Cambridge Pre-U

Cambridge International Examinations
Cambridge Pre-U Certificate

CANDIDATE NAME	
CENTRE NUMBER	
CANDIDATE NUMBER	

0159522207

CHEMISTRY (PRINCIPAL) **9791/03**

Paper 3 Part B Written **May/June 2016**

2 hours 15 minutes

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.
DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.
Electronic calculators may be used.
You may lose marks if you do not show your working, if you do not use appropriate units or if you do not give your answer to appropriate significant figures.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	
2	
3	
4	
5	
Total	

The syllabus is approved for use in England, Wales and Northern Ireland as a Cambridge International Level 3 Pre-U Certificate.

This document consists of **20** printed pages and **4** blank pages.

CAMBRIDGE International Examinations

1 **(a)** The kinetic theory of gases makes assumptions about the behaviour of an ideal gas. Boyle and Charles were amongst the first scientists to make detailed experimental measurements of the behaviour of gases.

(i) State **three** assumptions of the kinetic theory of gases.

.....

.....

.....

.....[3]

(ii) State Boyle's law.

.....

.....[1]

(iii) State Charles's law.

.....

.....[1]

(iv) State the conditions of temperature and pressure under which you might expect the behaviour of a real gas to be **least** like that of an ideal gas. Explain your answers.

temperature .....

explanation .....

.....

.....

pressure .....

explanation .....

.....

.....
[3]

(v) Suggest the order in which you would expect the following real gases to deviate from the behaviour of an ideal gas. List the gas with the **most** ideal behaviour first. Explain your order.

CH_4, CH_3Cl, H_2, Cl_2

order ……>……>……>……
most ideal *least ideal*

explanation .....

.....

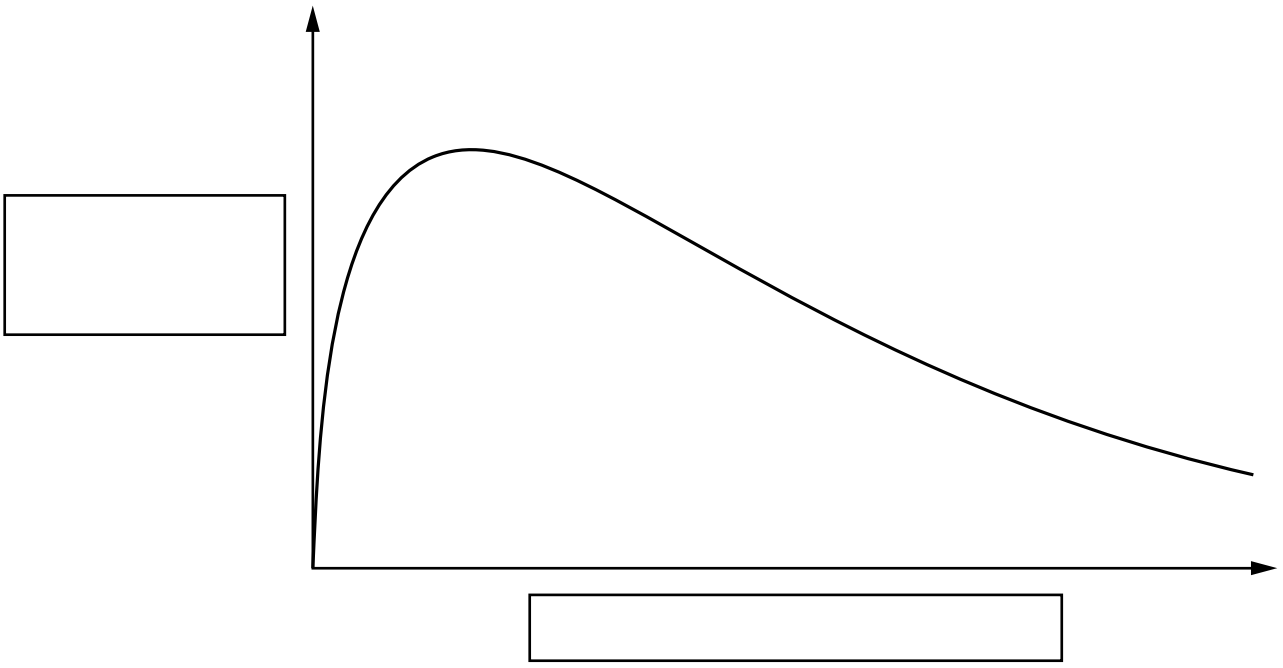
.....

.....

.....[4]

(b) The Boltzmann distribution was originally deduced theoretically and subsequently verified by experiment. It can be used to explain how the rate of reaction between gases varies with temperature.

(i) Label the axes on the Boltzmann distribution.



[2]

(ii) Draw and label a second curve on the axes above to represent the Boltzmann distribution for the same sample of gas at a **lower** temperature. [2]

(iii) Use the curves to explain the effect of temperature on reaction rate.

.....

.....

.....

.....[2]

(c) The kinetics of the gas phase reaction

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

were studied at a temperature of 80K in a 1.00 dm^3 flask and the initial reaction rates were measured for varying initial amounts of the reactants.

experiment	initial amount/mol		initial rate of NO_2 formation / $mol\,dm^{-3}\,s^{-1}$
	NO	O_2	
1	1.25×10^{-3}	1.25×10^{-3}	1.15×10^{-14}
2	2.50×10^{-3}	1.25×10^{-3}	4.61×10^{-14}
3	1.25×10^{-3}	2.50×10^{-3}	2.30×10^{-14}

(i) Explain how the data can be used to determine the orders of reaction with respect to NO and O_2 and hence derive the rate equation for this reaction.

.....

.....

.....

.....

.....

rate equation .....

[3]

(ii) Use the data from experiment 1 to calculate the value of the rate constant, *k*, at 80 K. Give the units of *k*.

k = ... units ..... [2]

(iii) Use the data from experiment 1 and the ideal gas equation to calculate the initial pressure in the flask.

pressure = ... Pa [2]

[Total: 25]

2 Some chemical reactions proceed to a dynamic equilibrium containing appreciable amounts of both reactants and products.

(a) (i) Give one characteristic of a dynamic equilibrium.

.....

.....[1]

(ii) State Le Chatelier's principle.

.....

.....

.....[1]

(b) Carbon dioxide and hydrogen react together to form an equilibrium mixture.

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

(i) Give the expression for K_c for this equilibrium.

$K_c =$

[1]

(ii) The values of K_c at two different temperatures are shown in the table.

temperature / °C	K_c
700	0.63
1000	1.66

State and explain what the values of K_c indicate about the enthalpy change for this reaction.

.....

.....[1]

(iii) State and explain the effect of increasing pressure on the position of this equilibrium.

.....

.....

.....[2]

(iv) 0.0100 mol of CO_2 and 0.0200 mol of H_2 were mixed and allowed to reach equilibrium at a temperature T. The final mixture contained 6.93×10^{-3} mol of H_2O.

Calculate the value of K_c at this temperature.

$K_c =$ ..... [3]

(c) A 0.100 mol sample of PCl_5 vapour was heated in a flask until the following equilibrium was established.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

The resulting mixture of gases was cooled rapidly to form solid PCl_5 and liquid PCl_3. The chlorine gas was pumped away and water was added to the mixture of chlorides to hydrolyse them. The following reactions occurred.

$$PCl_5(s) + 4H_2O(l) \longrightarrow 5HCl(aq) + H_3PO_4(aq)$$

$$PCl_3(l) + 3H_2O(l) \longrightarrow 3HCl(aq) + H_3PO_3(aq)$$

The solution resulting from hydrolysis of the chlorides was made up to 1.00 dm^3 and labelled solution **A**.

A 10.0 cm^3 sample of solution **A** required 31.40 cm^3 of 0.200 mol dm^{-3} sodium hydroxide solution, NaOH(aq), for neutralisation.

Assume that in the neutralisation 1 mole of H_3PO_4 reacts with 2 moles of NaOH.
Assume that in the neutralisation 1 mole of H_3PO_3 reacts with 2 moles of NaOH.

(i) Calculate the total amount, in mol, of $OH^-(aq)$ needed for neutralisation of the 1.00 dm^3 of solution **A**.

amount of OH^- (aq) = ... mol [2]

(ii) Calculate the amount, in mol, of PCl_5 in the equilibrium mixture.

amount of PCl_5 = ... mol [3]

[Total: 14]

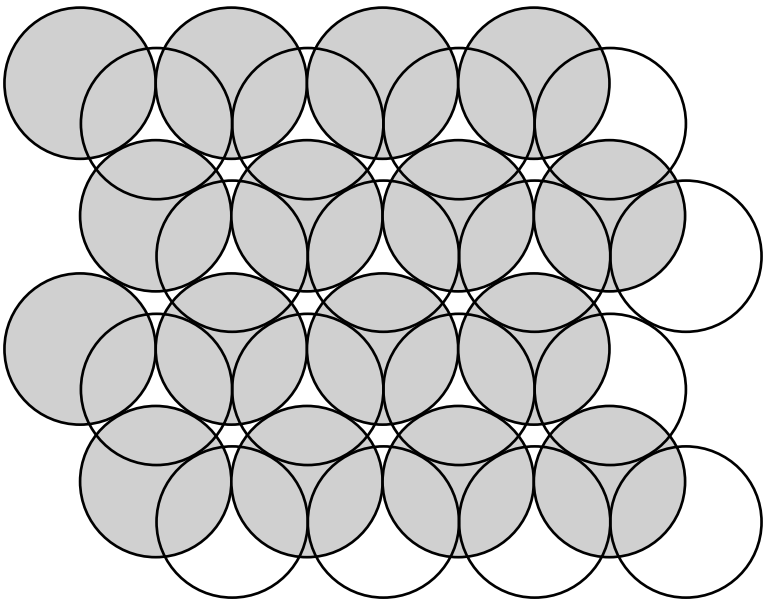
3 **(a)** Most metals have a close-packed structure based on one of two possible arrangements of atoms, CCP or HCP.

(i) What is the co-ordination number of an atom in a close-packed structure?

..... [1]

(ii) Both of the close-packed structures can be represented as a layer structure.

Two layers are shown with the shaded circles representing atoms in the first layer and the unshaded circles representing atoms in the second layer.



Add labels to the diagram to show clearly the positions of

- the centres of **two** atoms in the third layer of a CCP structure, labelled *,
- a tetrahedral hole, labelled **T**,
- an octahedral hole, labelled **O**.

[3]

(iii) In terms of the type of holes occupied and the ratio of holes to ions, describe the lattice structure of calcium fluoride.

.....

.....

.....[2]

(b) Tin forms two chlorides, $SnCl_2$ and $SnCl_4$.

(i) A sample of a mixture of these chlorides was found to contain 50.0% by mass of tin.

Calculate the percentage by mass of $SnCl_2$ in the sample.
You must show your working.

% = ... [3]

(ii) Heating tin with hydrochloric acid produces hydrogen gas. Careful evaporation of the water and dehydration with ethanoic anhydride produces white solid $SnCl_2$.

Passing chlorine gas over heated tin produces colourless liquid $SnCl_4$ as the only product.

Discuss whether the following standard electrode potentials support the production of $SnCl_2$ with hydrochloric acid and the production of $SnCl_4$ with chlorine.

$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$ $\quad E^\ominus = -0.14V$

$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$ $\quad E^\ominus = 0.00V$

$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$ $\quad E^\ominus = +0.15V$

$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $\quad E^\ominus = +1.36V$

.....

.....

.....

.....

.....

.....[3]

(c) Each element in Group 14 can form a monoxide.

(i) Draw a dot-cross diagram, showing outer-shell electrons only, to show the bonding in carbon monoxide, CO.

[1]

(ii) State and explain the trend in the type of **bonding** in the monoxides down Group 14.

.....

.....

.....

.....[2]

[Total: 15]

4 **(a)** Heating 1-bromopropane under reflux with potassium cyanide in ethanol produces butanenitrile.

$$CH_3CH_2CH_2Br + CN^- \longrightarrow CH_3CH_2CH_2CN + Br^-$$

(i) This reaction proceeds via a transition state.

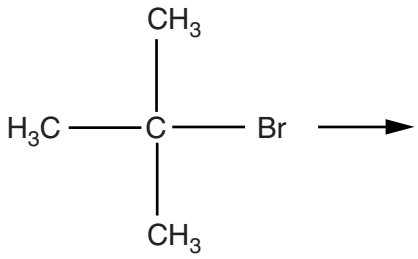
Draw the first step of the mechanism leading to the formation of the transition state. Include all relevant lone pairs of electrons, dipoles and curly arrows.

Draw the three-dimensional structure of the transition state and give the bond angles. Represent the ethyl group as C_2H_5.

[5]

(ii) Complete the first step of the mechanism for the reaction of 2-methyl-2-bromopropane with cyanide ions. Include all relevant lone pairs of electrons, dipoles and curly arrows.

Explain why the mechanism is different from that of the reaction involving 1-bromopropane with cyanide ions.



.....

.....

.....

[3]

(b) Butanenitrile, C_3H_7CN, reacts with aqueous acid to form an intermediate compound, **S**, which then reacts further to form compound **T**.

(i) Write an equation to show the formation of **S** from C_3H_7CN.

.....[1]

(ii) Write an equation to show the formation of **T** from **S**.

.....[1]

(iii) Identify the type of reaction involved in the overall conversion of C_3H_7CN to **T**.

Justify your answer with reference to functional group level.

.....

.....

.....[2]

(c) Butanenitrile, C_3H_7CN, reacts with lithium tetrahydridoaluminate, $LiAlH_4$, to form compound **U**.

Identify **U** and the type of reaction involved in the conversion of C_3H_7CN to **U**.

Justify your answer with reference to functional group level.

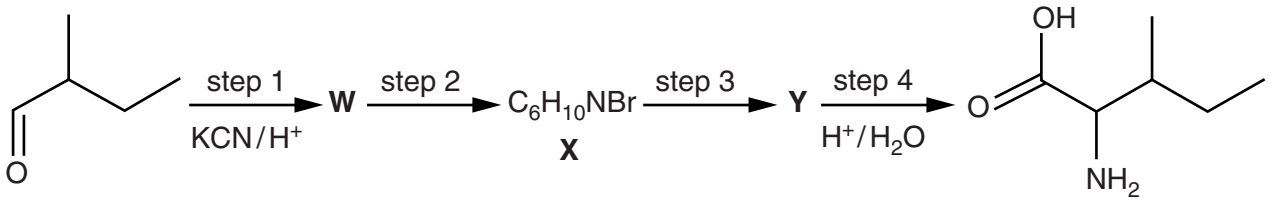
.....

.....

.....[3]

(d) A nitrile group can react with carbonyl compounds. This reaction can form the basis for the synthesis of amino acids.

The amino acid isoleucine can be prepared by a four-step sequence starting from 2-methylbutanal and cyanide ions.



(i) Give the full name of the reaction mechanism involved in step 1.

.....[1]

(ii) Draw the **skeletal** formula for **W**.

[1]

(iii) Suggest the full name of the reaction mechanism involved in step 2.

.....[1]

(iv) State the reagent needed for step 2.

.....[1]

(v) State the reagents and conditions needed for step 3.

.....

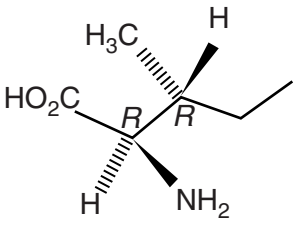
.....[2]

(vi) Give the **structural** formula of **Y**.

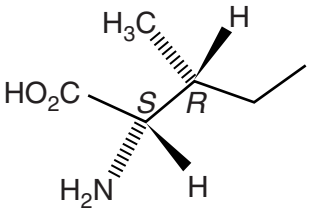
.....[1]

[Turn over

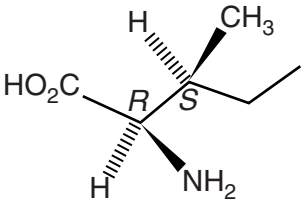
(vii) There are four stereoisomers of isoleucine.



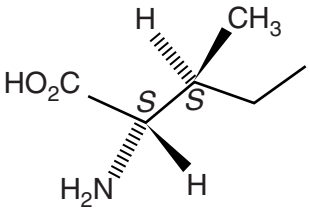
A



B



C



D

Identify by letter all those **pairs** of isomers that are either enantiomers or diastereoisomers of each other.

enantiomers .....

diastereoisomers .....

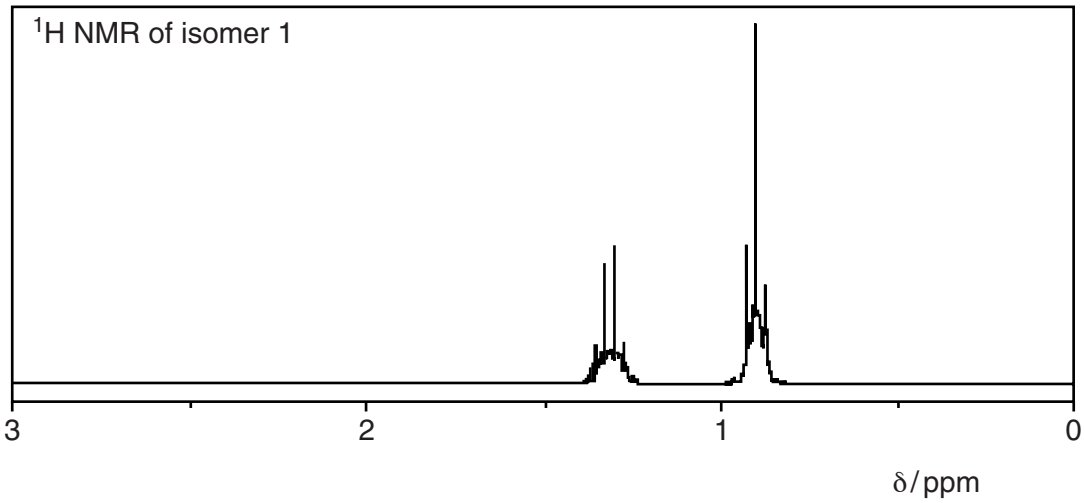
[3]

[Total: 25]

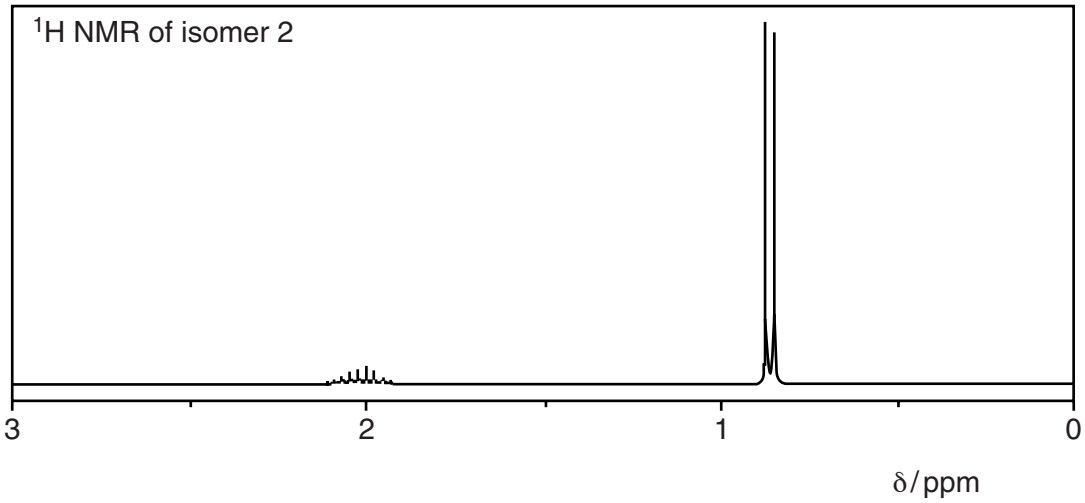
BLANK PAGE

5 **(a)** Two hydrocarbons have a molecular ion peak at m/z of 58.

The ^{1}H NMR spectrum of isomer 1 may be analysed by seeing that it consists predominantly of a triplet and a quartet.



The ^{1}H NMR spectrum of isomer 2 consists of a doublet and a dectet (10 peaks).



(i) What is the molecular formula of both isomers?

.....[1]

(ii) Give the structural formula of each isomer and explain the splitting patterns of the signals in each ^{1}H NMR spectrum.

isomer 1

.....

.....

.....

isomer 2

.....

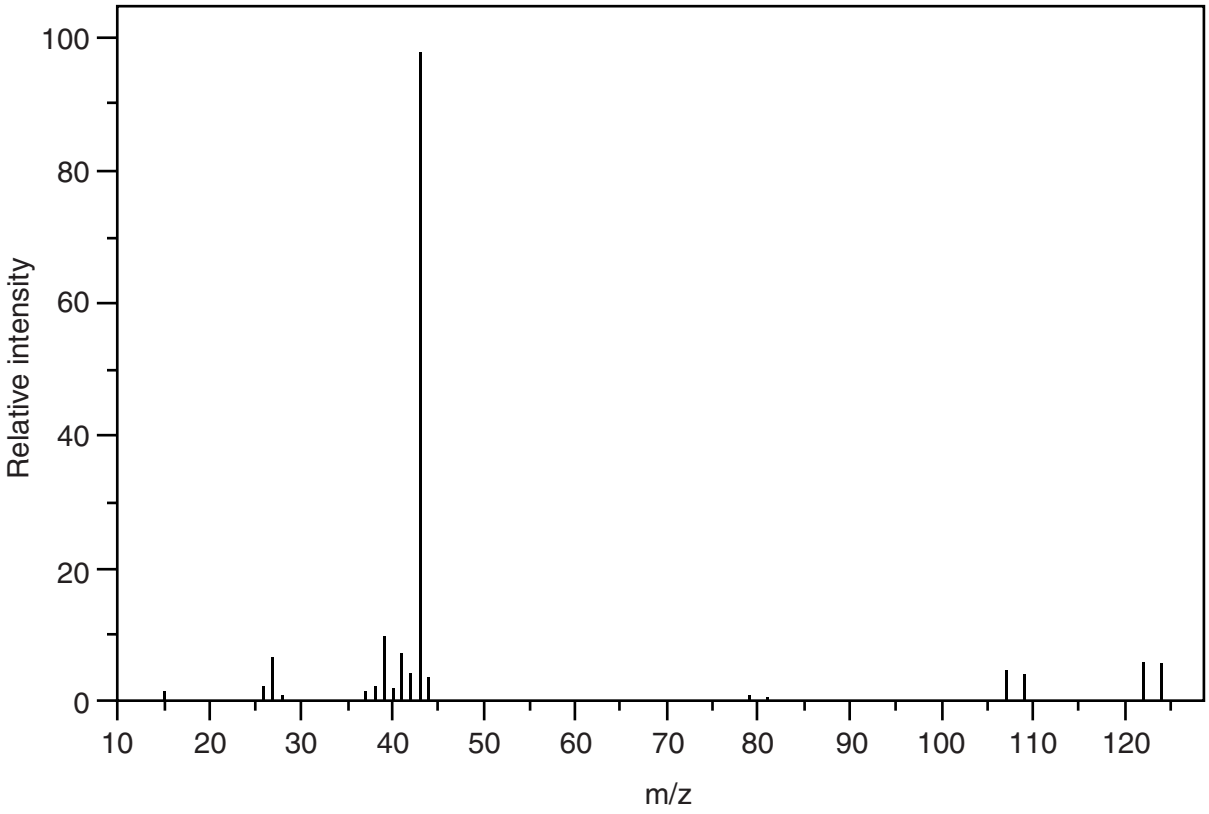
.....

.....

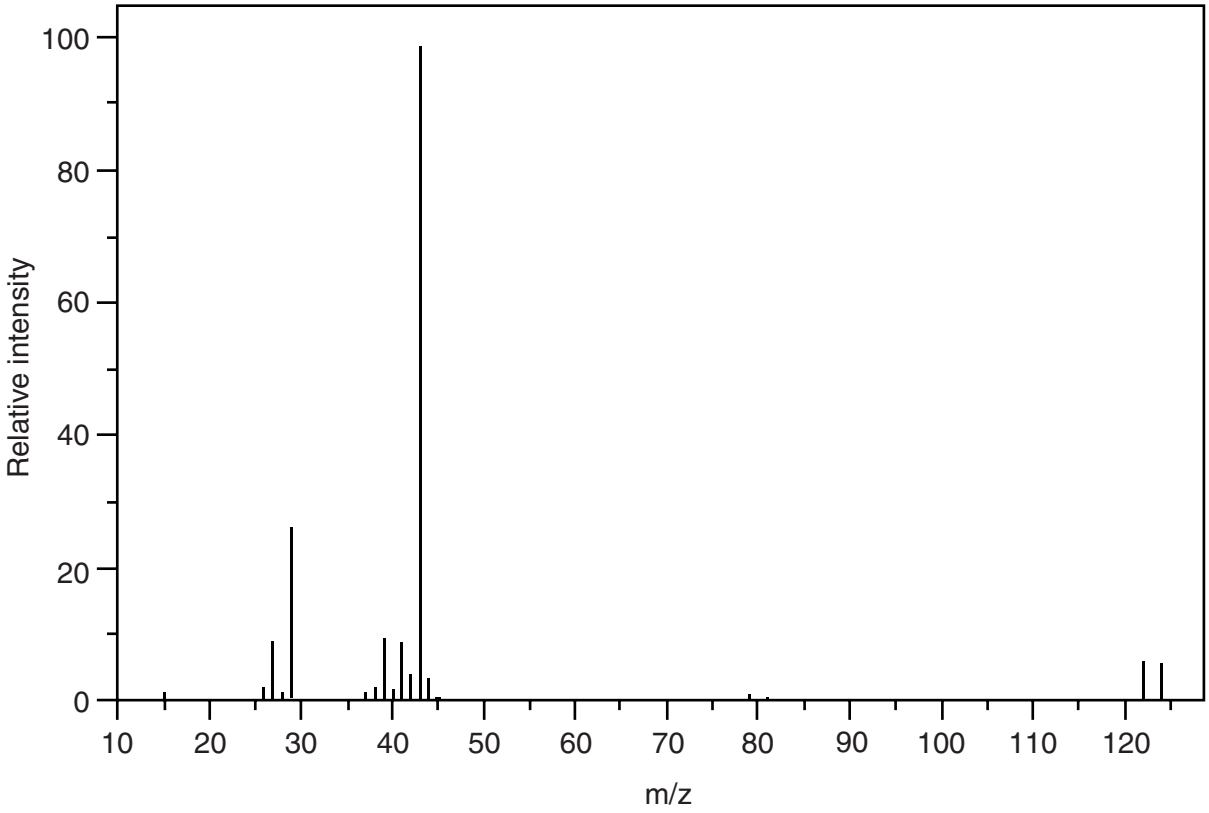
[3]

(b) Two isomeric halogenoalkanes have the mass spectra shown.

Isomer 3 has key peaks at m/z values of 124, 122, 109, 107 and 43.



Isomer 4 has key peaks at m/z values of 124, 122, 43 and 29.



(i) Explain the significance of the peaks at m/z 124 and 122 in both spectra and their equal relative intensities.

.....

.....

.....[2]

(ii) What is the molecular formula of the two isomers?

.....[1]

(iii) Give the structural formulae of isomers 3 and 4 and explain your choice by referring to the key peaks which are unique to each spectrum.

isomer 3

isomer 4

explanation .....

.....

.....

.....
[3]

(iv) Starting from the molecular ion, write an equation to explain the formation of the fragment responsible for the peak at m/z 43.

.....[2]

(c) Three unbranched carbonyl compounds have the molecular formula $C_5H_{10}O$.

Each is converted to an alcohol by reaction with anhydrous ethyl magnesium bromide, followed by acid hydrolysis.

Isomer 5 forms a chiral secondary alcohol.

Isomer 6 forms a chiral tertiary alcohol.

Isomer 7 forms a tertiary alcohol that is not chiral.

(i) Give the structural formula of each isomer and the structural formula of the alcohol formed from it.

isomer 5	alcohol formed from isomer 5
isomer 6	alcohol formed from isomer 6
isomer 7	alcohol formed from isomer 7

[3]

(ii) Write an equation for the overall reaction of methanal with ethyl magnesium bromide, followed by hydrolysis.

.....[2]

(d) Four aromatic compounds have the molecular formula C_7H_8O.

All four isomers react with sodium to form hydrogen gas.

Isomers 8, 9 and 10 react with sodium hydroxide to form salts, but isomer 11 does not.

The ^{13}C NMR spectrum of isomer 8 and isomer 9 both show seven separate signals.

The ^{13}C NMR spectrum of isomer 10 only shows five signals.

(i) Suggest a possible structure for each isomer.

isomer 8 isomer 9

isomer 10 isomer 11

[3]

(ii) Give approximate chemical shift values for the peaks you would expect to see in the ^{13}C NMR spectrum of isomer 11.

.....

.....[1]

[Total: 21]

BLANK PAGE

BLANK PAGE

BLANK PAGE