



Cambridge International AS & A Level

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CHEMISTRY

9701/41

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.



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

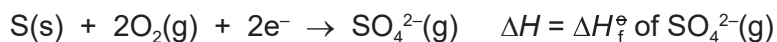
barium [1]

- (c) The solubility product, K_{sp} , of BaSO_4 is $1.08 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$ 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]

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



Calculate the standard enthalpy change of formation, $\Delta H_f^\ominus$, of $\text{SO}_4^{2-}\text{(g)}$. 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, $\text{BaSO}_4\text{(s)}$	–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 $\text{S(g)} \rightarrow \text{S}^{2-}\text{(g)}$	+440
standard enthalpy change for $\text{O(g)} \rightarrow \text{O}^{2-}\text{(g)}$	+657
O=O bond energy	+496

$\Delta H_f^\ominus$ of $\text{SO}_4^{2-}\text{(g)} = \dots\dots\dots \text{kJ mol}^{-1}$ [3]

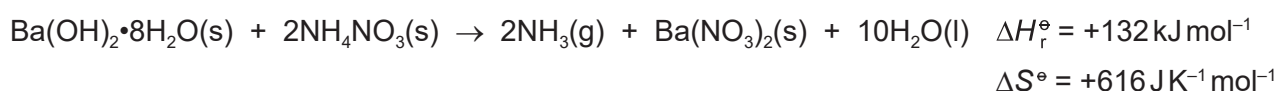
- (ii) Suggest how the lattice energy of $\text{BaSO}_4(\text{s})$ differs from the lattice energy of $\text{Cs}_2\text{SO}_4(\text{s})$. Explain your answer.

.....

 [2]

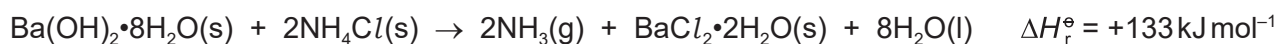
- (e) The reaction of solid hydrated barium hydroxide, $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, with ammonium salts is endothermic.

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



temperature = ... °C [2]

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



Some relevant standard entropies are given in Table 1.2.

Table 1.2

substance	$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}(\text{s})$	$\text{NH}_4\text{Cl}(\text{s})$	$\text{NH}_3(\text{g})$	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}(\text{s})$	$\text{H}_2\text{O}(\text{l})$
$S^\ominus / \text{JK}^{-1} \text{ mol}^{-1}$	427	95	192	203	70

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

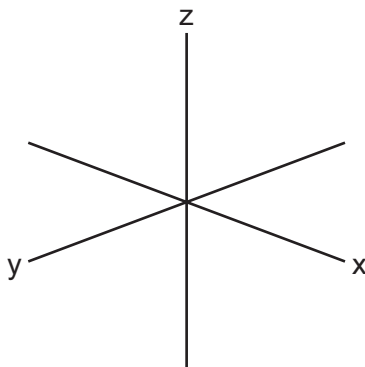
$\Delta G^\ominus = \dots\dots\dots \text{ kJ mol}^{-1}$ [3]

[Total: 16]

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 HCl.

- (i) Write the ionic equation, and state the type of reaction, for the reaction of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ with NaOH(aq).

ionic equation

type of reaction

[2]

- (ii) Write the ionic equation, and state the type of reaction, for the reaction of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ with concentrated HCl.

ionic equation

type of reaction

[2]

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

Table 2.1

electrode reaction	E°/V
$\text{Mn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mn}$	-1.18
$\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	+1.36
$2\text{HOCl} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Cl}_2 + 2\text{H}_2\text{O}$	+1.64
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 2\text{H}_2\text{O}$	+1.23
$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{MnO}_2 + 2\text{H}_2\text{O}$	+1.67

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

State the type of reaction.

formula of manganese species formed

type of reaction

[1]

[Total: 13]

- 3 (a) The rate of reaction between 2-chloro-2-methylpropane, $(\text{CH}_3)_3\text{CCl}$, and methanol is investigated. When a large excess of methanol is used, the overall reaction is first order.

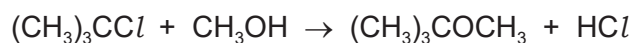


Fig. 3.1 shows the results obtained.

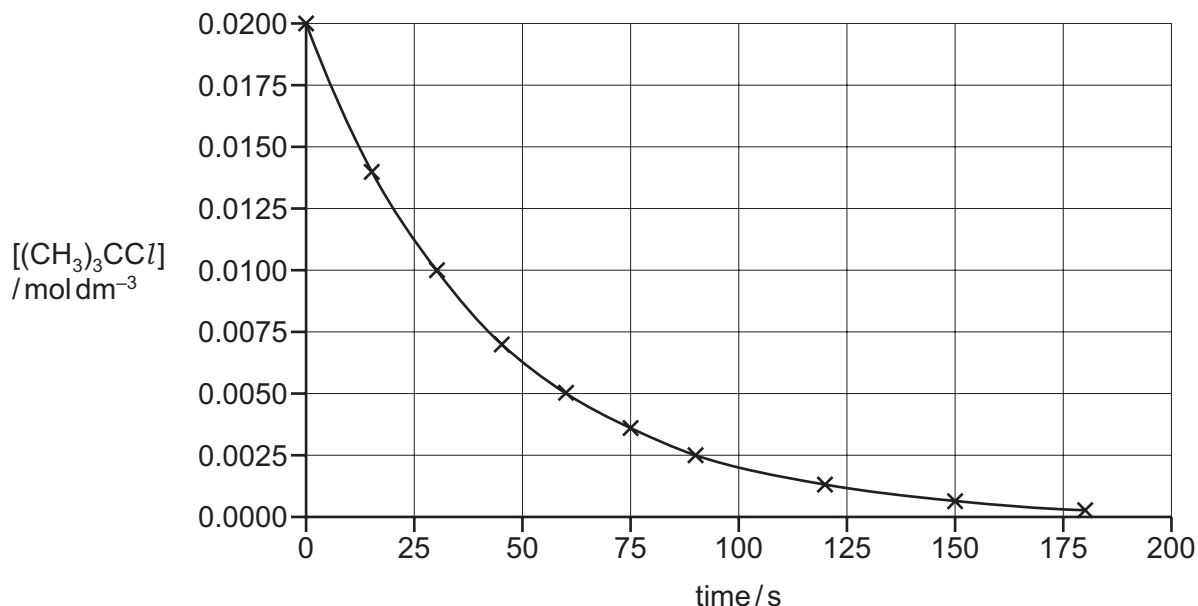


Fig. 3.1

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

rate = ... $\text{mol dm}^{-3} \text{s}^{-1}$ [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° .

.....

 [1]

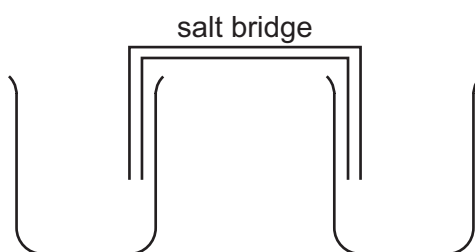
- (ii) A salt bridge is used in an electrochemical cell.

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° of the $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$, $\text{H}^+(\text{aq})/\text{Cr}^{3+}(\text{aq})$ electrode against the standard hydrogen electrode.

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



[3]

- (iv) The E° of the $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$, $\text{H}^+(\text{aq})/\text{Cr}^{3+}(\text{aq})$ 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]

- (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°/V
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+1.33
$\text{CH}_3\text{CHO} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{CH}_3\text{CH}_2\text{OH}$	-0.61
$\text{CH}_3\text{COOH} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{CH}_3\text{CHO} + \text{H}_2\text{O}$	-0.94
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.23

- (i) Ethanal is oxidised to ethanoic acid in the presence of $\text{Cr}_2\text{O}_7^{2-}$ ions.

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

ionic equation

$$E^\circ_{\text{cell}} = \dots\dots\dots \text{V}$$

[2]

- (ii) In an ethanol-oxygen fuel cell, $\text{CH}_3\text{CH}_2\text{OH}(\text{l})$ and $\text{O}_2(\text{g})$ are in contact with two inert electrodes immersed in an acidic solution.

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



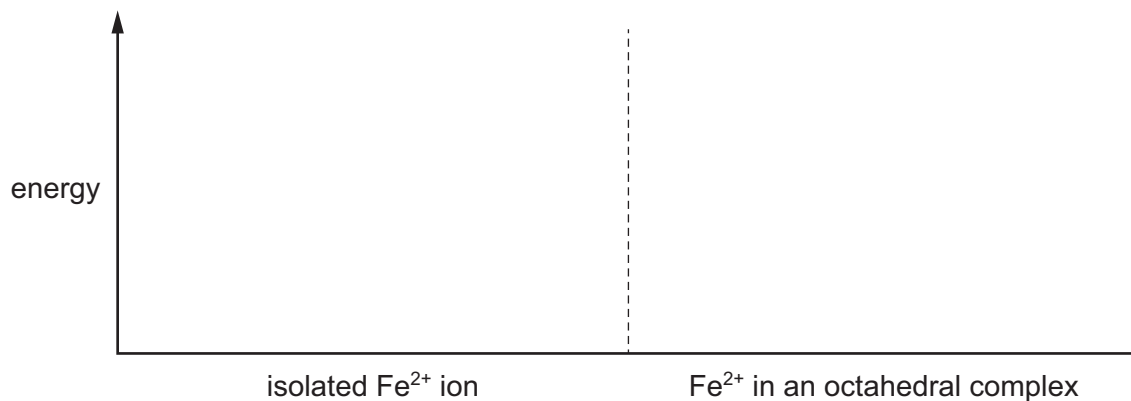
Calculate ΔG° , in kJ mol^{-1} , for the oxidation of ethanol by oxygen.

$$\Delta G^\circ = \dots\dots\dots \text{kJ mol}^{-1} \quad [2]$$

[Total: 15]

- 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.

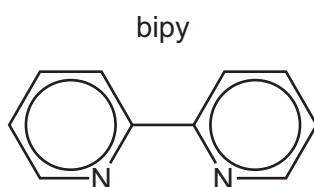


Fig. 4.1

Explain what is meant by bidentate ligand.

.....

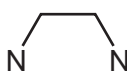
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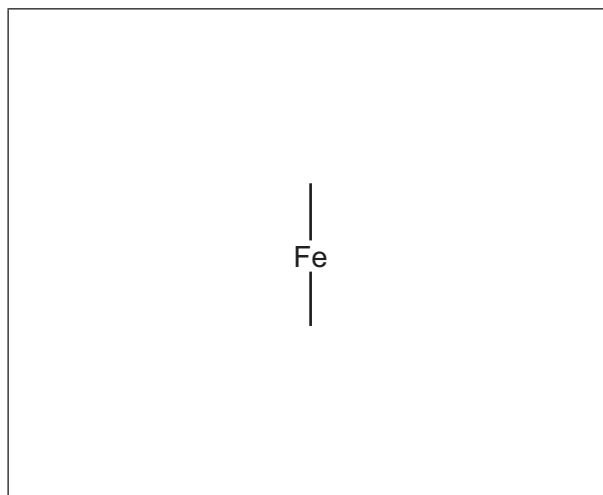
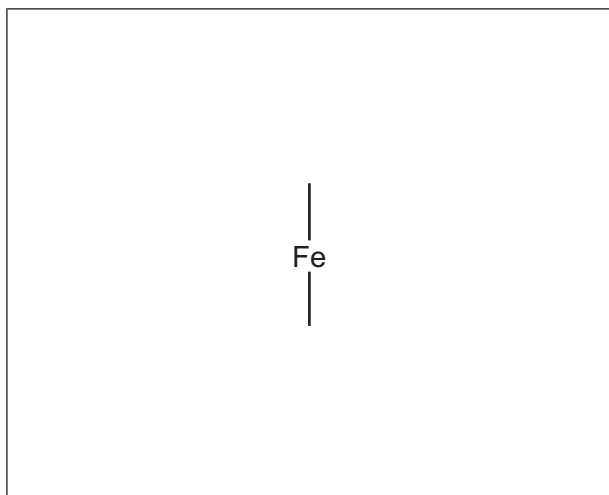
..... [2]

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

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

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 $\text{Fe}^{3+}/\text{Fe}^{2+}$ systems.

Table 4.1

electrode reaction	$E^\ominus/\text{V}$
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + \text{e}^- \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	+0.77
$[\text{Fe}(\text{CN})_6]^{3-} + \text{e}^- \rightleftharpoons [\text{Fe}(\text{CN})_6]^{4-}$	+0.36
$[\text{Fe}(\text{bipy})_3]^{3+} + \text{e}^- \rightleftharpoons [\text{Fe}(\text{bipy})_3]^{2+}$	+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]

- 5 (a) Compare the relative acidities of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$), phenylmethanol ($\text{C}_6\text{H}_5\text{CH}_2\text{OH}$), and phenol ($\text{C}_6\text{H}_5\text{OH}$). 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 (X) in the box if no reaction occurs.

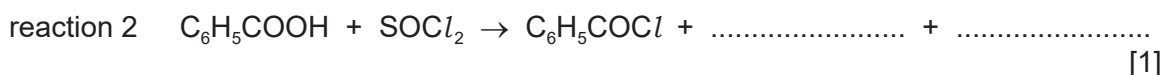
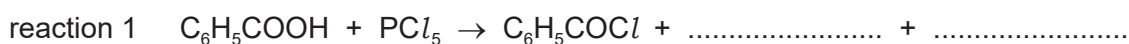
Table 5.1

	benzoic acid	phenylmethanol	phenol
Na(s)			
NaOH(aq)			
$\text{Na}_2\text{CO}_3(\text{aq})$			

[3]

- (c) (i) Benzoyl chloride, $\text{C}_6\text{H}_5\text{COCl}$, can be synthesised by the reaction of benzoic acid with either PCl_5 or SOCl_2 .

Complete the equations for these reactions.



[1]

- (ii) Use your answer to (c)(i) to suggest why it is easier to isolate, in a pure form, the $\text{C}_6\text{H}_5\text{COCl}$ 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 $\text{C}_6\text{H}_5\text{COCl}$ 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.

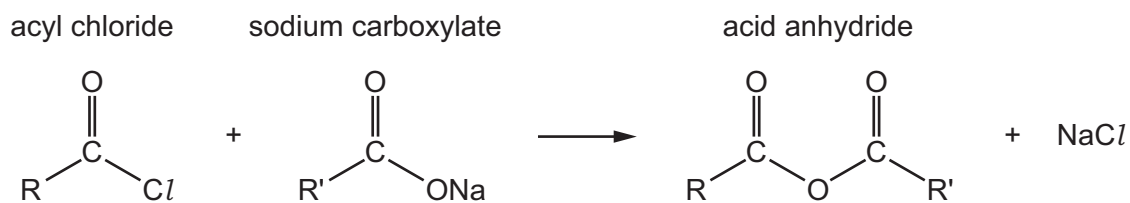


Fig. 5.1

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

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

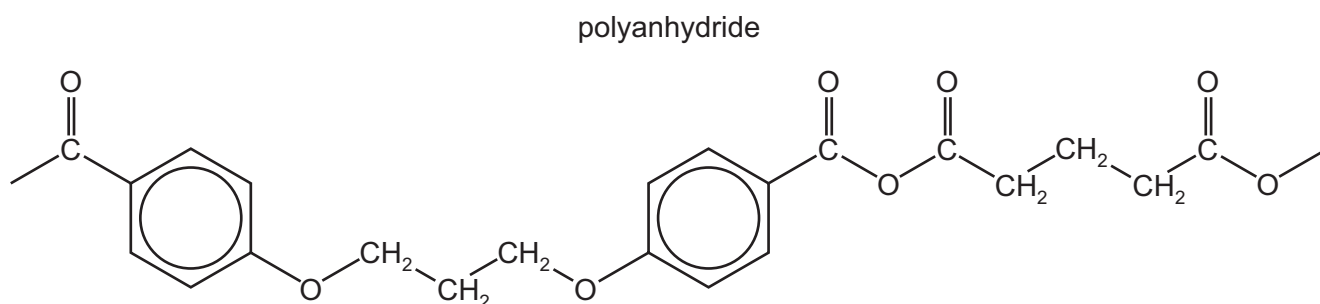


Fig. 5.2

(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.

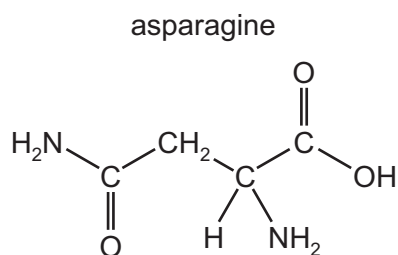


Fig. 6.1

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]

- (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.

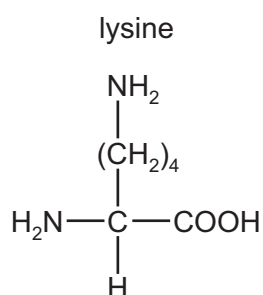


Fig. 6.2

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.

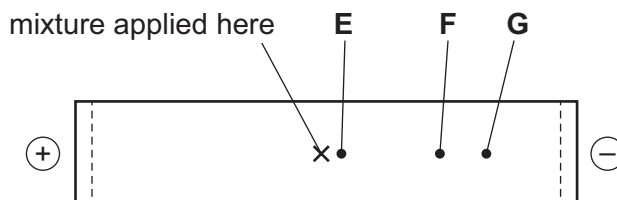


Fig. 6.3

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.

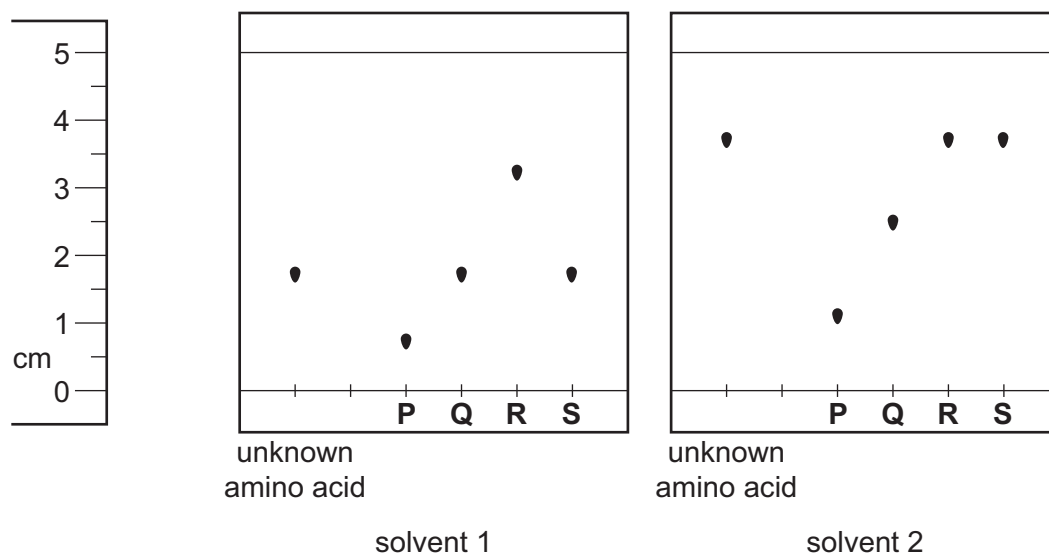


Fig. 6.4

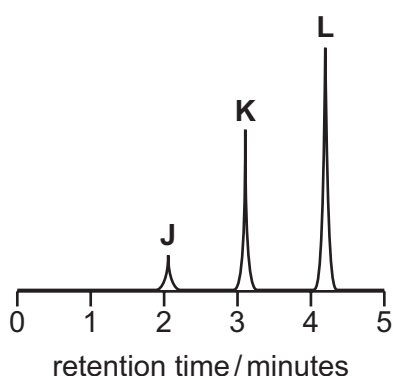
Identify the unknown amino acid. Justify your answer.

.....

.....

..... [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 $5.52 \times 10^{-2} \text{ g dm}^{-3}$.

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.

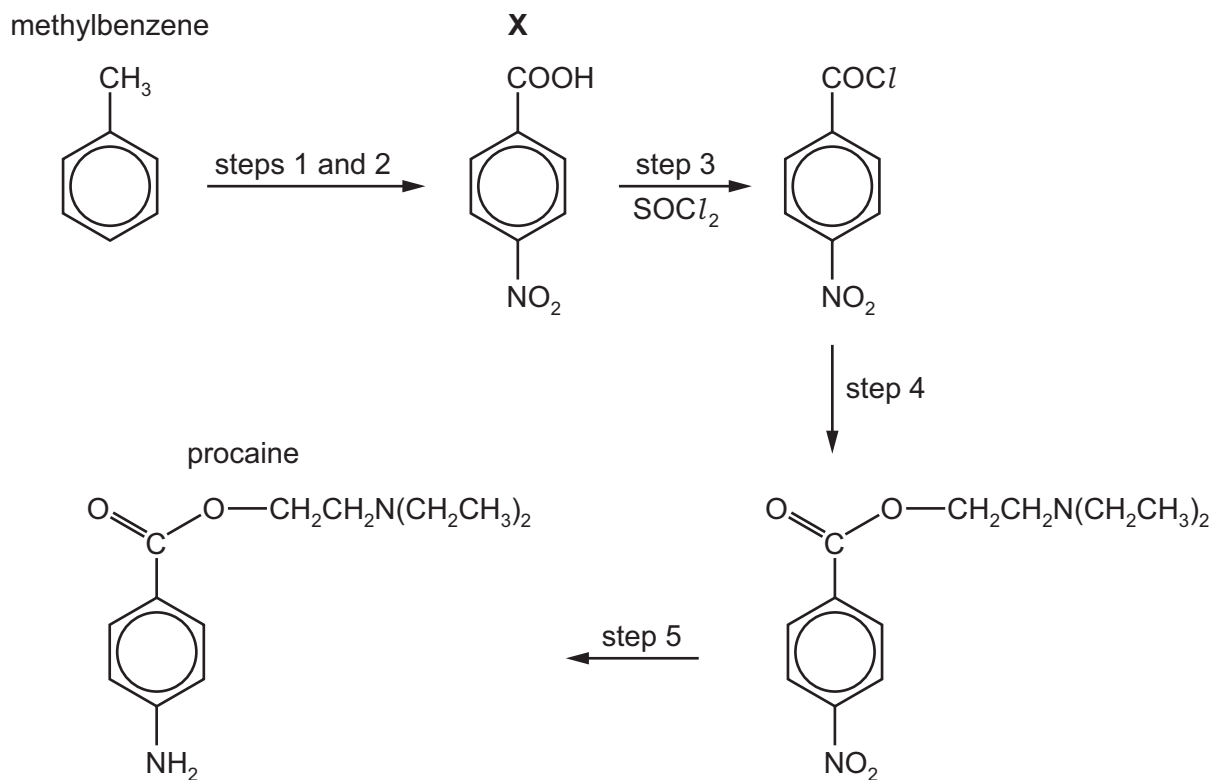


Fig. 7.1

- (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]

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

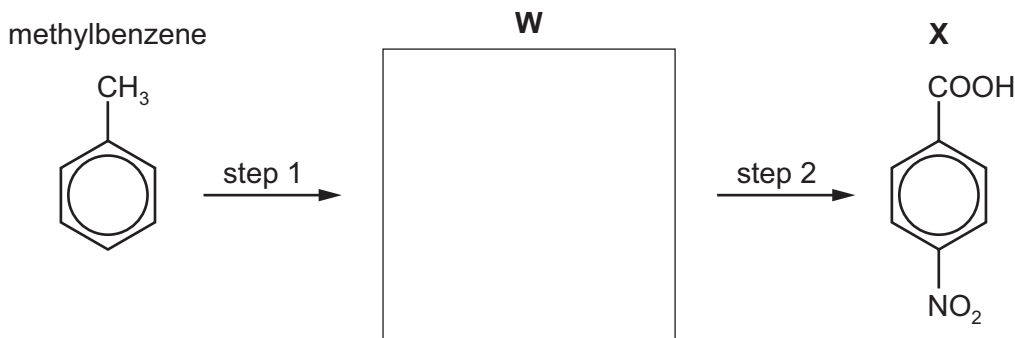


Fig. 7.2

(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 cm³ of water is shaken with 50.0 cm³ 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]

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 J g ⁻¹ K ⁻¹)

The Periodic Table of Elements

Group																			
1	2	Key												13	14	15	16	17	18
		atomic number atomic symbol name relative atomic mass												1 H hydrogen 1.0					
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	lanthanoids		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 —	actinoids		104 Rf rutherfordium —	105 Db dubnium —	106 Sg seaborgium —	107 Bh bohrium —	108 Hs hassium —	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 oganeson —		

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	euporium	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
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	226.0
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	—

lanthanoids

actinoids



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CHEMISTRY

9701/42

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.



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

- 1 (a) The solubility of the Group 2 hydroxides increases down the group.

Explain this trend.

.....

.....

.....

.....

..... [3]

- (b) The solubility of $\text{Be}(\text{OH})_2$ in water is $2.40 \times 10^{-6} \text{ g dm}^{-3}$ at 298 K.

- (i) Write an expression for the solubility product, K_{sp} , of $\text{Be}(\text{OH})_2$ and state its units.

$K_{\text{sp}} =$

units = ... [2]

- (ii) Calculate the numerical value of K_{sp} for $\text{Be}(\text{OH})_2$ at 298 K.

$K_{\text{sp}} =$ [2]

- (c) $\text{Be}(\text{OH})_2$ is soluble in aqueous solutions containing an excess of hydroxide ions and forms the complex ion $[\text{Be}(\text{OH})_4]^{2-}$. This complex ion has a similar shape to that of $[\text{CuCl}_4]^{2-}$.

- (i) Define the term complex ion.

.....

..... [1]

- (ii) Draw a three-dimensional diagram to show the structure of the complex ion $[\text{Be}(\text{OH})_4]^{2-}$. Name the shape of the $[\text{Be}(\text{OH})_4]^{2-}$ complex ion.

shape [1]

- (d) (i) Explain why transition elements can form complex ions.

.....
 [1]

- (ii) Complete Table 1.1 to show the coordination number of each metal ion, and the shapes and overall polarities of the complex ions listed.

Table 1.1

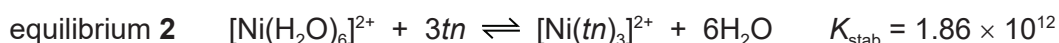
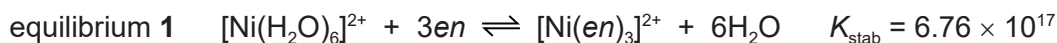
complex ion	shape	coordination number	polar or non-polar
<i>cis</i> -[Pt(H ₂ NCH ₂ CH ₂ NH ₂)Cl ₂]	square planar		
[Ag(NH ₃) ₂] ⁺			non-polar
[Fe(C ₂ O ₄) ₃] ³⁻		6	

[2]

- (e) (i) Define stability constant, K_{stab} .

.....
 [1]

- (ii) Nickel can form complexes with the ligands *en*, H₂NCH₂CH₂NH₂, and *tn*, H₂NCH₂CH₂CH₂NH₂, as shown.



Construct an expression for the stability constant, K_{stab} , for equilibrium 1.
 State the units for K_{stab} .

$$K_{\text{stab}} =$$

units = ...
 [2]

- (iii) Describe what the K_{stab} values indicate about the position of equilibrium for equilibrium 1 and 2. Use the K_{stab} values to deduce which complex, $[\text{Ni}(\text{en})_3]^{2+}$ or $[\text{Ni}(\text{tn})_3]^{2+}$, is more stable.

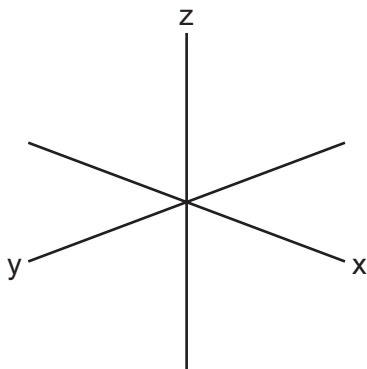
.....
 [1]

[Total: 16]

- 2 (a) Explain why transition elements have variable oxidation states.

.....
..... [1]

- (b) Sketch the shape of a $3d_{xy}$ orbital.



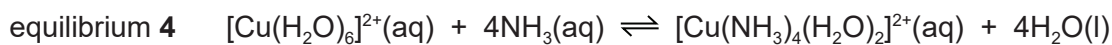
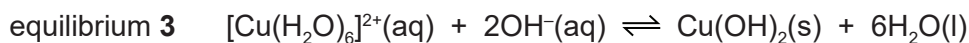
[1]

- (c) Explain why transition elements form coloured compounds.

.....
.....
.....
.....
.....
..... [3]

(d) Aqueous solutions of copper(II) salts contain $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ions.

Equilibrium 3 and equilibrium 4 show two reactions of these ions.



(i) State the colour of $\text{Cu}(\text{OH})_2(\text{s})$ and $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}(\text{aq})$.

colour of $\text{Cu}(\text{OH})_2(\text{s})$

colour of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}(\text{aq})$

[1]

(ii) Use Le Chatelier's principle to explain why a precipitate is formed when $\text{NaOH}(\text{aq})$ is added dropwise to $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$.

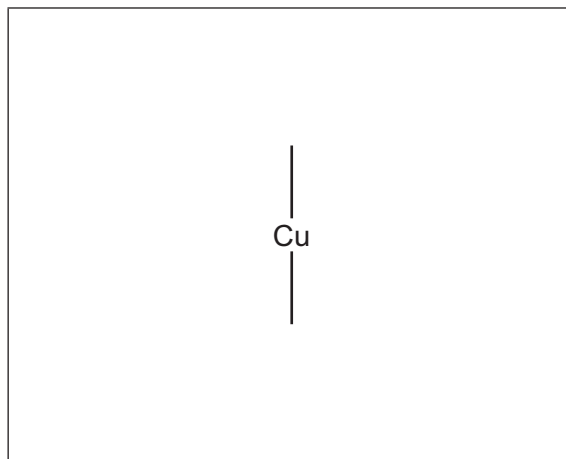
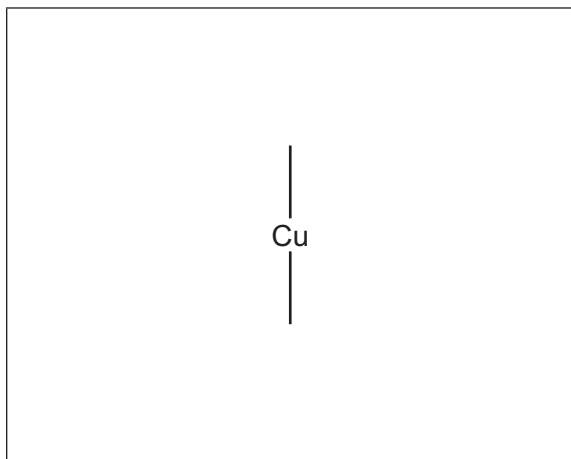
.....

.....

..... [1]

(e) There are two possible stereoisomers with the formula $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$.

Draw three-dimensional diagrams to show the two stereoisomers.



[2]

[Total: 9]

3 (a) (i) Define first electron affinity.

.....

 [2]

(ii) The first electron affinity of an atom is usually an exothermic process, whereas the second electron affinity is an endothermic process.

Suggest why.

.....
 [1]

(iii) Describe the general trend in first electron affinities for Cl, Br and I. Explain your answer.

.....

 [2]

(b) Table 3.1 shows energy changes to be used in this question and in (c).

Table 3.1

energy change	value / kJ mol ⁻¹
standard enthalpy change of atomisation of zinc	+131
first ionisation energy of zinc	+906
second ionisation energy of zinc	+1733
standard enthalpy change of formation of ZnI ₂ (s)	-208
lattice energy, $\Delta H_{\text{latt}}^{\circ}$, of zinc iodide, ZnI ₂ (s)	-2605
first ionisation energy of iodine	+1008
second ionisation energy of iodine	+1846
I–I bond energy	+151
enthalpy change of sublimation of iodine, I ₂ (s) → I ₂ (g)	+62

Calculate the first electron affinity for iodine. Use relevant data from Table 3.1 in your working. It may be helpful to draw a labelled energy cycle. Show all working.

first electron affinity for iodine = ... kJ mol^{-1} [3]

- (c) Predict how $\Delta H_{\text{latt}}^{\ominus}$ of $\text{CdI}_2(\text{s})$ differs from $\Delta H_{\text{latt}}^{\ominus}$ of $\text{ZnI}_2(\text{s})$. Place a tick (✓) in the appropriate box in Table 3.2.

Table 3.2

$\Delta H_{\text{latt}}^{\ominus}$ of $\text{CdI}_2(\text{s})$ is less negative than $\Delta H_{\text{latt}}^{\ominus}$ of $\text{ZnI}_2(\text{s})$	$\Delta H_{\text{latt}}^{\ominus}$ of $\text{CdI}_2(\text{s})$ is the same as $\Delta H_{\text{latt}}^{\ominus}$ of $\text{ZnI}_2(\text{s})$	$\Delta H_{\text{latt}}^{\ominus}$ of $\text{CdI}_2(\text{s})$ is more negative than $\Delta H_{\text{latt}}^{\ominus}$ of $\text{ZnI}_2(\text{s})$

Explain your answer.

.....
 [1]

[Total: 9]

- 4 (a) Calcium carbonate decomposes on heating.



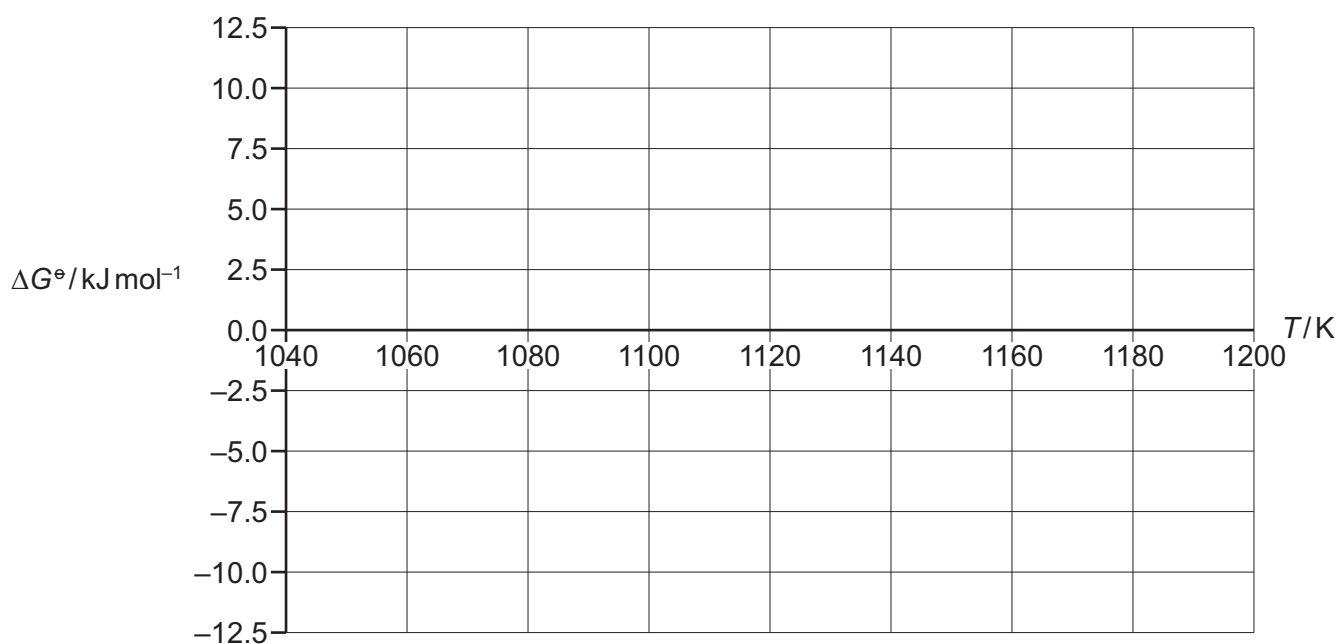
Table 4.1 shows the values of the Gibbs free energy change, ΔG° , for this reaction at various temperatures.

Table 4.1

T/K	$\Delta G^\circ/\text{kJ mol}^{-1}$
1050	9.9
1085	4.3
1120	-1.3
1148	-5.8
1176	-10.3

Assume the standard enthalpy change, ΔH° , and the standard entropy change, ΔS° , for this reaction remain constant over this temperature range.

- (i) Use the data in Table 4.1 to plot a graph of ΔG° against T on the grid.



[2]

- (ii) Calculate the gradient of your graph. Determine the ΔS° in $\text{JK}^{-1} \text{mol}^{-1}$ for this reaction. Show all working.

$$\Delta S^\circ = \dots\dots\dots \text{JK}^{-1} \text{mol}^{-1} \quad [2]$$

- (b) Group 1 hydrogencarbonates, MHCO_3 , decompose on gentle heating to give the corresponding metal carbonate, carbon dioxide and water vapour.

(i) Write an ionic equation for the decomposition of the hydrogencarbonate ion.

..... [1]

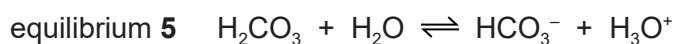
(ii) The thermal stability of Group 1 hydrogencarbonates increases down the group.

Suggest an explanation for the trend in thermal stability of the Group 1 hydrogencarbonates.

.....

 [2]

- (c) The buffer system in seawater contains a mixture of HCO_3^- and H_2CO_3 .



(i) Define a buffer solution.

.....

 [2]

(ii) Construct **two** equations to show how equilibrium 5 acts as a buffer solution.

.....
 [2]

(iii) The $[\text{HCO}_3^-]/[\text{H}_2\text{CO}_3]$ ratio in a sample of seawater is 14.1.

Calculate the pH of this sample.

$[\text{p}K_{\text{a}}: \text{H}_2\text{CO}_3, 6.35]$

pH = ... [3]

[Total: 14]

- 5 (a) Complete Table 5.1 to predict the substance liberated at each electrode during electrolysis of the indicated electrolyte with inert electrodes.

Table 5.1

electrolyte	substance liberated at the anode	substance liberated at the cathode
$\text{PbBr}_2(\text{l})$		
concentrated $\text{NaCl}(\text{aq})$		
$\text{Cu}(\text{NO}_3)_2(\text{aq})$		

[3]

- (b) An electrolytic cell is set up to determine a value for the Avogadro constant, L . The electrolyte is dilute sulfuric acid and both electrodes are copper.

When a current of 0.600 A is passed through the acid for 30.0 minutes, the anode decreases in mass by 0.350 g.

- (i) State the relationship between the Faraday constant, F , and the Avogadro constant, L .

..... [1]

- (ii) Use the experimental information in (b) and data from the table on page 23 to calculate a value for the Avogadro constant, L .

Show all working.

Avogadro constant, $L =$ [4]

[Total: 8]

- 6 (a) The reagent and conditions required for the nitration of benzene, benzoic acid and phenol are shown in Table 6.1.

Table 6.1

compound	reagents and conditions for nitration
benzene	concentrated HNO_3 , 50°C , concentrated H_2SO_4 catalyst
benzoic acid	concentrated HNO_3 , 100°C , concentrated H_2SO_4 catalyst
phenol	dilute $\text{HNO}_3(\text{aq})$, 20°C

Concentrated HNO_3 reacts with concentrated H_2SO_4 to generate the electrophile NO_2^+ .

- (i) Complete Fig. 6.1 to show the mechanism of the reaction between benzene and NO_2^+ . Include all relevant curly arrows and charges.

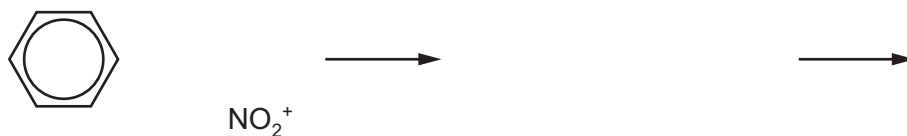


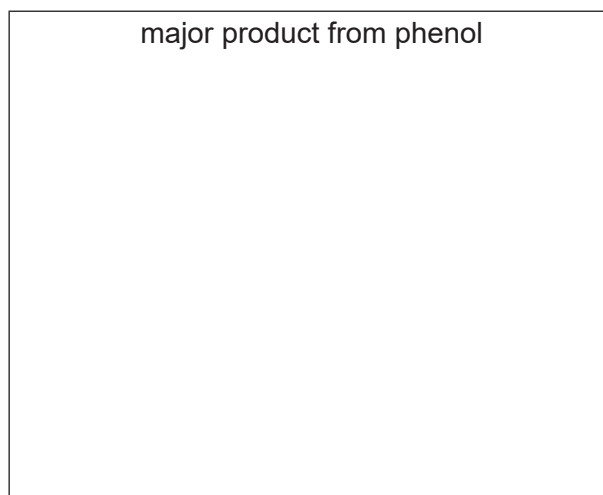
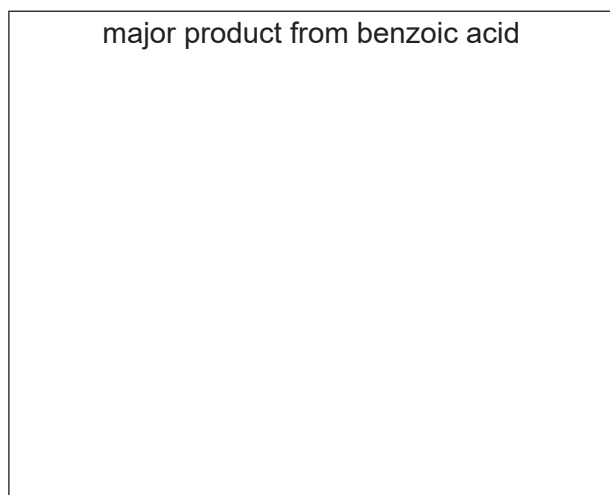
Fig. 6.1

[3]

- (ii) Write an equation to show how H_2SO_4 is regenerated.

..... [1]

- (b) Draw the major products from the mononitration of benzoic acid and of phenol.



[2]

- (c) Compare the relative ease of nitration of benzene, benzoic acid and phenol. Explain your reasoning; include reference to the structures of the three compounds in your answer.

..... > >
easiest least easy

.....

.....

.....

.....

.....

[4]

- (d) The azo compound Congo Red is used as an acid–base indicator and can be made by the route shown in Fig. 6.2.

In step 3 of this synthesis, compound **Y** reacts with compound **Z**. Compound **Z** is made from compound **X**. Assume that the SO_3^-Na^+ groups do not react.

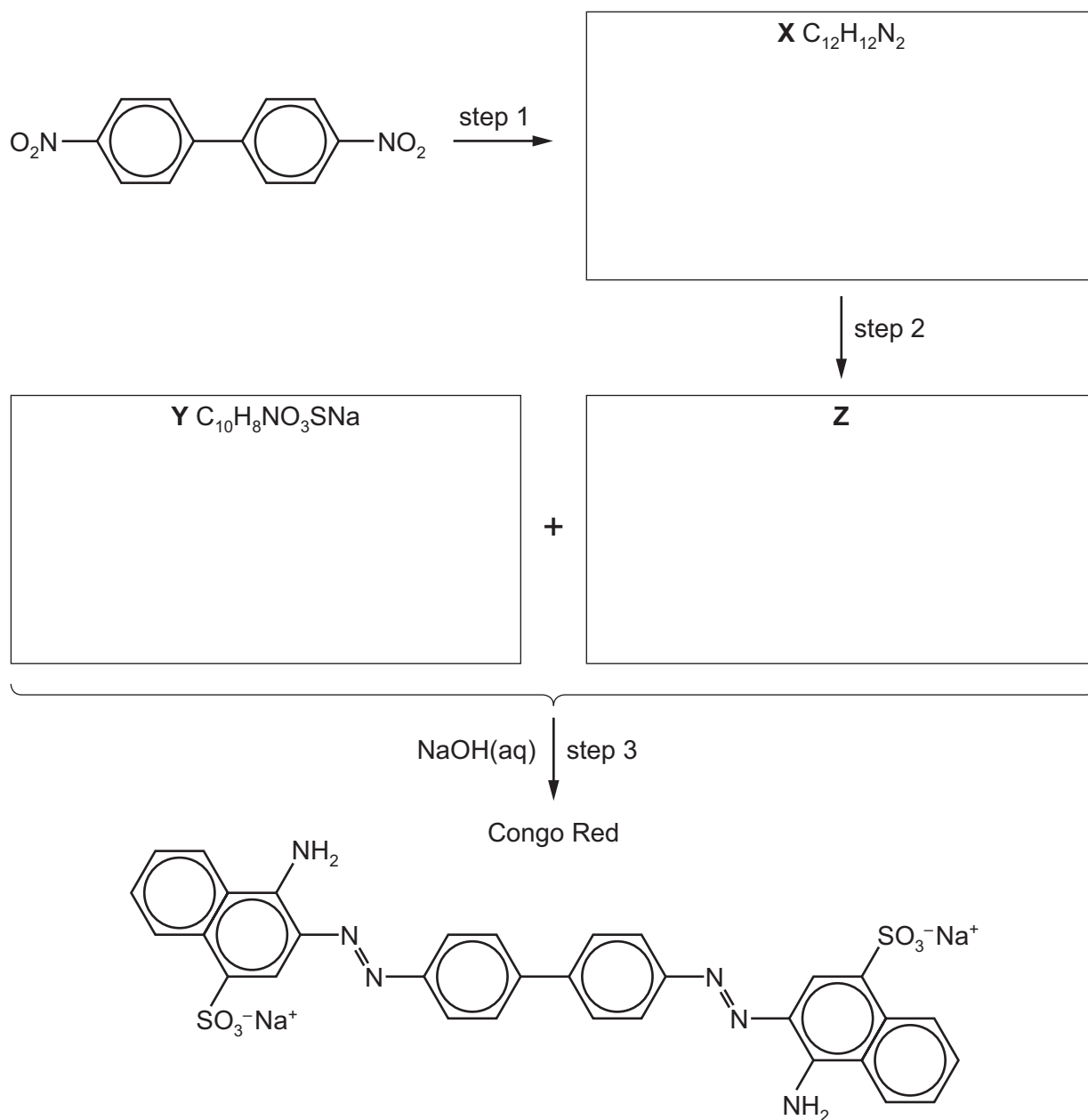


Fig. 6.2

- (i) Suggest structures for compounds **X**, **Y** and **Z** and draw them in the boxes in Fig. 6.2. [3]
- (ii) Give the reagents and conditions for step 1 and step 2.

step 1

step 2

[3]

[Total: 16]

- 7 (a) State the uses of TMS and D₂O in NMR spectroscopy.

TMS

D₂O

[1]

- (b) The three isomeric ketones with molecular formula C₅H₁₀O are:

- pentan-2-one
- pentan-3-one
- 3-methylbutanone.

- (i) Complete Table 7.1 to show the number of peaks observed in the proton (¹H) NMR spectrum and in the carbon-13 NMR spectrum for each compound listed.

Table 7.1

ketone	number of peaks observed in the proton (¹ H) NMR spectrum	number of peaks observed in the carbon-13 NMR spectrum
pentan-2-one		
pentan-3-one		
3-methylbutanone		

[2]

- (ii) State **all** the ketones with molecular formula C₅H₁₀O that have:

a doublet in their proton (¹H) NMR spectrum

.....

a singlet in their proton (¹H) NMR spectrum.

.....

[2]

- (c) Cortisone, $C_{21}H_{28}O_5$, is a naturally occurring chemical that contains chiral carbon atoms.

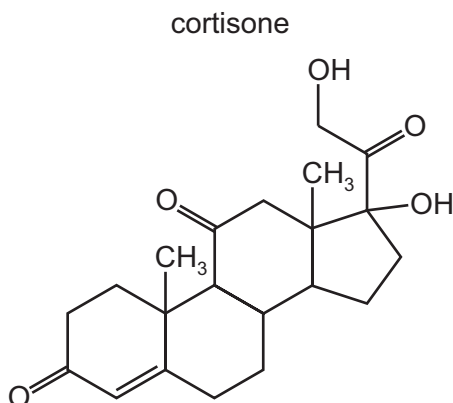


Fig. 7.1

- (i) Deduce the number of chiral carbon atoms in one molecule of cortisone.

..... [1]

- (ii) Cortisone is reacted with an excess of $NaBH_4$.

State the molecular formula of the organic compound formed.

..... [1]

- (iii) Cortisone is an optically active molecule.

Explain what is meant by optically active.

.....

 [1]

[Total: 8]

- 8 (a) Compare the relative acidities of ethanol, ethanoic acid, chloroethanoic acid and phenol. Explain your reasoning.

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

.....

.....

.....

.....

.....

.....

[4]

- (b) An excess of ethanedioic acid, $\text{HOOC}\text{COOH}(\text{aq})$, is reacted with warm acidified $\text{KMnO}_4(\text{aq})$.

State the type of reaction undergone by ethanedioic acid.

Describe what you would observe.

Write an equation for this reaction.

Your equation can use [O] or [H] as necessary.

type of reaction

observations

equation

[2]

- (c) A section of a polyester is shown.

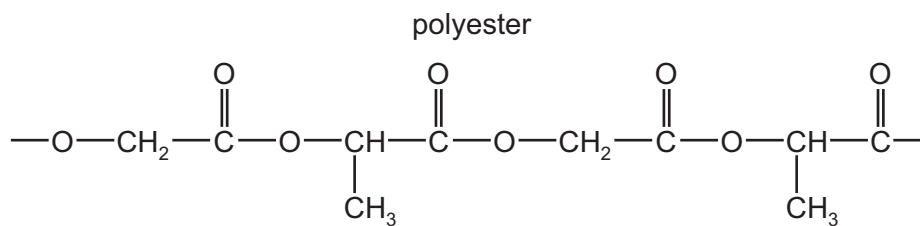


Fig. 8.1

Draw the structures of the two monomers that form this polyester.



[2]

- (d) Serine can polymerise to form two different types of condensation polymer; a polyester and a polypeptide.

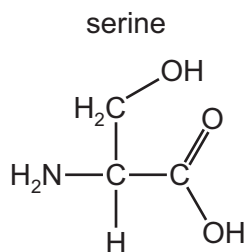


Fig. 8.2

Draw the structure of the polypeptide showing **two** repeat units. The peptide linkage should be shown displayed.

[2]

- (e) Explain why condensation polymers normally biodegrade more readily than addition polymers.

.....

..... [1]

[Total: 11]

- 9 The structure of cyclohexylamine is shown in Fig. 9.1.

cyclohexylamine

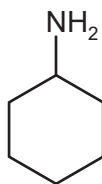


Fig. 9.1

- (a) Compare the relative basicities of ammonia, cyclohexylamine and phenylamine. Explain your reasoning.

..... > >

most basic least basic

.....

.....

.....

.....

.....

[3]

(b) Cyclohexylamine reacts with ethanoyl chloride to form the corresponding amide, **L**.

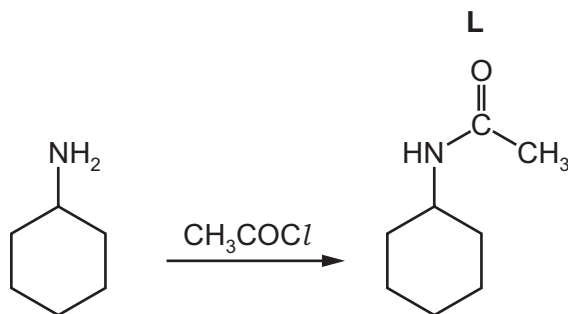


Fig. 9.2

(i) Name the mechanism for the reaction shown in Fig. 9.2.

..... [1]

(ii) Complete the mechanism of the reaction between cyclohexylamine and CH_3COCl .

R-NH_2 is used to represent cyclohexylamine.

Include all relevant lone pairs of electrons, curly arrows, charges and partial charges.



[4]

(iii) The reaction between cyclohexylamine and an excess of CH_3COCl forms compound **M**. Compound **M** has the molecular formula $\text{C}_{10}\text{H}_{17}\text{NO}_2$.

Suggest and draw the structure of **M**.

[1]

[Total: 9]

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 J g ⁻¹ K ⁻¹)

The Periodic Table of Elements

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

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
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



CANDIDATE
NAME

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CENTRE
NUMBER

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CANDIDATE
NUMBER

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9701/43

May/June 2022

2 hours

You must answer on the question paper.

No additional materials are needed.

- 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.

- 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.

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

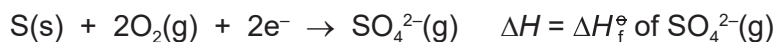
barium [1]

- (c) The solubility product, K_{sp} , of BaSO_4 is $1.08 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$ 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]

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



Calculate the standard enthalpy change of formation, $\Delta H_f^\ominus$, of $\text{SO}_4^{2-}(\text{g})$. 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, $\text{BaSO}_4(\text{s})$	–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 $\text{S}(\text{g}) \rightarrow \text{S}^{2-}(\text{g})$	+440
standard enthalpy change for $\text{O}(\text{g}) \rightarrow \text{O}^{2-}(\text{g})$	+657
O=O bond energy	+496

$\Delta H_f^\ominus$ of $\text{SO}_4^{2-}(\text{g}) = \dots\dots\dots \text{kJ mol}^{-1}$ [3]

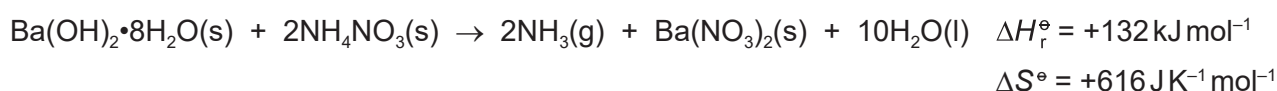
- (ii) Suggest how the lattice energy of $\text{BaSO}_4(\text{s})$ differs from the lattice energy of $\text{Cs}_2\text{SO}_4(\text{s})$. Explain your answer.

.....

 [2]

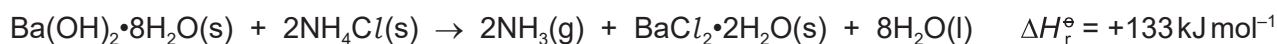
- (e) The reaction of solid hydrated barium hydroxide, $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, with ammonium salts is endothermic.

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



temperature = ... °C [2]

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



Some relevant standard entropies are given in Table 1.2.

Table 1.2

substance	$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}(\text{s})$	$\text{NH}_4\text{Cl}(\text{s})$	$\text{NH}_3(\text{g})$	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}(\text{s})$	$\text{H}_2\text{O}(\text{l})$
$S^\ominus / \text{JK}^{-1} \text{ mol}^{-1}$	427	95	192	203	70

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

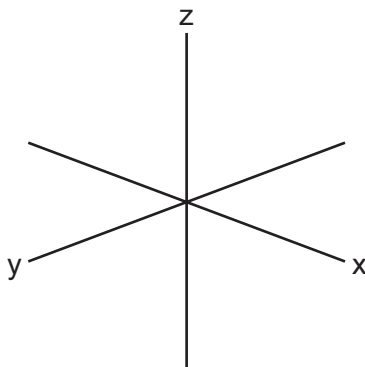
$\Delta G^\ominus = \dots\dots\dots \text{ kJ mol}^{-1}$ [3]

[Total: 16]

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 HCl.

- (i) Write the ionic equation, and state the type of reaction, for the reaction of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ with NaOH(aq).

ionic equation

type of reaction

[2]

- (ii) Write the ionic equation, and state the type of reaction, for the reaction of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ with concentrated HCl.

ionic equation

type of reaction

[2]

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

Table 2.1

electrode reaction	E°/V
$\text{Mn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mn}$	-1.18
$\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	+1.36
$2\text{HOCl} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Cl}_2 + 2\text{H}_2\text{O}$	+1.64
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 2\text{H}_2\text{O}$	+1.23
$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{MnO}_2 + 2\text{H}_2\text{O}$	+1.67

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

State the type of reaction.

formula of manganese species formed

type of reaction

[1]

[Total: 13]

- 3 (a) The rate of reaction between 2-chloro-2-methylpropane, $(\text{CH}_3)_3\text{CCl}$, and methanol is investigated. When a large excess of methanol is used, the overall reaction is first order.

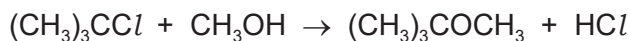


Fig. 3.1 shows the results obtained.

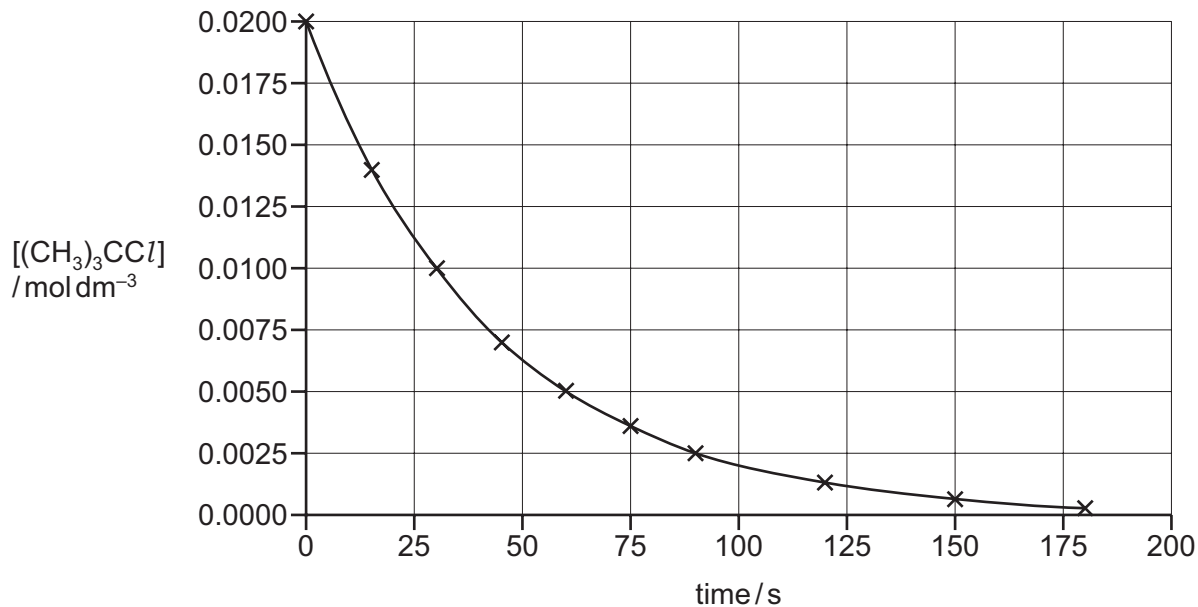


Fig. 3.1

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

rate = ... $\text{mol dm}^{-3} \text{s}^{-1}$ [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° .

.....

 [1]

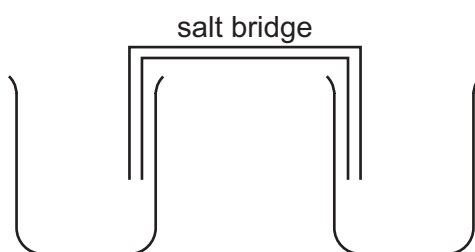
- (ii) A salt bridge is used in an electrochemical cell.

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° of the $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$, $\text{H}^+(\text{aq})/\text{Cr}^{3+}(\text{aq})$ electrode against the standard hydrogen electrode.

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



[3]

- (iv) The E° of the $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$, $\text{H}^+(\text{aq})/\text{Cr}^{3+}(\text{aq})$ 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]

- (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°/V
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+1.33
$\text{CH}_3\text{CHO} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{CH}_3\text{CH}_2\text{OH}$	-0.61
$\text{CH}_3\text{COOH} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{CH}_3\text{CHO} + \text{H}_2\text{O}$	-0.94
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.23

- (i) Ethanal is oxidised to ethanoic acid in the presence of $\text{Cr}_2\text{O}_7^{2-}$ ions.

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

ionic equation

$$E^\circ_{\text{cell}} = \dots\dots\dots \text{V}$$

[2]

- (ii) In an ethanol-oxygen fuel cell, $\text{CH}_3\text{CH}_2\text{OH}(\text{l})$ and $\text{O}_2(\text{g})$ are in contact with two inert electrodes immersed in an acidic solution.

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



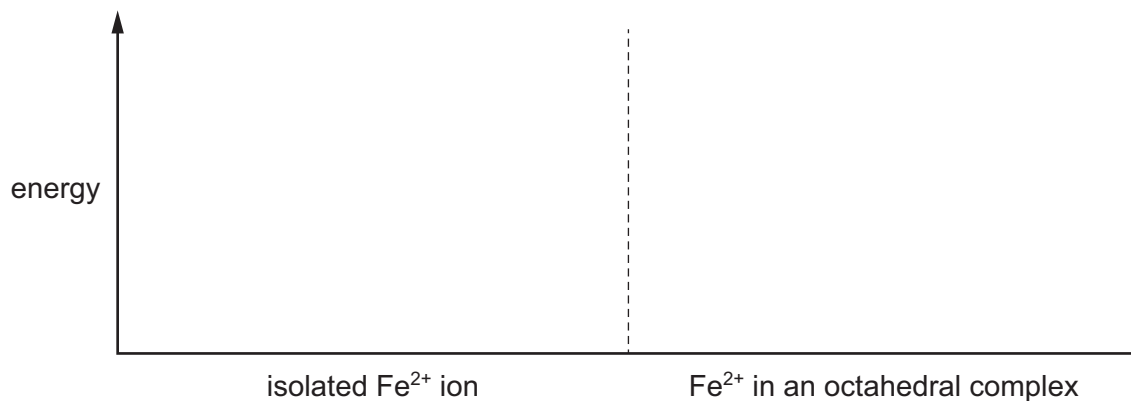
Calculate ΔG° , in kJ mol^{-1} , for the oxidation of ethanol by oxygen.

$$\Delta G^\circ = \dots\dots\dots \text{kJ mol}^{-1} \quad [2]$$

[Total: 15]

- 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.

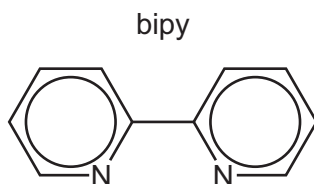


Fig. 4.1

Explain what is meant by bidentate ligand.

.....

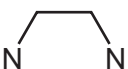
.....

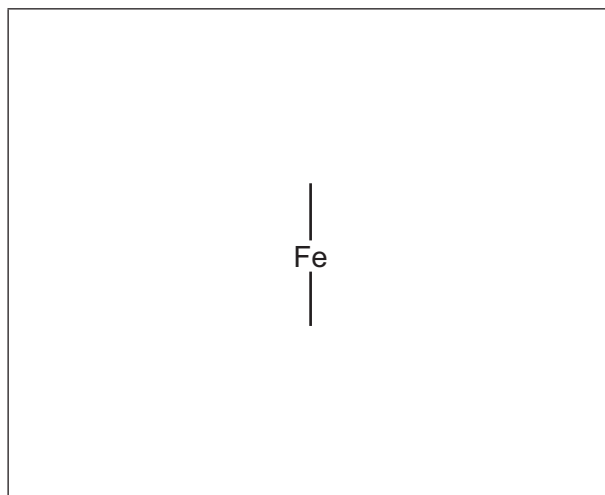
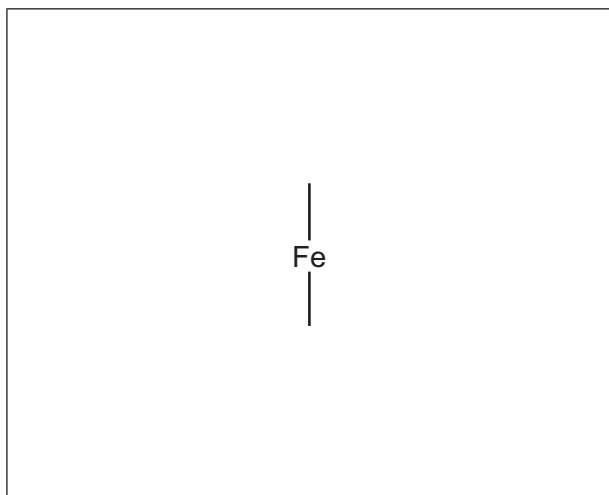
..... [2]

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

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

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 $\text{Fe}^{3+}/\text{Fe}^{2+}$ systems.

Table 4.1

electrode reaction	E°/V
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + \text{e}^- \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	+0.77
$[\text{Fe}(\text{CN})_6]^{3-} + \text{e}^- \rightleftharpoons [\text{Fe}(\text{CN})_6]^{4-}$	+0.36
$[\text{Fe}(\text{bipy})_3]^{3+} + \text{e}^- \rightleftharpoons [\text{Fe}(\text{bipy})_3]^{2+}$	+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]

- 5 (a) Compare the relative acidities of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$), phenylmethanol ($\text{C}_6\text{H}_5\text{CH}_2\text{OH}$), and phenol ($\text{C}_6\text{H}_5\text{OH}$). 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 (X) in the box if no reaction occurs.

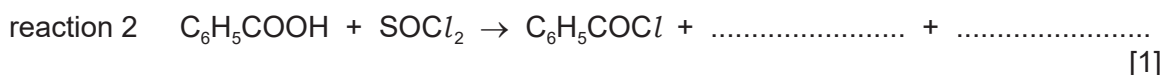
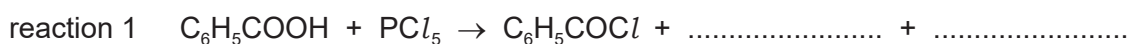
Table 5.1

	benzoic acid	phenylmethanol	phenol
Na(s)			
NaOH(aq)			
$\text{Na}_2\text{CO}_3(\text{aq})$			

[3]

- (c) (i) Benzoyl chloride, $\text{C}_6\text{H}_5\text{COCl}$, can be synthesised by the reaction of benzoic acid with either PCl_5 or SOCl_2 .

Complete the equations for these reactions.



[1]

- (ii) Use your answer to (c)(i) to suggest why it is easier to isolate, in a pure form, the $\text{C}_6\text{H}_5\text{COCl}$ 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 $\text{C}_6\text{H}_5\text{COCl}$ 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.

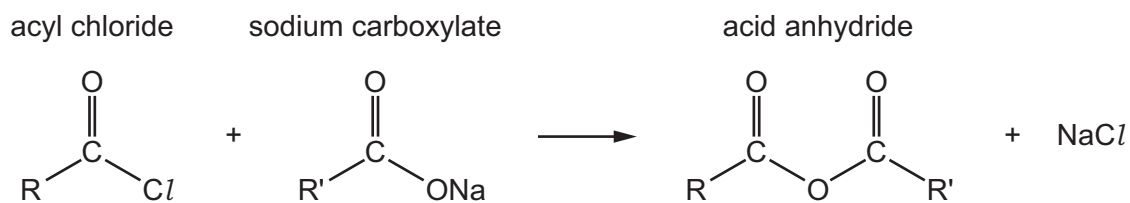


Fig. 5.1

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

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

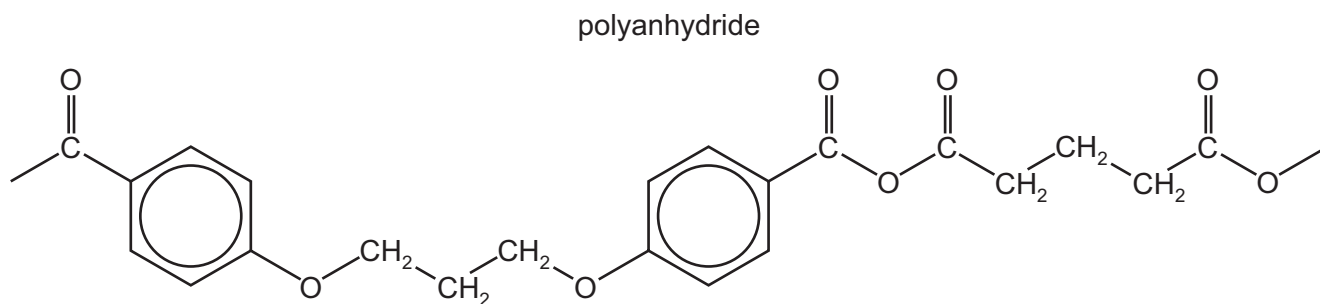


Fig. 5.2

(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.

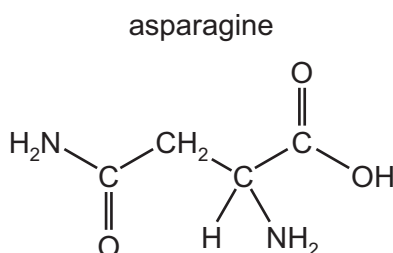


Fig. 6.1

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]

- (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.

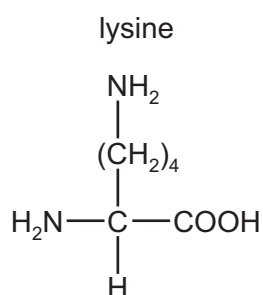


Fig. 6.2

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.

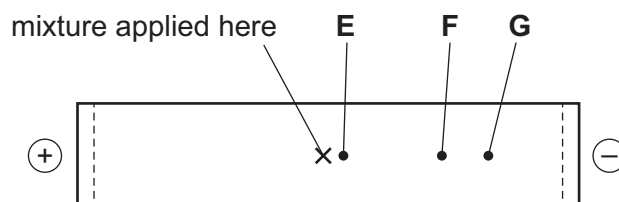


Fig. 6.3

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.

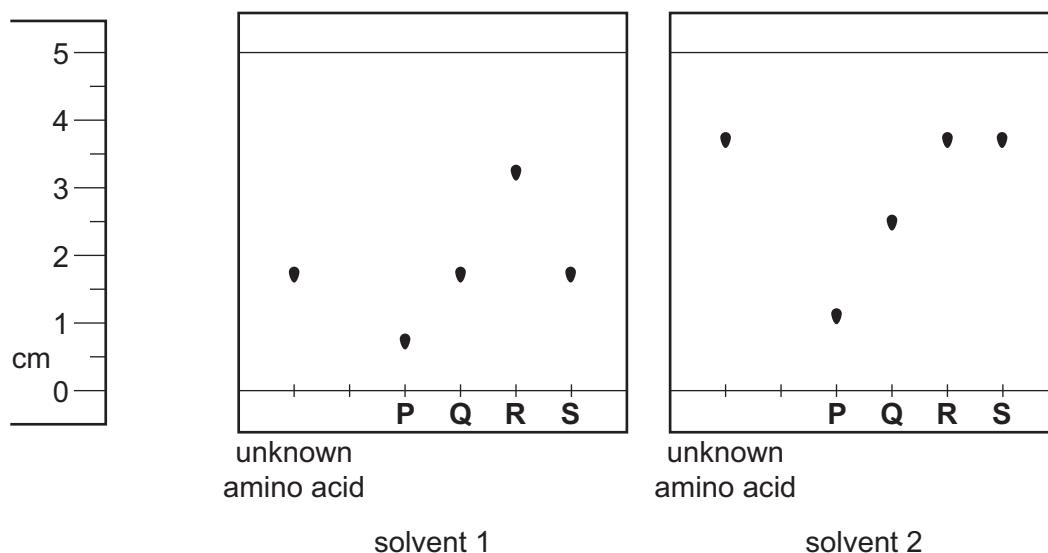


Fig. 6.4

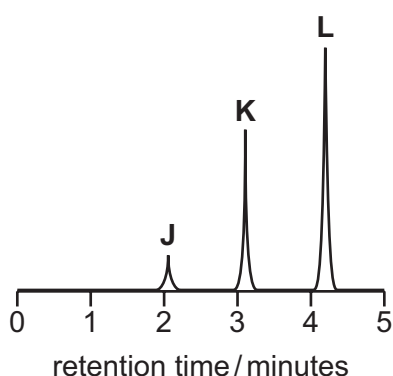
Identify the unknown amino acid. Justify your answer.

.....

.....

..... [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 $5.52 \times 10^{-2} \text{ g dm}^{-3}$.

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.

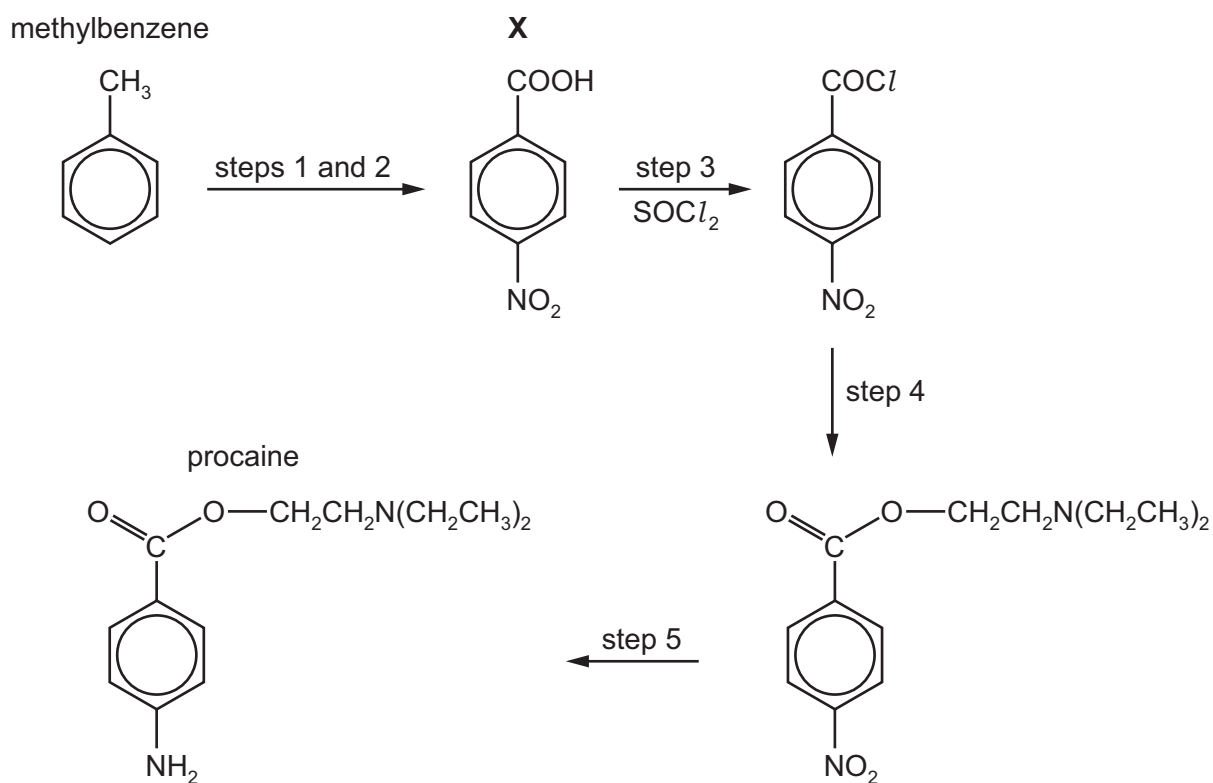


Fig. 7.1

- (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]

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

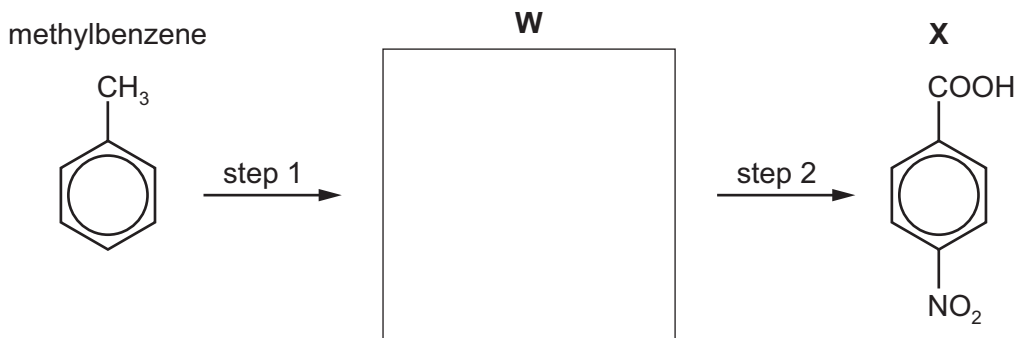


Fig. 7.2

(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 cm³ of water is shaken with 50.0 cm³ 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]

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 J g ⁻¹ K ⁻¹)

The Periodic Table of Elements

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

lanthanoids

actinoids

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	euporium	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
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	226.0
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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