Cambridge Assessment International Education

Cambridge International AS & A Level

CANDIDATE NAME

CENTRE NUMBER | CANDIDATE NUMBER

8519262883

CHEMISTRY **9701/43**

Paper 4 A Level Structured Questions **May/June 2023**

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 **28** pages. Any blank pages are indicated.

DC (LK) 326947

1 **(a)** Group 2 nitrates decompose when heated.

Describe how the thermal stability of Group 2 nitrates changes with increasing proton number.

Explain your answer.

....

....

....

....

.... [3]

(b) Copper(II) nitrate decomposes in a similar manner to Group 2 nitrates.

Write an equation for the decomposition of $Cu(NO_3)_2$.

.... [1]

(c) $Cu(NO_3)_2$ is added to water to form solution **A**.
Fig. 1.1 shows some reactions of solution **A**.

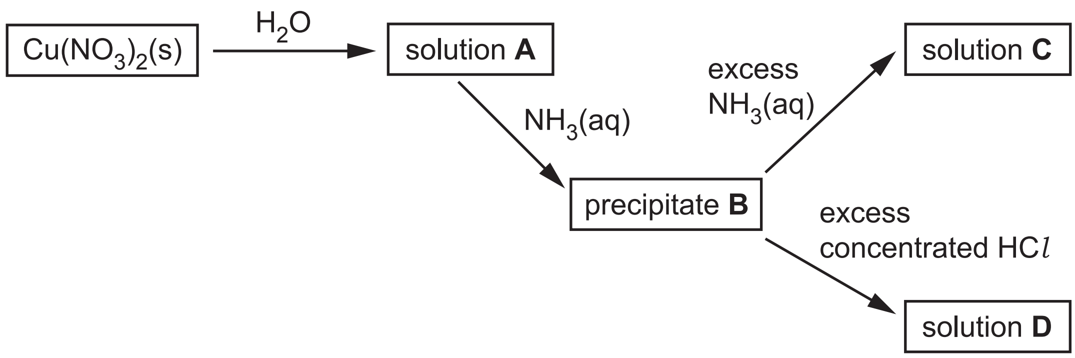

Fig. 1.1

Complete Table 1.1 to show the formula and colour of each of the copper-containing species present in **A**, **B**, **C** and **D**.

Table 1.1

	formula of copper-containing species formed	colour of copper-containing species formed
A		
B		
C		
D		

[4]

(d) $EDTA^{4-}$ is a polydentate ligand.

(i) Explain what is meant by a polydentate ligand.

....

....

.... [2]

(ii) Group 2 metal ions can form complexes similar to those of transition elements.

A solution of $EDTA^{4-}$ is added to water containing $[Ca(H_2O)_6]^{2+}$ to form a new complex, $[CaEDTA]^{2-}$, as shown.

equilibrium 1 $[Ca(H_2O)_6]^{2+} + EDTA^{4-} \rightleftharpoons [CaEDTA]^{2-} + 6H_2O$

Circle on the structure of $EDTA^{4-}$ in Fig. 1.2 the **six** atoms that form bonds with the metal ion.

EDTA^{4-}

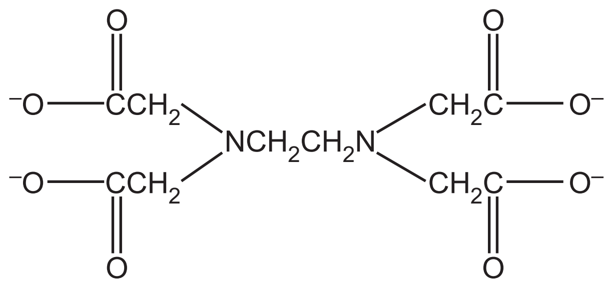

Fig. 1.2

[1]

(iii) The calcium ions in $[Ca(H_2O)_6]^{2+}$ and $[CaEDTA]^{2-}$ have a coordination number of 6.

Explain what is meant by coordination number.

....

.... [1]

(iv) The complex $[CaEDTA]^{2-}$ can be used to remove toxic metals from the body.

Table 1.2 shows the numerical values for the stability constants, K_{stab}, for some metal ions with $EDTA^{4-}$.

Table 1.2

complex	K_{stab}
$[CaEDTA]^{2-}$	5.0×10^{10}
$[CrEDTA]^{-}$	2.5×10^{23}
$[FeEDTA]^{-}$	1.3×10^{25}
$[PbEDTA]^{2-}$	1.1×10^{18}

An aqueous solution containing $[CaEDTA]^{2-}$ is added to a solution containing equal concentrations of $Cr^{3+}(aq)$, $Fe^{3+}(aq)$ and $Pb^{2+}(aq)$. The resulting mixture is left to reach a state of equilibrium.

State the type of reaction when $[CaEDTA]^{2-}$ reacts with $Cr^{3+}(aq)$, $Fe^{3+}(aq)$ and $Pb^{2+}(aq)$.

.... [1]

(v) Deduce the relative concentrations of $[CrEDTA]^{-}$, $[FeEDTA]^{-}$ and $[PbEDTA]^{2-}$ present in the resulting mixture.

Explain your answer.

.... > .... > ....

highest concentration lowest concentration

....

....

.... [1]

(e) The number of moles of water of crystallisation in a hydrated ionic salt can be determined by titration using aqueous $EDTA^{4-}$ ions with a suitable indicator.

- 0.255 g of hydrated chromium(III) sulfate, $Cr_2(SO_4)_3 \cdot nH_2O$, is dissolved in water and made up to 100 cm^3 in a volumetric flask.
- 25.0 cm^3 of this solution requires 26.2 cm^3 of 0.00800 mol dm^{-3} aqueous $EDTA^{4-}$ ions to reach the end-point.

The reaction occurs as shown.

$$[Cr(H_2O)_6]^{3+} + EDTA^{4-} \longrightarrow [CrEDTA]^{-} + 6H_2O$$

Use the data to calculate the value of *n* in the formula of $Cr_2(SO_4)_3 \cdot nH_2O$.

Show your working.

n = ... [3]

(f) A solution of $Cr^{3+}(aq)$ and a solution of $Fe^{3+}(aq)$ have different colours.

Explain why the two complexes have different colours.

....

....

....

.... [2]

[Total: 19]

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2 **(a)** Some transition element complexes can show stereoisomerism.

State **two** types of stereoisomerism shown by transition element complexes.

1 ....

2 ....
[1]

(b) The complexes $[Pt(NH_3)_2Cl_2]$ and $[Pt(en)_2]^{2+}$ have the same geometry (shape) around the metal ion.

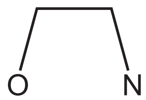
$[Pt(NH_3)_2Cl_2]$ exists as two stereoisomers whereas $[Pt(en)_2]^{2+}$ only has one possible structure.

State the geometry around the metal ion.

.... [1]

(c) The complex $[Cr(en)_3]^{2+}$ exists as two stereoisomers whereas the complex $[Cr(OCH_2CH_2NH_2)_3]^-$ exists as four stereoisomers.

Complete the three-dimensional diagrams in Fig. 2.1 to show the four stereoisomers of $[Cr(OCH_2CH_2NH_2)_3]^-$.

Represent the ligand $^-OCH_2CH_2NH_2$ by using 

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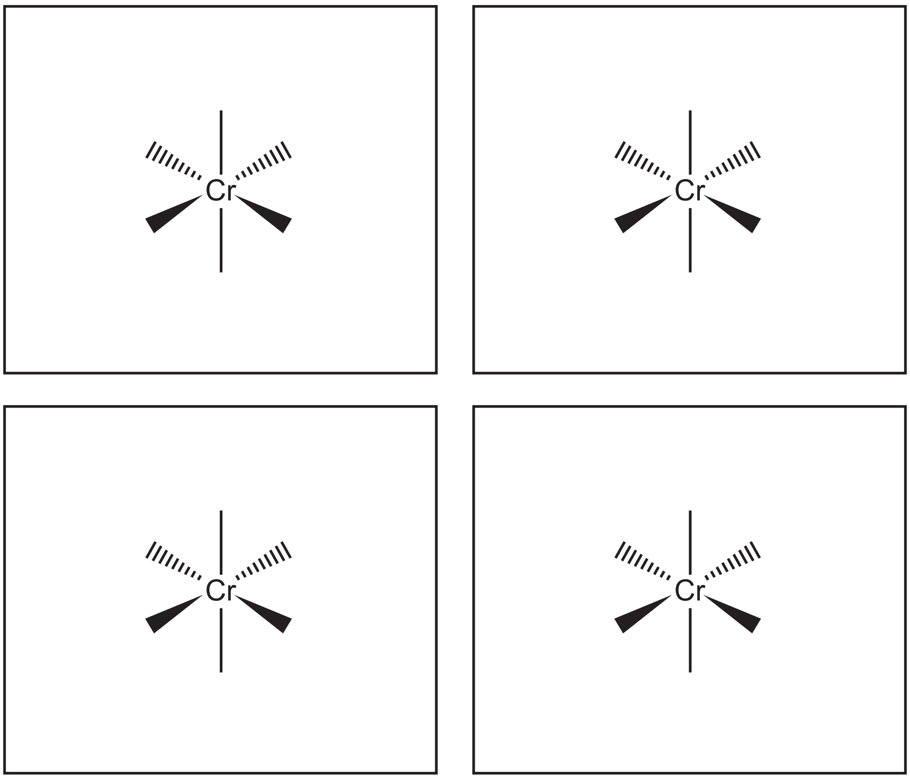

Fig. 2.1

[3]

[Turn over

(d) The complex $[Cr(OCH_2CH_2NH_2)_3]^-$ is formed by reacting $Cr^{2+}(aq)$ with the conjugate base of 2-aminoethanol.

A synthesis of 2-aminoethanol is shown in Fig. 2.2.

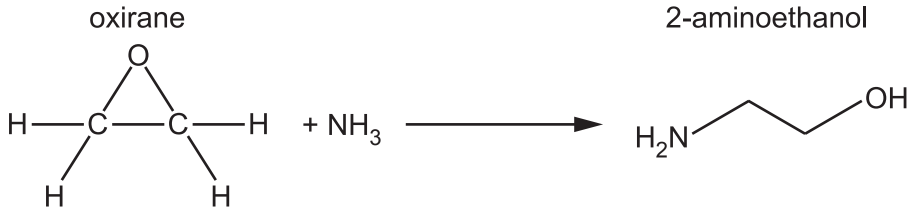

Fig. 2.2

(i) Suggest the mechanism for step 1 of the reaction of oxirane with ammonia in Fig. 2.3.

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

Draw the structure of the organic intermediate.

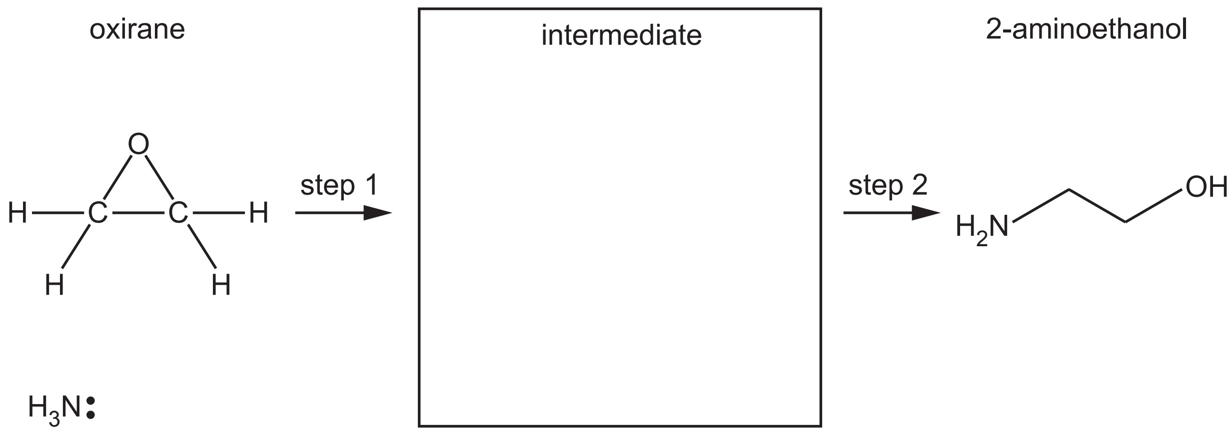

Fig. 2.3

[3]

(ii) A small amount of by-product **E**, shown in Fig. 2.4, is produced during the reaction shown in Fig. 2.2.

E

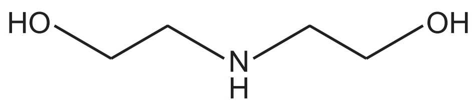

Fig. 2.4

Suggest how the formation of by-product **E** can be minimised.

....

.... [1]

(iii) Compound **F**, C_4H_9NO, can be formed from the reaction of by-product **E**, $C_4H_{11}NO_2$, with concentrated H_2SO_4.

Compound **F** is a **saturated** and basic organic compound.

Suggest a structure for compound **F**. State the type of reaction undergone by **E** to form **F**.

F

type of reaction ....

[2]

[Total: 11]

3 **(a)** Aqueous acidified iodate(V) ions, IO_3^-, react with iodide ions, as shown.

$$IO_3^- + 6H^+ + 5I^- \rightarrow 3I_2 + 3H_2O$$

The initial rate of this reaction is investigated. Table 3.1 shows the results obtained.

Table 3.1

experiment	$[IO_3^-]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}	initial rate / mol dm^{-3} min^{-1}
1	0.0400	0.0150	0.0250	4.20×10^{-2}
2	0.120	to be calculated	0.0125	7.09×10^{-2}

The rate equation for this reaction is rate = $k[IO_3^-][H^+]^2[I^-]^2$.

(i) Explain what is meant by order of reaction.

....

....

.... [1]

(ii) Complete Table 3.2.

Table 3.2

the order of reaction with respect to $[IO_3^-]$	
the order of reaction with respect to $[H^+]$	
the order of reaction with respect to $[I^-]$	
the overall order of reaction	

[1]

(iii) Use your answer to **(a)(ii)** to sketch lines in Fig. 3.1 to show the relationship between the initial rates and the concentrations of $[IO_3^-]$ and $[I^-]$.

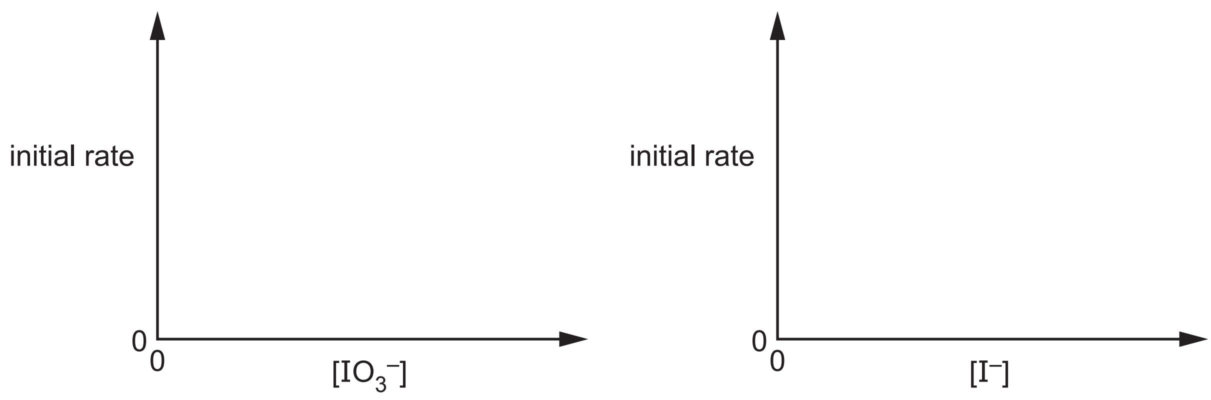

Fig. 3.1

[1]

(iv) Use data from Table 3.1 to calculate the rate constant, *k*, for this reaction.

Include the units of *k*.

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

(v) Use data from Table 3.1 to calculate the concentration of hydrogen ions, $[H^+]$, in experiment 2.

$[H^+]$ = ... $mol\,dm^{-3}$ [1]

(vi) This reaction is repeated in two separate experiments.

The experiments are carried out at the same temperature and with the same concentrations of I^- and IO_3^-.

One experiment takes place at pH 1.0 and the other experiment takes place at pH 2.0.

Calculate the value of $\frac{\text{rate at pH 1.0}}{\text{rate at pH 2.0}}$.

value of $\frac{\text{rate at pH 1.0}}{\text{rate at pH 2.0}}$ = ... [1]

(b) In aqueous solution, iron(III) ions react with iodide ions, as shown.

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

The initial rate of reaction is first order with respect to Fe^{3+} and second order with respect to I^-.

The mechanism for this reaction has three steps.

Each step involves only **two** ions reacting together.

Suggest equations for the **three** steps of this mechanism. Identify the rate-determining step.

step 1 ....

step 2 ....

step 3 ....

rate-determining step = ...

[3]

[Total: 10]

4 **(a)** State the hybridisation of the carbon atoms and the C–C–H bond angle in benzene, C_6H_6. Explain how orbital overlap leads to the formation of σ and π bonds in benzene.

....

....

....

....

.... [3]

(b) Compound **Z** can be synthesised from benzene in three steps by the route shown in Fig. 4.1.

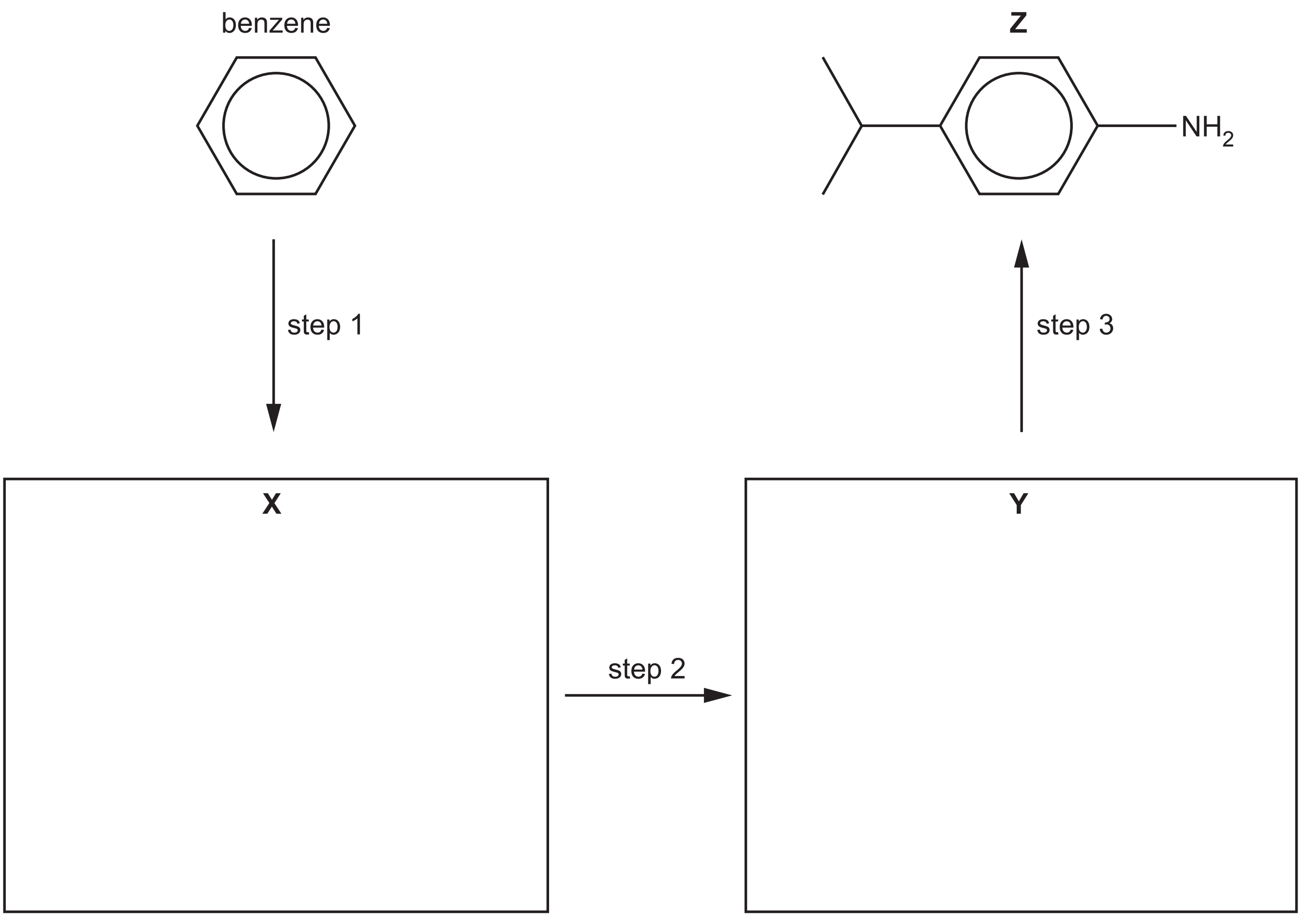

Fig. 4.1

(i) Draw structures for **X** and **Y** in Fig. 4.1. [2]

(ii) Give the reagents and conditions for steps 1, 2 and 3.

step 1 ....

step 2 ....

step 3 ....

[3]

(c) Compound **W** is an isomer of **Z**.

W

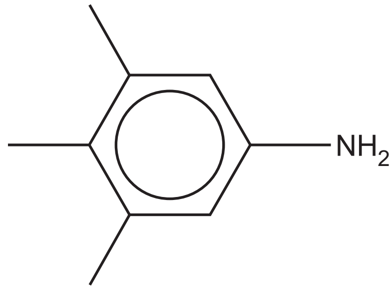

Fig. 4.2

Give the systematic name of **W**.

.... [1]

(d) Complete Table 4.1 to show the number of peaks observed in the carbon-13 NMR spectrum for **W** and **Z**.

Table 4.1

compound	number of peaks observed
W	
Z	

[1]

[Total: 10]

5 **(a)** The exhaust systems of most modern gasoline-fuelled cars contain a catalytic converter with three metal catalysts.

These metals act as heterogeneous catalysts.

(i) Name **three** metal catalysts used in catalytic converters.

1 .... 2 .... 3 .... [1]

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

....

.... [1]

(b) The exhaust systems of many diesel-fuelled cars contain an additional system to reduce vehicle emissions. This uses a liquid that is added to the exhaust system.

This liquid contains urea, $(NH_2)_2CO$, which decomposes on heating to isocyanic acid, HNCO, and ammonia.

reaction 1 $(NH_2)_2CO \rightarrow HNCO + NH_3$

Isocyanic acid reacts with water vapour to form ammonia and carbon dioxide.

reaction 2 $HNCO(g) + H_2O(g) \rightarrow NH_3(g) + CO_2(g)$

Some values for standard enthalpy changes of formation, $\Delta H_f^{\ominus}$, and standard entropies, $S^{\ominus}$, are given in Table 5.1.

Table 5.1

compound	$\Delta H_f^{\ominus}$ / kJ mol^{-1}	$S^{\ominus}$ / J K^{-1} mol^{-1}
HNCO(g)	–101.7	+238.2
$H_2O(g)$	–241.8	+188.8
$NH_3(g)$	–45.9	+192.8
$CO_2(g)$	–393.5	+213.8

(i) Explain what is meant by the term entropy of a system.

....

.... [1]

(ii) Use the data in Table 5.1 to calculate $\Delta G^{\ominus}$ for **reaction 2** at 25 °C.
Show your working.

$\Delta G^{\ominus}$ = ... $kJ\,mol^{-1}$ [4]

(c) The ammonia formed in reactions 1 and 2 can be used to remove nitrogen dioxide from exhaust emissions, as shown.

reaction 3 $8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O$

Use the equations for reactions 1, 2 and 3 to construct an overall equation for the reduction of NO_2 by $(NH_2)_2CO$.

.... [1]

(d) Isocyanic acid, HNCO, can form cyanuric acid, $C_3H_3N_3O_3$, under certain conditions.

$C_3H_3N_3O_3$ has a cyclic structure containing alternating carbon and nitrogen atoms in the ring system.

Suggest a structure for cyanuric acid.

[1]

(e) Isocyanic acid, HNCO, is a weak acid.

$$HNCO + H_2O \rightleftharpoons H_3O^+ + NCO^- \qquad pK_a = 3.70 \text{ at } 25\,°C$$

(i) Write the mathematical expressions for pK_a and pH.

pK_a = ...

pH = ...
[1]

(ii) Calculate the pH of 0.120 mol dm^{-3} HNCO(aq).
Give your answer to **three** significant figures.

pH = ... [2]

(iii) Calculate the percentage of HNCO molecules that are ionised in 0.120 mol dm^{-3} HNCO.

percentage ionisation of HNCO = ... [1]

[Total: 13]

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6 **(a)** Compound **H** has the structural formula $CH_2{=}CHCH(NH_2)COOH$.

(i) Name all the functional groups in **H**.

....

.... [2]

(ii) Compound **H** exhibits stereoisomerism.

Draw three-dimensional structures for the two stereoisomers of **H**.
Name this type of stereoisomerism.

type of stereoisomerism ....
[2]

(b) Compound **H** can be prepared from the reaction of **J** with an excess of hot aqueous acid.

J

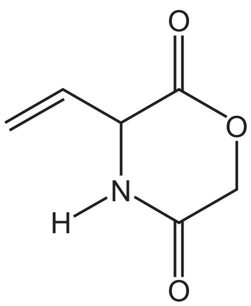
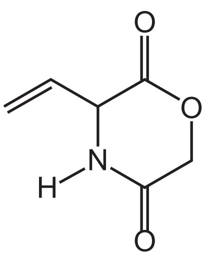


Fig. 6.1

(i) Complete Fig. 6.2 to show the equation for this reaction.



\+ → $CH_2{=}CHCH(NH_2)COOH$ +

Fig. 6.2

[1]

(ii) Name the type of reaction in **(b)(i)**.

.... [1]

(c) Polymers consist of monomers joined together by undergoing either addition or condensation polymerisation.

Compound **H** can react to form an addition polymer, **K**, or a condensation polymer, **L**, depending on the conditions.

(i) Draw **one** repeat unit of addition polymer **K**.

[1]

(ii) Draw **two** repeat units of condensation polymer **L**.

The new functional group formed should be displayed.

[2]

(iii) Explain why condensation polymers can normally biodegrade more readily than addition polymers.

....

.... [1]

[Total: 10]

7 (a) State the relative basicities of ethanamide, diethylamine and ethylamine in aqueous solution.

Explain your answer.

.... > .... > ....

most basic — least basic

....

....

....

....

.... [4]

(b) The amino acid alanine, $H_2NCH(CH_3)COOH$, can act as a buffer.

(i) Define a buffer solution.

....

....

.... [2]

(ii) Write **two** equations to show how an aqueous solution of alanine can act as a buffer solution.

....

.... [2]

(c) Glutamic acid is another amino acid that acts as a buffer.

glutamic acid

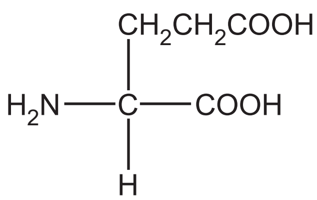


Fig. 7.1

(i) Draw the **skeletal** formula for glutamic acid.

[1]

(ii) Draw the structure for the dipeptide, ala-glu, formed from one molecule of alanine and one molecule of glutamic acid.

The peptide bond formed should be displayed.

[2]

(d) The isoelectric point of alanine is 6.0 and of glutamic acid is 3.2.

A mixture of the dipeptide, ala-glu, and its two constituent amino acids, alanine and glutamic acid, is analysed by electrophoresis using a buffer at pH 6.0.

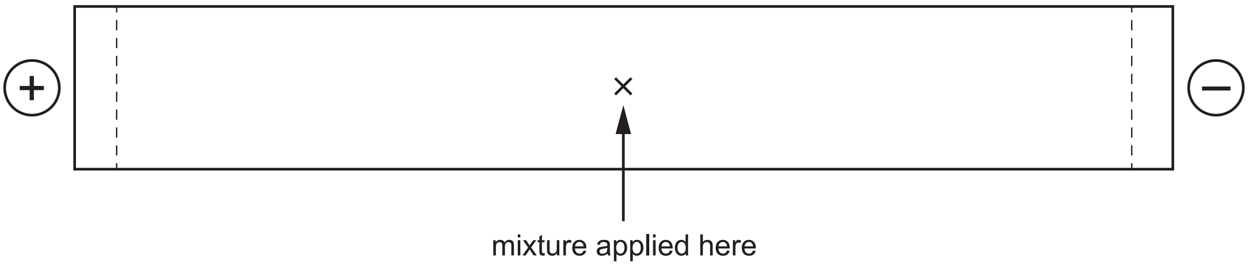


Fig. 7.2

Draw and label **three** spots on Fig. 7.2 to indicate the predicted position of each of these three species after electrophoresis.

Explain your answer.

....

....

....

....

.... [3]

(e) Alanine, $H_2NCH(CH_3)COOH$, reacts with methanol to form the ester **G** under certain conditions.

The proton (^1H) NMR spectrum of **G** dissolved in D_2O is shown in Fig. 7.3.

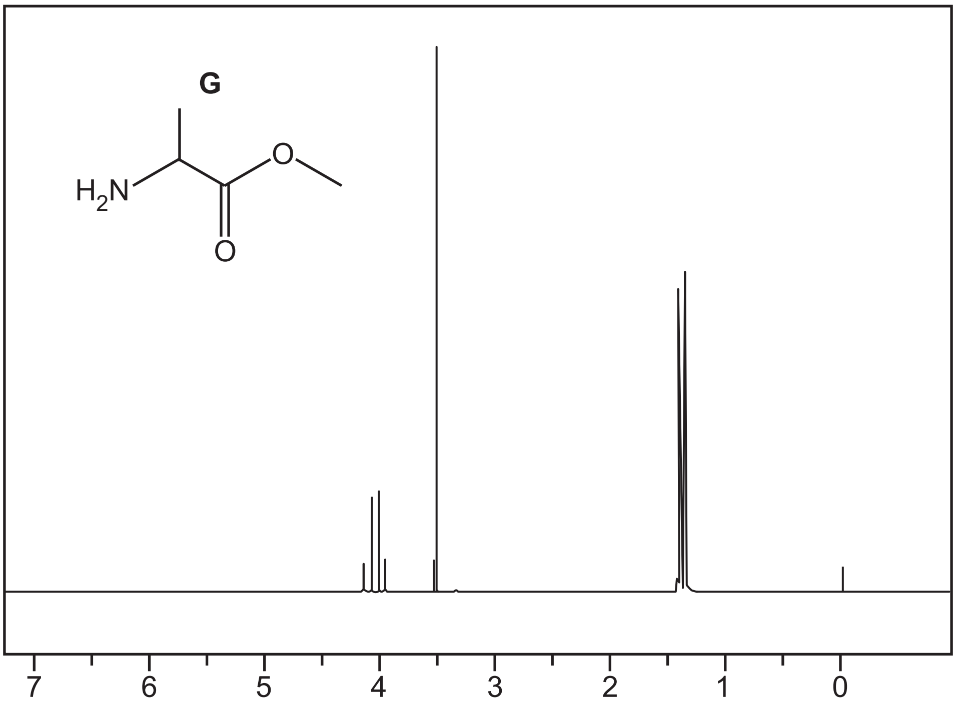


Fig. 7.3

Table 7.1

environment of proton	example	chemical shift range, δ / ppm
alkane	–C**H**$_3$, –C**H**$_2$–, >C**H**–	0.9–1.7
alkyl next to C=O	C**H**$_3$–C=O, –C**H**$_2$–C=O, >C**H**–C=O	2.2–3.0
alkyl next to aromatic ring	C**H**$_3$–Ar, –C**H**$_2$–Ar, >C**H**–Ar	2.3–3.0
alkyl next to electronegative atom	C**H**$_3$–O, –C**H**$_2$–O, –C**H**$_2$–C*l*	3.2–4.0
attached to alkene	=C**H**R	4.5–6.0
attached to aromatic ring	**H**–Ar	6.0–9.0
aldehyde	**H**COR	9.3–10.5
alcohol	RO**H**	0.5–6.0
phenol	Ar–O**H**	4.5–7.0
carboxylic acid	RCOO**H**	9.0–13.0
alkyl amine	R–N**H**–	1.0–5.0
aryl amine	Ar–N**H**$_2$	3.0–6.0
amide	RCON**H**R	5.0–12.0

(i) Complete Table 7.2 for the proton (^1H) NMR spectrum of **G**.

Table 7.2

chemical shift (δ)	splitting pattern	number of ^1H atoms responsible for the peak	number of protons on adjacent carbon atoms
1.4			
3.5			
4.0			

[3]

(ii) The proton (^1H) NMR spectrum of **G** dissolved in $CDCl_3$ is obtained.

Describe the difference observed between this spectrum and the proton NMR spectrum in D_2O shown in Fig 7.3.

Explain your answer.

....

....

.... [1]

[Total: 18]

8 **(a)** Complete Table 8.1 by placing **one** tick (✓) in each row to indicate the sign of each type of energy change under standard conditions.

Table 8.1

energy change	always positive	always negative	can be either negative or positive
lattice energy			
enthalpy change of hydration			
enthalpy change of solution			

[1]

(b) Define enthalpy change of hydration.

....

....

.... [1]

(c) Table 8.2 shows various energy changes which can be used in the following questions.

Table 8.2

energy change	value / $kJ\,mol^{-1}$
standard enthalpy change of atomisation of calcium	+178.2
first ionisation energy of calcium	+590
second ionisation energy of calcium	+1145
standard enthalpy change of atomisation of bromine	+111.9
Br–Br bond energy	+192.9
standard enthalpy change of solution of calcium bromide, $CaBr_2(s)$	–103.1
standard enthalpy change of formation of calcium bromide, $CaBr_2(s)$	–682.8
standard enthalpy change of hydration of Ca^{2+}	–1579
first electron affinity of bromine	–324.6
first ionisation energy of bromine	+1140

(i) Select and use relevant data from Table 8.2 to calculate the lattice energy, $\Delta H^{\ominus}_{latt}$, of $CaBr_2(s)$.

It may be helpful to draw a labelled energy cycle.

Show your working.

$\Delta H^{\ominus}_{latt}$ of $CaBr_2(s)$ = ... $kJ\,mol^{-1}$ [3]

(ii) Select and use relevant data from Table 8.2 and your answer to **(c)(i)** to calculate the standard enthalpy change of hydration, $\Delta H^{\ominus}_{hyd}$, of Br^-.

It may be helpful to draw a labelled energy cycle.

If you were not able to answer **(c)(i)**, use –2500 $kJ\,mol^{-1}$ as your value for $\Delta H^{\ominus}_{latt}$ of $CaBr_2(s)$. This is **not** the correct value.

Show your working.

$\Delta H^{\ominus}_{hyd}$ of Br^- = ... $kJ\,mol^{-1}$ [2]

(iii) The enthalpy change of hydration of the Br^- ion is more negative than the enthalpy change of hydration of the I^- ion. Explain why.

....

....

.... [2]

[Total: 9]

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Important values, constants and standards

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

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		**Key** atomic number atomic symbol name relative atomic mass									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	3	4	5	6	7	8	9	10	11	12	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 –

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 –