UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS
General Certificate of Education Advanced Level

CANDIDATE NAME									
CENTRE NUMBER						CANDIDATE NUMBER				

3430056738

CHEMISTRY **9701/42**

Paper 4 Structured Questions **October/November 2010**

1 hour 45 minutes

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions.

Section B
Answer **all** questions.

You may lose marks if you do not show your working or if you do not use appropriate units.
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	
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7	
8	
9	
Total	

This document consists of **17** printed pages and **3** blank pages.

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Section A

For Examiner's Use

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

1 **(a)** Write a balanced equation for the reaction of each of the following chlorides with water.

phosphorus(V) chloride .....

silicon(IV) chloride.....
[2]

(b) When sulfur is heated under pressure with chlorine, the major product is SCl_2 (Cl-S-Cl).

$$S_8(g) + 8Cl_2(g) \longrightarrow 8SCl_2(g)$$

Use data from the *Data Booklet* to calculate the enthalpy change, ΔH, for this reaction. The eight sulfur atoms in the S_8 molecule are all joined in a single ring by single bonds.

ΔH = ...kJ mol^{-1}
[2]

(c) Under suitable conditions, SCl_2 reacts with water to produce a yellow precipitate of sulfur and a solution **A**. Solution **A** contains a mixture of SO_2(aq) and compound **B**.

(i) What is the oxidation number of sulfur in SCl_2?.....

(ii) Work out how the oxidation number of sulfur changes during the reaction of SCl_2 with water.

.....

.....

(iii) Suggest the identity of compound **B**. .....

(iv) Construct an equation for the reaction between SCl_2 and water.

.....

(v) What would you observe when each of the following reagents is added to separate samples of solution **A**?

$AgNO_3$(aq).....

$K_2Cr_2O_7$(aq) .....
[7]

[Total: 11]

2 **(a)** **(i)** What is meant by the term *ligand* in the context of transition element chemistry?

For Examiner's Use

.....

.....

(ii) Decide which of the following species could be a ligand, and which could not be. Place a tick (✓) in the appropriate column.

species	can be a ligand	cannot be a ligand
OH^-		
NH_4^+		
CH_3OH		
CH_3NH_2		

[3]

(b) Read the following description of some reactions of copper(II) sulfate, and answer the questions that follow.

When 0.1 mol of white anhydrous $CuSO_4$ is dissolved in liquid ammonia at –33 °C, a deep blue solution **C** results.
When 0.2 mol of solid NaOH is added to solution **C**, and the ammonia solvent allowed to evaporate, a solid residue is obtained.
Heating this residue to 200 °C produces a dark coloured mixture of two solids.
When water is added to this mixture, a black solid **D** and a colourless solution **E** are formed. Neither **D** nor **E** contains nitrogen.
Adding $BaCl_2$(aq) to solution **E** produces a white precipitate **F**.
Solid **D** dissolves in HNO_3(aq) on warming, without evolution of gas, to give a pale blue solution containing $Cu(NO_3)_2$(aq).

(i) Suggest the formula of the compound contained in each of the following.

solution **C** .....

solid **D** .....

solution **E** .....

white precipitate **F** .....

(ii) Name the type of reaction that is occurring when **D** reacts with HNO_3(aq).

.....

[5]

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(c) (i) Describe what you would observe when a solid sample of anhydrous $Cu(NO_3)_2$ is strongly heated.

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.....

.....

(ii) Write an equation for this reaction.

.....

[2]

[Total: 10]

3 The electrolytic purification of copper can be carried out in an apparatus similar to the one shown below.

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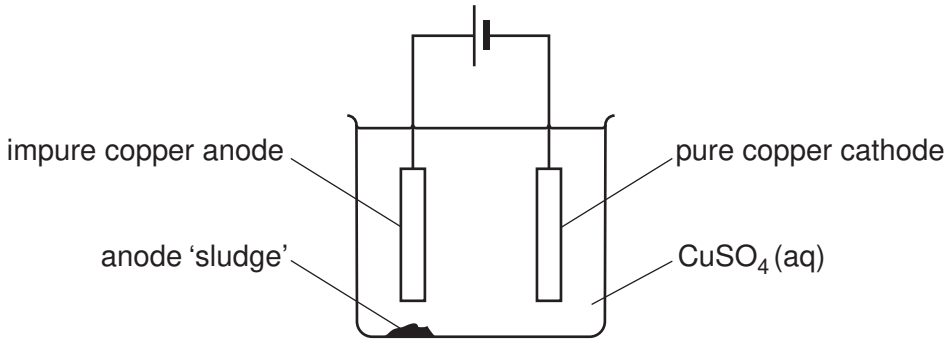

The impure copper anode contains small quantities of metallic nickel, zinc and silver, together with inert oxides and carbon resulting from the initial reduction of the copper ore with coke. The copper goes into solution at the anode, but the silver remains as the metal and falls to the bottom as part of the anode 'sludge'. The zinc also dissolves.

(a) (i) Write a half equation including state symbols for the reaction of copper at the anode.

.....

(ii) Use data from the *Data Booklet* to explain why silver remains as the metal.

.....

(iii) Use data from the *Data Booklet* to predict what happens to the nickel at the anode.

.....

.....

(iv) Write a half equation including state symbols for the main reaction at the cathode.

.....

(v) Use data from the *Data Booklet* to explain why zinc is not deposited on the cathode.

.....

.....

(vi) Suggest why the blue colour of the electrolyte slowly fades as the electrolysis proceeds.

.....

.....

[7]

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(b) Most of the current passed through the cell is used to dissolve the copper at the anode and precipitate pure copper onto the cathode. However, a small proportion of it is 'wasted' in dissolving the impurities at the anode which then remain in solution.
When a current of 20.0 A was passed through the cell for 10.0 hours, it was found that 225 g of pure copper was deposited on the cathode.

(i) Calculate the following, using appropriate data from the *Data Booklet*.

- number of moles of copper produced at the cathode

- number of moles of electrons needed to produce this copper

- number of moles of electrons that passed through the cell

(ii) Hence calculate the percentage of the current through the cell that has been 'wasted' in dissolving the impurities at the anode.

[4]

(c) Nickel often occurs in ores along with iron. After the initial reduction of the ore with coke, a nickel-iron alloy is formed.
Use data from the *Data Booklet* to explain why nickel can be purified by a similar electrolysis technique to that used for copper, using an impure nickel anode, a pure nickel cathode, and nickel sulfate as the electrolyte. Explain what would happen to the iron during this process.

.....

.....

.....

.....[2]

[Total: 13]

4 The most typical oxides of tin and lead are SnO, SnO_2, PbO and PbO_2.

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The following two generalisations can be made about the oxides of the elements in Group IV.

- As the metallic character of the elements increases down the Group, the oxides become more basic.
- The oxides of the elements in their higher oxidation states are more acidic than the oxides of the elements in their lower oxidation states.

(a) Use these generalisations to suggest which of the above oxides of tin or lead is **most likely** to react with each of the following reagents. In each case write a balanced equation for the reaction.

(i) with NaOH(aq)

formula of oxide .....

equation .....

(ii) with HC*l*(aq)

formula of oxide .....

equation .....

[4]

(b) 'Red lead' is used as a pigment, and as a metal primer paint to prevent the corrosion of steel. It is an oxide of lead that contains 9.30% oxygen by mass.

Calculate to **3 significant figures** the number of moles of oxygen and lead contained in a 100.0 g sample of red lead. Hence calculate its empirical formula.

empirical formula: .....[2]

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(c) Lead(II) chloride is slightly soluble in water.

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$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq) \qquad K_{sp} = 2.0 \times 10^{-5}$$

(i) Write an expression for the solubility product, K_{sp} for lead(II) chloride and state its units.

K_{sp} = ... units .....

(ii) Calculate $[Pb^{2+}(aq)]$ in a saturated solution of $PbCl_2$.

.....

.....

An excess of $PbCl_2(s)$ is stirred with 0.50 mol dm^{-3} $NaCl$ until equilibrium has been established. The excess $PbCl_2(s)$ is then filtered off.

(iii) Assuming $[Cl^-]$ remains at 0.50 mol dm^{-3} throughout, calculate the $[Pb^{2+}(aq)]$ in the remaining solution.

.....

.....

(iv) Suggest an explanation for the difference between this value and the value that you calculated in **(ii)**.

.....

[4]

[Total: 10]

5 **(a)** Compound **G** can be synthesised from benzene by the route shown below.

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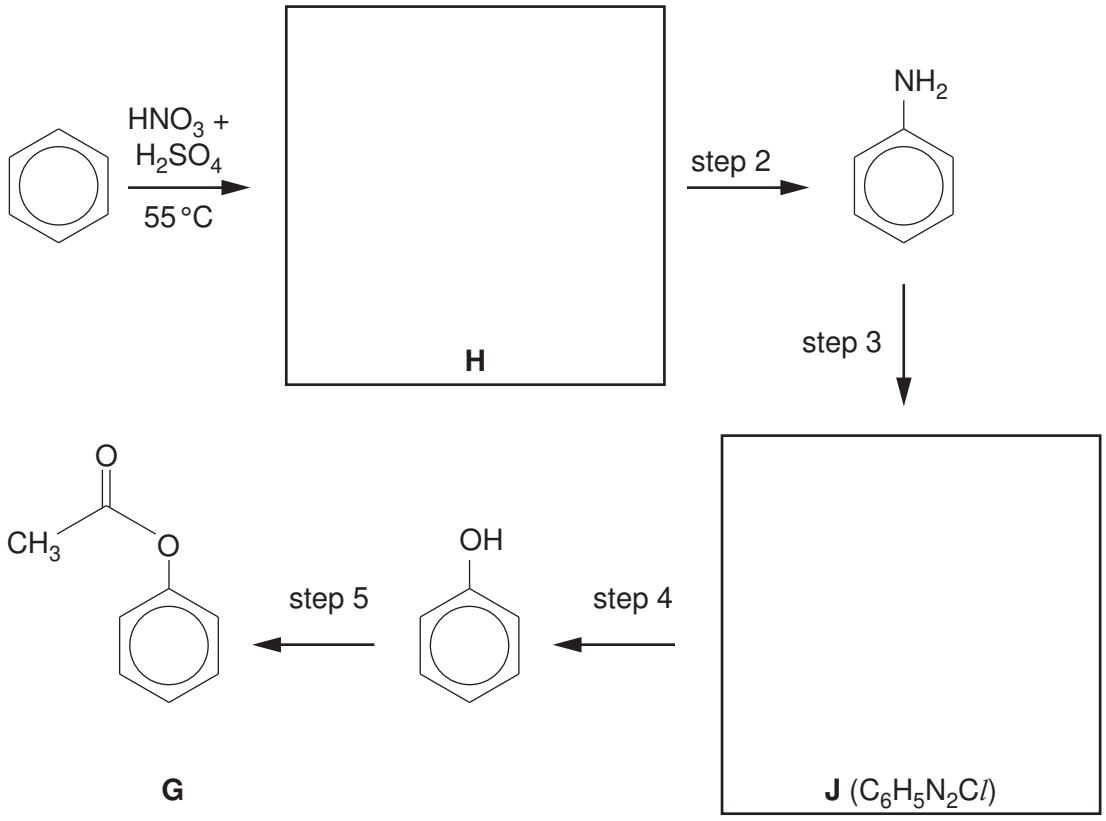

(i) **Name** the functional group formed in step 5.

.....

(ii) Draw the structures of the intermediates **H** and **J** in the boxes above.

(iii) Suggest reagents and conditions for the following.

step 2 .....

step 3 .....

step 4 .....

step 5 .....

[7]

(b) In a reaction discovered just over 100 years ago by the German chemist Karl Fries, compound **G** is converted into compound **K** when it is heated with $AlCl_3$. Compound **K** is a structural isomer of **G**.

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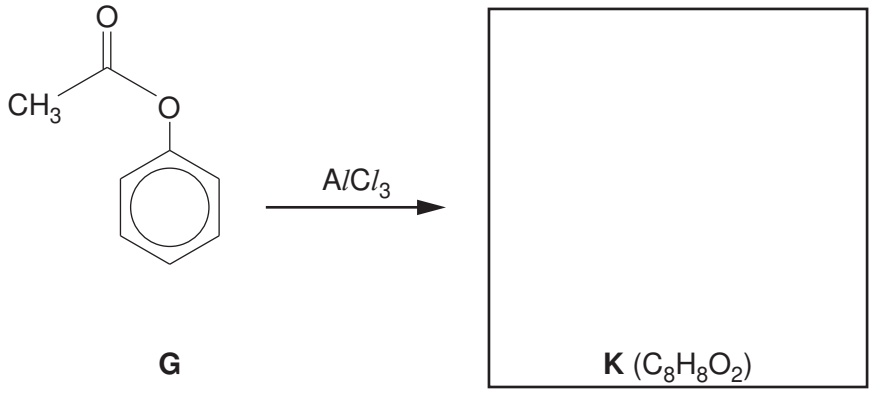


Compound **K** is a 1,4-disubstituted benzene derivative. It is insoluble in water, but dissolves in NaOH(aq). It gives a white precipitate with Br_2(aq), and a yellow precipitate with alkaline aqueous iodine.

(i) What is meant by the term *structural isomerism*?

.....

.....

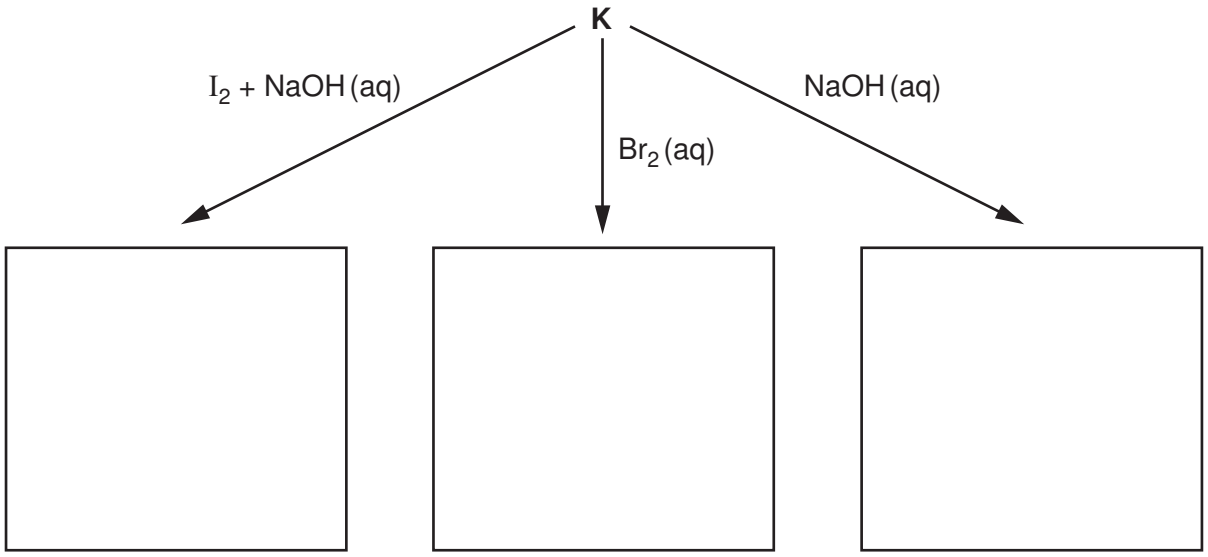
(ii) Use the information given above to **name** two functional groups in compound **K**.

.....

.....

(iii) Suggest the structural formula of **K**, and draw it in the box above.

(iv) Suggest structures for the aromatic products of the following reactions.



[7]

[Total: 14]

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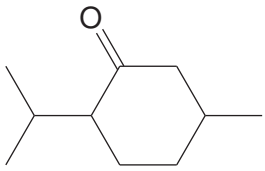
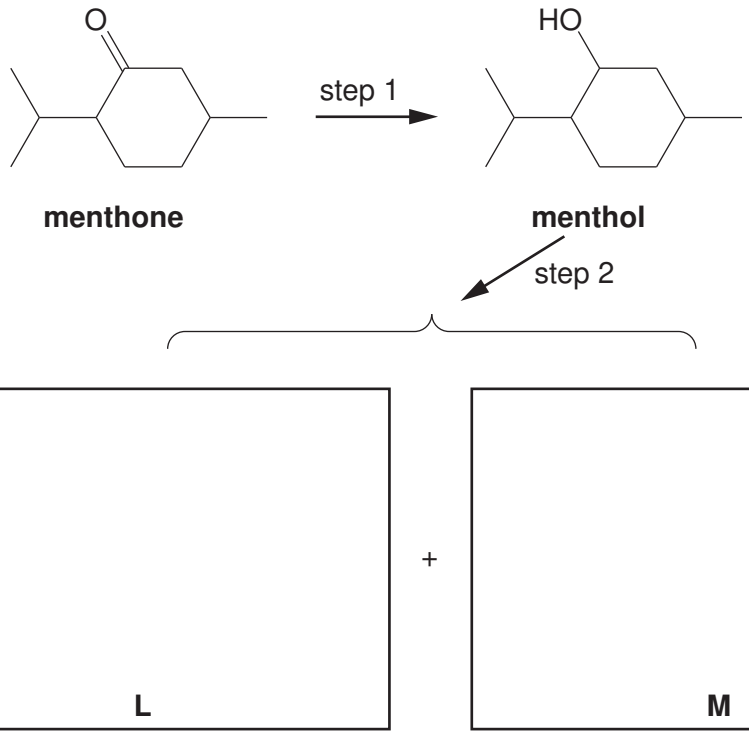
6 Menthone, $C_{10}H_{18}O$, is a cyclic ketone that occurs in oil of peppermint.



menthone

(a) Use asterisks (*) on the formula above to identify any chiral centres in the molecule of menthone. [2]

(b) Menthone can be reduced to menthol, which can be dehydrated to a mixture of two alkenes, **L** and **M**.



(i) Suggest reagents for

step 1, ...

step 2. .....

(ii) Suggest structures for **L** and **M** and draw them in the boxes above. [4]

(c) When heated with concentrated, acidified $KMnO_4(aq)$, one of the two alkenes **L** or **M** produces the dicarboxylic acid **N**.

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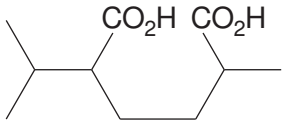


N

(i) Give the letter of the alkene that produced **N** by this reaction.

.....

(ii) Suggest the structure of the product, **P**, of the reaction between the other alkene you have drawn and hot concentrated acidified $KMnO_4$.

P

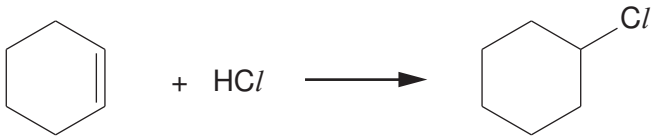
(iii) Suggest **one** chemical test that would enable you to distinguish between **N** and **P**.

reagent(s).....

observation.....

[3]

(d) Chlorocyclohexane can be prepared by bubbling HC*l*(g) through a solution of cyclohexene.



Suggest the mechanism of this 2-stage reaction by means of a diagram. Include all whole or partial charges, and represent the movements of electron pairs by curly arrows.

[3]

[Total: 12]

Section B

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

7 Whilst small amounts of some metal ions are vital in the human body, others can be highly toxic.

(a) Hg^{2+} ions are toxic for a number of reasons. Hg^{2+} ions can react with the R–S–S–R group, which is found in proteins.

$$R–S–S–R + 2Hg^{2+} + H_2 \longrightarrow 2\ R–S–Hg^{+} + 2H^{+} \qquad \text{reaction 1}$$

(i) What is the name of the R–S–S–R group in proteins?

.....

(ii) Which level of protein structure will be affected by reaction 1?

.....

.....

(iii) Why will this affect the activity of an enzyme?

.....

.....

[3]

(b) Ag^{+} ions can combine with free –COOH groups in the side chains of the amino acid residues in proteins to form partially covalent silver carboxylates.

$$RCOOH + Ag^{+} \longrightarrow RCOOAg + H^{+} \qquad \text{reaction 2}$$

(i) What type of behaviour is the –COOH group showing in reaction 2?

.....

.....

(ii) What types of R group interactions will be affected by reaction 2? Explain your answer.

.....

.....

.....

.....

.....

[4]

(c) By contrast, iron is an extremely important metal used in haemoglobin to transport oxygen molecules from the lungs to muscle cells and to carry carbon dioxide in the reverse direction.

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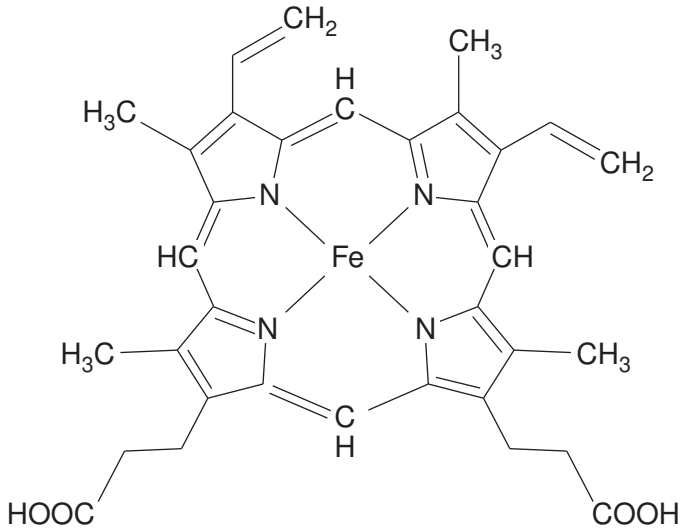
One haemoglobin molecule contains four haem groups, each of which contains one iron atom. In the haem group four nitrogen atoms are in the same plane as the iron atom. The oxygen molecule is attached above this plane, and the iron atom is joined to a protein chain below this plane.



haem

(i) How many oxygen **atoms** could one haemoglobin molecule transport?

.....

(ii) By what type of bonding is the oxygen molecule likely to be held to the iron atom in haem?

.....

(iii) What is the geometry of bonding around the iron atom?

.....

[3]

[Total: 10]

For Examiner's Use

8 **(a)** NMR spectroscopy and X-ray crystallography are two techniques that use electromagnetic radiation to look at the structures of large molecules.

For each technique state the sub-atomic particle involved, and explain how this particle interacts with the radiation.

NMR.....

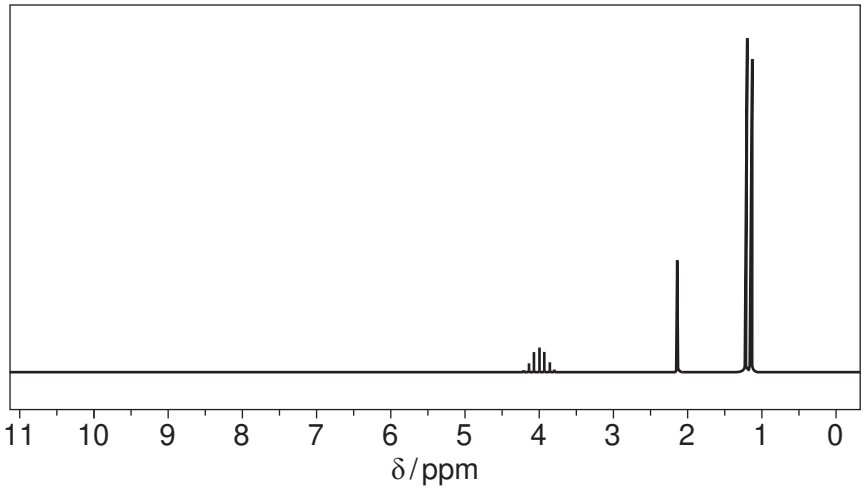
.....

X-ray .....

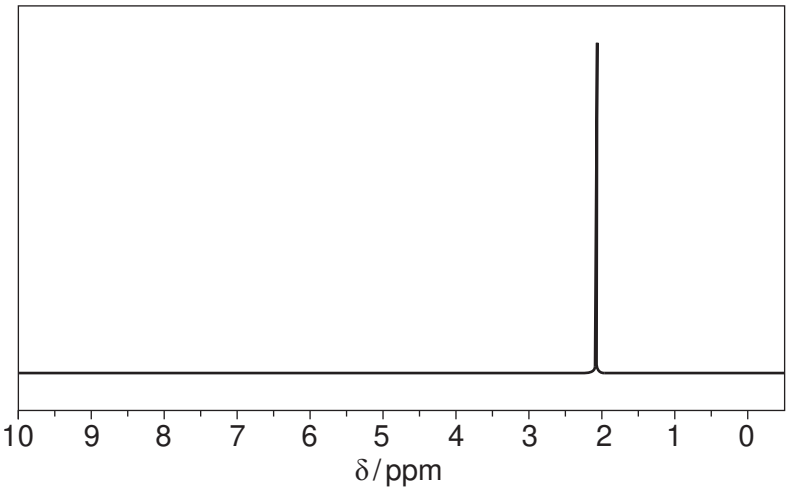
.....

[4]

(b) The two NMR spectra **1** and **2** were obtained before and after an alcohol, **Y**, was oxidised to give compound **Z**. The numbers of hydrogen atoms responsible for each peak have **not** been shown. All the peaks have been shown.



1



2

(i) State which spectrum, **1** or **2**, was produced by the alcohol, giving a reason for your answer.

For Examiner's Use

spectrum .....

reason .....

.....

(ii) The mass spectrum of **Y** showed an M : M + 1 peak ratio of 17.6:0.6.
Use this and other information in the question to suggest the identities of both **Y** and **Z**.

(iii) Draw a displayed formula for **Y** in the box provided

Y is

(iv) Explain why the NMR spectrum of **Z** only shows one peak.

.....

.....

[7]

[Total: 11]

For Examiner's Use

9 A possible source of energy for the road vehicles of the future is hydrogen. One of the problems still to be solved is the storage of the hydrogen in the vehicle. A conventional tank holding liquid hydrogen would have to be pressurised and refrigerated. In a crash, this type of tank could break resulting in the rapid release of hydrogen and an explosion.

One alternative is to use a fuel tank packed with carbon nanotubes. The hydrogen in the tank would be adsorbed onto the surface of the nanotubes at a pressure of no more than a few atmospheres.

(a) (i) What is the approximate width of a carbon nanotube?

.....

(ii) In what structural form is the carbon in a nanotube?

.....

(iii) What forces could be responsible for holding the hydrogen on the surface of the nanotubes? Explain your answer.

.....

.....

.....

[4]

(b) The hydrogen atoms in a fuel tank packed with nanotubes are closer together than in liquid hydrogen. Suggest **one** advantage of this.

.....

.....[1]

(c) When a nanotube-packed fuel tank is full of hydrogen there is a steady pressure of hydrogen in the tank. While hydrogen gas is being removed from the fuel tank to power the car, the pressure in the fuel tank drops very little for some time. State Le Chatelier's principle, and suggest how it explains this observation.

.....

.....

.....

.....

.....

.....[4]

[Total: 9]

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