

# Cambridge International AS & A Level

CANDIDATE NAME		
CENTRE NUMBER		CANDIDATE NUMBER
CHEMISTRY		9701/41
Paper 4 A Leve	el Structured Questions	May/June 2024
		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.



[Turn over

1 (a) (i) Describe the trend in the solubility of the hydroxides of magnesium, calcium and strontium.

		Explain your answer.
		most soluble least soluble
		[4]
	(ii)	Suggest the variation in pH of saturated solutions of the hydroxides of magnesium, calcium and strontium.
		Explain your answer.
		[1]
(b)	Bari	um hydroxide, Ba(OH) <sub>2</sub> , is a strong base.
	A 25 wate	$50.0 \mathrm{cm^3}$ solution of Ba(OH) <sub>2</sub> with a pH of 12.2 is made by dissolving Ba(OH) <sub>2</sub> in distilled er.
	Calo	culate the mass of Ba(OH) <sub>2</sub> required to make this solution.

Show your working.

[*M*<sub>r</sub>: Ba(OH)<sub>2</sub>, 171.3]

- (c) The solubility of iron(II) hydroxide,  $Fe(OH)_2$ , is  $5.85 \times 10^{-6} \text{ mol dm}^{-3}$  at 298 K.
  - (i) Write the expression for the solubility product,  $K_{sp}$ , of Fe(OH)<sub>2</sub>.

$$K_{\rm sp}$$
 =

[1]

(ii) Calculate the value of  $K_{\rm sp}$  of Fe(OH)<sub>2</sub>. Include its units.

K<sub>sp</sub> = ..... units = .....[2]

[Total: 12]





[1]

- (c) Tollens' reagent can be used to distinguish between aldehydes and ketones. Tollens' reagent contains [Ag(NH<sub>3</sub>)<sub>2</sub>]OH, which can be prepared in a two-step process.
  - **step 1** Aqueous NaOH is added dropwise to aqueous AgNO<sub>3</sub> to form Ag<sub>2</sub>O as a brown precipitate.
  - step 2 Aqueous  $NH_3$  is added dropwise to  $Ag_2O$  to form a colourless solution containing  $[Ag(NH_3)_2]OH$ .

Construct equations for each of the steps in the preparation of  $[Ag(NH_3)_2]OH$ .

step 1 ..... step 2 ......[2]

4

(d) Name the shape of the complex ion  $[Ag(NH_3)_2]^+$ .

bond angle for N-Ag-N = ...... °

[2]

(e) An electrochemical cell uses Ag<sub>2</sub>O as the positive electrode and Zn as the negative electrode immersed in an alkaline electrolyte.

The overall cell reaction is shown.

 $Ag_2O + Zn + H_2O \rightarrow 2Ag + Zn(OH)_2$ 

Complete the half-equation for the reaction at each electrode.

at the positive electrode	Ag <sub>2</sub> O +
at the negative electrode	Zn +[2]

(f) Coordination polymers are made when a bidentate ligand acts as a bridge between different metal ions.

Under certain conditions  $Ru^{3+}(aq)$  and the bidentate ligand *dps* can form a coordination polymer containing ( $[Ru(dps)Cl_4]^-)_n$  chains.



Fig. 2.2

The bidentate ligand *dps* uses each of the nitrogen atoms to bond to a different Ru<sup>3+</sup>.

Complete Fig. 2.3 by drawing the structure for the coordination polymer  $([Ru(dps)Cl_4]^-)_n$ . Show **two** repeat units.

The *dps* ligand can be represented using  $\dot{N}$ .



Fig. 2.3

[2]

[Total: 12]

3 (a) When a sample of hydrated lithium ethanedioate, Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub>•H<sub>2</sub>O, is gently heated, two gaseous products are formed and a white solid residue remains.

The residue is added to HNO<sub>3</sub>(aq). A gas is produced that turns limewater milky.

Complete the equation for the decomposition of  $Li_2C_2O_4$ •H<sub>2</sub>O.

 $\text{Li}_{2}\text{C}_{2}\text{O}_{4}\text{+}\text{H}_{2}\text{O} \rightarrow \dots + \dots + \dots + \dots$ 

(b) The trend in the decomposition temperatures of the Group 2 ethanedioates is similar to that of the Group 2 nitrates.

Suggest which of  $CaC_2O_4$  and  $BaC_2O_4$  will decompose at the **lower** temperature. Explain your answer.

(c) Potassium iron(III) ethanedioate,  $K_3[Fe(C_2O_4)_3]$ , dissolves in water to form a green solution.

Explain why transition elements can form coloured complexes.

(d) The anhydrous iron(III) compound K<sub>3</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>] decomposes on heating to form a mixture of K<sub>2</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>], K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and CO<sub>2</sub>.

Complete the equation for the decomposition of  $K_3[Fe(C_2O_4)_3]$ .

..... 
$$K_3[Fe(C_2O_4)_3] \rightarrow \dots K_2[Fe(C_2O_4)_2] + \dots K_2C_2O_4 + \dots CO_2$$
[1]

[1]

(e) The  $[Fe(C_2O_4)_3]^{3-}$  complex ion shows stereoisomerism.

Complete the three-dimensional diagrams in Fig. 3.1 to show the **two** stereoisomers of  $[Fe(C_2O_4)_3]^{3-}$ .

The  $C_2 O_4^{2-}$  ligand can be represented using O.





[2]

(f) Buffer solutions are used to regulate pH. Write **two** equations to describe how a solution containing  $HC_2O_4^-$  ions acts as a buffer solution when small amounts of acid or alkali are added.

(g) A fuel cell is an electrochemical cell that can be used to generate electrical energy by using oxygen to oxidise a fuel.

Ethanedioic acid, (COOH)<sub>2</sub>, dissolved in an alkaline electrolyte is being investigated as a fuel.

The relevant standard electrode potentials,  $E^{\Theta}$ , for the cell are shown.

$O_2(g) + 2H_2O(I) + 4e^-$	$\rightleftharpoons$	4OH <sup>_</sup> (aq)	$E^{\oplus} = +0.40  \text{V}$
2CO <sub>2</sub> (g) + 2e <sup>-</sup>	$\rightarrow$	C <sub>2</sub> O <sub>4</sub> <sup>2–</sup> (aq)	$E^{\oplus} = -0.59  \text{V}$

Use these equations to deduce the overall cell reaction. Calculate the value of  $E_{cell}^{\Phi}$ .

overall cell reaction .....

 $E_{\text{cell}}^{\Theta}$  = .....V[2]

4 (a) Define standard electrode potential,  $E^{\bullet}$ , including a description of standard conditions.

(b) (i) An electrochemical cell is set up to measure E<sup>o</sup> of the Ag<sup>+</sup>(aq)/Ag(s) electrode.
 Draw a labelled diagram of this electrochemical cell.

Include all necessary substances. It is not necessary to state conditions used.

[3]

(ii) A separate electrochemical cell is set up using a **lower** concentration of Ag<sup>+</sup>(aq) than that used in (b)(i).

Suggest how the electrode potential, E, for the Ag<sup>+</sup>(aq)/Ag(s) electrode would change from its  $E^{o}$  value. Explain your answer.

......[1]

(c) Define enthalpy change of solution,  $\Delta H_{sol}^{\Theta}$ .

......[1]

(d) Some relevant energy changes for  $AgNO_3$  are shown in Table 4.1.

### Table 4.1

energy change	value/kJmol <sup>-1</sup>
enthalpy change of solution of AgNO <sub>3</sub> (s)	+22.6
enthalpy change of hydration of silver ions	-475
enthalpy change of hydration of nitrate ions	-314

(i) Complete the energy cycle in Fig. 4.1 to show the relationship between the lattice energy,  $\Delta H_{\text{latt}}^{\circ}$ , of AgNO<sub>3</sub>(s) and the energy changes shown in Table 4.1.

Include state symbols for all the species.



Fig. 4.1

[2]

(ii) Calculate the lattice energy,  $\Delta H_{latt}^{\Theta}$ , of AgNO<sub>3</sub>(s).

 $\Delta H_{\text{latt}}^{\Theta} = \dots \quad \text{kJ mol}^{-1} \quad [1]$ 

(e) Suggest the trend in the magnitude of the lattice energies of the metal nitrates, NaNO<sub>3</sub>(s), Mg(NO<sub>3</sub>)<sub>2</sub>(s) and RbNO<sub>3</sub>(s).

Explain your answer. most exothermic least exothermic
[3]

[Total: 13]

5 (a) In aqueous solution, persulfate ions,  $S_2O_8^{2-}$ , react with iodide ions, as shown in reaction 1.

reaction 1 
$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$$

The rate of reaction 1 is investigated.

A sample of  $S_2O_8^{2-}$  is mixed with a large excess of iodide ions of known concentration. The graph in Fig. 5.1 shows the results obtained.



Fig. 5.1

(i) Use Fig. 5.1 to determine the initial rate of reaction 1. Show your working.

rate = .....  $mol dm^{-3} min^{-1}$  [1]

(ii) The rate equation for reaction 1 is rate =  $k [S_2O_8^{2-}] [I^-]$ .

Suggest why a large excess of iodide ions allows the rate constant to be determined from the half-life in this investigation.

......[1]

(b) The reaction of persulfate ions,  $S_2O_8^{2-}$ , with iodide ions is catalysed by Fe<sup>2+</sup> ions.

Write **two** equations to show how  $Fe^{2+}$  catalyses reaction 1.

equation 1 .....

(c) Describe the effect of an increase in temperature on the rate constant and the rate of reaction 1.

.....[1]

(d) In aqueous solution, thiosulfate ions,  $S_2O_3^{2-}$ , react with hydrogen ions, as shown in reaction 2.

reaction 2  $S_2O_3^{2-} + 2H^+ \rightarrow SO_2 + S + H_2O_2$ 

The rate of reaction is first order with respect to  $[S_2O_3^{2-}]$  and zero order with respect to  $[H^+]$  under certain conditions.

The rate constant, *k*, for this reaction is  $1.58 \times 10^{-2} \text{ s}^{-1}$ .

Calculate the half-life,  $t_{\frac{1}{2}}$ , for reaction 2.

 $t_{\frac{1}{2}}$  = .....s [1]

(e) The compound nitrosyl bromide, NOBr, can be formed as shown in reaction 3.

reaction 3  $2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$ 

The rate is first order with respect to [NO] and first order with respect to [Br<sub>2</sub>].

The reaction mechanism has two steps.

Suggest equations for the **two** steps of this mechanism. State which is the rate-determining step.

step 1 ..... step 2 ..... rate-determining step = .....

[2]

[2]

[Total: 8]

6 (a) (i) State what is meant by partition coefficient,  $K_{\rm pc}$ .

(ii) The partition coefficient,  $K_{pc}$ , for a compound, **X**, between carbon disulfide, CS<sub>2</sub>, and water is 10.5.

1.85 g of **X** is dissolved in water and made up to  $100.0 \text{ cm}^3$  in a volumetric flask. 40.0 cm<sup>3</sup> of this aqueous solution is shaken with 25.0 cm<sup>3</sup> of CS<sub>2</sub>. The mixture is left to reach equilibrium.

Calculate the mass of X, in g, extracted into the CS<sub>2</sub> layer.

mass of **X** = ..... g [2]

(b) The compound  $C_6H_6$  has many structural isomers. Four suggested structures of  $C_6H_6$  are shown in Fig. 6.1.

Kekulé benzene

Dewar benzene

Ladenburg benzene delocalise

delocalised benzene











Using Fig. 6.1, complete Table 6.1 to predict the number of carbon atoms that have sp, sp<sup>2</sup> and sp<sup>3</sup> hybridisation in Kekulé benzene, Dewar benzene and Ladenburg benzene.

Table (	6.1
---------	-----

C <sub>6</sub> H <sub>6</sub> structure	sp hybridised	sp <sup>2</sup> hybridised	sp <sup>3</sup> hybridised
Kekulé benzene			
Dewar benzene			
Ladenburg benzene			

[2]

(c) Describe the shape of delocalised benzene.

Include the geometry of each carbon, the C-C-H bond angle and the type of bond(s) between the carbon atoms and between the carbon and hydrogen atoms.

(d) Suggest why Dewar benzene and Ladenburg benzene are unstable isomers of C<sub>6</sub>H<sub>6</sub>. [1]

(e) Complete Table 6.2 to predict the number of peaks in the proton (<sup>1</sup>H) NMR spectrum for Dewar benzene, Ladenburg benzene and delocalised benzene.

### Table 6.2

number of peaks

[1]

(f) The reaction of phenylethanone with 1,4-dibromobutane, BrCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br, in the presence of FeBr<sub>3</sub> is shown in Fig. 6.2.

16







The mechanism of this reaction is similar to that of the alkylation of benzene.

(i) Construct an equation for the formation of the electrophile,  $BrCH_2CH_2CH_2CH_2^+$ .

......[1]

(ii) Complete the mechanism in Fig. 6.3 for the reaction of phenylethanone with BrCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub><sup>+</sup> ions.

Include all relevant curly arrows and charges. Draw the structure of the organic intermediate.





(iii) The reaction shown in Fig. 6.2 forms small amounts of two by-products, **Y** ( $C_{20}H_{22}O_2$ ) and **Z** ( $C_{12}H_{14}O$ ).

Suggest structures for  $\mathbf{Y}$  and  $\mathbf{Z}$  in the boxes in Fig. 6.4.



[2]

[Total: 15]

**7** Four esters, **A**, **B**, **C** and **D**, with the molecular formula  $C_6H_{12}O_2$  are shown in Fig. 7.1.





(a) Give the systematic name of ester A.

......[1]

(b) A mixture of these esters, A, B, C and D, is analysed by gas-liquid chromatography.

The chromatogram produced is shown in Fig. 7.2. The number above each peak represents the area under the peak.

The area under each peak is proportional to the mass of the respective ester in the mixture.





(i) State what is meant by retention time.

.....

......[1]

(ii) Calculate the percentage by mass of ester **D** in the original mixture.

percentage by mass of ester **D** = ..... % [1]

- (c) Separate samples of the esters, **A**, **B**, **C** and **D**, are analysed using proton (<sup>1</sup>H) NMR and carbon-13 NMR spectroscopy.
  - (i) Complete Table 7.1 to show the number of peaks in each NMR spectrum for esters **B** and **C**.

#### Table 7.1

ester	number of peaks in proton ( <sup>1</sup> H) NMR spectrum	number of peaks in carbon-13 NMR spectrum
В		
С		

(ii) Identify all of the esters from A, B, C and D that have at least one triplet peak in their proton (<sup>1</sup>H) NMR spectrum.

Question 7 continues on page 20.

[2]

(d) Compound F, C<sub>6</sub>H<sub>8</sub>O<sub>3</sub>, shows stereoisomerism and effervesces with Na<sub>2</sub>CO<sub>3</sub>(aq).
 Compound F reacts with alkaline I<sub>2</sub>(aq) to form yellow precipitate G and compound H.
 Compound F reacts with LiA*l*H<sub>4</sub> to form compound J, C<sub>6</sub>H<sub>12</sub>O<sub>2</sub>.
 Compound F reacts with SOC*l*<sub>2</sub> to form compound K, C<sub>6</sub>H<sub>7</sub>O<sub>2</sub>C*l*.

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Compound K reacts with propan-2-ol to form compound L.

Draw the structures of compounds F, G, H, J, K and L in the boxes in Fig. 7.3.



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8 Neotame is an artificial sweetener added to some foods.



Fig. 8.1

(a)	(i)	State the number of chiral carbon atoms in a molecule of neotame.	
			[1]
	(ii)	Neotame contains the arene functional group.	
		Identify all the <b>other</b> functional groups present in neotame.	
			[2]
(b)	Neo	otame reacts with an excess of hot NaOH(aq) to form three organic products.	
	(i)	State the <b>two</b> types of reaction that occur when neotame reacts with hot NaOH(aq).	
		1	
		2	[2]
			[-]



Fig. 8.1

(ii) Draw the structures of the **three** organic products formed from the reaction of neotame with an excess of hot NaOH(aq).





[Total: 8]

9 (a) Samples of phenol,  $C_6H_5OH$ , are reacted separately with sodium and with dilute nitric acid.



Fig. 9.1

- (i) Write the equation for the reaction of  $C_6H_5OH$  with Na.
  - ......[1]
- (ii) Draw the structures of the **two** major isomeric organic products formed in the reaction of phenol with dilute HNO<sub>3</sub>.



[1]

(b) Salicylic acid can be synthesised from phenol.



Fig. 9.2

One of the steps in this synthesis is the electrophilic substitution reaction of carbon dioxide with the phenoxide ion,  $C_6H_5O^-$ .

Complete the mechanism in Fig. 9.3 for the reaction of  $\rm C_6H_5O^-$  with  $\rm CO_2.$ 

Include all relevant curly arrows, dipoles and charges. Draw the structure of the organic intermediate.



Fig. 9.3

[3]

- (c) Some syntheses use Diels–Alder reactions, which normally involve a diene and an alkene reacting together to form a cyclohexene.
  - (i) Draw three curly arrows in Fig. 9.4 to complete the mechanism for the Diels–Alder reaction between buta-1,3-diene and ethene.





(ii) Another Diels–Alder reaction of buta-1,3-diene is shown in Fig. 9.5.

Predict the product formed in this reaction.





[1]

[1]

[Total: 7]

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## 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
$K_{\rm w} = 1.00 \times 10^{-14} {\rm mol}^2 {\rm dm}^{-6} ({\rm at}298{\rm K}(25{}^{\circ}{\rm C}))$
$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 Tal	The Periodic Table of Elements	ments							
							Group	dno								
-	2										13	14	15	16	17	18
	-					-				1						2
						т										He
			Key			hydrogen 1.0										helium 4.0
3	4		atomic number	_	_						5	9	7	8	6	10
	Be	đ	atomic symbol	bol							Ш	U	z	0	ш	Ne
6.9 ber	beryllium 9.0	<u> </u>	name relative atomic mass	ass							boron 10.8	carbon 12.0	nitrogen 14.0	oxygen 16.0	fluorine 19.0	neon 20.2
	12				_					-	13	14	15	16	17	18
	٨g										Ρl	N.	٩	ა	Cl	Ar
sodium mag 23.0 2	magnesium 24.3 3	4	5	9	7	Ø	6	10	11	12	aluminium 27.0	silicon 28.1	phosphorus 31.0	sulfur 32.1	chlorine 35.5	argon 39.9
			23	24	25	26	27	28	29	30	31	32	33	34	35	36
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	38 39		41	42	43	4	45	46	47	48	49	50	51	52	53	54
				Mo	р	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Ч	Ι	Xe
rubidium stro 85.5 8	strontium yttrium 87.6 88.9	N	niobium a2 a	molybdenum a5 a	technetium	ruthenium 101 1	rhodium 102 a	palladium 106 4	silver 107 a	cadmium 112 A	indium 114 R	tin 118.7	antimony 121 R	tellurium 127 6	iodine 126 a	xenon 1313
+	-	+	+	74	75	76	77	78	79	80	81	82	83	84	85	86
		loids Hf	Та	>	Re	Os	Ir	Ę	Au	Ha	11	Pb	Ē	Ро	At	Rn
	barium 137.3	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 -
		-		106	107	108	109	110	111	112	113	114	115	116	117	118
ц	Raactinoids	ids Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	C	ЧN	Fl	Mc	۲	Тs	Og
francium ra	radium -	rutherfordium -	dubnium –	seaborgium -	bohrium –	hassium -	meitnerium -	darmstadtium -	roentgenium -	copernicium -	nihonium –	flerovium -	moscovium -	livermorium -	tennessine -	oganesson 
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	57	28	59	60	61	62	63	64	65	66	67	68	69	70	71	
lanthanoids	Lo	_	ŗ	Νd	Ът	Sm	Eu	Вd	Тb	DV	Чо	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		91	92	93	94	95	96	97	98	66	100	101	102	103	
actinoids	Ac		Ра	⊃	dN	Pu	Am	Cm	ų	Ç	Еs	Е Н	Md	No	L	
	actinium -	um thorium 232.0	protactinium 231.0	uranium 238.0	neptunium -	plutonium –	americium -	curium	berkelium -	californium –	einsteinium -	fermium -	mendelevium -	nobelium -	lawrencium -	

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