

# Cambridge International AS & A Level

CANDIDATE NAME		
CENTRE NUMBER		CANDIDATE NUMBER
CHEMISTRY		9701/41
Paper 4 A Leve	I 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.



**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.

(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**.





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

Та	b	е	1	.1	

	formula of copper-containing species formed	colour of copper-containing species formed
A		
В		
С		
D		

[4]

- (d) EDTA<sup>4-</sup> is a polydentate ligand.
  - (i) Explain what is meant by a polydentate ligand.

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

A solution of EDTA<sup>4–</sup> 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<sup>4–</sup> in Fig. 1.2 the **six** atoms that form bonds with the metal ion.





(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]

[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,  $K_{\rm stab}$ , for some metal ions with EDTA<sup>4–</sup>.

complex	K <sub>stab</sub>
[CaEDTA] <sup>2–</sup>	5.0 × 10 <sup>10</sup>
[CrEDTA] <sup>-</sup>	2.5 × 10 <sup>23</sup>
[FeEDTA] <sup>-</sup>	1.3 × 10 <sup>25</sup>
[PbEDTA] <sup>2–</sup>	1.1 × 10 <sup>18</sup>

Table	1.2
-------	-----

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  $Pb^{2+}(aq)$ .

(v) Deduce the relative concentrations of [CrEDTA]<sup>-</sup>, [FeEDTA]<sup>-</sup> and [PbEDTA]<sup>2-</sup> 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<sup>4–</sup> ions with a suitable indicator.
  - 0.255 g of hydrated chromium(III) sulfate, Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>•nH<sub>2</sub>O, is dissolved in water and made up to 100 cm<sup>3</sup> in a volumetric flask.
  - 25.0 cm<sup>3</sup> of this solution requires 26.2 cm<sup>3</sup> of 0.00800 mol dm<sup>-3</sup> aqueous EDTA<sup>4-</sup> ions to reach the end-point.

The reaction occurs as shown.

 $[Cr(H_2O)_6]^{3+}$  + EDTA<sup>4-</sup>  $\rightarrow$   $[CrEDTA]^-$  +  $6H_2O$ 

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

Show your working.

(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]

## **BLANK PAGE**

6

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

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



(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



Fig. 2.1

(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.





(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.





[3]

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





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.

 $\mathrm{IO_3^-} + \mathrm{6H^+} + \mathrm{5I^-} \longrightarrow \mathrm{3I_2} + \mathrm{3H_2O}$ 

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

## Table 3.1

experiment	$[IO_3^{-}]/moldm^{-3}$	$[H^+]/moldm^{-3}$	$[I^-]/moldm^{-3}$	initial rate/moldm <sup>-3</sup> min <sup>-1</sup>
1	0.0400	0.0150	0.0250	$4.20 \times 10^{-2}$
2	0.120	to be calculated	0.0125	7.09 × 10 <sup>-2</sup>

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  $[I^-]$ .





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

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

 $[H^+] = \dots \mod dm^{-3}$  [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<sup>-</sup> 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  $\frac{\text{rate at pH 1.0}}{\text{rate at pH 2.0}}$ .

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

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

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

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]

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  $\sigma$  and  $\pi$  bonds in benzene.

12



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



Fig. 4.1

 (c) Compound W is an isomer of Z.



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**.

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 h	eterogeneous 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,  $\Delta H_{f}^{e}$ , and standard entropies,  $S^{e}$ , are given in Table 5.1.

compound	$\Delta H_{\rm f}^{\rm \Theta}/{\rm kJmol^{-1}}$	S <sup>⇔</sup> /JK <sup>−1</sup> mol <sup>−1</sup>
HNCO(g)	-101.7	+238.2
H <sub>2</sub> O(g)	-241.8	+188.8
NH <sub>3</sub> (g)	-45.9	+192.8
CO <sub>2</sub> (g)	-393.5	+213.8

Table 5.1

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

......[1]

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

 $\Delta G^{\oplus}$  = ...... kJ mol<sup>-1</sup> [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.

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

HNCO + 
$$H_2O \implies H_3O^+$$
 + NCO<sup>-</sup>  $pK_a = 3.70$  at 25 °C

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

(ii) Calculate the pH of 0.120 mol dm<sup>-3</sup> HNCO(aq). Give your answer to **three** significant figures.

pH = ......[2]

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

percentage ionisation of HNCO = ......[1]

[Total: 13]

## **BLANK PAGE**

17

(a) Compound H has the structural formula CH<sub>2</sub>=CHCH(NH<sub>2</sub>)COOH.
(i) Name all the functional groups in H.
(ii) Compound H exhibits stereoisomerism.
Draw three-dimensional structures for the two stereoisomers of H. Name this type of stereoisomerism.



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

[2]

[1]



Fig. 6.1

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



6

(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.

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

The new functional group formed should be displayed.

[2]

[1]

(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. Define a buffer solution. (i) Write two equations to show how an aqueous solution of alanine can act as a buffer (ii) solution. (c) Glutamic acid is another amino acid that acts as a buffer. glutamic acid





(i) Draw the skeletal formula for glutamic acid.

(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.





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<sub>2</sub>NCH(CH<sub>3</sub>)COOH, reacts with methanol to form the ester **G** under certain conditions.



The proton (<sup>1</sup>H) 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, $\delta/ppm$
alkane	-CH <sub>3</sub> , -CH <sub>2</sub> -, >CH-	0.9–1.7
alkyl next to C=O	CH <sub>3</sub> -C=O, -CH <sub>2</sub> -C=O, >CH-C=O	2.2–3.0
alkyl next to aromatic ring	CH <sub>3</sub> –Ar, –CH <sub>2</sub> –Ar, >CH–Ar	2.3–3.0
alkyl next to electronegative atom	CH <sub>3</sub> -O, -CH <sub>2</sub> -O, -CH <sub>2</sub> -C <i>l</i>	3.2–4.0
attached to alkene	=CHR	4.5–6.0
attached to aromatic ring	<b>H</b> –Ar	6.0–9.0
aldehyde	HCOR	9.3–10.5
alcohol	ROH	0.5–6.0
phenol	Ar–O <b>H</b>	4.5–7.0
carboxylic acid	RCOOH	9.0–13.0
alkyl amine	R–N <b>H</b> –	1.0–5.0
aryl amine	Ar–NH <sub>2</sub>	3.0–6.0
amide	RCONHR	5.0–12.0

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

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

#### Table 7.2

[3]

(ii) The proton (<sup>1</sup>H) NMR spectrum of **G** dissolved in  $CDCl_3$  is obtained.

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

Explain your answer.

......[1]

[Total: 18]

	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	[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/kJmol <sup>-1</sup>
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 <sub>2</sub> (s)	-103.1
standard enthalpy change of formation of calcium bromide, $CaBr_2(s)$	-682.8
standard enthalpy change of hydration of Ca <sup>2+</sup>	-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,  $\Delta H_{latt}^{e}$ , of CaBr<sub>2</sub>(s).

It may be helpful to draw a labelled energy cycle.

Show your working.

 $\Delta H_{latt}^{\Theta}$  of CaBr<sub>2</sub>(s) = ......kJmol<sup>-1</sup> [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,  $\Delta H_{hyd}^{e}$ , of Br<sup>-</sup>.

It may be helpful to draw a labelled energy cycle.

If you were not able to answer (c)(i), use  $-2500 \text{ kJmol}^{-1}$  as your value for  $\Delta H_{\text{latt}}^{\Theta}$  of CaBr<sub>2</sub>(s). This is **not** the correct value.

Show your working.

 $\Delta H_{\text{hyd}}^{\Theta}$  of Br<sup>-</sup> = ...... kJ mol<sup>-1</sup> [2]

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

.....[2]

# **BLANK PAGE**

## Important values, constants and standards

$R = 8.31 \mathrm{J}\mathrm{K}^{-1}\mathrm{mol}^{-1}$
$F = 9.65 \times 10^4 \mathrm{C  mol^{-1}}$
$L = 6.022 \times 10^{23} \mathrm{mol}^{-1}$
$e = -1.60 \times 10^{-19} \mathrm{C}$
$V_{\rm m}$ = 22.4 dm <sup>3</sup> mol <sup>-1</sup> at s.t.p. (101 kPa and 273 K) $V_{\rm m}$ = 24.0 dm <sup>3</sup> mol <sup>-1</sup> at room conditions
$K_{\rm w}$ = 1.00 × 10 <sup>-14</sup> mol <sup>2</sup> dm <sup>-6</sup> (at 298 K (25 °C))
$c = 4.18 \mathrm{kJ} \mathrm{kg}^{-1} \mathrm{K}^{-1} $ (4.18 J g <sup>-1</sup> K <sup>-1</sup> )

						The Pe	riodic Ta	The Periodic Table of Elements	ements							
							Grc	Group								
1 2											13	14	15	16	17	18
						-										2
						Т										He
			Key			hydrogen 1.0										helium 4.0
3 4			atomic number								5	9	7	80	6	10
		atc	atomic symbol	bol							В	U	z	0	ш	Ne
lithium beryllium 6.9 9.0	Ę	rel	name relative atomic mass	SSE							boron 10.8	carbon 12.0	nitrogen 14.0	oxygen 16.0	fluorine 19.0	neon 20.2
										-	13	14	15	16	17	18
											Al	<u>S</u>	٩	ა	Cl	Ar
sodium magnesium 23.0 24.3	3 3	4	5	9	7	8	6	10	11	12	aluminium 27.0	silicon 28.1	phosphorus 31.0	sulfur 32.1	chlorine 35.5	argon 39.9
		22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
		F	>	ں د	Mn	Fe	ပိ	ïZ	Cu	Zn	Ga	Ge	As	Se	Ŗ	Ϋ́
39.1 calcium	m scandium 1 45.0	titanium 47.9	vanadium 50.9	chromium 52.0	manganese 54.9	iron 55.8	cobalt 58.9	nickel 58.7	copper 63.5	zinc 65.4	gallium 69.7	germanium 72.6	arsenic 74.9	selenium 79.0	bromine 79.9	krypton 83.8
37 38		40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
		Zr	qN	Mo		Ru	RЧ	Pd	Ag	Cq	In	Sn	Sb	Те	Ι	Xe
rubidium strontium 85.5 87.6	um yttrium 88.9	zirconium 91.2	niobium 92.9	molybdenum 95.9		ruthenium 101.1	rhodium 102.9	palladium 106.4	silver 107.9	cadmium 112.4	indium 114.8	tin 118.7	antimony 121.8	tellurium 127.6	iodine 126.9	xenon 131.3
	-	72	73	74		76	77	78	79	80	81	82	83	84	85	86
		Hf	Та	8	Re	Os	Ir	£	Au	Hg	11	Pb	Bi	Ро	At	Rn
caesium barium 132.9 137.3	۳.	hafnium 178.5	tantalum 180.9	tungsten 183.8	rhenium 186.2	osmium 190.2	iridium 192.2	platinum 195.1	gold 197.0	mercury 200.6	thallium 204.4	lead 207.2	bismuth 209.0	polonium –	astatine -	radon -
		104		106	107	108	109	110	111	112	113	114	115	116	117	118
Fr Ra	actinoids	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	С	ЧN	Fl	Mc	۲	Ts	Öğ
	٤	rutherfordium -	_	seaborgium -	bohrium –	hassium -	meitnerium -	darmstadtium -	roentgenium -	copernicium -	nihonium –	flerovium -	moscovium -	livermorium -	tennessine -	oganesson -
-	-	-														
	57	58	59	60	61	62	63	25	65	66	67	68	69	70	71	
lanthanoids	La	Ce	ሻ	ΡN	Pm	Sm	Еu	Ъд	Тb	Dy	Ю	ц	Tm	γb	Lu	
	lanthanum 138.9		praseodymium 140.9	ne	promethium -	samarium 150.4	europium 152.0	gadolinium 157.3	terbium 158.9	dysprosium 162.5	holmium 164.9	erbium 167.3	thulium 168.9	ytterbium 173.1	lutetium 175.0	
	89	06	91	92	93	94	95	96	97	98	66	100	101	102	103	
actinoids	Ac	Th	Pa		ЧN	Pu	Am	СЗ	剐	ç	Es	Е	РМ	No	Ļ	
	actinium -	thorium 232.0	protactinium 231.0	uranium 238.0	neptunium -	plutonium –	americium -	curium	berkelium -	californium –	einsteinium -	fermium -	mendelevium -	nobelium -	lawrencium -	

To avoid the issue of disclosure of answer-related information to candidates, all copyright acknowledgements are reproduced online in the Cambridge Assessment International Education Copyright Acknowledgements Booklet. This is produced for each series of examinations and is freely available to download at www.cambridgeinternational.org after the live examination series.