, the victim will die.

Carbon monoxide is odourless, so this adds to the danger. This is why faulty gas heaters in which incomplete combustion occurs can kill unsuspecting people in rooms with poor ventilation.

As well as releasing carbon monoxide, road traffic also releases acidic nitrogen oxides, mainly NO and NO2.

These contribute to the problem of acid rain. Acid rain can kill trees and aquatic animals in lakes. Acid rain also erodes limestone buildings and statues, as well as corroding metals, such as iron.

In normal combustion, nitrogen gas in the air is not oxidised. However, in the very high temperatures in car engines, oxidation of nitrogen does take place. A variety of nitrogen oxides can be formed and released in the car's exhaust fumes

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

As well as toxic carbon monoxide and acidic nitrogen oxides, cars also release unburnt hydrocarbons, often referred to as volatile organic compounds (VOCs), into the air. Some of these are carcinogens (they cause cancers) and can form PAN, a contributor to photochemical smog

Reducing traffic emissions

Motor vehicles can now be fitted with catalytic converters in their exhaust systems. Once warmed up, a catalytic converter can cause the following reactions to take place:

- the oxidation of carbon monoxide to form carbon dioxide
- the reduction of nitrogen oxides to form harmless nitrogen gas
- the oxidation of unburnt hydrocarbons to form carbon dioxide and water.

Unfortunately, catalytic converters can do nothing to reduce the amount of carbon dioxide (a greenhouse gas) given off in the exhaust gases of cars and trucks.

18. Many reactions take place in the engine and catalytic converter of a car.
Which pair of substances is produced **both** by the reactions in a car engine and in a catalytic converter?

A carbon dioxide and unburnt hydrocarbons
B carbon dioxide and water
C carbon monoxide and nitrogen
D carbon monoxide and unburnt hydrocarbons

19. Which emission from an internal combustion engine contributes to the erosion of marble statues?

A carbon monoxide
B nitrogen
C nitrogen dioxide
D unburnt hydrocarbons

20. Exhaust gases from an internal combustion engine are made less harmful by passing them through a catalytic converter. A number of reactions take place in the catalytic converter. Two such reactions are described in the table. Which row is correct?

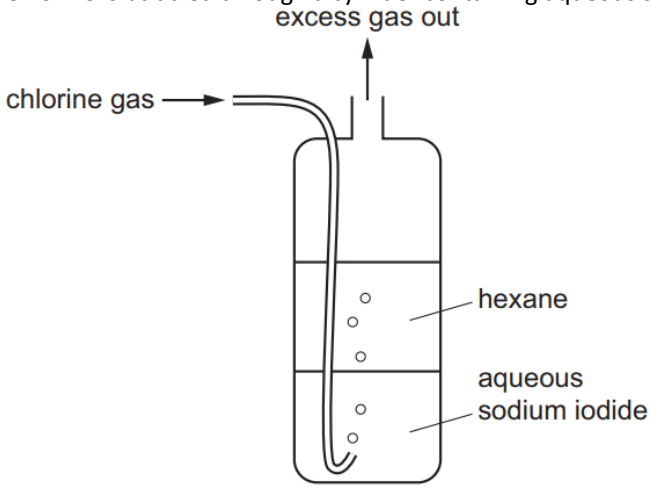
	the type of reaction that removes unburned hydrocarbons	the type of reaction that removes carbon monoxide
A	oxidation	oxidation
B	oxidation	reduction
C	reduction	reduction
D	reduction	oxidation

21. NO, NO_2, CO and unburnt hydrocarbons are present in the exhaust gases of internal combustion engines. When catalytic converters are used to remove these compounds from the exhaust gases, redox reactions occur. What happens to each compound in the catalytic converter?

	NO	NO_2	CO	unburnt hydrocarbons
A	oxidised	oxidised	reduced	oxidised
B	oxidised	oxidised	oxidised	oxidised
C	reduced	reduced	oxidised	oxidised
D	reduced	reduced	reduced	reduced

18. Molecule **M** is present in petrol, a fuel used in cars. M is a saturated, non-cyclic hydrocarbon.
M contains eight carbon atoms.
When petrol is burned in an internal combustion engine, oxides of nitrogen are released into the atmosphere.
Oxides of nitrogen are responsible for the formation of acid rain.
(i) Suggest the conditions required for the production of oxides of nitrogen during combustion of **M** in an internal combustion engine. Use an appropriate equation in your answer. [2]

22. Chlorine is bubbled through a cylinder containing aqueous sodium iodide and an immiscible layer of hexane.



As the bubbles pass through the cylinder, what is observed in the lower and upper layers?

	lower aqueous layer	upper hexane layer
A	colourless solution becomes brown	colourless liquid becomes coloured
B	colourless solution becomes brown	colourless liquid is unchanged
C	brown solution becomes colourless	colourless liquid becomes coloured
D	brown solution becomes colourless	colourless liquid is unchanged