Cambridge Assessment International Education

Cambridge International AS & A Level

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

0724726256

CHEMISTRY **9701/43**

Paper 4 A Level Structured Questions **May/June 2022**

2 hours

You must answer on the question paper.

No additional materials are needed.

INSTRUCTIONS

- Answer **all** questions.
- Use a black or dark blue pen. You may use an HB pencil for any diagrams or graphs.
- Write your name, centre number and candidate number in the boxes at the top of the page.
- Write your answer to each question in the space provided.
- Do **not** use an erasable pen or correction fluid.
- Do **not** write on any bar codes.
- You may use a calculator.
- You should show all your working and use appropriate units.

INFORMATION

- The total mark for this paper is 100.
- The number of marks for each question or part question is shown in brackets [ ].
- The Periodic Table is printed in the question paper.
- Important values, constants and standards are printed in the question paper.

This document has **24** pages. Any blank pages are indicated.

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

1 **(a)** The solubility of the Group 2 sulfates decreases down the group.

Explain this trend.

.....

.....

.....

.....

..... [3]

(b) Describe what is observed when magnesium and barium are reacted separately with an excess of dilute sulfuric acid.

magnesium .....

barium .....
[1]

(c) The solubility product, K_{sp}, of $BaSO_4$ is 1.08×10^{-10} mol^2 dm^{-6} at 298 K.

Calculate the solubility of $BaSO_4$ in g per 100 cm^3 of solution.

solubility of $BaSO_4$ = ... g per 100 cm^3 of solution
[2]

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(d) (i) The equation for the formation of a gaseous sulfate ion is shown.

$$S(s) + 2O_2(g) + 2e^- \rightarrow SO_4^{2-}(g) \quad \Delta H = \Delta H_f^{\ominus} \text{ of } SO_4^{2-}(g)$$

Calculate the standard enthalpy change of formation, $\Delta H_f^{\ominus}$, of $SO_4^{2-}(g)$. It may be helpful to draw a labelled energy cycle. Use relevant data from Table 1.1 in your calculations.

Table 1.1

energy change	value / kJ mol^{-1}
lattice energy of barium sulfate, $BaSO_4(s)$	–2469
standard enthalpy change of formation of barium sulfate	–1473
standard enthalpy change of atomisation of barium	+180
first ionisation energy of barium	+503
second ionisation energy of barium	+965
standard enthalpy change of atomisation of sulfur	+279
standard enthalpy change for $S(g) \rightarrow S^{2-}(g)$	+440
standard enthalpy change for $O(g) \rightarrow O^{2-}(g)$	+657
O=O bond energy	+496

$\Delta H_f^{\ominus}$ of $SO_4^{2-}(g)$ = ... kJ mol^{-1} [3]

(ii) Suggest how the lattice energy of $BaSO_4(s)$ differs from the lattice energy of $Cs_2SO_4(s)$. Explain your answer.

.....

.....

..... [2]

(e) The reaction of solid hydrated barium hydroxide, $Ba(OH)_2 \cdot 8H_2O$, with ammonium salts is endothermic.

(i) Calculate the **minimum** temperature at which the reaction of $Ba(OH)_2 \cdot 8H_2O$ with NH_4NO_3 becomes feasible. Show all your working.

$Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4NO_3(s) \rightarrow 2NH_3(g) + Ba(NO_3)_2(s) + 10H_2O(l)$ $\Delta H_r^{\ominus} = +132\,kJ\,mol^{-1}$

$\Delta S^{\ominus} = +616\,J\,K^{-1}\,mol^{-1}$

temperature = ... °C [2]

(ii) Barium hydroxide reacts readily with ammonium chloride on mixing at room temperature.

$Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4Cl(s) \rightarrow 2NH_3(g) + BaCl_2 \cdot 2H_2O(s) + 8H_2O(l)$ $\Delta H_r^{\ominus} = +133\,kJ\,mol^{-1}$

Some relevant standard entropies are given in Table 1.2.

Table 1.2

substance	$Ba(OH)_2 \cdot 8H_2O(s)$	$NH_4Cl(s)$	$NH_3(g)$	$BaCl_2 \cdot 2H_2O(s)$	$H_2O(l)$
$S^{\ominus}$ / $J\,K^{-1}\,mol^{-1}$	427	95	192	203	70

Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for this reaction at 25 °C.

$\Delta G^{\ominus}$ = ... $kJ\,mol^{-1}$ [3]

[Total: 16]

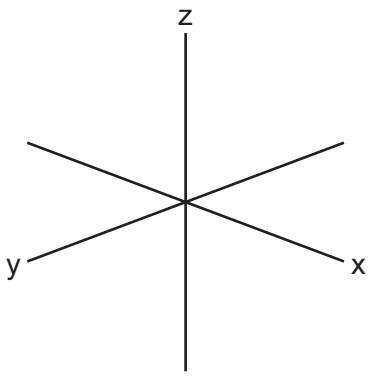
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2 **(a)** Define transition element.

.....

..... [1]

(b) Sketch the shape of a $3d_{z^2}$ orbital.



[1]

(c) Manganese(IV) oxide, MnO_2, acts as a heterogeneous catalyst in the decomposition of hydrogen peroxide, H_2O_2.

(i) Explain what is meant by a heterogeneous catalyst.

.....

..... [1]

(ii) Describe the mode of action of a heterogeneous catalyst in a reaction.

.....

.....

.....

..... [3]

(d) Manganese(VII) oxide, Mn_2O_7, can be made by treatment of $KMnO_4$ with concentrated sulfuric acid (reaction 1).

Mn_2O_7 readily decomposes at room temperature to form manganese(IV) oxide and a colourless diatomic gas (reaction 2).

Construct equations for **both** the reactions described.

reaction 1 .....

reaction 2 .....

[2]

(e) Aqueous manganese(II) ions show similar chemical properties to aqueous copper(II) ions when reacted separately with NaOH(aq) and with concentrated HC*l*.

(i) Write the ionic equation, and state the type of reaction, for the reaction of $[Mn(H_2O)_6]^{2+}$ with NaOH(aq).

ionic equation .....

type of reaction .....
[2]

(ii) Write the ionic equation, and state the type of reaction, for the reaction of $[Mn(H_2O)_6]^{2+}$ with concentrated HC*l*.

ionic equation .....

type of reaction .....
[2]

(iii) Table 2.1 lists relevant electrode potentials for some electrode reactions.

Table 2.1

electrode reaction	$E^{\ominus}$/V
$Mn^{2+} + 2e^- \rightleftharpoons Mn$	–1.18
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$2HOCl + 2H^+ + 2e^- \rightleftharpoons Cl_2 + 2H_2O$	+1.64
$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$	+1.23
$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2 + 2H_2O$	+1.67

Suggest the formula of the manganese species formed when Mn^{2+}(aq) reacts with Cl_2.

State the type of reaction.

formula of manganese species formed .....

type of reaction .....
[1]

[Total: 13]

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3 **(a)** The rate of reaction between 2-chloro-2-methylpropane, $(CH_3)_3CCl$, and methanol is investigated. When a large excess of methanol is used, the overall reaction is first order.

$$(CH_3)_3CCl + CH_3OH \rightarrow (CH_3)_3COCH_3 + HCl$$

Fig. 3.1 shows the results obtained.

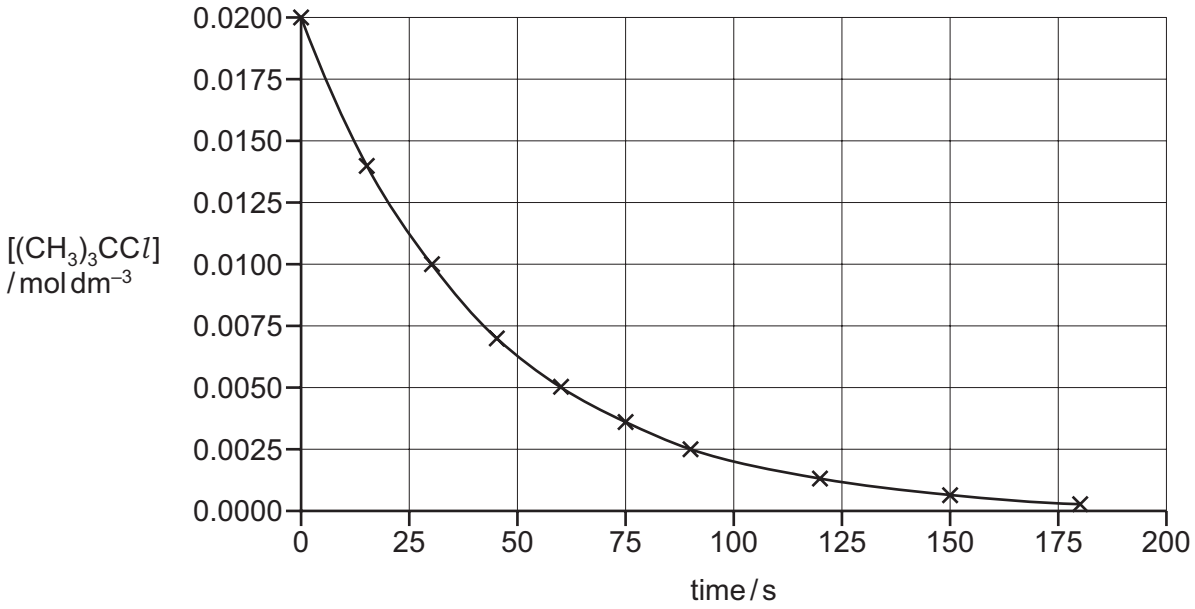


Fig. 3.1

(i) Use the graph to determine the rate of reaction at 40 s. Show all your working.

rate = ... $mol\,dm^{-3}\,s^{-1}$ [1]

(ii) Use the graph to show that the overall reaction is first order. Explain your answer.

.....

.....

..... [2]

(b) In a different reaction, which is also a first order reaction, 75% of the reactant is consumed in 320 s.

Calculate the rate constant, *k*, for this reaction. State the units for *k*.

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

(c) (i) Define standard electrode potential, $E^{\ominus}$.

.....

.....

..... [1]

(ii) A salt bridge is used in an electrochemical cell.

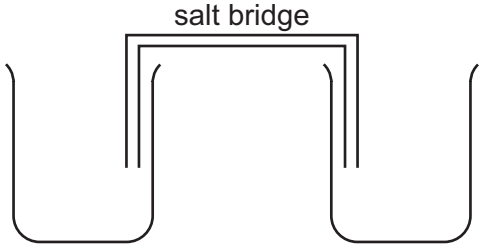
State the function of the salt bridge. Explain your answer.

.....

..... [1]

(iii) Complete the diagram of the apparatus that can be used to measure the $E^{\ominus}$ of the $Cr_2O_7^{2-}(aq)$, $H^+(aq)/Cr^{3+}(aq)$ electrode against the standard hydrogen electrode.

Your diagram should be fully labelled to identify all apparatus, substances and conditions.



[3]

(iv) The $E^{\ominus}$ of the $Cr_2O_7^{2-}(aq)$, $H^+(aq)/Cr^{3+}(aq)$ electrode is +1.33 V.

Label the negative electrode and the direction of electron flow in the external circuit when the current flows in your diagram in **(c)(iii)**. [1]

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(d) Table 3.1 lists relevant electrode potentials for some electrode reactions for use in **(d)(i)** and **(d)(ii)**.

Table 3.1

electrode reaction	$E^{\ominus}$/V
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
$CH_3CHO + 2H^+ + 2e^- \rightleftharpoons CH_3CH_2OH$	–0.61
$CH_3COOH + 2H^+ + 2e^- \rightleftharpoons CH_3CHO + H_2O$	–0.94
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23

(i) Ethanal is oxidised to ethanoic acid in the presence of $Cr_2O_7^{2-}$ ions.

Construct the ionic equation for the oxidation of ethanal to ethanoic acid using dichromate(VI) in acid conditions. Calculate the $E^{\ominus}_{cell}$ for this reaction.

ionic equation .....

$E^{\ominus}_{cell}$ = ... V
[2]

(ii) In an ethanol-oxygen fuel cell, $CH_3CH_2OH(l)$ and $O_2(g)$ are in contact with two inert electrodes immersed in an acidic solution.

The cell reaction for the oxidation of ethanol by oxygen is shown.

$$2CH_3CH_2OH + O_2 \rightarrow 2CH_3COOH + 2H_2O \qquad E^{\ominus}_{cell} = +2.01\,V$$

Calculate $\Delta G^{\ominus}$, in kJ mol^{-1}, for the oxidation of ethanol by oxygen.

$\Delta G^{\ominus}$ = ... kJ mol^{-1} [2]

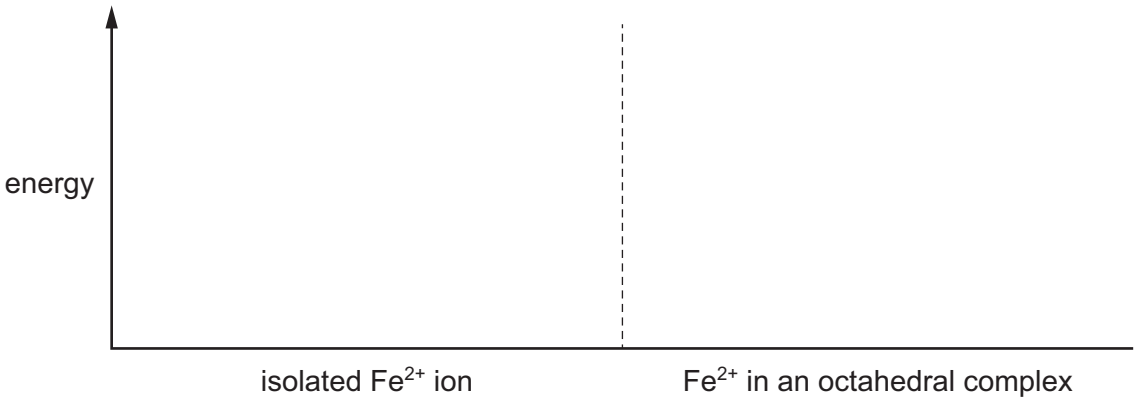
[Total: 15]

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[Turn over

4 **(a)** The 3d orbitals in an isolated Fe^{2+} ion are degenerate.

Complete the diagram to show the splitting of the 3d orbital energy levels in an isolated Fe^{2+} ion and when Fe^{2+} forms an octahedral complex.



[2]

(b) **(i)** Bipyridine, bipy, is a bidentate ligand.

bipy

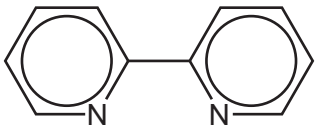


Fig. 4.1

Explain what is meant by bidentate ligand.

.....

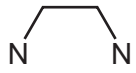
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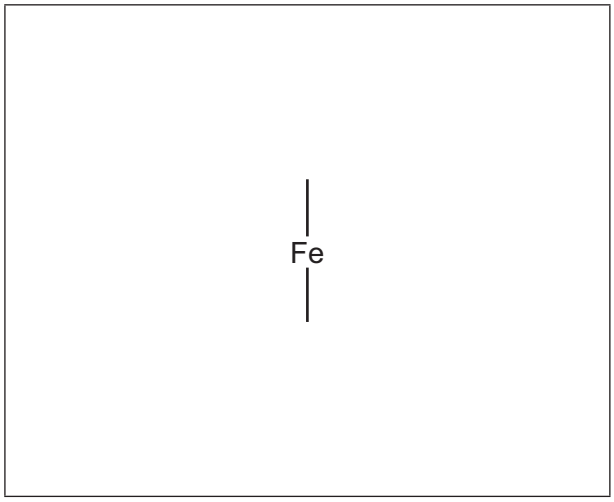
..... [2]

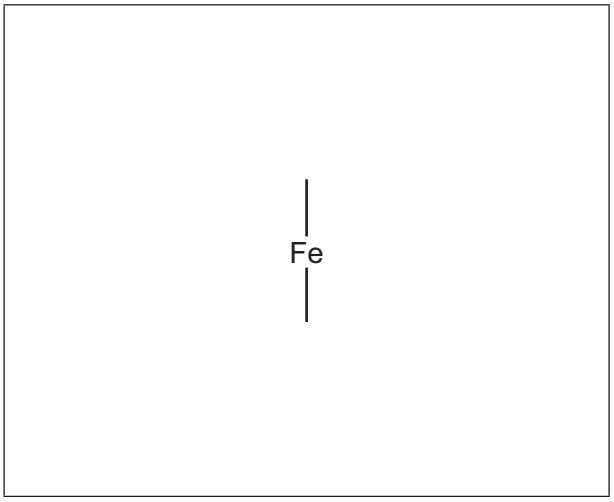
(ii) The complex $[Fe(bipy)_3]^{2+}$ exists as two stereoisomers.

Complete the three-dimensional diagrams to show the two stereoisomers of $[Fe(bipy)_3]^{2+}$.

State the type of stereoisomerism shown.

Use  to represent bipy in your diagrams.





type of stereoisomerism .....

[3]

(c) Standard electrode potentials can be used to compare the stability of different complex ions for a given transition element.

Table 4.1 lists electrode potentials for some electrode reactions for Fe^{3+}/Fe^{2+} systems.

Table 4.1

electrode reaction	$E^{\ominus}$/V
$[Fe(H_2O)_6]^{3+} + e^- \rightleftharpoons [Fe(H_2O)_6]^{2+}$	+0.77
$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$	+0.36
$[Fe(bipy)_3]^{3+} + e^- \rightleftharpoons [Fe(bipy)_3]^{2+}$	+0.96

Use relevant data from Table 4.1 to state which iron(III) complex is hardest to reduce. Explain your choice.

iron(III) complex .....

explanation .....

.....

[1]

(d) The ligand bipyridine consists of two pyridine rings.

Pyridine, C_5H_5N, and benzene, C_6H_6, have similar planar, cyclic structures.

pyridine



Fig. 4.2

By reference to the hybridisation of the carbon atoms and the nitrogen atom, and orbital overlap, suggest how the σ and π bonds are formed in a pyridine molecule.

.....

.....

.....

.....

..... [3]

(e) Pyridine reacts with Cl_2 in the presence of $AlCl_3$ as shown in Fig. 4.3.

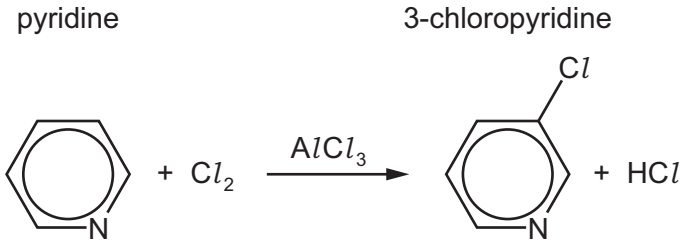
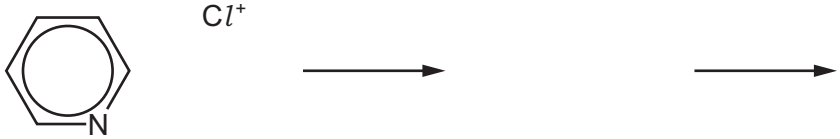


Fig. 4.3

The mechanism of this reaction is similar to that of the chlorination of benzene. $AlCl_3$ reacts with chlorine to generate an electrophile, Cl^+.

Complete the diagram to show the mechanism for the reaction of pyridine with Cl^+. Include all relevant charges, dipoles, lone pairs of electrons and curly arrows as appropriate.



[3]

[Total: 14]

5 **(a)** Compare the relative acidities of benzoic acid (C_6H_5COOH), phenylmethanol ($C_6H_5CH_2OH$), and phenol (C_6H_5OH).
Explain your reasoning.

..... > ..... > .....
most acidic least acidic

.....

.....

.....

.....

.....
[3]

(b) A series of nine separate experiments is carried out as shown in Table 5.1.

Complete the table by placing a tick (✓) in the relevant box if a reaction occurs. Place a cross (✗) in the box if no reaction occurs.

Table 5.1

	benzoic acid	phenylmethanol	phenol
Na(s)			
NaOH(aq)			
Na_2CO_3(aq)			

[3]

(c) **(i)** Benzoyl chloride, C_6H_5COCl, can be synthesised by the reaction of benzoic acid with either PCl_5 or $SOCl_2$.

Complete the equations for these reactions.

reaction 1 $C_6H_5COOH + PCl_5 \rightarrow C_6H_5COCl +$ ..... + ...

reaction 2 $C_6H_5COOH + SOCl_2 \rightarrow C_6H_5COCl +$ ..... + ...
[1]

(ii) Use your answer to **(c)(i)** to suggest why it is easier to isolate, in a pure form, the C_6H_5COCl from reaction 2 compared to reaction 1.

.....

..... [1]

(d) Benzoyl chloride is hydrolysed by water at room temperature to form benzoic acid.

(i) Complete the diagram to show the mechanism for the reaction between C_6H_5COCl and H_2O.

Include charges, dipoles, lone pairs of electrons and curly arrows as appropriate.



[4]

(ii) Name the type of mechanism you showed in **(d)(i)**.

..... [1]

(e) Acyl chlorides react with sodium carboxylates to form acid anhydrides as shown in Fig. 5.1.

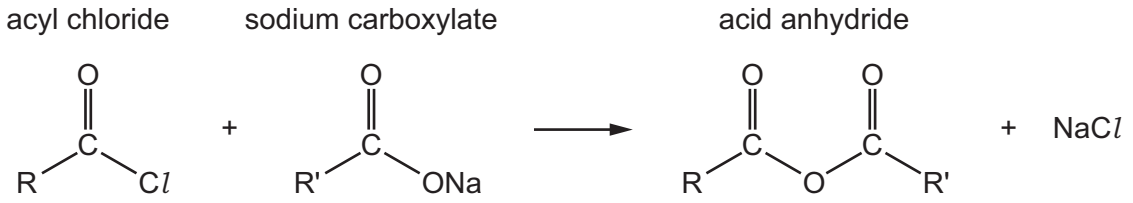


Fig. 5.1

The condensation polymers, polyanhydride and polyester, are formed by similar methods.

The repeat unit for a polyanhydride is shown in Fig. 5.2.

polyanhydride

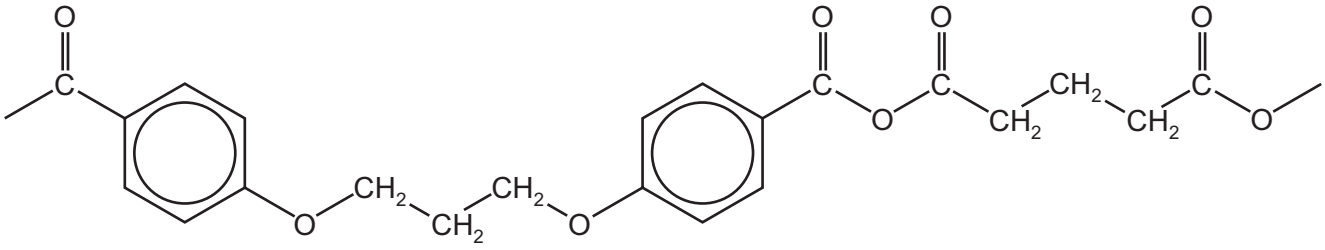


Fig. 5.2

(i) Use Fig. 5.1 and Fig. 5.2 to suggest the structures of the two monomers used to make this polyanhydride.

[2]

(ii) Polyanhydrides are biodegradable polymers.

Suggest how this polyanhydride can be degraded.

.....

..... [1]

[Total: 16]

6 **(a)** Describe what is meant by a racemic mixture.

.....

..... [1]

(b) Asparagine is an amino acid that contains a chiral carbon atom and displays stereoisomerism.

Separate samples of asparagine are dissolved in $CDCl_3$ and analysed using carbon-13 and proton (^1H) NMR spectroscopy.

asparagine

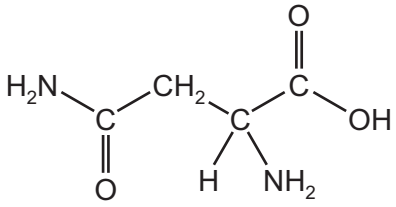


Fig. 6.1

Predict the number of peaks seen in the carbon-13 and proton (^1H) NMR spectra of asparagine.

	carbon-13 NMR	proton (^1H) NMR
number of peaks		

[1]

(c) The isoelectric point of asparagine, asn, is at pH 5.4.

(i) Describe the meaning of the term isoelectric point.

.....

..... [1]

(ii) Draw the structure of asparagine at pH 1.0.

[1]

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(d) Asparagine can polymerise to form poly(asparagine).

Draw the structure of poly(asparagine), showing **two** repeat units. The peptide linkage should be shown displayed.

[2]

(e) The isoelectric point of lysine, lys, is at pH 9.8.

lysine

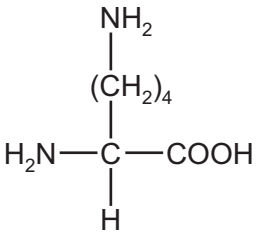


Fig. 6.2

A mixture of the dipeptide lys-asn and its two constituent amino acids, asparagine and lysine, is analysed by electrophoresis using a buffer at pH 5.0. The results obtained are shown in Fig. 6.3.

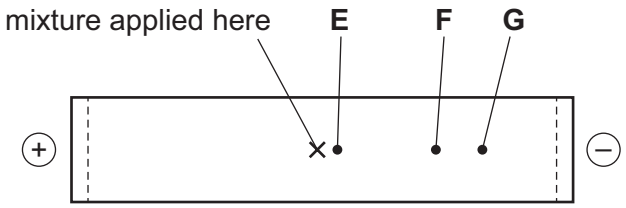


Fig. 6.3

Suggest identities for the species responsible for spots **E**, **F** and **G**. Explain your answers.

spot	identity
E	
F	
G	

.....

.....

.....

[3]

(f) Thin-layer and gas-liquid chromatography can be used to analyse mixtures of substances.

Each type of chromatography makes use of a stationary phase and a mobile phase.

(i) Complete Table 6.1 with an example of each of these.

Table 6.1

	stationary phase	mobile phase
thin-layer chromatography		
gas-liquid chromatography		

[1]

(ii) An unknown amino acid is analysed using thin-layer chromatography. Two chromatographs of the unknown amino acid and four reference amino acids, **P**, **Q**, **R** and **S**, are obtained using two different solvents.

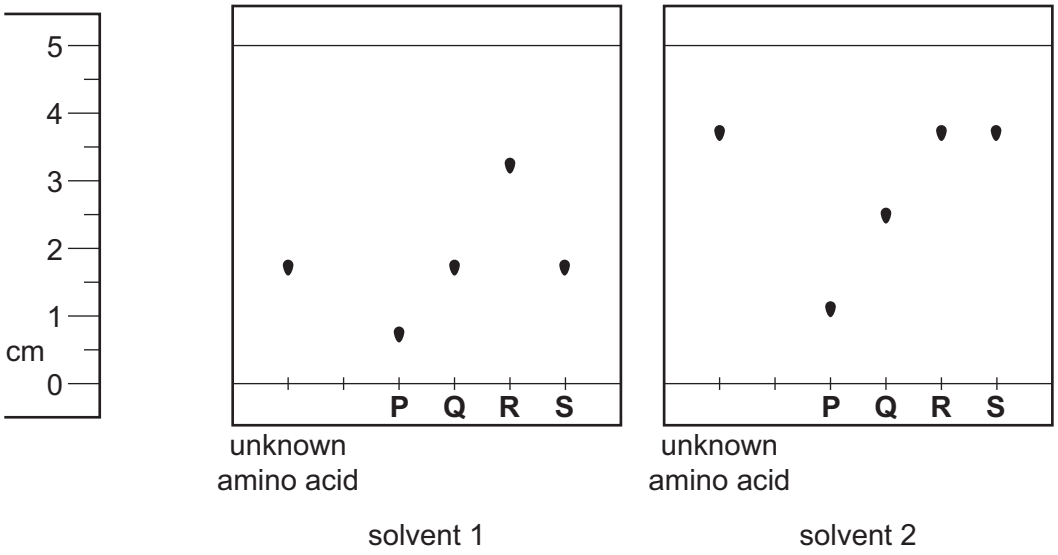


Fig. 6.4

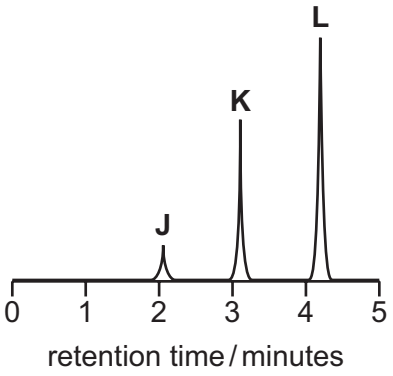
Identify the unknown amino acid. Justify your answer.

.....

.....

..... [1]

(g) A mixture containing three organic compounds is analysed by gas chromatography and mass spectrometry. The gas chromatogram is shown.



peak	J	K	L
area / mm^2	8	44	58

Fig. 6.5

The area underneath each peak is proportional to the mass of the respective compound in the mixture.

The concentration of **K** in the mixture is 5.52×10^{-2} g dm^{-3}.

Calculate the concentration, in mol dm^{-3}, of compound **L** in the mixture.
[M_r: **L**, 116]

concentration of **L** = ... mol dm^{-3} [1]

[Total: 12]

7 Procaine is used as an anaesthetic in medicine. It can be synthesised from methylbenzene in five steps as shown in Fig. 7.1.

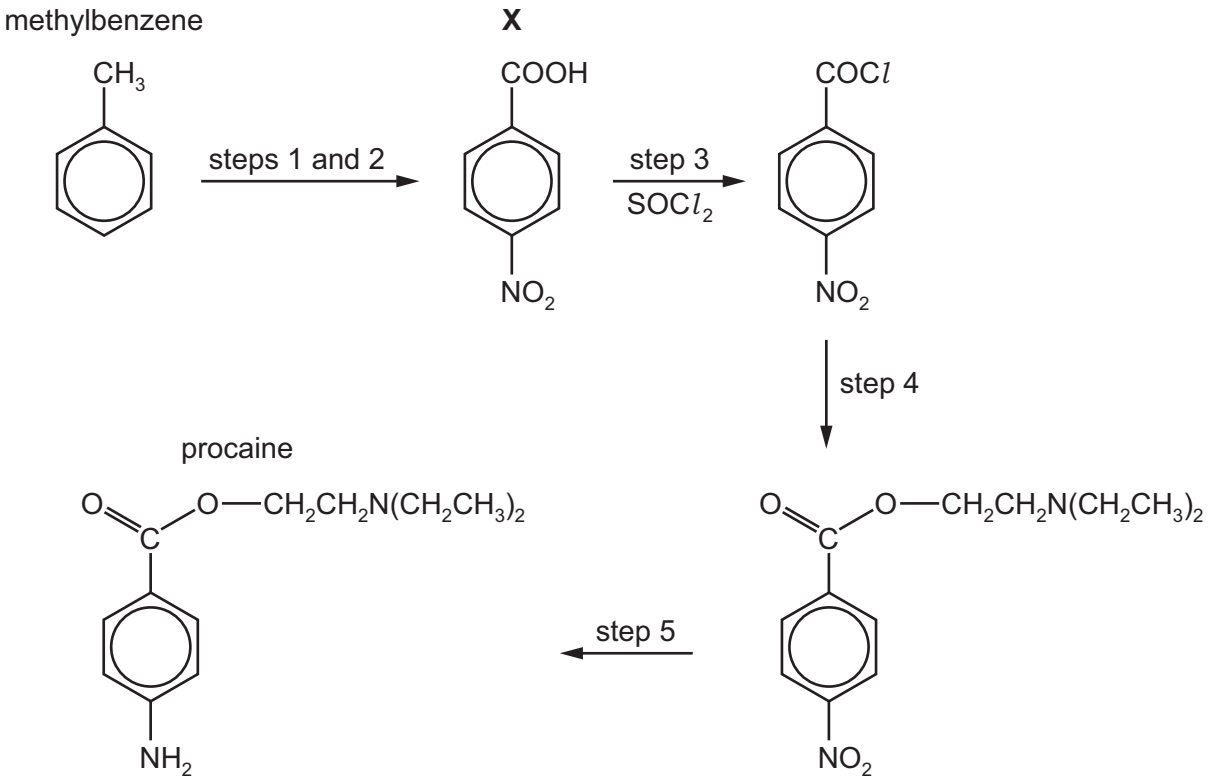


Fig. 7.1

(a) (i) Name all the functional groups present in procaine.

..... [1]

(ii) A molecule of procaine has 13 carbon atoms.

State the number of carbon atoms that are sp, sp^2 and sp^3 hybridised in procaine.

sp carbons = ... sp^2 carbons = ... sp^3 carbons = ... [1]

(b) The proton (^1H) NMR spectrum of procaine dissolved in D_2O is recorded.

Predict the number of peaks observed.

..... [1]

(c) State why procaine can act as a base.

.....

..... [1]

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(d) Compound **X** can be synthesised in two steps from methylbenzene.

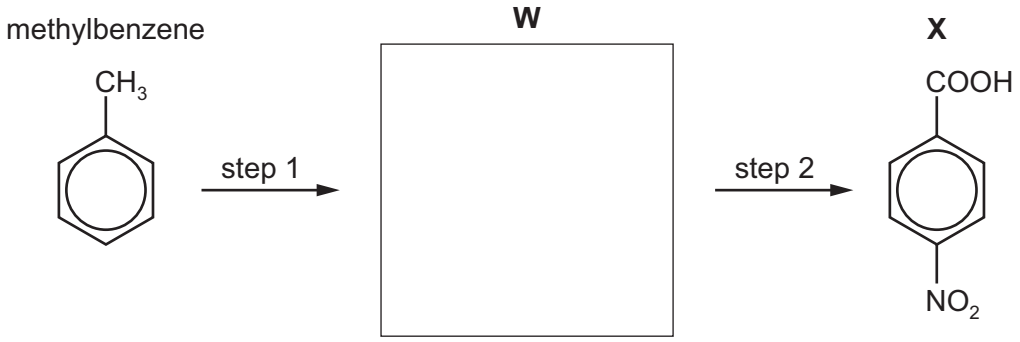


Fig. 7.2

(i) Draw the structure of compound **W** in the box provided. [1]

(ii) State the reagents and conditions for step 1 and step 2.

step 1 .....

step 2 .....
[2]

(e) Procaine is synthesised in three steps from **X**.

Suggest the reagents and conditions for step 4 and for step 5 in Fig. 7.1.

step 4 .....

step 5 .....
[3]

(f) **(i)** Explain what is meant by partition coefficient, K_{pc}.

.....

..... [2]

(ii) The partition coefficient of procaine between octan-1-ol and water is 1.77.

Octan-1-ol and water are immiscible. A solution containing 0.500 g of procaine in 75.0 cm^3 of water is shaken with 50.0 cm^3 of octan-1-ol.

Calculate the mass of procaine that is extracted into the octan-1-ol.

mass of procaine extracted = ... g [2]

[Total: 14]

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Important values, constants and standards

molar gas constant	$R = 8.31\,\text{J K}^{-1}\,\text{mol}^{-1}$
Faraday constant	$F = 9.65 \times 10^{4}\,\text{C mol}^{-1}$
Avogadro constant	$L = 6.022 \times 10^{23}\,\text{mol}^{-1}$
electronic charge	$e = -1.60 \times 10^{-19}\,\text{C}$
molar volume of gas	$V_m = 22.4\,\text{dm}^3\,\text{mol}^{-1}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0\,\text{dm}^3\,\text{mol}^{-1}$ at room conditions
ionic product of water	$K_w = 1.00 \times 10^{-14}\,\text{mol}^2\,\text{dm}^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18\,\text{kJ kg}^{-1}\,\text{K}^{-1}$ ($4.18\,\text{J g}^{-1}\,\text{K}^{-1}$)

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The Periodic Table of Elements

Group																		
1	2											13	14	15	16	17	18
								1 H hydrogen 1.0									2 He helium 4.0
3 Li lithium 6.9	4 Be beryllium 9.0											5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2
11 Na sodium 23.0	12 Mg magnesium 24.3											13 Al aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 Cl chlorine 35.5	18 Ar argon 39.9
19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium –	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –
87 Fr francium –	88 Ra radium –	89–103 actinoids	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –	113 Nh nihonium –	114 Fl flerovium –	115 Mc moscovium –	116 Lv livermorium –	117 Ts tennessine –	118 Og oganesson –

Key

atomic number
atomic symbol
name
relative atomic mass

lanthanoids	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.4	61 Pm promethium –	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
actinoids	89 Ac actinium –	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium –	94 Pu plutonium –	95 Am americium –	96 Cm curium –	97 Bk berkelium –	98 Cf californium –	99 Es einsteinium –	100 Fm fermium –	101 Md mendelevium –	102 No nobelium –	103 Lr lawrencium –

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