Cambridge Assessment International Education

Cambridge International AS & A Level

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

1573904526

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.

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

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

K_{sp} =

units = ...
[2]

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

K_{sp} = ... [2]

(c) $Be(OH)_2$ is soluble in aqueous solutions containing an excess of hydroxide ions and forms the complex ion $[Be(OH)_4]^{2-}$. This complex ion has a similar shape to that of $[CuCl_4]^{2-}$.

(i) Define the term complex ion.

....

.... [1]

(ii) Draw a three-dimensional diagram to show the structure of the complex ion $[Be(OH)_4]^{2-}$.
Name the shape of the $[Be(OH)_4]^{2-}$ 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
cis-$[Pt(H_2NCH_2CH_2NH_2)Cl_2]$	square planar		
$[Ag(NH_3)_2]^+$			non-polar
$[Fe(C_2O_4)_3]^{3-}$		6	

[2]

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

....

.... [1]

(ii) Nickel can form complexes with the ligands *en*, $H_2NCH_2CH_2NH_2$, and *tn*, $H_2NCH_2CH_2CH_2NH_2$, as shown.

equilibrium **1** $[Ni(H_2O)_6]^{2+} + 3en \rightleftharpoons [Ni(en)_3]^{2+} + 6H_2O$ $K_{stab} = 6.76 \times 10^{17}$

equilibrium **2** $[Ni(H_2O)_6]^{2+} + 3tn \rightleftharpoons [Ni(tn)_3]^{2+} + 6H_2O$ $K_{stab} = 1.86 \times 10^{12}$

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

K_{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, $[Ni(en)_3]^{2+}$ or $[Ni(tn)_3]^{2+}$, is more stable.

....

.... [1]

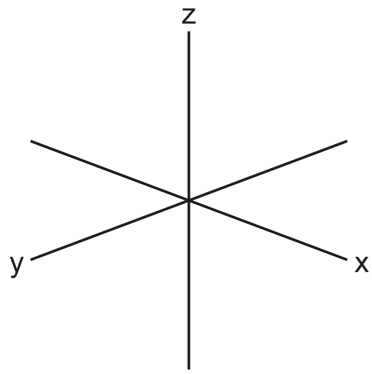
[Total: 16]

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 $[Cu(H_2O)_6]^{2+}$ ions.

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

equilibrium **3** $[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s) + 6H_2O(l)$

equilibrium **4** $[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$

(i) State the colour of $Cu(OH)_2(s)$ and $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$.

colour of $Cu(OH)_2(s)$ ....

colour of $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$ ....
[1]

(ii) Use Le Chatelier's principle to explain why a precipitate is formed when NaOH(aq) is added dropwise to $[Cu(H_2O)_6]^{2+}(aq)$.

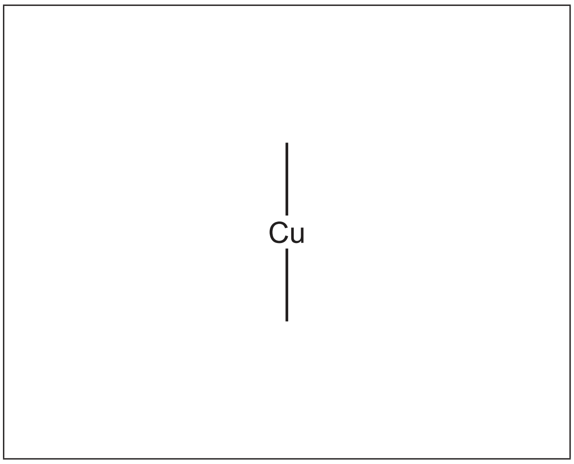
....

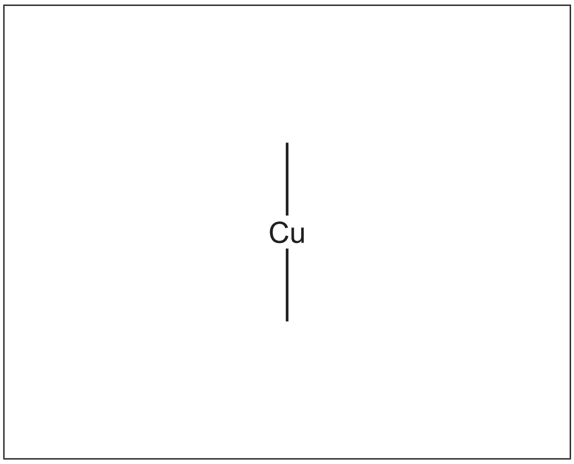
....

.... [1]

(e) There are two possible stereoisomers with the formula $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

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 C*l*, 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, $\Delta H^{\ominus}_{latt}$, 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, $I_2(s) \rightarrow I_2(g)$	+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 $\Delta H^{\ominus}_{latt}$ of CdI_2(s) differs from $\Delta H^{\ominus}_{latt}$ of ZnI_2(s).
Place a tick (✓) in the appropriate box in Table 3.2.

Table 3.2

$\Delta H^{\ominus}_{latt}$ of CdI_2(s) is less negative than $\Delta H^{\ominus}_{latt}$ of ZnI_2(s)	$\Delta H^{\ominus}_{latt}$ of CdI_2(s) is the same as $\Delta H^{\ominus}_{latt}$ of ZnI_2(s)	$\Delta H^{\ominus}_{latt}$ of CdI_2(s) is more negative than $\Delta H^{\ominus}_{latt}$ of ZnI_2(s)

Explain your answer.

....

.... [1]

[Total: 9]

4 **(a)** Calcium carbonate decomposes on heating.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

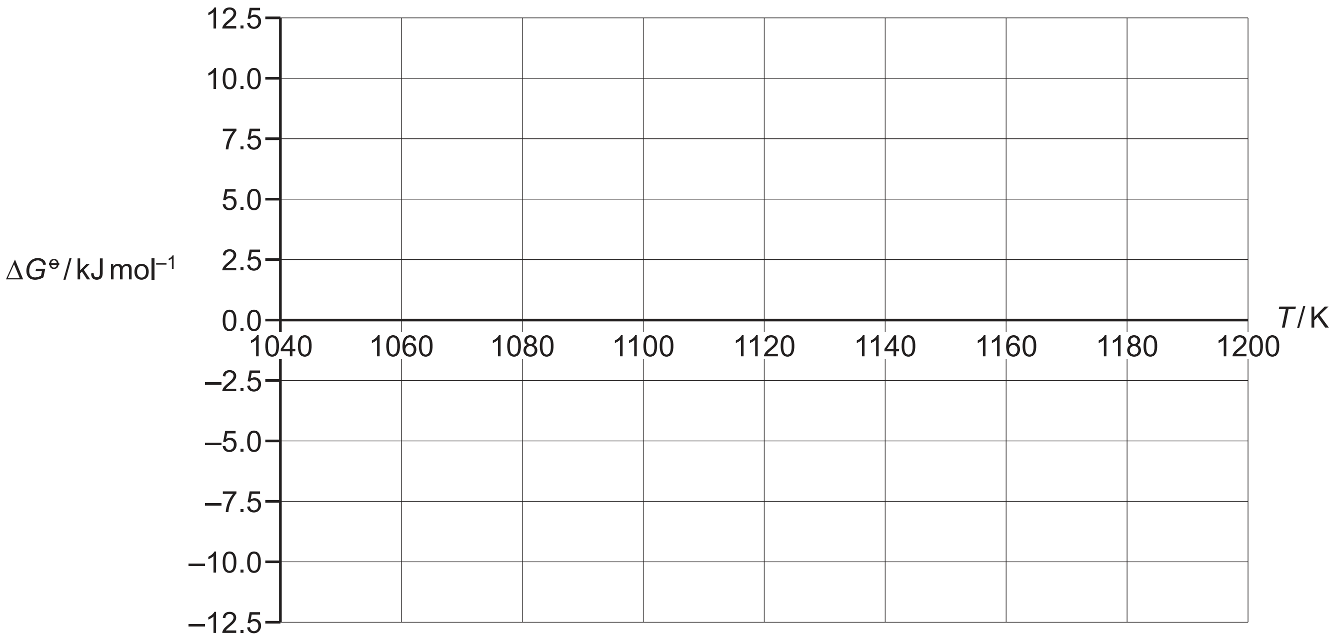
Table 4.1 shows the values of the Gibbs free energy change, $\Delta G^{\ominus}$, for this reaction at various temperatures.

Table 4.1

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

Assume the standard enthalpy change, $\Delta H^{\ominus}$, and the standard entropy change, $\Delta S^{\ominus}$, for this reaction remain constant over this temperature range.

(i) Use the data in Table 4.1 to plot a graph of $\Delta G^{\ominus}$ against T on the grid.



[2]

(ii) Calculate the gradient of your graph. Determine the $\Delta S^{\ominus}$ in J K^{-1} mol^{-1} for this reaction. Show all working.

$\Delta S^{\ominus}$ = ... J K^{-1} mol^{-1} [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.

equilibrium **5** $H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$

(i) Define a buffer solution.

....

....

.... [2]

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

....

.... [2]

(iii) The $[HCO_3^-]/[H_2CO_3]$ ratio in a sample of seawater is 14.1.

Calculate the pH of this sample.
[pK_a: H_2CO_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
$PbBr_2(l)$		
concentrated $NaCl(aq)$		
$Cu(NO_3)_2(aq)$		

[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 HNO_3(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.

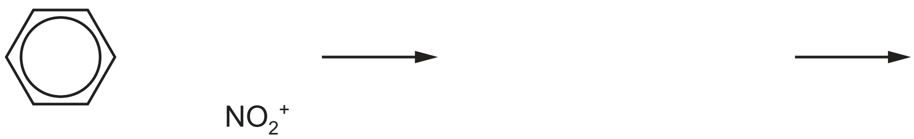


Fig. 6.1

[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.

major product from benzoic acid	major product from 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.

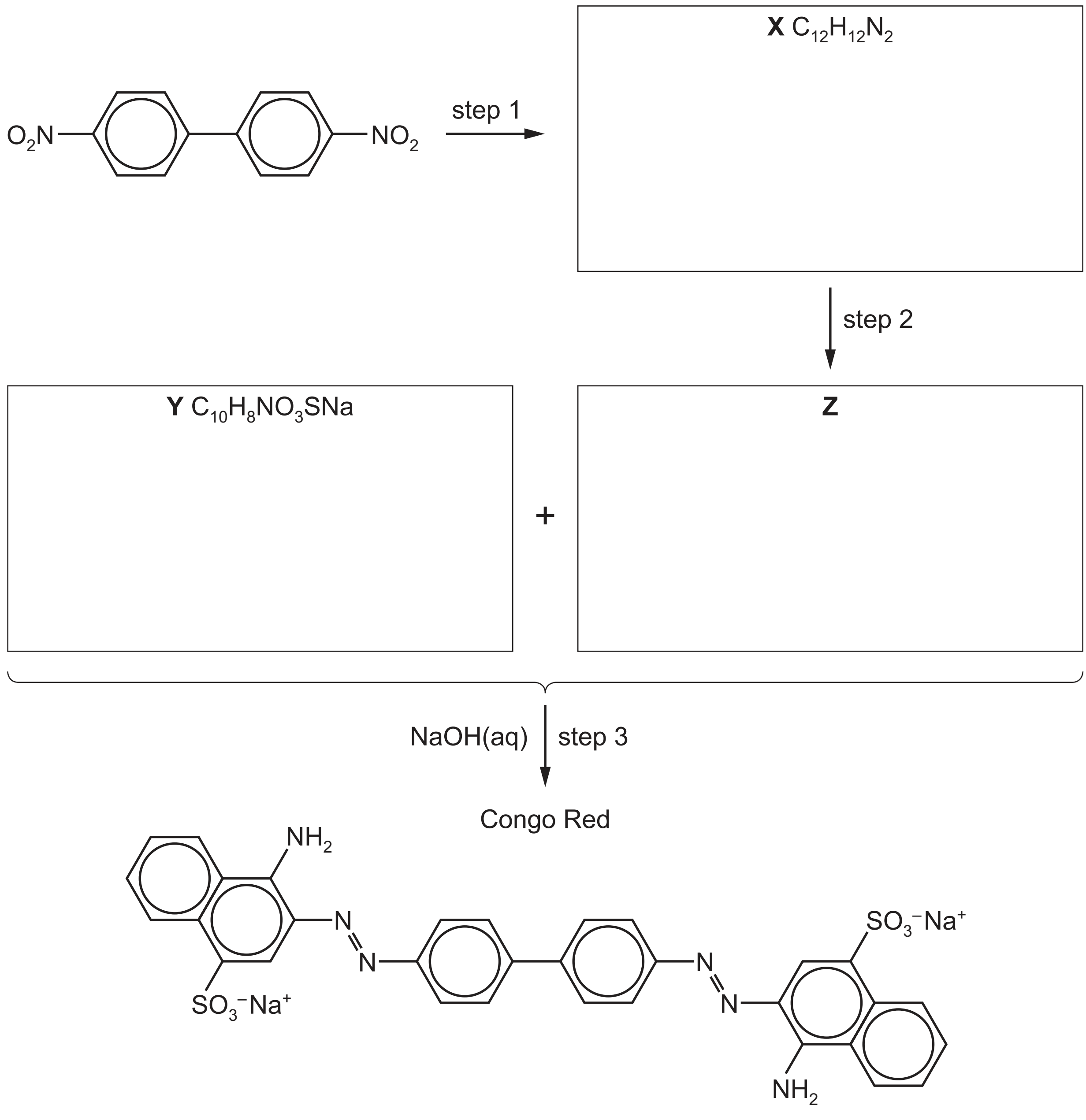


Fig. 6.2

(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 D_2O in NMR spectroscopy.

TMS ....

D_2O ....
[1]

(b) The three isomeric ketones with molecular formula $C_5H_{10}O$ 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 (^1H) 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 $C_5H_{10}O$ 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.

cortisone

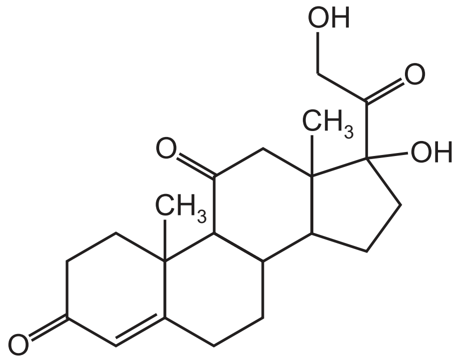


Fig. 7.1

(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, HOOCCOOH(aq), is reacted with warm acidified $KMnO_4$(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.

polyester

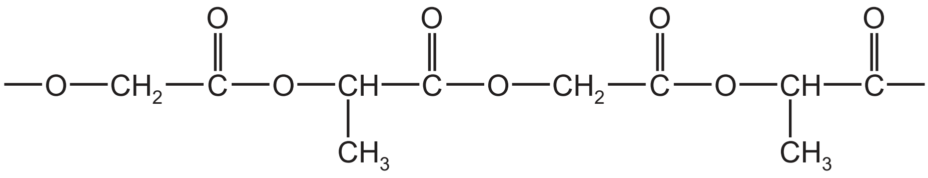


Fig. 8.1

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.

serine

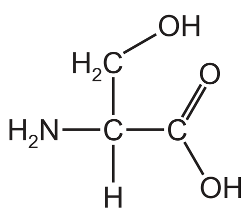


Fig. 8.2

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

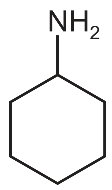


Fig. 9.1

(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**.

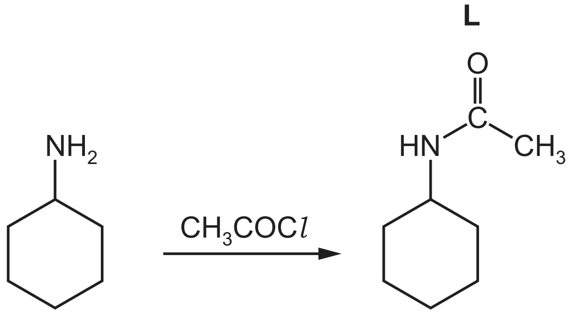


Fig. 9.2

(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 $C_{10}H_{17}NO_2$.

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

[1]

[Total: 9]

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Important values, constants and standards

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

The Periodic Table of Elements

Key

atomic number atomic symbol name relative atomic mass

Group																	
1	2	3	4	5	6	7	8	9	10	11	12	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 A*l* aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 C*l* 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 T*l* 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 F*l* flerovium –	115 Mc moscovium –	116 Lv livermorium –	117 Ts tennessine –	118 Og oganesson –

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 –