UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS
General Certificate of Education
Advanced Subsidiary Level and Advanced Level

CANDIDATE NAME	

CENTRE NUMBER					

CANDIDATE NUMBER			

CHEMISTRY   **9701/42**

Paper 4 Structured Questions   **October/November 2012**

                                                                                  2 hours

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 a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.
DO **NOT** WRITE IN 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	
2	
3	
4	
5	
6	
7	
8	
Total	

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

UNIVERSITY *of* CAMBRIDGE
International Examinations

[Turn over

Section A

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

1 (a) Write down what you would see, and write equations for the reactions that occur, when silicon(IV) chloride and phosphorus(V) chloride are separately mixed with water.
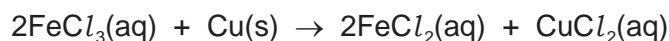
silicon(IV) chloride

....

....

phosphorus(V) chloride

....

....

[4]

(b) Iron(III) chloride, $FeCl_3$, is used to dissolve unwanted copper from printed circuit boards (PCBs) by the following reaction.

$$2FeCl_3(aq) + Cu(s) \rightarrow 2FeCl_2(aq) + CuCl_2(aq)$$

A solution in which $[Fe^{3+}(aq)]$ was originally equal to $1.50\,mol\,dm^{-3}$ was re-used several times to dissolve copper from the PCBs, and was then titrated as follows.

A $2.50\,cm^3$ sample of the partially-used-up solution was acidified and titrated with $0.0200\,mol\,dm^{-3}$ $KMnO_4$.
This oxidised any $FeCl_2$ in the solution back to $FeCl_3$.
It was found that $15.0\,cm^3$ of $KMnO_4(aq)$ was required to reach the end point.

(i) Construct an ionic equation for the reaction between Fe^{2+} and MnO_4^- in acid solution.

....

(ii) State here the $Fe^{2+} : MnO_4^-$ ratio from your equation in **(i)**. ....

(iii) Calculate the number of moles of MnO_4^- used in the titration.

**(iv)** Calculate the number of moles of Fe^{2+} in $2.50\,cm^3$ of the partially-used-up solution.

(v) Calculate the $[Fe^{2+}]$ in the partially-used-up solution.

(vi) Calculate the mass of copper that could still be dissolved by 100 cm³ of the partially-used-up solution.

mass of copper = ... g

[6]

(c) When $SiCl_4$ vapour is passed over Si at red heat, Si_2Cl_6 is formed. Si_2Cl_6 contains a Si-Si bond.
The reaction of Si_2Cl_6 and Cl_2 re-forms $SiCl_4$.

$$Si_2Cl_6(g) \; + \; Cl_2(g) \; \rightarrow \; 2SiCl_4(g)$$
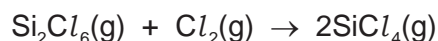
Use bond energy data from the *Data Booklet* to calculate $\Delta H^\ominus$ for this reaction.

$\Delta H^\ominus$ = ... kJ mol⁻¹
[2]

(d) Calcium forms three calcium silicides, Ca_2Si, $CaSi$ and $CaSi_2$. The first of these reacts with water as follows.

.........Ca_2Si + ...H_2O → ....$Ca(OH)_2$ + ...SiO_2 + ...H_2

(i) Balance this equation. You may find the use of oxidation numbers helpful.

(ii) During this reaction, state

which element(s) have been oxidised, ...

which element(s) have been reduced. ....
[2]

[Total: 14]

2 (a) The diagram below shows an incomplete experimental set-up needed to measure the E_{cell} of a cell composed of the standard Cu^{2+}/Cu electrode and an Ag^+/Ag electrode.

copper electrode

solution **A**

electrode **B**

saturated solution of $AgCl$

solid $AgCl$
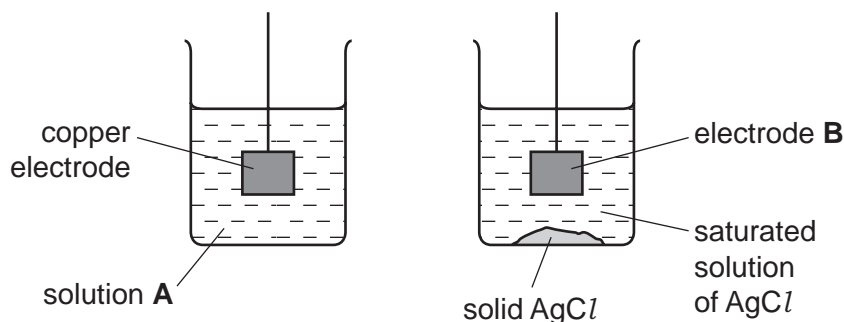
(i) State the chemical composition of

solution **A**, ...

electrode **B**. ....

(ii) Complete the diagram to show the whole experimental set-up.

[4]

(b) The above cell is not under standard conditions, because the $[Ag^+]$ in a saturated solution of $AgCl$ is much less than $1.0\,mol\,dm^{-3}$. The $E_{electrode}$ is related to $[Ag^+]$ by the following equation.

equation 1 $\qquad E_{electrode} = E^{\ominus}_{electrode} + 0.06\,\log[Ag^+]$

(i) Use the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ if the cell was operating under standard conditions.

$E^{\ominus}_{cell} = $ V

In the above experiment, the E_{cell} was measured at +0.17V.

(ii) Calculate the value of $E_{electrode}$ for the Ag^+/Ag electrode in this experiment.

....

(iii) Use equation 1 to calculate $[Ag^+]$ in the saturated solution.

$[Ag^+] = $ .... $mol\,dm^{-3}$

[3]

(c) (i) Write an expression for K_{sp} of silver sulfate, Ag_2SO_4, including units.

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

Using a similar experimental set-up to that illustrated opposite, it is found that $[Ag^+]$ in a saturated solution of Ag_2SO_4 is $1.6 \times 10^{-2}\,mol\,dm^{-3}$.

(ii) Calculate the value of K_{sp} of silver sulfate.

K_{sp} = ...
[3]

(d) Describe how the colours of the silver halides, and their relative solubilities in $NH_3(aq)$, can be used to distinguish between solutions of the halide ions Cl^-, Br^- and I^-.

....

....

....

....

....

....

.... [4]

(e) Describe and explain the trend in the solubilities of the sulfates of the elements in Group II.

....

....

....

....

....

....

.... [4]

[Total: 18]

3 (a) Catalysts can be described as homogeneous or heterogeneous.

(i) What is meant by the terms *homogeneous* and *heterogeneous*?

....

....

(ii) By using iron and its compounds as examples, outline the different modes of action of homogeneous and heterogeneous catalysis.
Choose **one** example of each type, and for **each** example you should

- state what the catalyst is, and whether it is acting as a homogeneous or a heterogeneous catalyst,
- write a balanced equation for the reaction,
- outline how the catalyst you have chosen works to decrease the activation energy.

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

[8]

(b) The reaction between SO_2, NO_2 and O_2 occurs in two steps.

$$NO_2 + SO_2 \rightarrow NO + SO_3 \qquad \Delta H_1^\ominus = -88\,\text{kJ}\,\text{mol}^{-1}$$
$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2 \qquad \Delta H_2^\ominus = -57\,\text{kJ}\,\text{mol}^{-1}$$

The activation energy of the first reaction, E_{a_1}, is higher than that of the second reaction, E_{a_2}.

Use the axes below to construct a fully-labelled reaction pathway diagram for this reaction, labelling E_{a_1}, E_{a_2}, $\Delta H_1^\ominus$ and $\Delta H_2^\ominus$.

energy

NO$_2$ + SO$_2$

extent of reaction

[2]

[Total: 10]

[Turn over
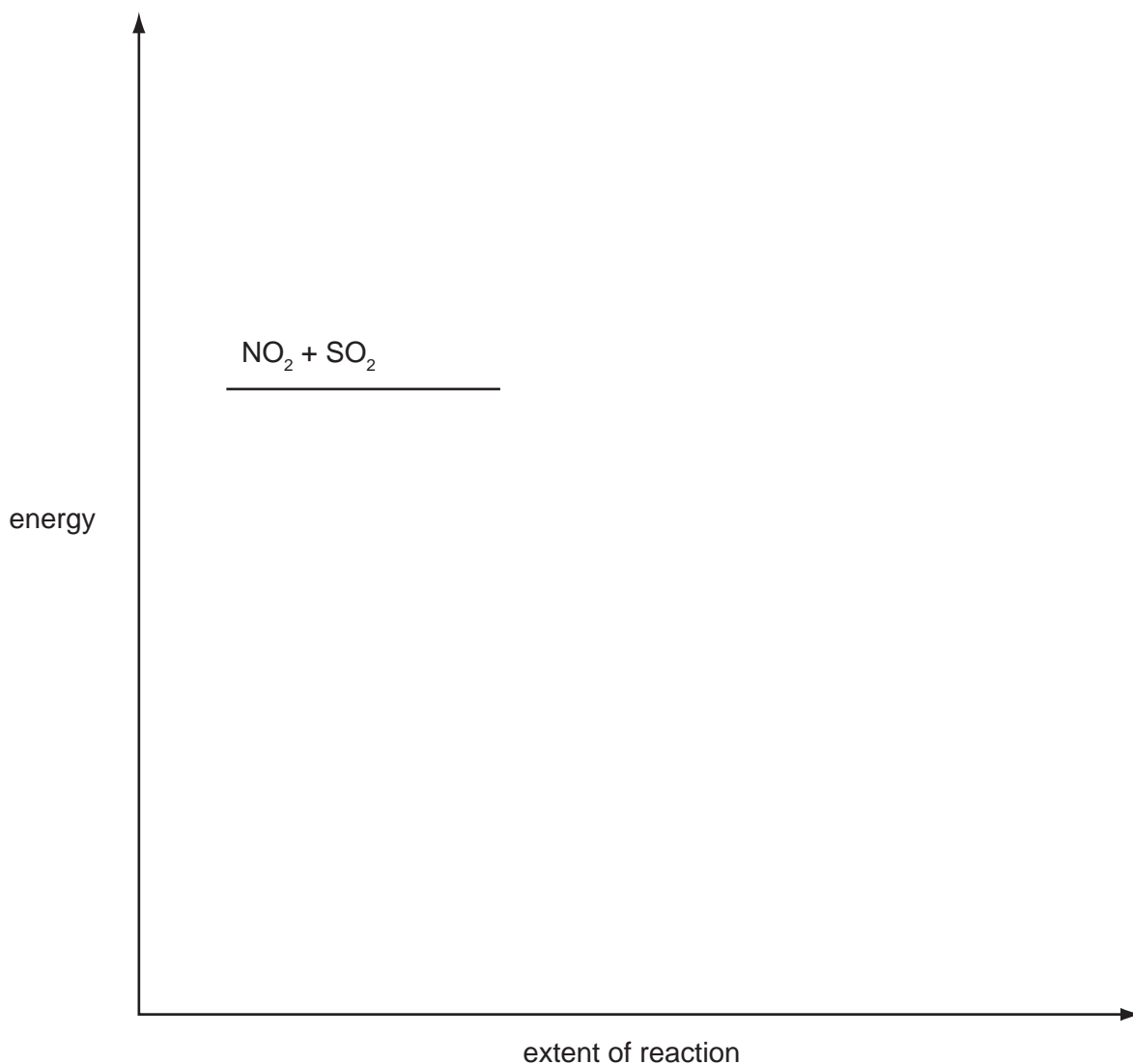
4 The compound responsible for the hot taste of chilli peppers is capsaicin. Its molecular structure can be deduced by the following reaction scheme.

capsaicin, $C_{18}H_{27}NO_3$

reaction 1 | boil with H_3O^+

HO—⟨benzene ring⟩—CH_2NH_2, OCH_3

+

C, $C_{10}H_{18}O_2$

reaction 2 | heat with concentrated acidified $KMnO_4$

D, $C_6H_{10}O_4$

+

E, $C_4H_8O_2$

reaction 5

reaction 3

$(CH_3)_2CHCH_2OH$

F, $C_6H_8N_2$

reaction 4 | heat with KCN

$Br(CH_2)_4Br$
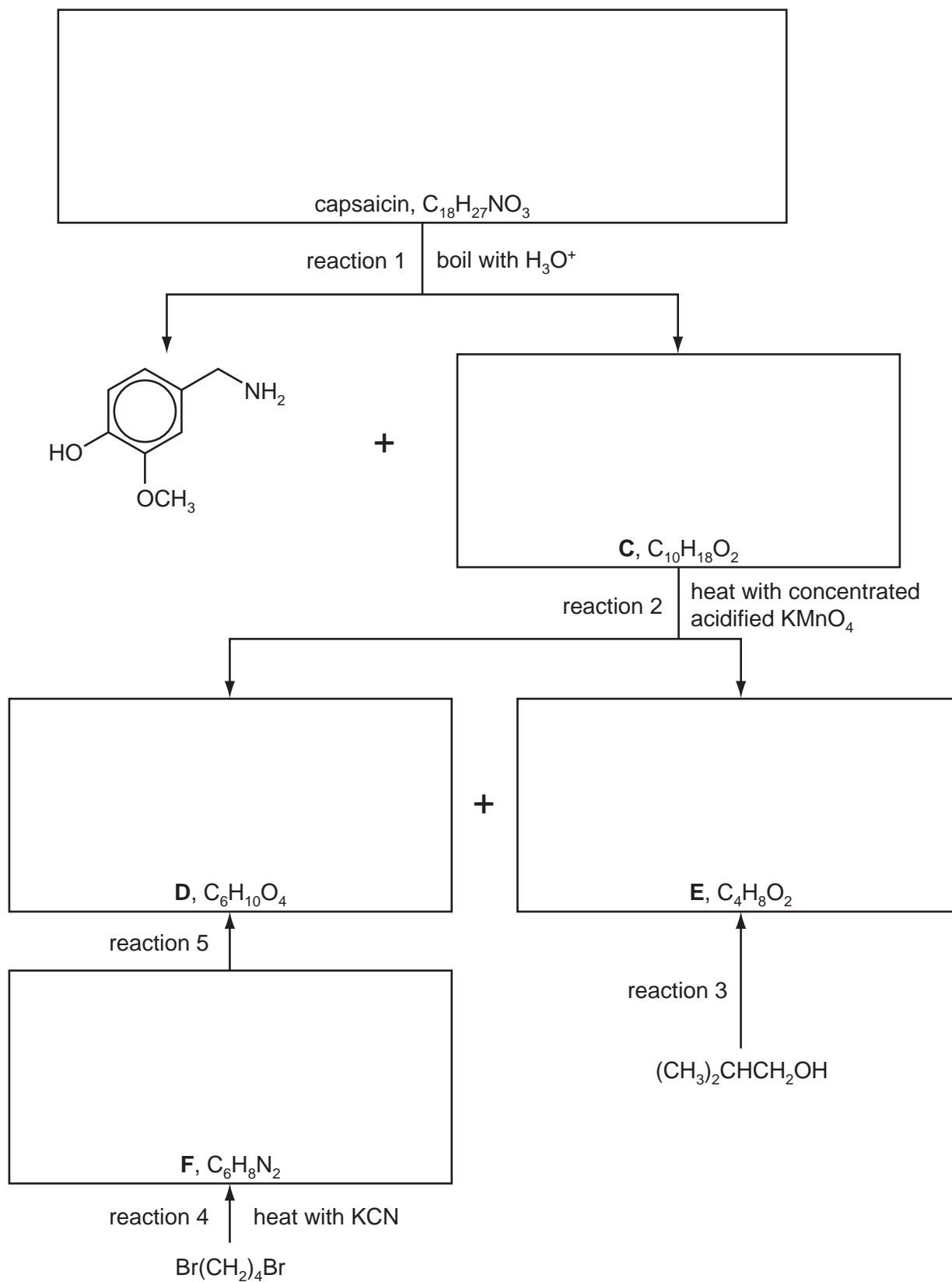
Compounds **C**, **D** and **E** all react with $Na_2CO_3(aq)$.

Answer the following questions.

(a) Suggest reagents and conditions for reaction 3.

.... [1]

(b) What *type of reaction* is reaction 4?

.... [1]

(c) Suggest reagents and conditions for reaction 5.

.... [1]

(d) Name the functional group in **C** that has reacted with hot concentrated acidified $KMnO_4$.

.... [1]

(e) Suggest the name of the functional group in capsaicin that has reacted in reaction 1.

.... [1]

(f) Work out structures for compounds **C**–**F** and capsaicin, and draw their structural formulae
in the boxes opposite. [5]

[Total: 10]

5 Compound **G** is a naturally occurring aromatic compound that is present in raspberries.
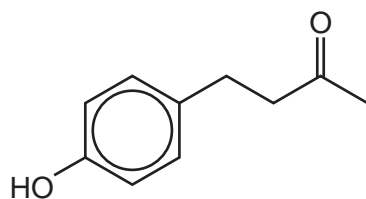
compound **G**

**(a)** Identify the functional groups present in compound **G**.

....

.... [2]

(b) Complete the following table with information about the reactions of the three stated reagents with compound **G**.

reagent	observation	structure of organic product	type of reaction
sodium metal			
aqueous bromine			
aqueous alkaline iodine			

[8]

(c) The dye **H** can be made from compound **G** by the route shown below.

J

step 1

K

compound **G**

step 2

dye **H**
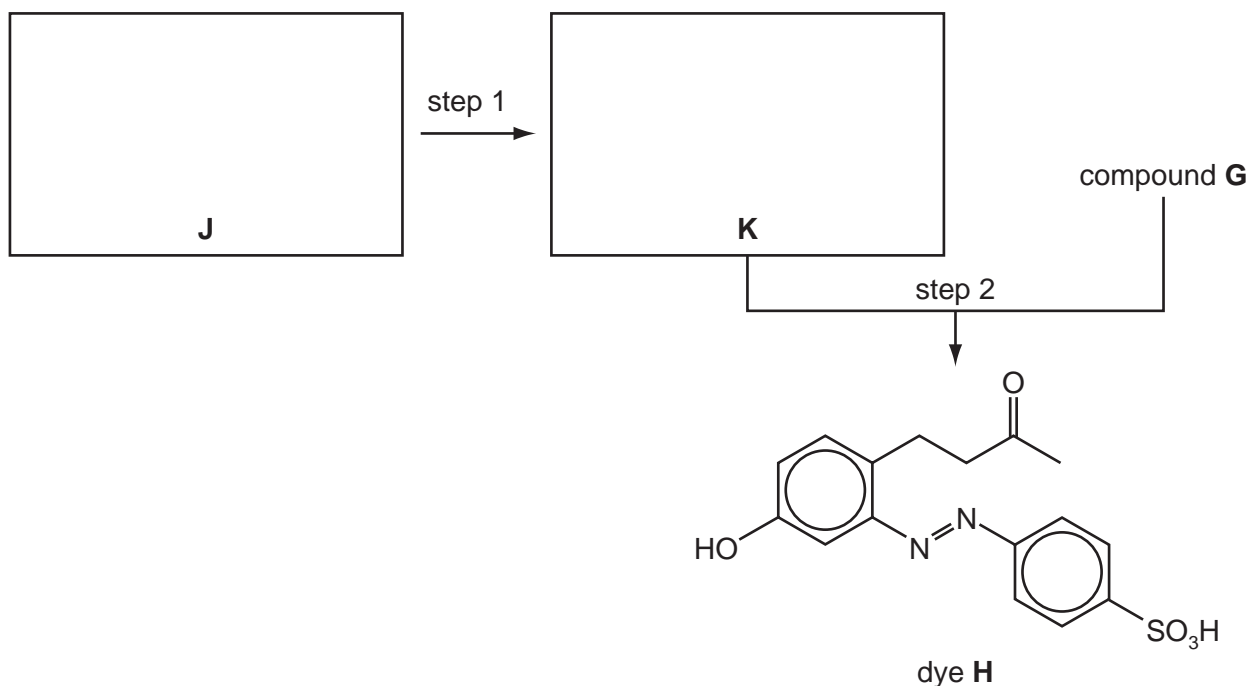
   (i) Draw the structures of the amine **J** and the intermediate **K** in the boxes above.

   (ii) Suggest reagents and conditions for

   step 1, ...

   step 2. ....

   [5]

(d) Suggest a reaction scheme by which compound **G** and propanoic acid could be converted into compound **L**.

compound **L**
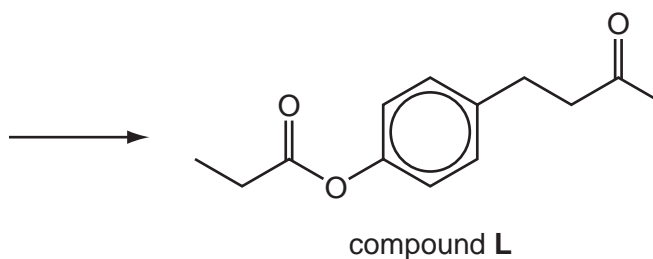
[3]

[Total: 18]

Section B

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

6 Proteins are complex molecules made up from long chains that are folded to give a three-dimensional structure.

(a) Study the table which describes aspects of bonding in proteins. For each description of a bonding type, indicate whether it contributes to the primary, secondary or tertiary structure of a protein.

bonding type	structure involved
disulfide bonds between parts of the chain	
hydrogen bonds in a β-pleated sheet	
ionic bonds between parts of the chain	
peptide links between amino acids	

[3]

(b) Explain, with the use of diagrams as appropriate, the difference between competitive and non-competitive inhibition of enzymes.
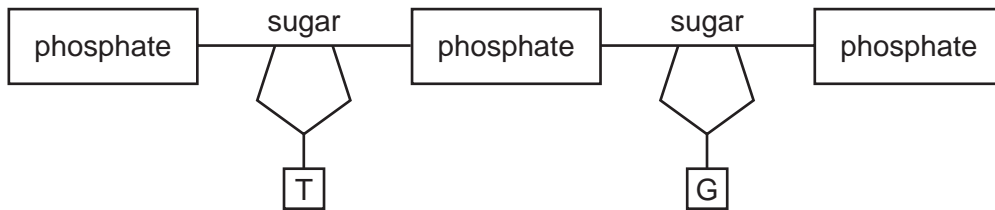
....

....

....

....

....

.... [4]

(c) The diagram shows one strand of DNA. Draw a matching strand showing clearly, with labels, the bonds holding the two strands together.
Name the bases in **your** strand, indicating clearly which base bonds to each base in the strand shown.

| phosphate | sugar | phosphate | sugar | phosphate |

T   G

names of bases ....

[3]

[Total: 10]

7 DNA fingerprinting has become an important analytical technique, largely due to its use in 'screening' crime suspects. It also has a range of applications in modern analysis including determining family links, medicine and archaeology.

(a) (i) DNA fingerprinting uses an analytical technique you have studied. What is the name of that technique?

....

(ii) In order to carry out DNA fingerprinting, the DNA must first be broken down into shorter lengths of polynucleotides. How is this accomplished?
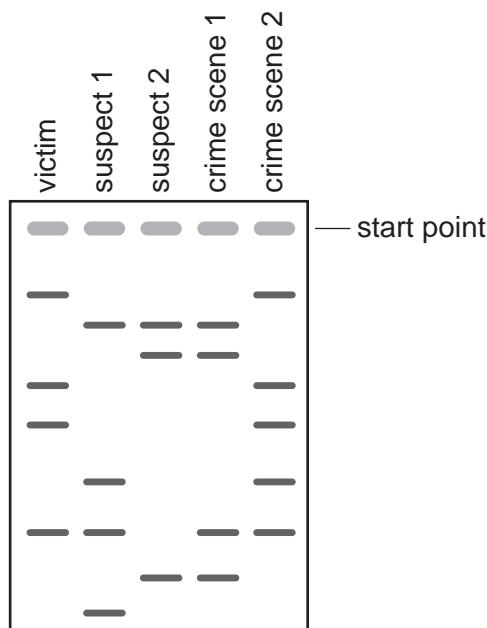
....

(iii) What part of the DNA fragments enables them to move in an electric field?

....

[3]

(b) The DNA fingerprints shown were obtained from a crime scene. DNA samples were recovered from two rooms in the house where the crime took place. The victim's DNA and that of two possible suspects were included in the analysis.

(i) Indicate with an **X** on the diagram, which lines from suspect 1 and from suspect 2 **cannot** distinguish which of them was present in the house.

(ii) Based on this evidence one suspect was arrested. Which suspect would you expect this to be? Explain your reasoning.

....

....
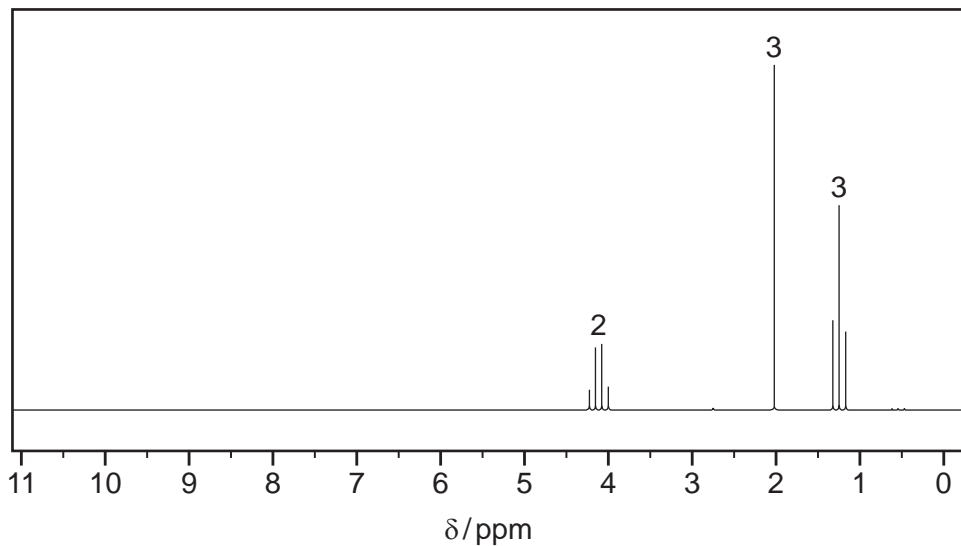
[2]

(c) A sample of a liquid, **P**, was found at the scene of the crime and was analysed using mass spectrometry and NMR spectroscopy.

The mass spectrum has M and M+1 peaks in the ratio of 5.1 : 0.22 with the M peak at $m/e = 88$.

The NMR spectrum is shown

Use the data to suggest a structure for **P**, explaining your answer.

....

....

....

....

....

....

....

structure of **P**

[5]

[Total: 10]

8 The increasing awareness of the diminishing supply of crude oil has resulted in a number of initiatives to replace oil-based polymers with those derived from natural products. One such polymer, 'polylactide' or PLA, is produced from corn starch and has a range of applications.

(a) The raw material for the polymer, lactic acid (2-hydroxypropanoic acid), is formed by the fermentation of corn starch using enzymes from bacteria.
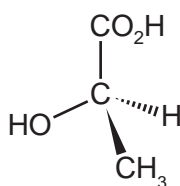
(i) Calcium hydroxide is added to the fermentation tanks to prevent the production of lactic acid from slowing down.
Why might high acidity reduce the effectiveness of the enzymes?

....

....

(ii) The structure of lactic acid is shown.

$$CO_2H$$
$$HO-C\text{'''}H$$
$$CH_3$$

What type of reaction takes place in this polymerisation?

....
[2]

(b) Lactic acid exists in two stereoisomeric forms. Draw the other form in the box.

[1]

(c) One of the reasons PLA has attracted so much attention is that it is biodegradeable. This does, however, restrict some potential uses. The simple polymer has a melting point of around 175 °C, but softens between 60-80 °C. However, its thermoplastic properties enable it to have a range of uses in fibres and in food packaging.

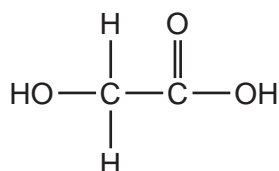**(i)** Explain why PLA would **not** be a suitable packaging material for foods pickled in vinegar.

....

....

(ii) PLA containers are not used for hot drinks. Suggest why.

....

....

[2]

(d) Lactic acid can also be co-polymerised with glycolic acid.

$$HO-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

glycolic acid

(i) Draw a section of the co-polymer showing one repeat unit.

(ii) Suggest what type(s) of bonding will occur between chains of this co-polymer, indicating the groups involved.

....

....

....

(iii) Suggest one property in which the co-polymer differs from PLA.

....

....

[5]

[Total: 10]

BLANK PAGE

BLANK PAGE

BLANK PAGE