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Section A

Answer **all** questions in the spaces provided.

1 Mass spectrometry can be used to identify isotopes of elements.

1 (a) (i) In terms of fundamental particles, state the difference between isotopes of an element.

.....

.....

(1 mark)

1 (a) (ii) State why isotopes of an element have the same chemical properties.

.....

.....

(1 mark)

1 (b) Give the meaning of the term *relative atomic mass.*

.....

.....

.....

(2 marks)

(Extra space).....

.....

1 (c) The mass spectrum of element **X** has four peaks. The table below gives the relative abundance of each isotope in a sample of element **X**.

m/*z*	64	66	67	68
Relative abundance	12	8	1	6

1 (c) (i) Calculate the relative atomic mass of element **X**.
Give your answer to one decimal place.

.....

.....

.....

.....

.....

(3 marks)

1 (c) (ii) Use the Periodic Table to identify the species responsible for the peak at *m*/*z* = 64

.....

(2 marks)

1 (d) Suggest **one** reason why particles with the same mass and velocity can be deflected by different amounts in the same magnetic field.

.....

.....

(1 mark)

1 (e) Explain how the detector in a mass spectrometer enables the abundance of an isotope to be measured.

.....

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(2 marks)

(Extra space) .....

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12

Do not write outside the box

2 Norgessaltpeter was the first nitrogen fertiliser to be manufactured in Norway. It has the formula $Ca(NO_3)_2$

2 (a) Norgessaltpeter can be made by the reaction of calcium carbonate with dilute nitric acid as shown by the following equation.

$$CaCO_3(s) + 2HNO_3(aq) \longrightarrow Ca(NO_3)_2(aq) + CO_2(g) + H_2O(l)$$

In an experiment, an excess of powdered calcium carbonate was added to 36.2 cm^3 of 0.586 mol dm^{-3} nitric acid.

2 (a) (i) Calculate the amount, in moles, of HNO_3 in 36.2 cm^3 of 0.586 mol dm^{-3} nitric acid. Give your answer to 3 significant figures.

.....

.....

(1 mark)

2 (a) (ii) Calculate the amount, in moles, of $CaCO_3$ that reacted with the nitric acid. Give your answer to 3 significant figures.

.....

.....

(1 mark)

2 (a) (iii) Calculate the minimum mass of powdered $CaCO_3$ that should be added to react with all of the nitric acid. Give your answer to 3 significant figures.

.....

.....

.....

(2 marks)

2 (a) (iv) State the type of reaction that occurs when calcium carbonate reacts with nitric acid.

.....

(1 mark)

2 (b) Norgessaltpeter decomposes on heating as shown by the following equation.

$$2Ca(NO_3)_2(s) \longrightarrow 2CaO(s) + 4NO_2(g) + O_2(g)$$

A sample of Norgessaltpeter was decomposed completely.

The gases produced occupied a volume of $3.50 \times 10^{-3}\,m^3$ at a pressure of 100 kPa and a temperature of 31 °C.
(The gas constant $R = 8.31\,J\,K^{-1}\,mol^{-1}$)

2 (b) (i) Calculate the total amount, in moles, of gases produced.

.....

.....

.....

.....

(3 marks)

2 (b) (ii) Hence calculate the amount, in moles, of oxygen produced.

.....

.....

(1 mark)

2 (c) Hydrated calcium nitrate can be represented by the formula $Ca(NO_3)_2.xH_2O$ where x is an integer.

A 6.04 g sample of $Ca(NO_3)_2.xH_2O$ contains 1.84 g of water of crystallisation.

Use this information to calculate a value for x.
Show your working.

.....

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(3 marks)

12

Do not write outside the box

3 Fluorine and iodine are elements in Group 7 of the Periodic Table.

3 (a) Explain why iodine has a higher melting point than fluorine.

.....

.....

.....

(2 marks)

(Extra space).....

.....

3 (b) (i) Draw the shape of the NHF_2 molecule and the shape of the BF_3 molecule.
Include any lone pairs of electrons that influence the shape.
In each case name the shape.

Shape of NHF_2 Shape of BF_3

Name of shape of NHF_2 .....

Name of shape of BF_3 .....

(4 marks)

3 (b) (ii) Suggest a value for the F—N—F bond angle in NHF_2

.....

(1 mark)

3 (c) State the strongest type of intermolecular force in a sample of NHF_2

.....

(1 mark)

Do not write outside the box

3 (d) A molecule of NHF_2 reacts with a molecule of BF_3 as shown in the following equation.

$$NHF_2 + BF_3 \longrightarrow F_2HNBF_3$$

State the type of bond formed between the N atom and the B atom in F_2HNBF_3
Explain how this bond is formed.

Name of type of bond .....

How bond is formed .....

.....

.....

(2 marks)

10

Turn over for the next question

4 There are several types of crystal structure and bonding shown by elements and compounds.

4 (a) (i) Name the type of bonding in the element sodium.

.....

(1 mark)

4 (a) (ii) Use your knowledge of structure and bonding to draw a diagram that shows how the particles are arranged in a crystal of sodium.
You should identify the particles and show a minimum of six particles in a two-dimensional diagram.

(2 marks)

4 (b) Sodium reacts with chlorine to form sodium chloride.

4 (b) (i) Name the type of bonding in sodium chloride.

.....

(1 mark)

4 (b) (ii) Explain why the melting point of sodium chloride is high.

.....

.....

.....

.....

(2 marks)

(Extra space) .....

.....

4 (c) The table below shows the melting points of some sodium halides.

	NaCl	NaBr	NaI
Melting point / K	1074	1020	920

Suggest why the melting point of sodium iodide is lower than the melting point of sodium bromide.

.....

.....

(1 mark)

7

Turn over for the next question

5 This question is about the first ionisation energies of some elements in the Periodic Table.

5 (a) Write an equation, including state symbols, to show the reaction that occurs when the first ionisation energy of lithium is measured.

.....

(1 mark)

5 (b) State and explain the general trend in first ionisation energies for the Period 3 elements aluminium to argon.

Trend .....

Explanation .....

.....

.....

(3 marks)

(Extra space).....

.....

5 (c) There is a similar general trend in first ionisation energies for the Period 4 elements gallium to krypton.
State how selenium deviates from this general trend and explain your answer.

How selenium deviates from this trend .....

Explanation .....

.....

.....

(3 marks)

(Extra space).....

.....

5 (d) Suggest why the first ionisation energy of krypton is lower than the first ionisation energy of argon.

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(1 mark)

5 (e) The table below gives the successive ionisation energies of an element.

	First	Second	Third	Fourth	Fifth
Ionisation energy / kJ mol^{-1}	590	1150	4940	6480	8120

Deduce the group in the Periodic Table that contains this element.

.....

(1 mark)

5 (f) Identify the element that has a 5+ ion with an electron configuration of $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$

.....

(1 mark)

10

Turn over for the next question

Section B

Answer **all** questions in the spaces provided.

6 (a) There is a risk of gas explosions in coal mines. This risk is mainly due to the presence of methane. If the percentage of coal-mine methane (CMM) in the air in the mine is greater than 15%, the explosion risk is much lower. CMM slowly escapes from the mine into the atmosphere.

Write an equation to show the complete combustion of methane.

Suggest **one** reason why there is a much lower risk of an explosion if the percentage of CMM is greater than 15%.

State why it is beneficial to the environment to collect the CMM rather than allowing it to escape into the atmosphere.

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(3 marks)

(Extra space) .....

.....

.....

6 (b) Methane can be obtained from crude oil. Some of this crude oil contains an impurity called methanethiol (CH_3SH). This impurity causes environmental problems when burned.

Write an equation to show the complete combustion of methanethiol.

State why calcium oxide can be used to remove the sulfur-containing product of this combustion reaction.

State **one** pollution problem that is caused by the release of this sulfur-containing product into the atmosphere.

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(3 marks)

(Extra space).....

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6

Turn over for the next question

Do not write outside the box

7 Pentane is a member of the alkane homologous series.

7 (a) Give the general formula for the homologous series of alkanes.

.....

(1 mark)

7 (b) One of the structural isomers of pentane is 2,2-dimethylpropane.

Draw the displayed formula of 2,2-dimethylpropane.

State the type of structural isomerism shown.

.....

(2 marks)

Do not write outside the box

7 (c) A molecule of hydrocarbon **Y** can be thermally cracked to form one molecule of pentane and two molecules of ethene only.

Deduce the molecular formula of **Y**.

State why high temperatures are necessary for cracking reactions to occur.

Give **one** reason why thermal cracking reactions are carried out in industry.

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(3 marks)

(Extra space) .....

.....

.....

7 (d) Write an equation for the incomplete combustion of pentane to form a solid pollutant.

Suggest why this solid pollutant is an environmental problem.

.....

.....

.....

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(2 marks)

(Extra space) .....

.....

Question 7 continues on the next page

Do not write outside the box

7 (e) Pentane can react with chlorine as shown in the following equation.

$$C_5H_{12} + Cl_2 \longrightarrow C_5H_{11}Cl + HCl$$

Calculate the percentage atom economy for the formation of $C_5H_{11}Cl$

Deduce how many straight-chain isomers of $C_5H_{11}Cl$ could be formed.

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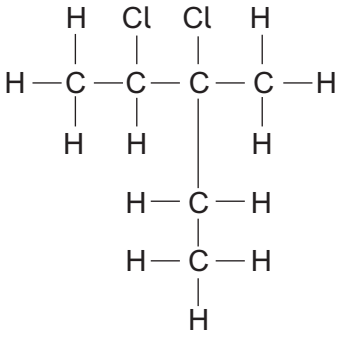
(3 marks)

(Extra space).....

.....

7 (f) Consider the following compound.



Name this compound.

Deduce the empirical formula of this compound.

.....

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.....

.....

(2 marks)

13

END OF QUESTIONS

Do not write outside the box

Section A

Answer **all** questions in the spaces provided.

1 The rate of a chemical reaction is influenced by the size of the activation energy. Catalysts are used to increase the rates of chemical reactions but are not used up in the reactions.

1 (a) Give the meaning of the term *activation energy*.

.....

.....

.....

.....

(2 marks)

1 (b) Explain how a catalyst increases the rate of a reaction.

.....

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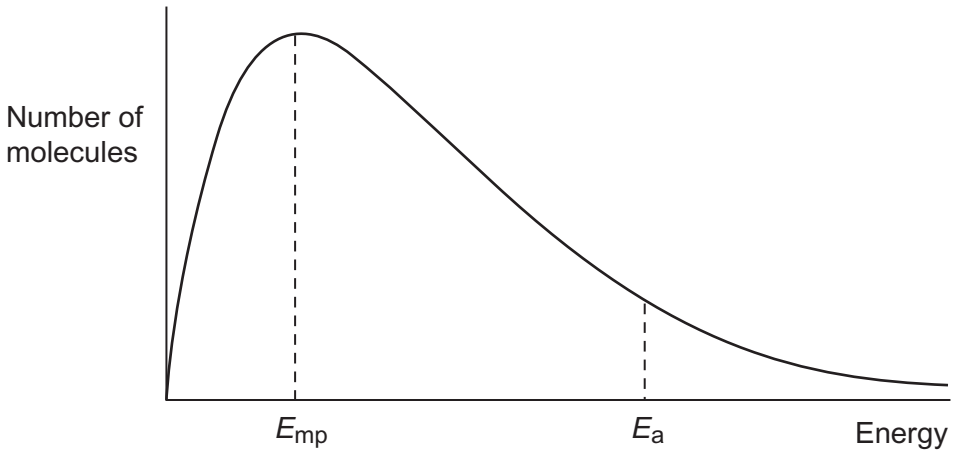
(2 marks)

1 (c) The diagram below shows the Maxwell–Boltzmann distribution of molecular energies, at a constant temperature, in a gas at the start of a reaction.
On this diagram the most probable molecular energy at this temperature is shown by the symbol E_{mp}
The activation energy is shown by the symbol E_a



To answer the questions **1 (c) (i)** to **1 (c) (iv)**, you should use the words **increases**, **decreases** or **stays the same**. You may use each of these answers once, more than once or not at all.

1 (c) (i) State how, if at all, the value of the most probable energy (E_{mp}) changes as the total number of molecules is increased at constant temperature.

.....

(1 mark)

1 (c) (ii) State how, if at all, the number of molecules with the most probable energy (E_{mp}) changes as the temperature is decreased without changing the total number of molecules.

.....

(1 mark)

1 (c) (iii) State how, if at all, the number of molecules with energy greater than the activation energy (E_a) changes as the temperature is increased without changing the total number of molecules.

.....

(1 mark)

1 (c) (iv) State how, if at all, the area under the molecular energy distribution curve changes as a catalyst is introduced without changing the temperature or the total number of molecules.

.....

(1 mark)

1 (d) For each of the following reactions, identify a catalyst and name the organic product of the reaction.

1 (d) (i) The fermentation of an aqueous solution of glucose.

Catalyst .....

Name of organic product .....

(2 marks)

1 (d) (ii) The hydration of but-2-ene.

Catalyst .....

Name of organic product .....

(2 marks)

12

Do not write outside the box

2 This question is about the extraction of titanium from titanium(IV) oxide by a two-stage process.
The first stage in the process produces titanium(IV) chloride. In the second stage, titanium(IV) chloride is converted into titanium.
The enthalpy change for the second stage can be determined using Hess's Law.

2 (a) Give **one** reason why titanium is **not** extracted directly from titanium(IV) oxide using carbon.

.....

.....

(1 mark)

2 (b) Give the meaning of the term *enthalpy change*.

.....

.....

.....

(1 mark)

2 (c) State Hess's Law.

.....

.....

.....

.....

(1 mark)

2 (d) Define the term *standard enthalpy of formation*.

.....

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(3 marks)

2 (e) The following standard enthalpy of formation data refer to the second stage in the extraction of titanium.

	$TiCl_4(g)$	Na(l)	NaCl(s)	Ti(s)
$\Delta H_f^{\ominus}$ / kJ mol^{-1}	–720	+3	–411	0

2 (e) (i) State why the value for the standard enthalpy of formation of Na(l) is **not** zero.

.....

.....

(1 mark)

2 (e) (ii) Use data from the table to calculate a value for the standard enthalpy change of the following reaction.

$$TiCl_4(g) + 4Na(l) \longrightarrow 4NaCl(s) + Ti(s)$$

.....

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.....

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(3 marks)

2 (e) (iii) State the role of sodium in this reaction.

.....

(1 mark)

11

Do not write outside the box

3 (a) Give the **formula** of a Group 2 metal hydroxide used in agriculture.

.....

(1 mark)

3 (b) Identify a sodium halide that does **not** undergo a redox reaction when added as a solid to concentrated sulfuric acid.

.....

(1 mark)

3 (c) Chlorine gas reacts with cold dilute sodium hydroxide solution to form sodium chloride and another chlorine-containing compound, **X**.
Give the **formula** of **X**.

.....

(1 mark)

3 (d) Give the **formula** of the substance responsible for the orange colour when chlorine gas is bubbled through an aqueous solution of sodium bromide.

.....

(1 mark)

3 (e) Solid sodium iodide undergoes a redox reaction with concentrated sulfuric acid.
Give the **formula** for each of the following in this reaction.

Formula of the solid reduction product .....

Formula of the oxidation product .....

(2 marks)

Do not write outside the box

3 (f) Draw the structure of each of the following organic compounds.

3 (f) (i) The hydrocarbon that is a chain isomer of methylpropene, but does **not** exhibit E–Z stereoisomerism.

(1 mark)

3 (f) (ii) The alcohol that is a position isomer of butan-2-ol.

(1 mark)

3 (f) (iii) The hydrocarbon that has a peak, due to its molecular ion, at $m/z = 44$ in its mass spectrum.

(1 mark)

3 (f) (iv) The bromoalkane that reacts with sodium cyanide to produce propanenitrile.

(1 mark)

10

Do not write outside the box

4 Metals are usually extracted from oxides.
Some of these oxides occur naturally. Other oxides are made by roasting sulfide ores in air, producing sulfur dioxide as a by-product.
For the extraction of some metals, the oxide needs to be converted into a chloride.

4 (a) The ore molybdenite contains molybdenum disulfide (MoS_2).
The first stage in the extraction of molybdenum is to roast the ore in air to form molybdenum oxide (MoO_3) and sulfur dioxide.

4 (a) (i) Write an equation for the first stage in this extraction.

.....

(1 mark)

4 (a) (ii) The release of sulfur dioxide into the atmosphere causes environmental problems and wastes a valuable resource. Identify **one** environmental problem and identify **one** use for the sulfur dioxide.

Environmental problem .....

.....

.....

Use for sulfur dioxide .....

.....

.....

(2 marks)

4 (a) (iii) Pure molybdenum is formed in the second stage by the reduction of MoO_3 using hydrogen.
Write an equation for this reaction.

.....

(1 mark)

4 (a) (iv) State **one** risk in using hydrogen gas in metal extractions.

.....

.....

(1 mark)

4 (b) Calcium is an expensive metal. It is extracted by the electrolysis of molten calcium chloride.

4 (b) (i) State why calcium chloride must be molten for electrolysis to occur.

.....

.....

(1 mark)

4 (b) (ii) Write an equation for the reaction that takes place at the negative electrode during this electrolysis.

.....

(1 mark)

4 (b) (iii) Identify the major cost in this extraction of calcium.

.....

.....

(1 mark)

8

Turn over for the next question

Do not write outside the box

5 A sample of nitrogen dioxide gas (NO_2) was prepared by the reaction of copper with concentrated nitric acid.

5 (a) (i) Balance the equation for the reaction of copper with concentrated nitric acid.

$$Cu + \ldots\ldots HNO_3 \longrightarrow Cu(NO_3)_2 + \ldots\ldots NO_2 + \ldots\ldots H_2O$$

(1 mark)

5 (a) (ii) Give the oxidation state of nitrogen in each of the following compounds.

HNO_3 .....

NO_2 .....

(2 marks)

5 (a) (iii) Deduce the half-equation for the conversion of HNO_3 into NO_2 in this reaction.

.....

(1 mark)

5 (b) The following equilibrium is established between colourless dinitrogen tetraoxide gas (N_2O_4) and dark brown nitrogen dioxide gas.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = +58\,kJ\,mol^{-1}$$

5 (b) (i) Give two features of a reaction at equilibrium.

Feature 1 .....

.....

.....

.....

Feature 2 .....

.....

.....

.....

(2 marks)

Do not write outside the box

5 (b) (ii) Use Le Chatelier's principle to explain why the mixture of gases becomes darker in colour when the mixture is heated at constant pressure.

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(2 marks)

5 (b) (iii) Use Le Chatelier's principle to explain why the amount of NO_2 decreases when the pressure is increased at constant temperature.

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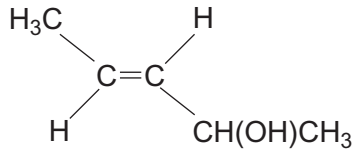
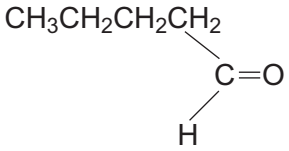
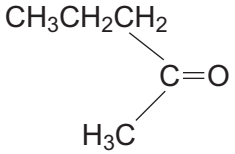
(2 marks)

10

Turn over for the next question

6 The table below shows the structures of three isomers with the molecular formula $C_5H_{10}O$

Isomer **1** 	(*E*)-pent-3-en-2-ol
Isomer **2** 	pentanal
Isomer **3** 	

6 (a) Complete the table by naming Isomer **3**. *(1 mark)*

6 (b) State the type of structural isomerism shown by these three isomers.

.....

(1 mark)

6 (c) The compound (*Z*)-pent-3-en-2-ol is a stereoisomer of (*E*)-pent-3-en-2-ol.

6 (c) (i) Draw the structure of (*Z*)-pent-3-en-2-ol.

(1 mark)

6 (c) (ii) Identify the feature of the double bond in (*E*)-pent-3-en-2-ol and that in (*Z*)-pent-3-en-2-ol that causes these two compounds to be stereoisomers.

.....

(1 mark)

6 (d) A chemical test can be used to distinguish between separate samples of Isomer **2** and Isomer **3**.
Identify a suitable reagent for the test.
State what you would observe with Isomer **2** and with Isomer **3**.

Test reagent .....

Observation with Isomer **2** .....

.....

Observation with Isomer **3** .....

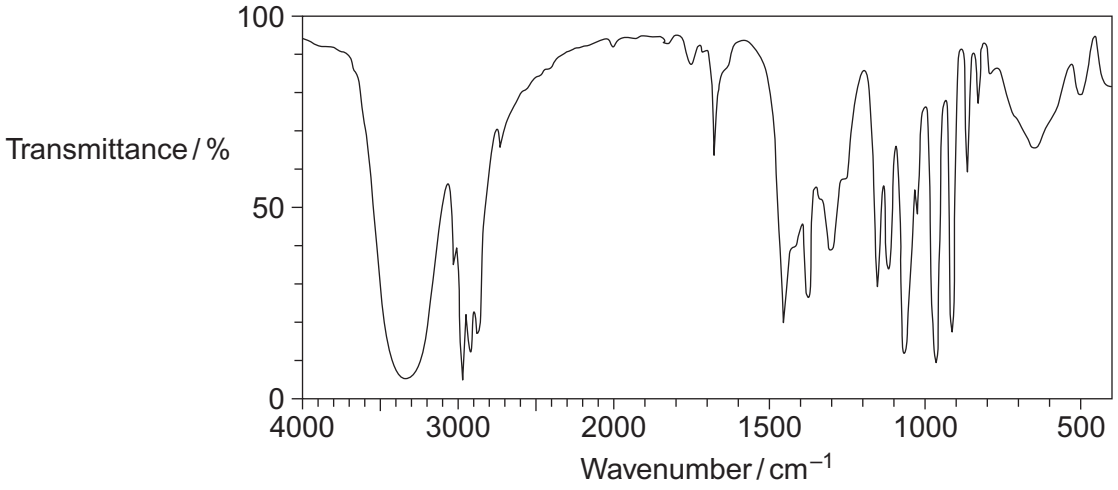
.....

(3 marks)

Question 6 continues on the next page

Do not write outside the box

6 (e) The following is the infrared spectrum of one of the isomers **1**, **2** or **3**.



6 (e) (i) Deduce which of the isomers (**1**, **2** or **3**) would give this infrared spectrum.
You may find it helpful to refer to **Table 1** on the Data Sheet.

.....

(1 mark)

6 (e) (ii) Identify two features of the infrared spectrum that support your deduction.
In each case, identify the functional group responsible.

Feature 1 and functional group .....

.....

.....

.....

Feature 2 and functional group .....

.....

.....

.....

(2 marks)

10

Turn over for the next question

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ANSWER IN THE SPACES PROVIDED

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7 Halogens are used to make halogenated organic compounds.

7 (a) The refrigerant used in air conditioners is a mixture of fluorinated alkanes.
These compounds are made by fluorination reactions.
The mechanism for the reaction of fluorine with an alkane or with a fluoroalkane is a free-radical substitution similar to the reaction of chlorine with methane.

7 (a) (i) Write the overall equation for the reaction of fluorine with methane to form trifluoromethane (CHF_3).

.....

(1 mark)

7 (a) (ii) Write equations for the following steps in the mechanism for the reaction of fluorine with trifluoromethane (CHF_3) to form tetrafluoromethane (CF_4).

Initiation step

.....

First propagation step

.....

Second propagation step

.....

A termination step leading to the formation of hexafluoroethane.

.....

(4 marks)

Do not write outside the box

7 (b) Chlorofluorocarbons (CFCs) were used as refrigerants.
In the upper atmosphere, ultra-violet radiation breaks bonds in the CFCs to produce a reactive intermediate that catalyses the decomposition of ozone.

7 (b) (i) An example of a CFC is 1,1,1-trichloro-2,2-difluoroethane.
Draw the displayed formula of this CFC.

(1 mark)

7 (b) (ii) Identify a bond in a CFC that is broken by ultra-violet radiation to produce a reactive intermediate.
Give the name of this reactive intermediate that catalyses the decomposition of ozone.
Write an overall equation for this decomposition of ozone.

Bond broken .....

Name of the reactive intermediate .....

Overall equation

.....

(3 marks)

9

Turn over for the next question

Section B

Answer **all** questions in the spaces provided.

8 (a) Some scientists thought that the waste water from a waste disposal factory contained **two** sodium halides.

They tested a sample of the waste water.

They added three reagents, one after the other, to the same test tube containing the waste water.

The table below shows their results.

Reagent added	Observations
1. Silver nitrate solution (acidified with dilute nitric acid)	A cream precipitate formed
2. Dilute ammonia solution	A yellow precipitate remained
3. Concentrated ammonia solution	The yellow precipitate did not dissolve

8 (a) (i) Identify the yellow precipitate that did **not** dissolve in concentrated ammonia solution.
Write the **simplest** ionic equation for the formation of this precipitate from silver ions and the correct halide ion.
Identify the other sodium halide that must be present in this mixture of two sodium halides.

.....

.....

.....

.....

(3 marks)

8 (a) (ii) Give **one** reason why the silver nitrate solution was acidified before it was used in this test.

.....

.....

.....

(1 mark)

Do not write outside the box

8 (a) (iii) The method that the scientists used could **not** detect one type of halide ion.
Identify this halide ion.
Give **one** reason for your answer.

.....

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.....

(2 marks)

8 (b) The scientists thought that the waste water also contained dissolved barium ions.
An aqueous solution of sodium sulfate can be used to test for the presence of dissolved barium ions.

Write the **simplest** ionic equation for the reaction between barium ions and sulfate ions to form barium sulfate.

State what is observed in this reaction.

Give a use for barium sulfate in medicine and explain why this use is possible, given that solutions containing barium ions are poisonous.

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(4 marks)

Question 8 continues on the next page

8 (c) The scientists also analysed the exhaust gases from an incinerator used to destroy waste poly(ethene).
Mass spectrometry showed that there was a trace gas with a precise M_r = 28.03176 in the exhaust gases from the incinerator.

The table below contains some precise relative atomic mass data.

Atom	Precise relative atomic mass
^{12}C	12.00000
^{1}H	1.00794
^{16}O	15.99491

Use the data to show that the trace gas is ethene. Show your working.

Suggest why both ethene and carbon monoxide might have been identified as the trace gas if the scientists had used relative atomic masses to a precision of only one decimal place.

Write an equation for the incomplete combustion of ethene to form carbon monoxide and water only.

Ethene is used to make poly(ethene).
Draw the displayed formula for the repeating unit of poly(ethene).
Name this type of polymer.

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(5 marks)

15

Do not write outside the box

9 Organic reaction mechanisms help chemists to understand how the reactions of organic compounds occur.
The following conversions illustrate a number of different types of reaction mechanism.

9 (a) When 2-bromopentane reacts with ethanolic KOH, two structurally isomeric alkenes are formed.

9 (a) (i) Name and outline a mechanism for the conversion of 2-bromopentane into pent-2-ene as shown below.

$$CH_3CH_2CH_2CHBrCH_3 \xrightarrow{\text{ethanolic KOH}} CH_3CH_2CH{=}CHCH_3$$

(4 marks)

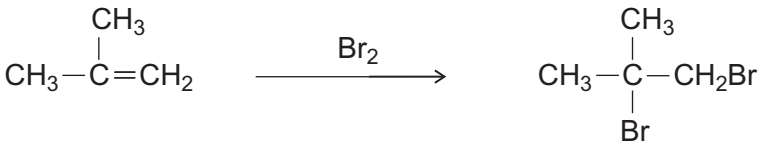
9 (a) (ii) Draw the structure of the other structurally isomeric alkene produced when 2-bromopentane reacts with ethanolic KOH.

(1 mark)

Question 9 continues on the next page

Do not write outside the box

9 (b) Name and outline a mechanism for the following conversion.



(5 marks)

Do not write outside the box

9 (c) Name and outline a mechanism for the following conversion.

$$CH_3CH_2CH_2Br \xrightarrow{NH_3} CH_3CH_2CH_2NH_2$$

(5 marks)

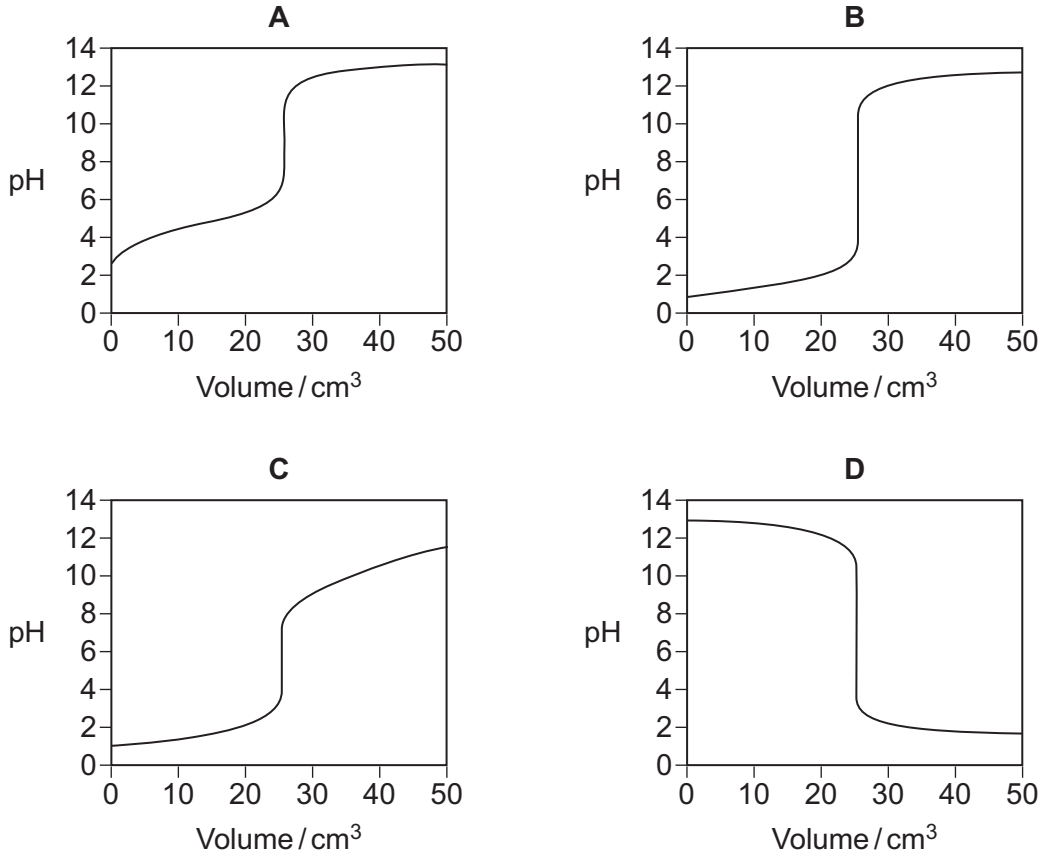
15

END OF QUESTIONS

Section A

Answer **all** questions in the spaces provided.

1 Titration curves labelled **A**, **B**, **C** and **D** for combinations of different aqueous solutions of acids and bases are shown below.
All solutions have a concentration of 0.1 mol dm^{-3}.



1 (a) In this part of the question write the appropriate letter in each box.

From the curves **A**, **B**, **C** and **D**, choose the curve produced by the addition of

ammonia to 25 cm^3 of hydrochloric acid ☐

sodium hydroxide to 25 cm^3 of ethanoic acid ☐

nitric acid to 25 cm^3 of potassium hydroxide ☐

(3 marks)

1 (b) A table of acid–base indicators is shown below.
The pH ranges over which the indicators change colour and their colours in acid and alkali are also shown.

Indicator	pH range	Colour in acid	Colour in alkali
Trapaeolin	1.3 – 3.0	red	yellow
Bromocresol green	3.8 – 5.4	yellow	blue
Cresol purple	7.6 – 9.2	yellow	purple
Alizarin yellow	10.1 – 12.0	yellow	orange

1 (b) (i) Select from the table an indicator that could be used in the titration that produces curve **B** but **not** in the titration that produces curve **A**.

.....

(1 mark)

1 (b) (ii) Give the colour change at the end point of the titration that produces curve **D** when cresol purple is used as the indicator.

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(1 mark)

5

Turn over for the next question

Do not write outside the box

2 This question is about the pH of some solutions containing potassium hydroxide and ethanoic acid.

Give all values of pH to 2 decimal places.

2 (a) (i) Write an expression for pH.

.....

(1 mark)

2 (a) (ii) Write an expression for the ionic product of water, K_w

.....

(1 mark)

2 (a) (iii) At 10 °C, a 0.154 mol dm^{-3} solution of potassium hydroxide has a pH of 13.72
Calculate the value of K_w at 10 °C.

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(2 marks)

(Extra space) .....

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Do not write outside the box

2 (b) At 25 °C, the acid dissociation constant K_a for ethanoic acid has the value 1.75×10^{-5} mol dm^{-3}.

2 (b) (i) Write an expression for K_a for ethanoic acid.

.....

.....

(1 mark)

2 (b) (ii) Calculate the pH of a 0.154 mol dm^{-3} solution of ethanoic acid at 25 °C.

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(3 marks)

(Extra space) .....

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Question 2 continues on the next page

Do not write outside the box

2 (c) At 25 °C, the acid dissociation constant K_a for ethanoic acid has the value 1.75×10^{-5} mol dm^{-3}.

2 (c) (i) Calculate the pH of the solution formed when 10.0 cm^3 of 0.154 mol dm^{-3} potassium hydroxide are added to 20.0 cm^3 of 0.154 mol dm^{-3} ethanoic acid at 25 °C.

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(4 marks)

(Extra space) .....

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2 (c) (ii) Calculate the pH of the solution formed when 40.0 cm^3 of 0.154 mol dm^{-3} potassium hydroxide are added to 20.0 cm^3 of 0.154 mol dm^{-3} ethanoic acid at 25 °C.

At 25 °C, K_w has the value 1.00×10^{-14} mol^2 dm^{-6}.

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(4 marks)

(Extra space) .....

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16

Turn over for the next question

3 The following dynamic equilibrium was established at temperature T in a closed container.

$$P(g) + 2Q(g) \rightleftharpoons 2R(g) \qquad \Delta H^{\ominus} = -50\ \text{kJ mol}^{-1}$$

The value of K_c for the reaction was 68.0 $\text{mol}^{-1}\ \text{dm}^3$ when the equilibrium mixture contained 3.82 mol of **P** and 5.24 mol of **R**.

3 (a) Give the meaning of the term *dynamic equilibrium*.

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(2 marks)

(Extra space) .....

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3 (b) Write an expression for K_c for this reaction.

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(1 mark)

3 (c) The volume of the container was 10.0 dm^3.

Calculate the concentration, in mol dm^{-3}, of **Q** in the equilibrium mixture.

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(4 marks)

(Extra space) .....

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Do not write outside the box

3 (d) State the effect, if any, on the equilibrium amount of **P** of increasing the temperature. All other factors are unchanged.

.....

(1 mark)

3 (e) State the effect, if any, on the equilibrium amount of **P** of using a container of larger volume. All other factors are unchanged.

.....

(1 mark)

3 (f) State the effect, if any, on the value of K_c of increasing the temperature. All other factors are unchanged.

.....

(1 mark)

3 (g) State the effect, if any, on the value of K_c of using a container of larger volume. All other factors are unchanged.

.....

(1 mark)

3 (h) Deduce the value of the equilibrium constant, at temperature *T*, for the reaction

$$2R(g) \rightleftharpoons P(g) + 2Q(g)$$

.....

.....

(1 mark)

12

Turn over for the next question

4 The amide or peptide link is found in synthetic polyamides and also in naturally-occurring proteins.

4 (a) (i) Draw the repeating unit of the polyamide formed by the reaction of propanedioic acid with hexane-1,6-diamine.

(2 marks)

4 (a) (ii) In terms of the intermolecular forces between the polymer chains, explain why polyamides can be made into fibres suitable for use in sewing and weaving, whereas polyalkenes usually produce fibres that are too weak for this purpose.

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(3 marks)

(Extra space) .....

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Do not write outside the box

4 (b) (i) Name and outline a mechanism for the reaction of CH_3CH_2COCl with CH_3NH_2

Name of mechanism.....

Mechanism

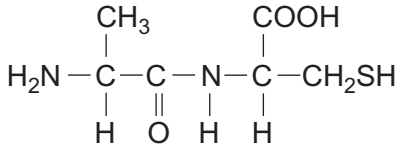
(5 marks)

4 (b) (ii) Give the name of the product containing an amide linkage that is formed in the reaction in part **4 (b) (i)**.

.....

(1 mark)

4 (c) The dipeptide shown below is formed from two different amino acids.



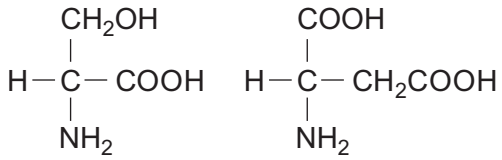
Draw the structure of the alternative dipeptide that could be formed by these two amino acids.

(1 mark)

Question 4 continues on the next page

Do not write outside the box

4 (d) The amino acids serine and aspartic acid are shown below.



4 (d) (i) Give the IUPAC name of serine.

.....

(1 mark)

4 (d) (ii) Draw the structure of the species formed when aspartic acid reacts with aqueous sodium hydroxide.

(1 mark)

4 (d) (iii) Draw the structure of the species formed when serine reacts with dilute hydrochloric acid.

(1 mark)

4 (d) (iv) Draw the structure of the species formed when serine reacts with an excess of bromomethane.

(1 mark)

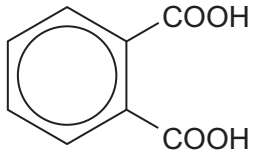
16

Do not write outside the box

5 Items softened with plasticisers have become an essential part of our modern society.

Compound **S**, shown below, is commonly known as phthalic acid.

Esters of phthalic acid are called phthalates and are used as plasticisers to soften polymers such as PVC, poly(chloroethene).



S

5 (a) Give the IUPAC name for phthalic acid.

.....

(1 mark)

5 (b) Draw the displayed formula of the repeating unit of poly(chloroethene).

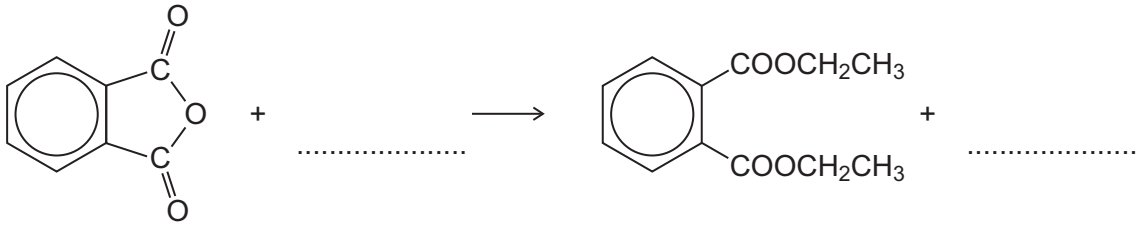
(1 mark)

Question 5 continues on the next page

Do not write outside the box

5 (c) The ester diethyl phthalate (DEP) is used in food packaging and in cosmetics.

5 (c) (i) Complete the following equation showing the formation of DEP from phthalic anhydride.



DEP

(2 marks)

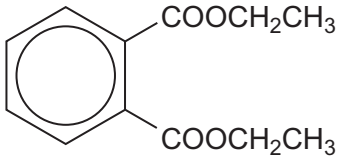
5 (c) (ii) Deduce the number of peaks in the ^{13}C n.m.r. spectrum of DEP.

.....

(1 mark)

5 (c) (iii) One of the peaks in the ^{13}C n.m.r. spectrum of DEP is at δ = 62 ppm.
Table 3 on the Data Sheet can be used to identify a type of carbon atom responsible for this peak.

Draw a circle around **one** carbon atom of this type in the structure below.



(1 mark)

5 (d) The mass spectrum of DEP includes major peaks at *m*/*z* = 222 (the molecular ion) and at *m*/*z* = 177

Write an equation to show the fragmentation of the molecular ion to form the fragment that causes the peak at *m*/*z* = 177

.....

(2 marks)

5 (e) Because of their many uses, phthalates have been tested for possible adverse effects to humans and to the environment.

The European Council for Plasticisers and Intermediates is an organisation that represents the manufacturers of plasticisers.

The text below is taken from a document written by the organisation.

'Research demonstrates that phthalates, at current and foreseeable exposure levels, do not pose a risk to human health or to the environment. Experimental evidence shows that phthalates are readily biodegradable and do not persist for long in the environment.'

5 (e) (i) Hydrolysis of DEP in an excess of water was found to follow first order kinetics.

Write a rate equation for this hydrolysis reaction using DEP to represent the ester.

.....

(1 mark)

5 (e) (ii) Suggest what needs to be done so that the public could feel confident that the research quoted above is reliable.

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(2 marks)

(Extra space) .....

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11

Do not write outside the box

6 (a) In the presence of the catalyst rhodium, the reaction between NO and H_2 occurs according to the following equation.

$$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$$

The kinetics of the reaction were investigated and the rate equation was found to be

$$\text{rate} = k[NO]^2[H_2]$$

The initial rate of reaction was 6.2×10^{-6} mol dm^{-3} s^{-1} when the initial concentration of NO was 2.9×10^{-2} mol dm^{-3} and the initial concentration of H_2 was 2.3×10^{-2} mol dm^{-3}.

6 (a) (i) Calculate the value of the rate constant under these conditions and give its units.

Calculation .....

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Units .....

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(3 marks)

6 (a) (ii) Calculate the initial rate of reaction if the experiment is repeated under the same conditions but with the concentrations of NO and of H_2 both doubled from their original values.

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(1 mark)

6 (b) Using the rate equation and the overall equation, the following three-step mechanism for the reaction was suggested. X and Y are intermediate species.

Step **1** $NO + NO \longrightarrow X$

Step **2** $X + H_2 \longrightarrow Y$

Step **3** $Y + H_2 \longrightarrow N_2 + 2H_2O$

Suggest which **one** of the three steps is the rate-determining step.

Explain your answer.

Rate-determining step.....

Explanation .....

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(2 marks)

(Extra space) .....

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6

Turn over for the next question

Section B

Answer **all** questions in the spaces provided.

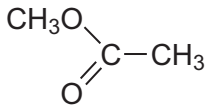
7 Organic chemists use a variety of methods to distinguish between compounds. These methods include analytical and spectroscopic techniques.

7 (a) The following compounds can be distinguished by observing what happens in test-tube reactions.

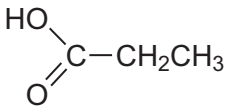
For each pair, suggest a suitable reagent or reagents that could be added separately to each compound in order to distinguish them.

Describe what you would observe with each compound.

7 (a) (i)



E



F

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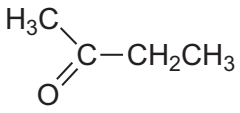
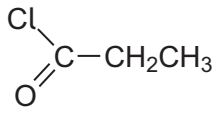
(3 marks)

Do not write outside the box

7 (a) (ii)



G



H

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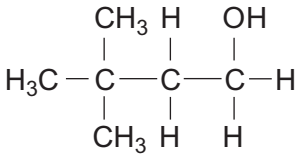
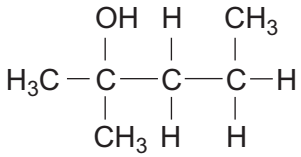
(3 marks)

7 (a) (iii)



J



K

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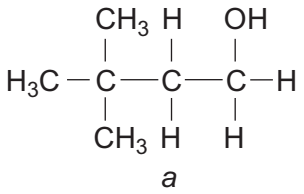
(3 marks)

Question 7 continues on the next page

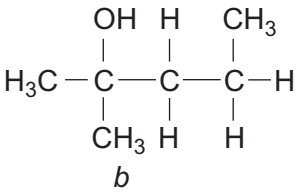
Do not write outside the box

7 (b) Compounds **J** and **K** can also be distinguished using spectroscopic techniques such as ^{1}H n.m.r.



a

J



b

K

7 (b) (i) Name compound **J**.

Give the total number of peaks in the ^{1}H n.m.r. spectrum of **J**.

State the splitting pattern, if any, of the peak for the protons labelled *a*.

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(3 marks)

7 (b) (ii) Name compound **K**.

Give the total number of peaks in the ^{1}H n.m.r. spectrum of **K**.

State the splitting pattern, if any, of the peak for the protons labelled *b*.

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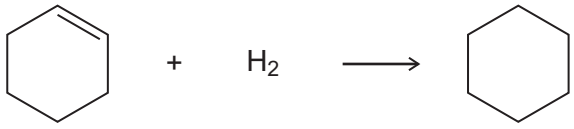
(3 marks)

15

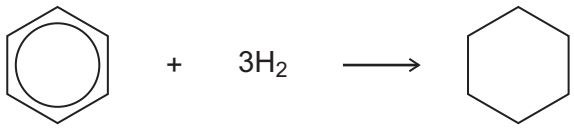
Do not write outside the box

8 The hydrocarbons benzene and cyclohexene are both unsaturated compounds. Benzene normally undergoes substitution reactions, but cyclohexene normally undergoes addition reactions.

8 (a) The molecule cyclohexatriene does not exist and is described as hypothetical. Use the following data to state and explain the stability of benzene compared with the hypothetical cyclohexatriene.



$\Delta H^{\ominus} = -120\,\text{kJ mol}^{-1}$



$\Delta H^{\ominus} = -208\,\text{kJ mol}^{-1}$

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(4 marks)

(Extra space) .....

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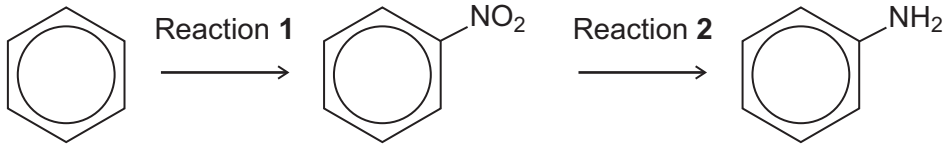
Question 8 continues on the next page

Do not write outside the box

8 (b) Benzene can be converted into amine **U** by the two-step synthesis shown below.



U

The mechanism of Reaction **1** involves attack by an electrophile.

Give the reagents used to produce the electrophile needed in Reaction **1**.

Write an equation showing the formation of this electrophile.

Outline a mechanism for the reaction of this electrophile with benzene.

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(6 marks)

(Extra space) .....

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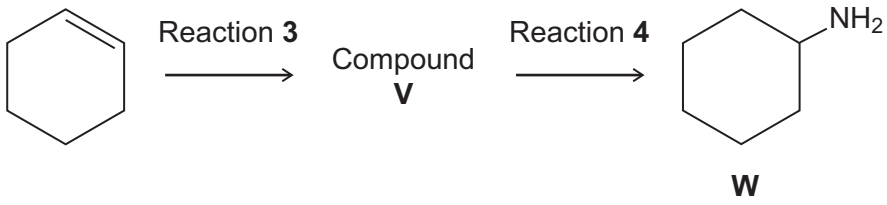
Do not write outside the box

8 (c) Cyclohexene can be converted into amine **W** by the two-step synthesis shown below.



W

Suggest an identity for compound **V**.

For Reaction **3**, give the reagent used and name the mechanism.

For Reaction **4**, give the reagent and condition used and name the mechanism.

Equations and mechanisms with curly arrows are **not** required.

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(6 marks)

(Extra space) .....

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Question 8 continues on the next page

Do not write outside the box

8 (d) Explain why amine **U** is a weaker base than amine **W**.

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(3 marks)

(Extra space) .....

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19

END OF QUESTIONS

Do not write outside the box

Section A

Answer **all** questions in the spaces provided.

1 Thermodynamics can be used to investigate the changes that occur when substances such as calcium fluoride dissolve in water.

1 (a) Give the meaning of each of the following terms.

1 (a) (i) enthalpy of lattice formation for calcium fluoride

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(2 marks)

1 (a) (ii) enthalpy of hydration for fluoride ions

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(1 mark)

1 (b) Explain the interactions between water molecules and fluoride ions when the fluoride ions become hydrated.

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(2 marks)

Do not write outside the box

1 (c) Consider the following data.

	$\Delta H^{\ominus}$/ kJ mol^{-1}
Enthalpy of lattice formation for CaF_2	–2611
Enthalpy of hydration for Ca^{2+} ions	–1650
Enthalpy of hydration for F^- ions	–506

Use these data to calculate a value for the enthalpy of solution for CaF_2

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(2 marks)

7

Turn over for the next question

There are no questions printed on this page

DO NOT WRITE ON THIS PAGE
ANSWER IN THE SPACES PROVIDED

2 When potassium nitrate (KNO_3) dissolves in water the value of the enthalpy change ΔH = +34.9 kJ mol^{-1} and the value of the entropy change ΔS = +117 J K^{-1} mol^{-1}.

2 (a) Write an equation, including state symbols, for the process that occurs when potassium nitrate dissolves in water.

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(1 mark)

2 (b) Suggest why the entropy change for this process is positive.

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(1 mark)

2 (c) Calculate the temperature at which the free-energy change, ΔG, for this process is zero.

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(3 marks)

2 (d) (i) Deduce what happens to the value of ΔG when potassium nitrate dissolves in water at a temperature lower than your answer to part **2 (c)**.

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(1 mark)

2 (d) (ii) What does this new value of ΔG suggest about the dissolving of potassium nitrate at this lower temperature?

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(1 mark)

7

Do not write outside the box

3 Ammonia can be manufactured by the Haber Process.

The equation for the reaction that occurs is shown below.

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

3 (a) The table below contains some bond enthalpy data.

	N≡N	H—H	N—H
Mean bond enthalpy / kJ mol^{-1}	944	436	388

3 (a) (i) Use data from the table to calculate a value for the enthalpy of formation for one mole of ammonia.

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(3 marks)

3 (a) (ii) A more accurate value for the enthalpy of formation of ammonia is –46 kJ mol^{-1}. Suggest why your answer to part **3 (a) (i)** is different from this value.

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(1 mark)

Do not write outside the box

3 (b) The table below contains some entropy data.

	$H_2(g)$	$N_2(g)$	$NH_3(g)$
$S^{\ominus}$ / J K^{-1} mol^{-1}	131	192	193

Use these data to calculate a value for the entropy change, with units, for the formation of one mole of ammonia from its elements.

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(3 marks)

3 (c) The synthesis of ammonia is usually carried out at about 800 K.

3 (c) (i) Use the ΔH value of -46 kJ mol^{-1} and your answer from part **3 (b)** to calculate a value for ΔG, with units, for the synthesis at this temperature.
(If you have been unable to obtain an answer to part **3 (b)**, you may assume that the entropy change is –112 J K^{-1} mol $^{-1}$. This is not the correct answer.)

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(3 marks)

3 (c) (ii) Use the value of ΔG that you have obtained to comment on the feasibility of the reaction at 800 K.

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(1 mark)

11

Do not write outside the box

4 This question is about the chemistry of the Period 3 elements and the trends in their properties.

4 (a) (i) Describe what you would observe when magnesium burns in oxygen. Write an equation for the reaction that occurs. State the type of bonding in the oxide formed.

Observations .....

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.....

.....

Equation .....

Type of bonding .....

(4 marks)

4 (a) (ii) Describe what you would observe when sulfur burns in oxygen. Write an equation for the reaction that occurs. State the type of bonding in the oxide formed.

Observations .....

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Equation .....

Type of bonding .....

(4 marks)

4 (b) State the type of bonding in sodium oxide. Explain why sodium oxide reacts to form an alkaline solution when added to water.

Type of bonding.....

Explanation.....

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.....

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(3 marks)

4 (c) Outline an experiment that could be used to show that aluminium oxide contains ions.

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(2 marks)

(Extra space) .....

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4 (d) Suggest **one** reason why a thin layer of aluminium oxide protects aluminium from corrosion in moist air.

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(1 mark)

4 (e) Write an ionic equation in each case to show how aluminium oxide reacts with the following

4 (e) (i) hydrochloric acid

.....

(1 mark)

4 (e) (ii) aqueous sodium hydroxide.

.....

(1 mark)

16

Turn over for the next question

Do not write outside the box

5 Redox reactions occur in the discharge of all electrochemical cells. Some of these cells are of commercial value.
The table below shows some redox half-equations and standard electrode potentials.

Half-equation	$E^{\ominus}$ / V
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	–0.76
$Ag_2O(s) + 2H^+(aq) + 2e^- \longrightarrow 2Ag(s) + H_2O(l)$	+0.34
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$	+1.23
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87

5 (a) In terms of electrons, state what happens to a reducing agent in a redox reaction.

.....

(1 mark)

5 (b) Use the table above to identify the strongest reducing agent from the species in the table.

Explain how you deduced your answer.

Strongest reducing agent .....

Explanation .....

.....

(2 marks)

5 (c) Use data from the table to explain why fluorine reacts with water.
Write an equation for the reaction that occurs.

Explanation .....

.....

.....

Equation .....

.....

(3 marks)

Do not write outside the box

5 (d) An electrochemical cell can be constructed using a zinc electrode and an electrode in which silver is in contact with silver oxide. This cell can be used to power electronic devices.

5 (d) (i) Give the conventional representation for this cell.

.....

(2 marks)

5 (d) (ii) Calculate the e.m.f. of the cell.

.....

(1 mark)

5 (d) (iii) Suggest **one** reason why the cell cannot be electrically recharged.

.....

.....

(1 mark)

5 (e) The electrode half-equations in a lead–acid cell are shown in the table below.

Half-equation	$E^{\ominus}$ / V
$PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$	+1.69
$PbSO_4(s) + H^+(aq) + 2e^- \longrightarrow Pb(s) + HSO_4^-(aq)$	to be calculated

5 (e) (i) The $PbO_2/PbSO_4$ electrode is the positive terminal of the cell and the e.m.f. of the cell is 2.15 V.

Use this information to calculate the missing electrode potential for the half-equation shown in the table.

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(1 mark)

5 (e) (ii) A lead–acid cell can be recharged.
Write an equation for the overall reaction that occurs when the cell is being recharged.

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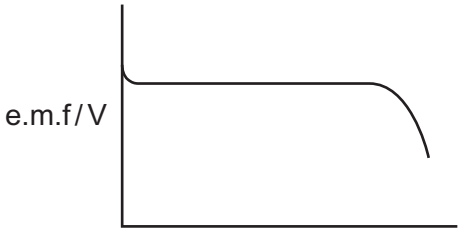
(2 marks)

Question 5 continues on the next page

Turn over ▶

5 (f) The diagrams below show how the e.m.f. of each of two cells changes with time when each cell is used to provide an electric current.

Lead–acid cell



Cell X

5 (f) (i) Give **one** reason why the e.m.f. of the **lead–acid cell** changes after several hours.

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(1 mark)

5 (f) (ii) Identify the type of cell that behaves like **cell X**.

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(1 mark)

5 (f) (iii) Explain why the voltage remains constant in **cell X**.

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(2 marks)

(Extra space) .....

.....

17

6 Transition metals and their complexes have characteristic properties.

6 (a) Give the electron configuration of the Zn^{2+} ion.
Use your answer to explain why the Zn^{2+} ion is **not** classified as a transition metal ion.

Electron configuration .....

Explanation .....

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(2 marks)

6 (b) In terms of bonding, explain the meaning of the term *complex*.

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(2 marks)

6 (c) Identify **one** species from the following list that does **not** act as a ligand. Explain your answer.

H_2 O^{2-} O_2 CO

Not a ligand .....

Explanation .....

(2 marks)

6 (d) The element palladium is in the d block of the Periodic Table. Consider the following palladium compound which contains the sulfate ion.

$[Pd(NH_3)_4]SO_4$

6 (d) (i) Give the oxidation state of palladium in this compound.

.....

(1 mark)

6 (d) (ii) Give the names of two possible shapes for the complex palladium ion in this compound.

Shape 1 .....

Shape 2 .....

(2 marks)

9

Do not write outside the box

Section B

Answer **all** questions in the spaces provided.

7 This question is about copper chemistry.

7 (a) Aqueous copper(II) ions $[Cu(H_2O)_6]^{2+}(aq)$ are blue.

7 (a) (i) With reference to electrons, explain why aqueous copper(II) ions are blue.

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(3 marks)

(Extra space) .....

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7 (a) (ii) By reference to aqueous copper(II) ions, state the meaning of each of the **three** terms in the equation $\Delta E = h\nu$.

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(3 marks)

(Extra space) .....

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Do not write outside the box

7 (a) (iii) Write an equation for the reaction, in aqueous solution, between $[Cu(H_2O)_6]^{2+}$ and an excess of chloride ions.
State the shape of the complex produced and explain why the shape differs from that of the $[Cu(H_2O)_6]^{2+}$ ion.

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(3 marks)

(Extra space) .....

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7 (b) Draw the structure of the ethanedioate ion ($C_2O_4^{2-}$).
Explain how this ion is able to act as a ligand.

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(2 marks)

Question 7 continues on the next page

Do not write outside the box

7 (c) When a dilute aqueous solution containing ethanedioate ions is added to a solution containing aqueous copper(II) ions, a substitution reaction occurs. In this reaction four water molecules are replaced and a new complex is formed.

7 (c) (i) Write an ionic equation for the reaction. Give the co-ordination number of the complex formed and name its shape.

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(4 marks)

7 (c) (ii) In the complex formed, the two water molecules are opposite each other.
Draw a diagram to show how the ethanedioate ions are bonded to a copper ion and give a value for one of the O—Cu—O bond angles. You are **not** required to show the water molecules.

(2 marks)

17

Do not write outside the box

8 Iron is an important element in living systems. It is involved in redox and in acid–base reactions.

8 (a) Explain how and why iron ions catalyse the reaction between iodide ions and $S_2O_8^{2-}$ ions. Write equations for the reactions that occur.

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(5 marks)

(Extra space) .....

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Question 8 continues on the next page

8 (b) Iron(II) compounds are used as moss killers because iron(II) ions are oxidised in air to form iron(III) ions that lower the pH of soil.

8 (b) (i) Explain, with the aid of an equation, why iron(III) ions are more acidic than iron(II) ions in aqueous solution.

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(3 marks)

8 (b) (ii) In a titration, 0.321 g of a moss killer reacted with 23.60 cm^3 of acidified 0.0218 mol dm^{-3} $K_2Cr_2O_7$ solution.

Calculate the percentage by mass of iron in the moss killer. Assume that all of the iron in the moss killer is in the form of iron(II).

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(5 marks)

8 (c) Some sodium carbonate solution was added to a solution containing iron(III) ions. Describe what you would observe and write an equation for the reaction that occurs.

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(3 marks)

16

END OF QUESTIONS

Answer ALL the questions. Write your answers in the spaces provided.

1 Solid **W** is a blue salt containing a transition metal complex cation and one anion.

(a) Give the formulae of **two** different transition metal ions which can form blue complex cations.

(2)

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(b) Complete the following table.

	Test	Observation	Inference(s)	
(i)	Heat compound **W**.	.....	Water	**(1)**
(ii)	Test any gas evolved with moist red litmus paper.	Red litmus paper turns blue	.....	**(1)**

(iii) Suggest **two** sources of the water which was given off when a pure dry sample of **W** was heated.

(2)

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.....

(c) The following tests are carried out on **separate** portions of an aqueous solution of **W**.

Complete the table.

Note: in the third column, the **formula** of the ion, molecule or compound giving rise to the observation is required.

	Test	Observation	**Formula**	
(i)	Add concentrated hydrochloric acid slowly,	..... -coloured precipitate	$Cu(OH)_2$	**(1)**
	until in excess.	green-yellow solution	.....	**(1)**
(ii)	Acidify with dilute hydrochloric acid and then add barium chloride solution.	white precipitate	.....	**(1)**
(iii)	Add dilute sulfuric acid until the solution is pale blue; then add potassium iodide solution.	white precipitate	.....	**(1)**
		in a brown solution	.....	**(1)**

(d) Suggest the **formula** of the complex cation in an aqueous solution of compound **W**.

(1)

.....

(Total for Question 1 = 12 marks)

2 The tertiary halogenoalkane 2-chloro-2-methylpropane reacts with hydroxide ions in solution as follows:

$$(CH_3)_3CCl + OH^- \rightarrow (CH_3)_3COH + Cl^-$$

The progress of the reaction can be followed by titrating the reaction mixture with a solution of hydrochloric acid of known concentration.

In an experiment designed to determine the order of the reaction, the following procedure was used.

1. 250 cm^3 of an ethanolic solution of 2-chloro-2-methylpropane, of concentration 0.100 mol dm^{-3}, was placed in a flask in a water bath at 25 °C. 250 cm^3 of aqueous sodium hydroxide solution, also of concentration 0.100 mol dm^{-3}, was placed in a similar flask in the same water bath. The temperature of the solutions was allowed to reach 25 °C.
2. A series of conical flasks were prepared, each containing about 40 cm^3 of propanone.
3. The reaction was started by mixing the halogenoalkane solution and the sodium hydroxide solution in a large flask in the water bath. A clock was started as the solutions were mixed.
4. At intervals, a 25 cm^3 pipette was used to withdraw samples of the reaction mixture. Each sample was added to a flask containing propanone and the time was noted. The propanone slows but does not completely stop the reaction.
5. Each sample was titrated immediately with a solution of hydrochloric acid of concentration 0.0500 mol dm^{-3}, using methyl orange as the indicator.

(a) (i) What colour change would you see at the end point of the titration?

(1)

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(ii) Explain why it is necessary to titrate the samples **immediately** after they have been withdrawn from the reaction mixture. State the effect, if any, on the titre if this were not done.

(2)

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(b) Suggest why it is necessary to use a solvent of aqueous ethanol rather than water alone for this reaction.

(1)

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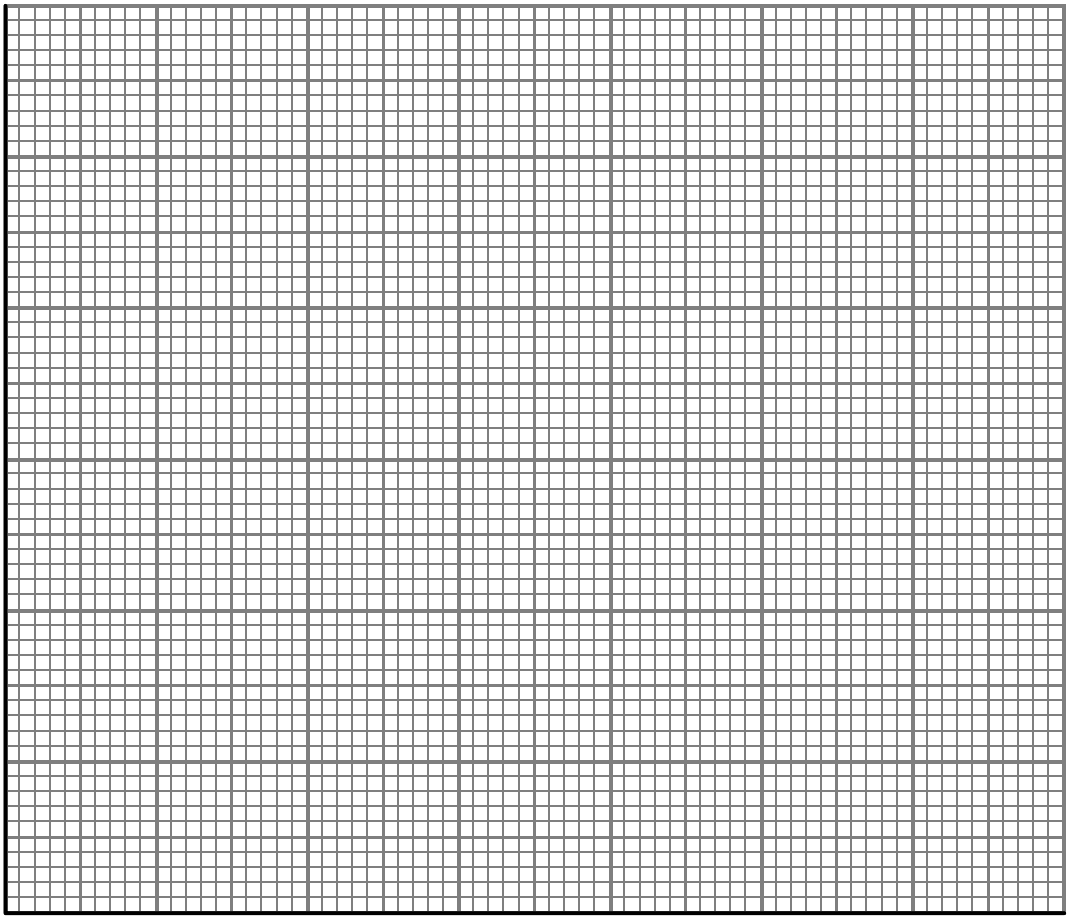
(c) In an experiment which was carried out as described above, the following data were obtained.

Time/min	1	5	12	20	32	49	65
Volume of HCl/cm^3	25.5	22.5	18.5	15.5	11.5	8.0	5.5

(i) Using the axes below, plot a suitable graph of these data.

(2)

Volume of HCl/cm^3



Time/min

(ii) Show **two** successive half-life measurements on your graph and write their values below.

(2)

First half-life .....

Second half-life .....

(iii) Explain how your answers to (ii) show that this reaction is first order.

(1)

.....

.....

(iv) Give the units of the rate constant for this reaction.

(1)

.....

(v) Because the initial concentrations of the reactants are the same, it is not possible to tell whether the rate equation is of the form

$$\text{rate} = k[(CH_3)_3CCl]$$

or of the form $\text{rate} = k[OH^-]$

Suggest a further experiment which could be carried out to show that it is in fact first order with respect to the halogenoalkane.

(2)

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(d) In a further experiment to investigate the hydrolysis, a solution of 2-chloro-2-methylpropane in aqueous ethanol was prepared at room temperature. The pH of this solution was measured at intervals using narrow-range pH paper. The reaction occurring is

$$(CH_3)_3CCl + H_2O \rightarrow (CH_3)_3COH + H^+ + Cl^-$$

(i) Suggest what the initial pH of the mixture would be. Justify your answer.

(1)

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.....

(ii) The pH rapidly falls to 2 or lower. Explain why this confirms that the rate of the hydrolysis of 2-chloro-2-methylpropane is independent of the hydroxide ion concentration in the reaction

$$(CH_3)_3CCl + OH^- \rightarrow (CH_3)_3COH + Cl^-$$

(2)

(iii) Assuming that the reaction rate follows the rate equation

$$\text{rate} = k[(CH_3)_3CCl]$$

write the equation for the rate-determining step.

(2)

(Total for Question 2 = 17 marks)

3 Propyl ethanoate is an ester which has a smell similar to that of bananas or pears. It can be made in the laboratory from propan-1-ol and ethanoic acid. The equation for the reaction is

$$CH_3COOH + CH_3CH_2CH_2OH \rightleftharpoons CH_3COOCH_2CH_2CH_3 + H_2O$$

Procedure

1. Propan-1-ol (50 cm^3) and ethanoic acid (50 cm^3) are mixed thoroughly in a 250 cm^3 round-bottomed flask.
2. Concentrated sulfuric acid (10 cm^3) is added drop by drop to the mixture, keeping the contents of the flask well-shaken and cooled in an ice-water bath.
3. When the acid has all been added, a reflux condenser is fitted to the flask and the mixture gently boiled over an electric heating mantle for about 30 minutes.
4. The mixture is cooled, and the apparatus rearranged for distillation. The crude ester (about 60 cm^3) is distilled off.
5. The distillate is placed in a separating funnel and shaken with about half its volume of 30% sodium carbonate solution, with the pressure being released at intervals. The lower aqueous layer is then discarded.
6. The crude ester is shaken in a separating funnel with about half its volume of 50% calcium chloride solution, which removes unreacted alcohol. The lower layer is discarded.
7. The ester is run into a clean, dry flask containing some anhydrous calcium chloride and swirled.
8. The ester is filtered into a clean, dry flask, with a few anti-bumping granules, and distilled. The fraction boiling between 100 °C and 103 °C is collected.

(a) (i) Explain why the concentrated sulfuric acid is added slowly with **cooling**.

(1)

.....

.....

.....

(ii) Explain why the mixture is heated **under reflux** for **about 30 minutes**.

(2)

Under reflux.....

.....

For about 30 minutes.....

.....

(iii) What is the **main** function of the sulfuric acid in this reaction?

(1)

(iv) Suggest the identity of **two** impurities that might be present in the crude distillate from step 4.

(2)

(v) What data would you need about propyl ethanoate to be sure that the instruction in step 5 to discard the lower layer is correct?

(1)

(vi) Step 5 requires that you release the pressure at intervals. Explain why the pressure in the funnel increases.

(2)

(vii) Explain why anhydrous calcium chloride is added in step 8 and state how the appearance of the liquid changes when this stage is complete.

(2)

(viii) What is the reason for adding anti-bumping granules in step 8?

(1)

(b) (i) Use the data in the table below to show, by calculating the numbers of moles, which reactant is in excess.

(2)

Substance	Density / g cm^{-3}	Molar mass / g mol^{-1}
Ethanoic acid	1.05	60.1
Propan-1-ol	0.804	60.1

(ii) The mass of the ester collected was 35.0 g. Calculate the percentage yield of the ester propyl ethanoate.

Assume the molar mass of propyl ethanoate is 102 g mol^{-1}.

(2)

(c) A student who carried out this experiment, according to the instructions, obtained a product that boiled at 95 °C. The student suspected that the alcohol originally provided was not propan-1-ol, but was 2-methylpropan-2-ol, since that would have given an ester with this boiling temperature.

(i) Draw the structural formula for the ester that is formed from the reaction of ethanoic acid with 2-methylpropan-2-ol.

(1)

(ii) Suggest a simple test-tube experiment that the student could carry out on the original alcohol to see if the suspicion could be correct. Give the reagents used and the expected result for both propan-1-ol and 2-methylpropan-2-ol. Explain why the results are different.

(4)

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(Total for Question 3 = 21 marks)

TOTAL FOR PAPER = 50 MARKS