Rewarding Learning

Centre Number

71

Candidate Number

ADVANCED
General Certificate of Education
2013

Chemistry

Assessment Unit A2 2

assessing

Analytical, Transition Metals, Electrochemistry and Further Organic Chemistry

[AC222]

MV18

TUESDAY 4 JUNE, AFTERNOON

TIME

2 hours, plus your additional time allowance.

INSTRUCTIONS TO CANDIDATES

Write your Centre Number and Candidate Number in the spaces provided at the top of this page.
Answer **all fourteen** questions.
Answer **all ten** questions in **Section A**. Record your answers by marking the appropriate letter on the answer sheet provided. Use only the spaces numbered 1 to 10. Keep in sequence when answering.
Answer **all four** questions in **Section B**. Write your answers in the spaces provided in this question paper.

INFORMATION FOR CANDIDATES

The total mark for this paper is 120.
Quality of written communication will be assessed in question **13(e)(iii)**.
In Section A all questions carry equal marks, i.e. **two** marks for each question.
In Section B the figures printed at the end of each question indicate the marks awarded to each question or part question.
A Periodic Table of the Elements, containing some data, is included in this question paper.

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(Questions start overleaf)

Section A

For each of the following questions only **one** of the lettered responses (A–D) is correct.

Select the correct response in each case and mark its code letter by connecting the dots as illustrated on the answer sheet.

1 The standard electrode potentials for some half-cells are listed below:

$Cu^{2+}(aq)$	+	$2e^-$	→	$Cu(s)$		+0.34 V
$AgCl(s)$	+	e^-	→	$Ag(s)$	+ $Cl^-(aq)$	+0.22 V
$H^+(aq)$	+	e^-	→	$\frac{1}{2}H_2(g)$		0.00 V
$Zn^{2+}(aq)$	+	$2e^-$	→	$Zn(s)$		–0.76 V

Which one of the following cell potentials could be obtained by combining two of these standard electrodes?

A 0.42 V

B 0.54 V

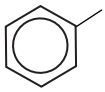
C 0.56 V

D 0.98 V

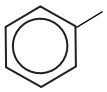
2 In which one of the following reactions is the inorganic reagent acting as an electrophile?

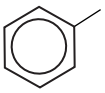
A $CH_3CH_3 + Cl_2 \rightarrow CH_3CH_2Cl + HCl$

B $CH_4 + 4Cl_2 \rightarrow CCl_4 + 4HCl$

C  $+ Br_2 \rightarrow$ 

$+ HBr$

D 

$+ Br_2 \rightarrow$ 

$+ HBr$

3 Which one of the following is the total number of isomers, both structural and stereoisomers, which are possible for the formula $C_4H_{10}O$?

A 3 or less

B 4

C 5

D 6 or more

4 Which one of the following is the name of the indicator used for the titration of magnesium ions with edta?

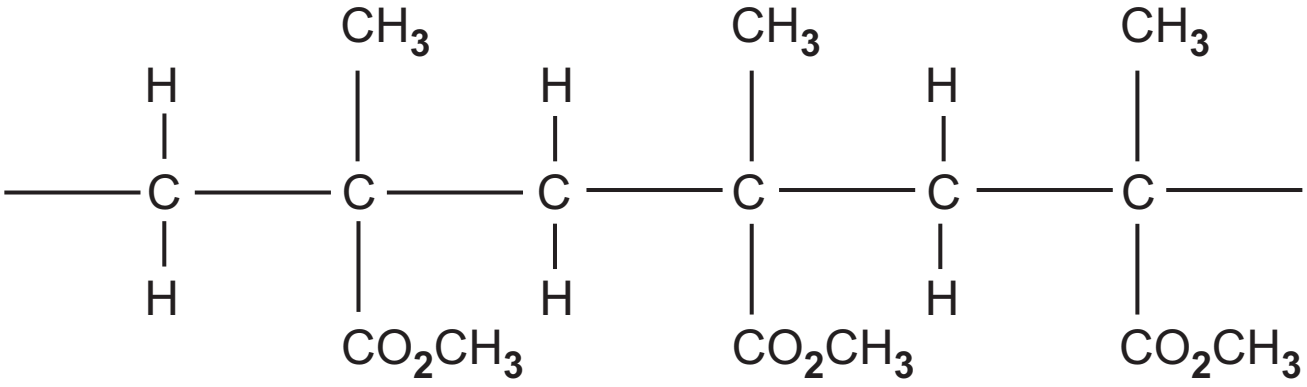
A Eriochrome

B Eriochrome T

C Eriochrome brown T

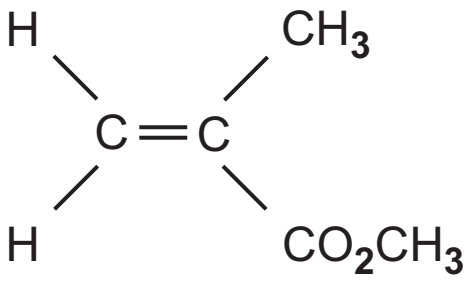
D Eriochrome black T

5 The structure of the polymer perspex is shown below.



Which one of the following structures is that of the monomer from which perspex is formed?

A



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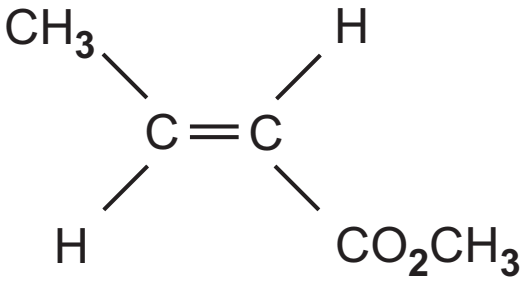
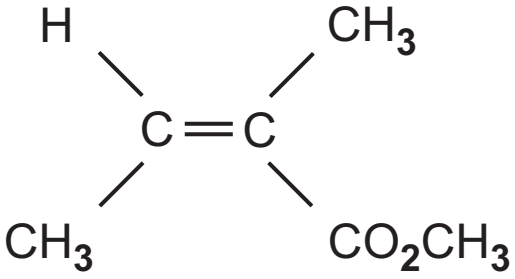
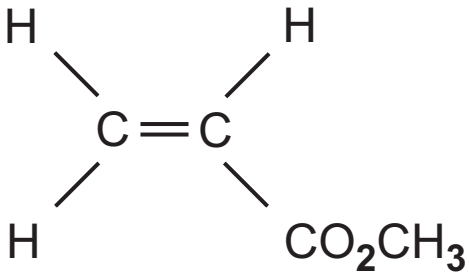


C



D



6 Which one of the following statements describes the primary structure of a protein?

A The formation of the α-helix

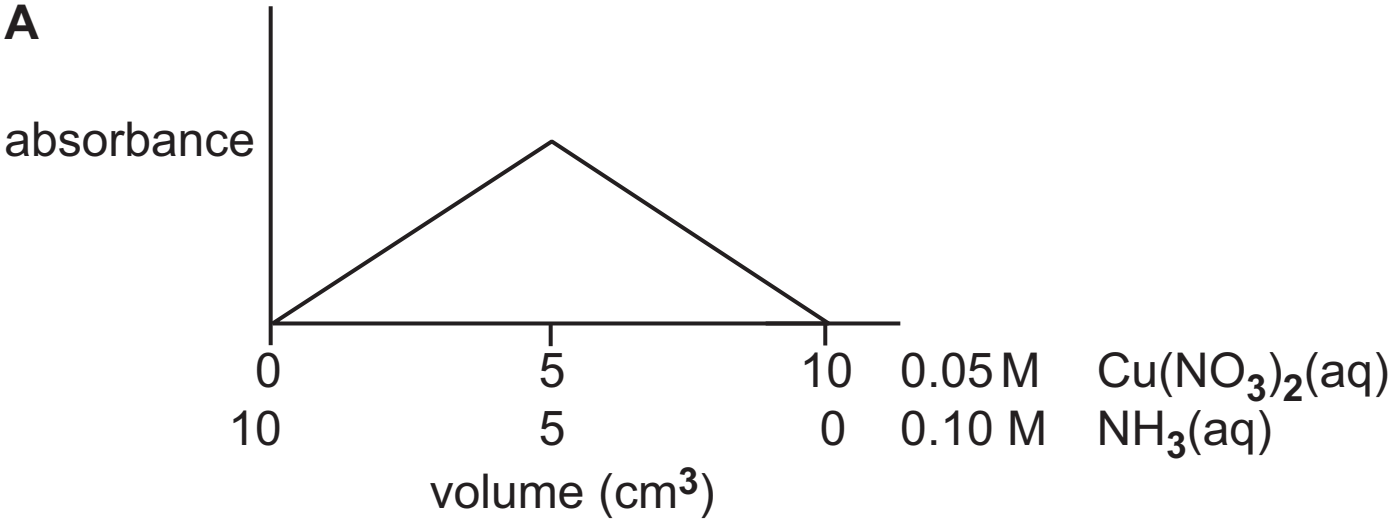
B The folding of the α-helix

C The sequence of the amino acids in the chain

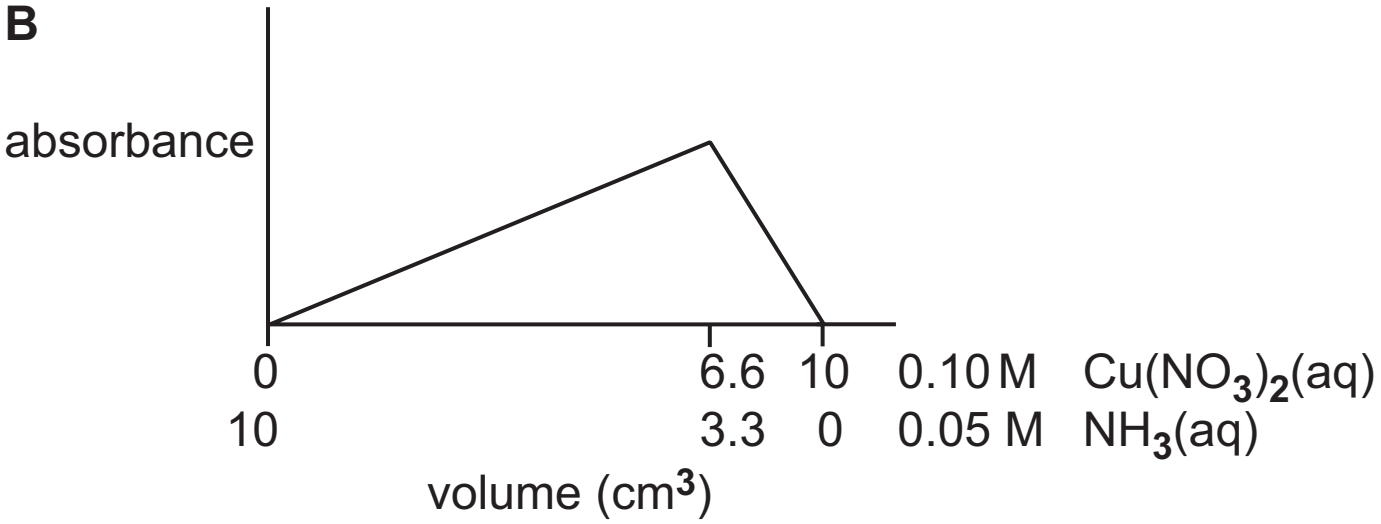
D The sequence of peptide links in the chain

7 Which one of the following graphs represents the absorbance against volume in a colorimetry experiment for the reaction of copper(II) nitrate with ammonia?

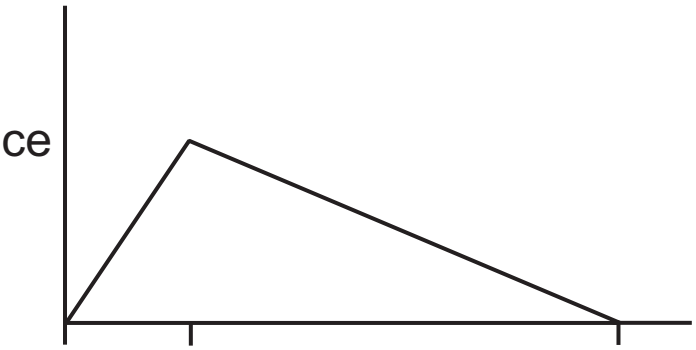
A



B



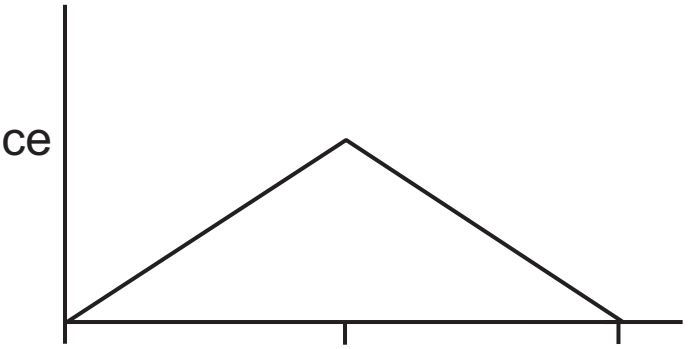
C



0	3.3	10	0.05 M	$Cu(NO_3)_2(aq)$
10	6.6	0	0.10 M	$NH_3(aq)$

volume (cm^3)

D



0	5	10	0.10 M	$Cu(NO_3)_2(aq)$
10	5	0	0.05 M	$NH_3(aq)$

volume (cm^3)

8 Which one of the following compounds is the least soluble in water at room temperature?

A $CH_3CH(NH_2)CO_2H$

B $CH_3CH_2CH_2NH_2$

C $C_6H_5CO_2Na$

D $C_6H_5NH_2$

9 In which one of the following reactions is the transition metal, transition metal compound or ion **not** acting as a catalyst?

A Iron in the production of ammonia

B Nickel in the formation of ethane from ethene

C Silver ions in the oxidation of ethanal

D Vanadium pentoxide in the manufacture of sulfuric acid

10 Complete combustion of 0.70 dm^3 of a gaseous organic compound at 20 °C and one atmosphere pressure gave 0.12 mole of carbon dioxide.

Which one of the following is the number of carbon atoms in one molecule of the compound?

A 1

B 2

C 4

D 6

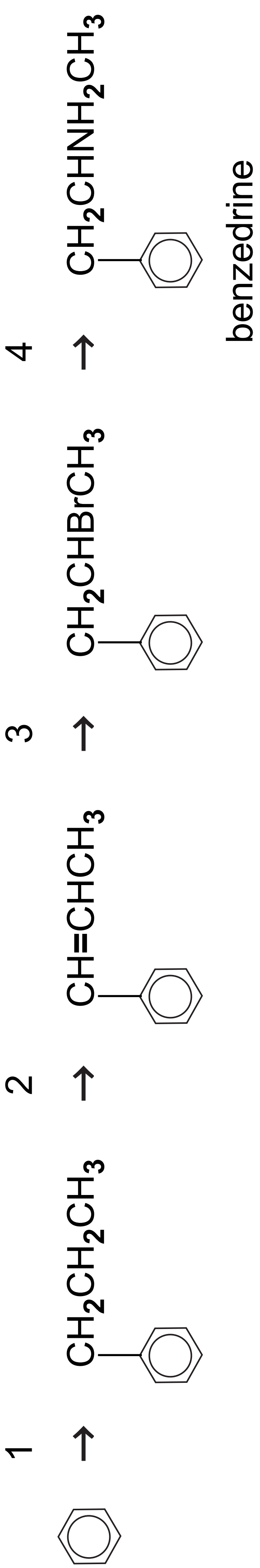
Section B

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

11 Benzedrine is the trade name for a mixture of the optical isomers of amphetamine. It was used as a stimulant in World War II and continues to be used in this way today.

(a) Benzedrine may be synthesised by the route shown opposite.

(i) In step 1 a reaction occurs which has a very similar mechanism to that of the monobromination of benzene. With bromination the electrophile is Br^+, in this case the electrophile is $CH_3CH_2CH_2^+$.
Draw a flow scheme for this reaction. [3]


1
$CH_2CH_2CH_3$
2
CH=CHCH$_3$
3
$CH_2CHBrCH_3$
4
$CH_2CHNH_2CH_3$
benzedrine

(ii) In step 2 the propylbenzene is broken down into smaller molecules (cracked) in the presence of zinc oxide. Suggest the role of the zinc oxide and the conditions under which the cracking is carried out. [3]

(iii) In step 3 name the reagent which adds across the double bond. [1]

(iv) In step 4 name the reagent which is used to replace the bromine atom in the compound. [1]

(b) (i) Deduce and explain whether benzedrine is a primary, secondary or tertiary amine. [2]

(ii) Explain its strength as a base compared with phenylamine. [2]

(c) Benzedrine forms salts with inorganic acids. The sulfate salt is often used as the main form of benzedrine in medicine.

(i) Write the equation for the formation of the sulfate salt of benzedrine. [2]

_____

(ii) Suggest why the formation of an ionic salt is more beneficial if tablets of the drug are used. [1]

_____

(iii) The amine can be liberated from the salt. Name the reagent and the conditions used for this reaction. [2]

_____

_____

(d) Benzedrine is optically active and exists in two forms one of which is more biologically active than the other. This variation in activity is explained in a similar way to that of enzyme activity.

(i) Explain why benzedrine is optically active. [1]

_____

(ii) Explain why one structure is more biologically active than the other. [1]

_____

_____

(e) The identification of many drugs uses the technique of GLC. Explain how this is carried out. [2]

12 Iron is a transition element that forms a wide variety of complexes and salts. For example, with ethanedioic acid (oxalic acid) iron can form salts such as iron(II) oxalate and iron(III) oxalate. It can also form complexes such as potassium iron(III) oxalate.

COOH
|
COOH

oxalic acid

(a) (i) Write the formulae of iron(II) oxalate and iron(III) oxalate. [1]/[1]

iron(II) oxalate _____

iron(III) oxalate _____

(ii) The oxalate ion is colourless. What are the expected colours of the aqueous oxalate solutions listed below? [1]/[1]

aqueous iron(II) oxalate _____

aqueous iron(III) oxalate _____

(iii) State and explain what would be observed when a solution of sodium hydroxide is added to each of the solutions. [4]

(b) Iron(II) oxalate, when heated, decomposes to produce iron(II) oxide and both oxides of carbon. Write the equation for the reaction. [1]

(c) Iron(II) oxalate is completely oxidised by acidified potassium manganate(VII). The iron(II) ion is oxidised to iron(III):

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

The oxalate ion is completely oxidised to carbon dioxide.

$$\begin{matrix} COO^- \\ | \\ COO^- \end{matrix} \rightarrow 2CO_2 + 2e^-$$

The electrons produced react with the manganate(VII) ion.

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

(i) Write the equation for the reaction of acidified manganate(VII) ions with iron(II) oxalate. [2]

(ii) Oxalic acid is used to remove iron stains because iron dissolves to form iron(II) oxalate. Calculate the mass of iron, in milligrams, dissolved in a 100 cm^3 solution if 20.0 cm^3 of the iron(II) oxalate solution reacts with 18.2 cm^3 of 0.002 M potassium manganate(VII) solution. [4]

(d) The oxalate ion also acts as a bidentate ligand. For example, iron(III) ions form the complex $K_3Fe(C_2O_4)_3$. The structure of the trisoxalato anion is based on an octahedron.

(i) Explain the meaning of the term **complex**. [2]

(ii) Explain the meaning of the term **bidentate ligand**. [2]

(iii) Suggest a 3D structure for the trisoxalato anion. [2]

(iv) Explain why the trisoxalato anion is optically active. [2]

_____

_____

_____

(e) If a solution of $K_3Fe(C_2O_4)_3$ is treated with edta a reaction takes place. Suggest what reaction takes place and explain why it occurs. [2]

_____

_____

_____

13 Propanamide is a white crystalline solid with a melting point of 80 °C. It is prepared by heating the ammonium salt of propanoic acid.

(a) (i) Write the equation for the reaction of propanoic acid with ammonia. [1]

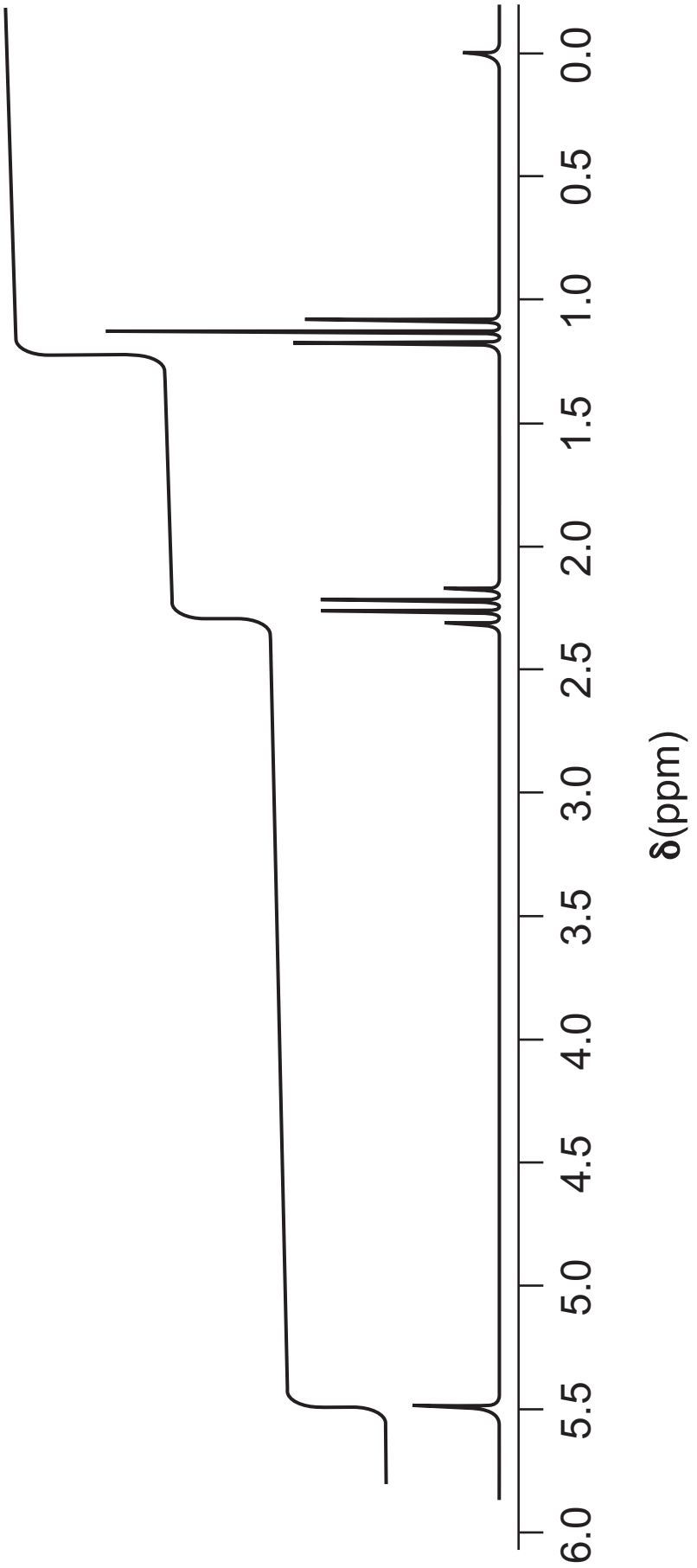
(ii) Write the equation for the decomposition of this ammonium salt to produce propanamide. [1]

(b) The nmr spectrum of propanamide is shown opposite.

(i) The signal at 0 ppm is due to TMS. Explain why TMS is used as a standard. [2]

(ii) Explain why the signal at 1.15 ppm is a triplet. [1]

(iii) Explain why the signal at 2.25 ppm is a quartet. [1]


6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ(ppm)

(iv) Explain why the signal at 5.5 ppm is at the highest chemical shift in the spectrum. [1]

(v) Explain **three ways** in which this spectrum would differ from the spectrum of the N-methylated compound, $CH_3CH_2CONHCH_3$. [3 marks]

(c) The mass spectrum of propanamide is shown opposite.

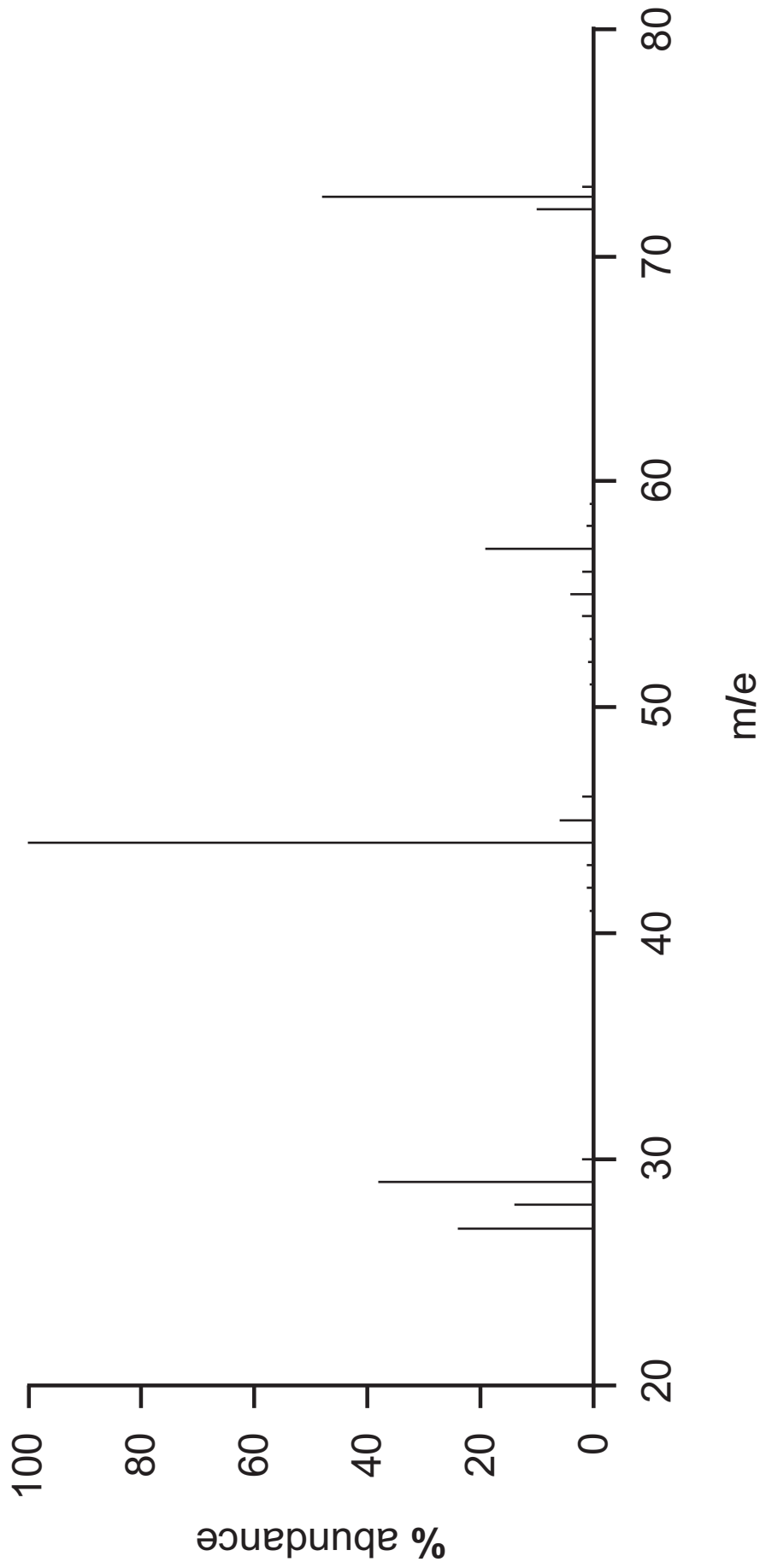
(i) Write the formulae of the fragment ions which have the following masses. [1]/[1]

29 _____

44 _____

(ii) Explain what is meant by the term **fragmentation**. [2]

(iii) Identify the base peak in the spectrum. [1]


% abundance
100
80
60
40
20
0
20
30
40
50
60
70
80
m/e

(d) The amide group is hydrolysed slowly with water, rapidly by acids and far more rapidly by alkalis.

(i) Write the equation for the reaction of propanamide with aqueous sodium hydroxide. [2]

_____

(ii) The relative reactivity may be explained by the reactive species present in the three reactions. Suggest why the hydroxide ion is a better reagent than the hydrogen ion to attack the amide group. [1]

_____

_____

(e) Polyamides such as nylon are important industrial chemicals.

(i) Write an equation to show the formation of a section of the nylon molecule using the industrial monomers. [3]

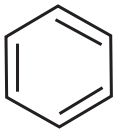
(ii) State **two** major uses of nylon. [2]

(iii) Nylon is far more easily disposed of than polythene. Explain using the chemical structure of nylon why this is so and state how waste polythene is disposed of apart from recycling. [4]

Quality of written communication [2]

14 Benzene, C_6H_6, was first isolated by Faraday in 1825. It is a colourless liquid with a melting point of 6 °C and a boiling point of 80 °C.

It is either represented by the Kekulé structure or by the more modern structure of a circle inside the ring.



Kekulé structure

modern structure

(a) What is the empirical formula of benzene? [1]

_____

(b) What is the shape of benzene? [1]

_____

(c) Benzene may be catalytically reduced in several steps to cyclohexane using nickel.

(i) Write the overall equation for the reduction. [1]

_____

(ii) Draw a flow scheme showing the structure of all the reduction products. [2]

(iii) Explain, in terms of chemisorption, the role of nickel in the reduction. [3]

(d) The enthalpy of hydrogenation of cyclohexene is $-120\,kJ\,mol^{-1}$.

(i) What does this suggest for the value for the hydrogenation of benzene? [1]

(ii) The actual hydrogenation value for benzene is $-208\,kJ\,mol^{-1}$.
Suggest the reason for the difference. [1]

_____

_____

(e) Draw a dot and cross diagram for the Kekulé structure of a benzene molecule using outer electrons only. [3]

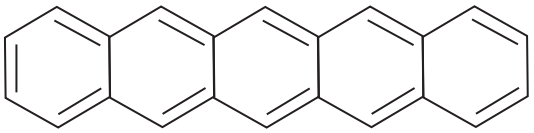
(f) Compare the reaction of bromine with benzene and ethene by drawing the following flow schemes:

(i) Draw a flow scheme to show the mechanism for the reaction of bromine with benzene. [3]

(ii) Draw a flow scheme to show the mechanism for the reaction of bromine with ethene where Br^+ is the electrophile. [3]

(iii) Explain why there are different mechanisms for the reactions. [2]

(g) Benzene is colourless but the solid pentacene is red.



pentacene

Explain why pentacene is coloured and benzene is not. [4]

THIS IS THE END OF THE QUESTION PAPER

For Examiner's use only	
Question Number	**Marks**
Section A	
1–10	
Section B	
11	
12	
13	
14	
Total Marks	