

Cambridge International AS & A Level

CENTRE		CANDIDATE
NUMBER CHEMISTRY		NUMBER 9701/43
Paper 4 A Level	Structured Questions	October/November 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 Fluorine reacts with chlorine dioxide, ClO_2 , as shown.

 $F_2(g) + 2ClO_2(g) \rightarrow 2FClO_2(g)$

The rate of the reaction is first order with respect to the concentration of F_2 and first order with respect to the concentration of ClO_2 . No catalyst is involved.

(a) (i) Suggest a two-step mechanism for this reaction.

step 1 \rightarrow step 2 \rightarrow [2]

(ii) Identify the rate-determining step in this mechanism. Explain your answer.

- (b) When the rate of the reaction is measured in moldm⁻³s⁻¹ the numerical value of the rate constant, k, is 1.22 under certain conditions.
 - (i) Complete the rate equation for this reaction, stating the overall order of the reaction.

rate =

overall order of reaction =

[1]

(ii) Use your rate equation in (i) to calculate the rate of the reaction when the concentrations of F_2 and ClO_2 are both 2.00 × 10⁻³ mol dm⁻³.

rate = mol dm⁻³s⁻¹ [1]

(c) Under different conditions, and in the presence of a large excess of ClO_2 , the rate equation is as shown.

rate =
$$k_1[F_2]$$

The half-life, $t_{\frac{1}{2}}$, of the concentration of F_2 is 4.00 s under these conditions.

(i) Calculate the numerical value of k_1 , giving its units.

Give your answer to three significant figures.

*k*₁ = units

[2]

(ii) An experiment is performed under these conditions in which the starting concentration of F_2 is 0.00200 mol dm⁻³.

Draw a graph on the grid in Fig. 1.1 to show how the concentration of F_2 changes over the first 12s of the reaction.



Fig. 1.1

[1]

(iii) Use your graph in Fig. 1.1 to find the rate of the reaction when the concentration of F_2 is 0.00100 mol dm⁻³. Show your working on the graph.

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

[Total: 9] [Turn over 4

2 (a) Define $K_{\rm w}$ mathematically by completing the expression.

K_w =[1]

(b) Two solutions, V and W, are described.

- V is HC*l*(aq).
- W is NaOH(aq).
- The concentration of HCl in **V** is the same as the concentration of NaOH in **W**.
- The pH values of V and W differ by exactly 11.00 at 298 K.
- (i) Calculate the concentration of HCl in V.

	concentration of HCl in V = mol dm ⁻³ [2]
(ii)	Equal volumes of the two solutions ${f V}$ and ${f W}$ are mixed, giving solution ${f X}$.
	Name solution X and state its pH.
	solution X pH [1]
(iii)	A 1 cm ³ sample of 1.0 mol dm ⁻³ HNO ₃ is added to 100 cm ³ of solution X , forming mixture Y .
	A 1 cm ³ sample of 1.0 mol dm ⁻³ KOH is added to 100 cm^3 of solution X , forming mixture Z .
	Estimate the pH of mixtures Y and Z . No calculations are required.
	mixture Y mixture Z [1]
(c) (i)	CH_3CH_2COOH , CH_3CCl_2COOH and H_2SO_4 are all acidic.
	Suggest the trend in the relative acid strength of these three compounds.
	Explain your answer.
	strongest acid weakest acid
	explanation
	[3]

(ii)	When concentrated H_2SO_4 is added to water a series of acid-base reactions occurs.
	There are three conjugate acid-base pairs that can be identified during this series of reactions.
	Write the formulae of these three conjugate acid-base pairs.
	conjugate acid 1
	conjugate acid 2 conjugate base 2
	conjugate acid 3[2]
The	e partition coefficient, K_{pc} , of a substance, Q , between hexane and water is 7.84 at 298 K.

Q is more soluble in hexane than it is in water.

(i) Define partition coefficient, K_{pc} .

(d)

.....

-[1]
- (ii) 5.00 g of **Q** is shaken with a mixture of 100.0 cm³ of water and 100.0 cm³ of hexane at 298 K and left until there is no further change in concentrations.

Calculate the mass of **Q** dissolved in the water.

mass of **Q** = g [1]

(iii) A sample of **Q** is shaken with a different mixture of water and hexane and left until there is no further change in concentrations.

It is found that the mass of **Q** dissolved in each solvent is the same.

Use the $K_{\rm pc}$ value to suggest possible values for the volume of water used and the volume of hexane used.

	volume of water = .	cm ³
	volume of hexane = .	cm ³ [1]
(iv)	Q is more soluble in hexane than it is in water.	
	It is suggested that Q is one of KCl, $CH_3(CH_2)_4OH$ or HCOOH.	
	Identify Q . Explain your answer.	
		[1]
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3 Hydrogen peroxide is a liquid at 298K. It is moderately stable under room conditions but will decompose quickly if a catalyst is added.

reaction 1 $2H_2O_2(I) \rightarrow 2H_2O(I) + O_2(g)$

(a) (i) Define entropy.

(ii) Predict the sign of the standard entropy change of reaction 1. Explain your answer. sign explanation

(b) Some bond energy data are shown in Table 3.1.

Table 3	3.1
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type of bond	bond energy /kJ mol ⁻¹
0–0	150
O–H	460
O=0	496

Use the data in Table 3.1 to show that the enthalpy change of the following reaction is $-196 \, k J \, mol^{-1}$.

 $2\mathrm{H}_2\mathrm{O}_2(\mathrm{g}) \to 2\mathrm{H}_2\mathrm{O}(\mathrm{g}) + \mathrm{O}_2(\mathrm{g})$

[1]

(c) Some standard entropies, S^{Θ} , are shown in Table 3.2.

substance	S ^e /JK ⁻¹ mol ⁻¹
H ₂ O ₂ (I)	+102
H ₂ O(I)	+70

Table 3.2

The enthalpy change and Gibbs free energy change for the following reaction are shown.

$$2H_2O_2(I) \rightarrow 2H_2O(I) + O_2(g) \qquad \Delta H^{\oplus} = -196 \text{ kJ mol}^{-1}$$

$$\Delta G^{\oplus} = -238 \text{ kJ mol}^{-1}$$

Use the data given to calculate the standard entropy of oxygen, S^{Θ} , $O_2(g)$.

 S^{Φ} , $O_2(g) = \dots J K^{-1} mol^{-1}$ [3]

 (e) The E^{\diamond} values for two electrode reactions are given.

$$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$$
 $E^{\oplus} = +1.77V$
 $Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$ $E^{\oplus} = -0.41V$

- (i) An electrochemical cell is constructed with the following half-cells (electrodes):
 - an acidified solution of H_2O_2 , a platinum wire Cr^{2+} mixed with Cr^{3+} , a platinum wire.

Identify the positive half-cell and calculate the standard cell potential, E_{cell}^{\bullet} .

positive half-cell E_{cell}^{Θ} = V [1]

Calculate the value of ΔG° for the cell reaction that occurs, per mole of H₂O₂. (ii)

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

(f) The E^{\diamond} values for two electrode reactions are given.

 $H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$ $E^{\oplus} = +1.77V$ $Co^{3+} + e^- \Longrightarrow Co^{2+}$ *E*[⊕] = +1.82∨

An electrochemical cell is constructed with the following half-cells.

- half-cell 1 an acidified solution of H2O2 under standard conditions, a platinum wire
- half-cell 2 a solution containing 0.020 mol dm⁻³Co³⁺ and 2.0 mol dm⁻³Co²⁺, a platinum wire
- (i) Use the Nernst equation to calculate the value of E, the electrode potential of half-cell 2 under these conditions.

E = V [2]

Write an equation for the cell reaction that occurs in this cell under these conditions. (ii)

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9

Define enthalpy change of hydration, ΔH_{hyd} . (g) (i)

>

(ii) Aluminium fluoride, AlF_3 , is an ionic solid.

Complete and label the energy cycle to show the relationship between:

- the enthalpy change of solution of AlF_3 , ΔH_{sol}^{Φ} the lattice energy of AlF_3 , ΔH_{latt}^{Φ} the enthalpy changes of hydration of Al^{3+} and F^- , ΔH_{hyd}^{Φ} . •

Include state symbols for all substances and ions.



[2]

(iii) Relevant data for this question are given.

$$\Delta H_{sol}^{\Theta} A l F_3 = -209 \text{ kJ mol}^{-1}$$
$$\Delta H_{hyd}^{\Theta} A l^{3+} = -4690 \text{ kJ mol}^{-1}$$
$$\Delta H_{hyd}^{\Theta} F^- = -506 \text{ kJ mol}^{-1}$$

Use these data and your energy cycle in (g)(ii) to calculate the ΔH_{latt}^{Θ} of AlF_3 .

 $\Delta H_{\text{latt}}^{\Theta}$ of $AlF_3 = \dots kJ \text{ mol}^{-1}$ [1]

[Total: 17]

[Turn over

- 4 (a) Cobalt(II) nitrate, $Co(NO_3)_2$, is a reddish-brown crystalline solid. It dissolves in water to form a solution containing $[Co(H_2O)_6]^{2+}$ complex ions.
 - (i) Complete Table 4.1 giving the formula of the cobalt-containing species that is formed in each of the three reactions described.

reactio	reagent added to $[Co(H_2O)_6]^{2+}(aq)$	cobalt-containing species formed	
1	NaOH(aq)		
2	an excess of NH ₃ (aq)		
3	an excess of conc. HC <i>l</i> (aq)		
(ii)	Describe the colour change seen in reaction of $[Co(H, \Omega)]^{2+}$	[2]	
	final colour after addition of an excess of	conc. HC <i>l</i> (aq)[1]	
	cium nitrate, Ca(NO ₃) ₂ , is a white crystallir proximately 500°C.	e solid. When heated, it starts to decompose at	
(i)	Write an equation for the decomposition	of $Ca(NO_3)_2$.	
		[1]	
(ii)	Suggest temperatures at which Mg(NO ₃)	$_2$ and Ba(NO $_3$) $_2$ start to decompose.	
	Explain your answer.		
	temperature at which $Mg(NO_3)_2$ starts to	decompose°C	
	temperature at which Ba(NO ₃) ₂ starts to decompose°C		
	explanation		
		[3]	
		[Total: 7]	

Table 4.1

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- **5** Transition elements behave as catalysts and can form complex ions.
 - (a) Explain why transition elements behave as catalysts.

......[2]

(b) Silver forms the linear complex ion $[Ag(CN)_2]^-$.

Copper forms the tetrahedral complex ion $[Cu(CN)_{d}]^{3-}$.

Titanium forms the complex $[TiCl_4(diars)_2]$, where diars is a neutral bidentate ligand.

(i) State the oxidation state and the coordination number of titanium in $[TiC l_4(diars)_2]$.

oxidation state

coordination number

[1]

(ii) Draw three-dimensional diagrams to show the shapes of $[Ag(CN)_2]^-$ and $[Cu(CN)_4]^{3-}$, in the boxes.

Label one bond angle on each diagram.



[2]

- (c) The numerical value of the stability constant, K_{stab} , of the copper(I) complex $[Cu(CN)_4]^{3-}$ is 2.0×10^{27} .
 - (i) Write an expression for the K_{stab} of $[Cu(CN)_4]^{3-}$.

$$K_{\rm stab} =$$

[1]

(ii) In a solution the concentrations of CN^- and $[Cu(CN)_4]^{3-}$ are both 0.0010 mol dm⁻³.

Use your expression from (c)(i) and the value of K_{stab} to calculate the concentration of Cu⁺(aq) in this solution.

concentration of $Cu^+(aq) = \dots mol dm^{-3}$ [1]

(d) A piece of a copper-containing alloy has a mass of 0.567 g. It is dissolved in an acid giving 100.0 cm³ of a blue solution in which all the copper is present as Cu²⁺ ions.

An excess of KI(aq) is added to a 25.0 cm³ sample of this solution.

All of the copper is precipitated as white CuI(s).

 Cu^{2+} ions are the only component in the solution that react with KI(aq). This is reaction 1.

reaction 1 $2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$

The liberated $\rm I_2$ is then titrated with 0.0200 mol dm^-3 $\rm S_2O_3{}^{2-}.$ This is reaction 2.

reaction 2 $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$

The titration requires 20.10 cm³ of 0.0200 mol dm⁻³ $S_2O_3^{2-}$ to reach the end-point.

(i) Calculate the number of moles of ${\rm I}_2$ that are reduced in this titration.

number of moles of I_2 = mol [1]

(ii) Calculate the number of moles of copper in the original piece of alloy.

number of moles of copper = mol [1]

(iii) Calculate the percentage of copper in the alloy.

percentage of copper = % [1]

(iv) Suggest why a solution of Cu²⁺ is coloured but solid CuI is white.

......[2]

[Total: 12]

6 (a) Five ligands are listed in Table 6.1.

Tab	le	6.	1
IUN		•	

ligand	type of ligand
NH ₃	
EDTA ⁴⁻	
CN⁻	
H ₂ NCH ₂ CH ₂ NHCH ₂ CH ₂ NH ₂	tridentate
C ₂ O ₄ ²⁻	

- (i) Complete Table 6.1 using the words monodentate, bidentate and polydentate only.Each of these three words may be used once, more than once, or not at all.
- (ii) The molecule $H_2NCH_2CH_2NHCH_2CH_2NH_2$ is a tridentate ligand.

Suggest the meaning of tridentate ligand.

[2]

-[1]
- (iii) Suggest how $H_2NCH_2CH_2NHCH_2CH_2NH_2$ acts as a tridentate ligand.

-[1]
- (b) Nickel forms the octahedral complex $[Ni(en)_2(H_2O)_2]^{2+}$. This complex can exist in three isomeric forms, listed in Table 6.2.

One of these forms is a trans isomer, the other forms are two different cis isomers.

Table 6.2

isomer	polarity
trans isomer	
cis isomer 1	
cis isomer 2	

(i) Complete Table 6.2 using the terms polar or non-polar.

	Each term may be used once, more than once, or not at all.	[1]
(ii)	Describe the difference between cis isomer 1 and cis isomer 2.	
		[1]
	[Tota	l: 6]

7 Sunset Yellow is an additive used for colouring foods.

A synthetic route for making Sunset Yellow is shown.

Molecules **E** and **G** each contain one $-SO_3^-$ group. These groups are unchanged in the formation of Sunset Yellow.







8 Capsaicin is found in chilli peppers.



You should assume the CH₃O group is unreactive in the reactions involved in this question.

- (a) Name all the functional groups in capsaic in addition to the CH_3O group.
 -[1]
- (b) Complete the equation for the reaction of capsaicin with an excess of $Br_2(aq)$ in the dark.

Draw the structure of the organic product in the labelled box.



(c) Capsaicin is heated with an excess of hydrogen gas in the presence of platinum metal.
 The six-membered ring reacts in the same way as benzene under these conditions.
 Draw the structure of the organic product formed.

- (d) When capsaicin is treated with reagent J under suitable conditions one of the products is methylpropanoic acid, CH₃CH(CH₃)COOH.
 - (i) Identify reagent J and any necessary conditions.

......[1]

(ii) There are three different peaks in the proton (¹H) NMR spectrum of $CH_3CH(CH_3)COOH$ in $CDCl_3$.

environment of proton	example	chemical shift range δ/ppm
alkane	-CH ₃ , -CH ₂ -, >CH-	0.9–1.7
alkyl next to C=O	CH ₃ -C=O, -CH ₂ -C=O, >CH-C=O	2.2–3.0
alkyl next to aromatic ring	CH_3 -Ar, $-CH_2$ -Ar, $>CH$ -Ar	2.3–3.0
alkyl next to electronegative atom	CH ₃ -O, -CH ₂ -O, -CH ₂ -C <i>l</i>	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	HCOR	9.3–10.5
alcohol	ROH	0.5–6.0
phenol	Ar–O H	4.5–7.0
carboxylic acid	RCOOH	9.0–13.0

Table 8.1

Use Table 8.1 to complete Table 8.2 and state:

- the typical proton (^{1}H) chemical shift values (δ) for the protons
- the splitting pattern (singlet, doublet, triplet, quartet or multiplet) shown by each peak
- the explanation for the splitting patterns of the CH₃ protons and the CH proton.

environment	δ/ppm	splitting pattern	explanation for splitting pattern
CH ₃			
СН			
СООН			

Table 8.2

[3]

(e) (i) Capsaicin is heated with an excess of hot aqueous NaOH.



Draw the structures of the two organic products **H** and **K**.



(ii) Name the **two** types of reaction occurring in (e)(i).

......[1]

(f) Draw the structure of the organic product L formed when capsaicin is treated with $LiAlH_4$ in dry ether.



[1]

[Total: 14]

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9 (a) Benzoyl chloride, C₆H₅COC*l*, can be made from ethyl benzene in a two-step process.
 A reaction scheme is shown.



(b) C_6H_5COCl reacts with phenol, C_6H_5OH , to give the ester phenyl benzoate, $C_6H_5COOC_6H_5$. An incomplete description of the mechanism of this reaction is shown in Fig. 9.1.



Fig. 9.1

- (i) Complete the mechanism in Fig. 9.1 and include:
 - all relevant dipoles (δ+ and δ-) and full electric charges (+ and -) on the species in box one and in box two
 - all relevant lone pairs on the species in box one and in box two
 - all relevant curly arrows to show the movement of electron pairs in box one and in box two
 - the formula of the second product in box three.

[4]

(ii) Name this mechanism.

......[1]

(c) Benzoyl chloride, chlorobenzene and chloroethane differ in their rates of hydrolysis when each compound is added separately to water at 25 °C.

Suggest the relative ease of hydrolysis of these three compounds.

Explain your answer.

hardest to hydrolyse easiest to hydrolyse
explanation

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Important values,	constants	and s	tandards

molar gas constant	$R = 8.31 \mathrm{J}\mathrm{K}^{-1}\mathrm{mol}^{-1}$
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	$e = -1.60 \times 10^{-19} \text{C}$
molar volume of gas	$V_{\rm m}$ = 22.4 dm ³ mol ⁻¹ at s.t.p. (101 kPa and 273 K) $V_{\rm m}$ = 24.0 dm ³ mol ⁻¹ at room conditions
ionic product of water	$K_{\rm w}$ = 1.00 × 10 ⁻¹⁴ 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 Pe	riodic Tal	The Periodic Table of Elements	ments							
								Grc	Group								
-	2											13	14	15	16	17	18
							- :										5
							T										He
				Key			hydrogen 1.0										4.0
m	4		.0	atomic number								5	9	7	8	6	10
	Be		ato	atomic symbol	loc							В	ပ	z	0	ш	Ne
b 6.9	beryllium 9.0		rela	name relative atomic mass	SS							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
	Mg											Al	N.	٩	ი	Cl	Ar
sodium ma 23.0	magnesium 24.3	ო	4	5	9	7	80	0	10	11	12	aluminium 27.0	silicon 28.1	phosphorus 31.0	sulfur 32.1	chlorine 35.5	argon 39.9
	20	21	22	23		25	26	27	28	29	30	31	32	33	34	35	36
	Ca	Sc	F	>		Mn	Ъe	ပိ	ïZ	Си	Zn	Ga	Ge	As	Se	Br	Кr
potassium 6 39.1	calcium 40.1	scandium 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
	38	39	40	41	42	43	4	45	46	47	48	49	50	51	52	53	54
	S	≻	Zr	qN	Mo		Ru	R	Ъd	Ag	РС	In	Sn	Sb	Te	I	Xe
rubidium st 85.5	strontium 87.6	yttrium 88.9	zirconium 91.2	niobium 92.9	molybdenum 95.9	technetium -	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
	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
	Ba	lanthanoids	Ħ	Та	≥		SO	Ir	Ŧ	ΡN	Нg	Ll	РЬ	B	Ро	At	Rn
caesium 132.9	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 -
	88	89-103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Ъг	Ra	actinoids	Ŗ	Db	Sg	Bh	Hs	Mt	Ds	Rg	ы	ЧN	Fl	Mc	L<	Ъ	Og
francium -	radium -		rutherfordium -	dubnium –	seaborgium -	bohrium I	hassium -	meitnerium -	darmstadtium -	roentgenium -	copernicium -	nihonium –	flerovium –	moscovium -	livermorium -	tennessine -	oganesson -
		57	58		60	61	62	63	64		66	67	68	69	70	71	
lanthanoids	(0	La		ŗ	ΡN		Sm	Еu	Ъд		Dy		ч	Tm	Υb	Lu	
		lanthanum 138.9	cerium 140.1	In	neodymium 144.4	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	
	I	89	06	91	92	93	94	95	96		98		100	101	102	103	
actinoids		Ac	Ч	Ра	⊃	ЧN	Pu	Am	CB	Ŗ	Ç	Es	Еm	Мd	No	Ļ	
		actinium -	thorium 232.0	protactinium 231.0	uranium 238.0	neptunium -	plutonium -	americium -	curium I	berkelium -	californium -	einsteinium -	fermium -	mendelevium -	nobelium -	lawrencium -	

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