

Cambridge International Examinations Cambridge International Advanced Subsidiary and Advanced Level

CHEMISTRY

9701/42 May/June 2017

Paper 4 A Level Structured Questions MARK SCHEME Maximum Mark: 100

Published

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Question	Answer	Marks
1(a)(i)	increases down the group	1
	radius / size of (cat)ion/M ²⁺ increases	1
	less polarisation / distortion of anion / carbonate ion / CO_3^{2-}	1
1(a)(ii)	Na⁺ has smaller ionic charge and larger ionic radii	1
	OR the charge density of the Na⁺ is lower	
1(b)(i)	$2KHCO_3 \longrightarrow K_2CO_3 + CO_2 + H_2O$	1
1(b)(ii)	NaHCO₃ because Na ⁺ is smaller OR charge density Na ⁺ is larger	1
1(c)(i)	$LE = \Delta H_{f} - 2(\Delta H_{at} + IE) - \frac{1}{2}(O=O) - (EA_{1} + EA_{2})$ = -361 - 2(89) - 2(418) - 496/2 - (-141+798) = -2280 (kJ mol ⁻¹) correct answer scores [3]	3 1 1 1
1(c)(ii)	LE of Na ₂ O will be more negative AND as Na ⁽⁺⁾ is smaller / larger charge density / smaller radii AND so greater attraction (between the ions) OR (ionic) bonds will be stronger	1
	Total:	10

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Question	Answer	Marks
2(a)	Add AgNO ₃ Cl^{-} gives a white ppt and I^{-} gives a yellow ppt.	1
	Add NH ₃ (aq); ppt dissolves and ppt is insoluble	1
2(b)(i)	conductivity decreases during the reaction, AND number of Na ⁺ / I ⁻ / ions are decreased / used up (from solution)	1
2(b)(ii)	(Equilibrate) solutions at 40 °C / with a water bath (cannot be after mixing)	3
	mix known volumes and start the clock / timing clearly mentioned/implied	
	measure conductance / conductivity at regular intervals / every measured time [method A] OR measure the time for conductance to go to zero / a specific value / to be constant [method B]	
	prepare a curve of conductance vs. time [related to method A] OR prepare a curve of conductance vs. concentration [related to method A] OR repeating the experiment at different concentrations [related to method A and B] any 3 points	
2(c)(i)	[R-C1]: rate increases by $5/3$ when concentration increases by $10/6$ ($5/3$), so order = 1	1
	[I ⁻]: rate increases by $5/3$ when concentration increases by $5/3$, so order = 1	1
2(c)(ii)	rate = $k[I^-][CH_3CH_2CHCICH_3]$ AND units of $k = dm^3 mol^{-1} s^{-1}$	1
2(c)(iii)	relative rate = 5 / 5.3	1

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Question	Answer	
2(d)(i)	either S _N 1 or S _N 2 mechanism $I \xrightarrow{CH_3}_{\substack{0 \\ 0 \\ 0 \\ H}} \xrightarrow{H_1}_{\substack{0 \\ 0 \\ 0 \\ H}} \xrightarrow{C_2H_5} \xrightarrow{C_2H_5} \xrightarrow{C_2H_5} \xrightarrow{C_2H_5} \xrightarrow{C_2H_5} \xrightarrow{C_2H_5} \xrightarrow{C_1}_{\substack{0 \\ 0 \\ 0 \\ H}}$	
	C-C1 dipole AND C-C1 curly arrow	1
	intermediate cation OR 5-valent transition state (charge essential)	1
	I [−] with lone pair AND other curly arrow	1
2(d)(ii)	If S _N 1 in 2(d)(i) mixture of / two optical isomers will be formed, AND the intermediate can be formed by the I ⁻ approaching from top or bottom plane If S _N 2 in 2(d)(i) one optical isomer AND attack always from fixed direction / opposite side	

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Question		Answer		Marks
2(e)(i)	4 peaks			1
2(e)(ii)	CH ₃ CH ₃ CH ₃ CH ₃	CH_{3} CH_{3} CH_{2} CH_{2} CH_{2} CH_{3} CH_{2} CH_{3} CH_{2} CH_{3} CH_{3} CH_{3} CH_{2} CH_{3} C		1 + 1
	number of peaks = 2	number of peaks = 3		1
			Total:	18

Question	Answer	Marks
3(a)	$\begin{array}{c} \cdot & \cdot \\ \cdot & \cdot \\$	
	four shared pairs: S=O and 2 × S-C <i>l</i>	1
	all (9) lone pairs	1
3(b)(i)	$NaOH + HCl \longrightarrow NaCl + H_2O$	1
	$2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$	1

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Question	Answer	Marks
3(b)(ii)	moles (at start) = $0.5 \times 60 / 1000 = 3 \times 10^{-2}$ AND moles (at end) = $0.5 \times 10.8 / 1000 = 5.4 \times 10^{-3}$	1
	moles reacted (= $(30-5.4) \times 10^{-3}$ =) 2.5 × 10 ⁻² correct ans. scores [2]	1
3(b)(iii)	moles of RCO ₂ H = $2.46 \times 10^{-2}/3 = 8.2 - 8.3 \times 10^{-3}$ mole	1
3(b)(iv)	$M_{\rm r} = 1.00 / (8.2 \times 10^{-3}) = 121.95 \ (=122)$	1
3(b)(v)	$C_7H_6O_2$ OR $C_6H_5CO_2H$	1
3(c)(i)	LiA <i>l</i> H ₄	1
3(c)(ii)	$\begin{array}{c} & & \\ & & \\ & \\ angelic \ acid \end{array} \qquad \begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $	3
3(c)(iii)	angelic acid: geometrical OR cis-trans compound T : optical	1
	Total:	14

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Question	Answer	Marks
4(a)(i)	$M_{\rm r} = 52 + 6 \times 18 + 3 \times 35.5 = 266.5$	
4(a)(ii)	$1.00g = 1/266.5 \text{ OR } 3.75 \times 10^{-3} \text{ moles (of complex in 1g)}$ for A , n=2 AND [Cr(H ₂ O) ₄ C <i>l</i> ₂]C <i>l</i> .2H ₂ O for B , n=1 AND [Cr(H ₂ O) ₅ C <i>l</i>]C <i>l</i> ₂ .H ₂ O for C , n=0; AND [Cr(H ₂ O) ₆]C <i>l</i> ₃	2
4(b)(i)	Geometric(al) / cis-trans	1
4(b)(ii)	$R_{3}P \xrightarrow{CN}_{Ni} PR_{3} R_{3}P \xrightarrow{Ni}_{PR_{3}} CN$ isomer 1 isomer 2	1
4(b)(iii)	isomer 2 AND dipoles do not cancel OR CN ⁻ are on the same side of the molecule	1
	Total:	6

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Question	Answer	Marks
5(a)(i)	<i>bidentate</i> : (a species that) forms <u>two</u> dative bonds / donates <u>two</u> lone pairs	1
	ligand: a species that uses a lone pair to form a dative bond to a metal atom / metal ion	1
5(a)(ii)	$ \boxed{ \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	3
5(b)(i)	$K_{\text{stab1}} = [Cu(NH_3)_4^{2+}]/[Cu^{2+}][NH_3]^4$	1
	$K_{\text{stab2}} = [Cu(en)_2^{2^+}]/[Cu^{2^+}][en]^2$	1
	$mol^{-4} dm^{12} AND mol^{-2} dm^{6}$	1
5(b)(ii)	$K_{eq3} = K_{stab2} / K_{stab1}$	1
5(b)(iii)	$K_{eq3} = K_{stab2} / K_{stab1} = 4.4(2) \times 10^{6}$	1
	mol ² dm ⁻⁶	1
5(c)(i)	$(\Delta S_{eq1} \text{ is negative as})$ more / 5 moles of reactants are forming (one mole of) the complex OR (ΔS_{eq2} is positive as) fewer / 3 moles of reactants are forming (one mole of) the complex	
5(c)(ii)	$\Delta G_{eq2} = -100 - 298 \times 40 / 1000 \text{ OR } \Delta G = \Delta H - T\Delta S$ = -112 or -111.9 (kJ mol ⁻¹) correct answer [2]	2 1 1

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Question	ion Answer	
5(c)(iii)	Since (ΔG_{eq2}) is more negative (than ΔG_{eq1}) AND equilibrium 2 is more feasible	1
5(c)(iv)	$\Delta H_{(3)} = -8 \text{ (kJ mol}^{-1})$	
5(c)(v)	ligand exchange / replacement / substitution / displacement	
	Total:	17

Question	Answer	Marks
6(a)(i)	the lower / smaller the pK_a , the stronger the acid	1
6(a)(ii)	$pK_a = -\log(K_a)$ or $pK_a = -\lg(K_a)$ or $K_a = 10^{-pka}$	1
6(a)(iii)	(stronger than ethanoic acid because) Cl is electron-withdrawing	1
	and so stabilises the RCO ₂ ⁻ anion / conjugate base or weakens O-H bond (so H ⁺ is more easily released)	1
6(b)(i)	$NH_{3}^{+}CH_{2}CO_{2}^{-} \longrightarrow NH_{2}CH_{2}CO_{2}^{-} + H^{+}$ $OR NH_{3}^{+}CH_{2}CO_{2}^{-} + H_{2}O \longrightarrow NH_{2}CH_{2}CO_{2}^{-} + H_{3}O^{+}$	1
6(b)(ii)	$\begin{split} \mathcal{K}_{a} &= 10^{-9.87} = 1.35 \times 10^{-10} \\ [\text{H}^{+}] &= \sqrt{(\mathcal{K}_{a}.c)} = 3.67 \times 10^{-6} \end{split}$	1
	pH = 5.4 (5.43–5.44) min 2sf	1

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Question	Answer	Marks
6(b)(iii)	curve starts at 5.4 and continuous	1
	vertical portion (end point) at vol added = 10.0 cm^3	1
	finishes at pH = 12.5 at 20 cm³ (and does not increase in pH)	1
	Total:	10

Question			Answer		Marks
7(a)	w	X	Y	Z	5
	acyl chloride / COC/	methyl ketone / CH3CO group aryl chloride	aldehyde / CHO chloro(alkane) / RC <i>l</i>	Alkene / C=C phenol / C ₆ H ₅ OH aryl chloride	
	0–1 [0]; 2 [1]; 3 [2]; 4 [3];	5 [4]; 6–8 [5]			

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Question	Answer	Marks
7(b)(i)	$\mathbf{w} \bigoplus_{\text{or}} \overset{\text{CH}_2\text{COCI}}{\underset{\text{CH}_3}{\text{or}}} \mathbf{x} \bigoplus_{\text{CI}} \overset{\text{COCH}_3}{\underset{\text{CI}}{\text{ci}}}$	1 + 1
	Y CHO or CH ₂ Cl Z HO CH ₂ Cl CH=CH ₂	1 + 1
7(b)(ii)	Y CHO OR any chiral atom correctly labelled	1
	Total:	10

Question	Answer	
8(a)(i)	step 1 electrophilic substitution ignore acylation	1
	step 2 nucleophilic addition	1
8(a)(ii)	hydrolysis	1

Question	Answer	Marks
8(a)(iii)	step 1 $ClCH_2CHO$ (allow Br, I for Cl)	1
	$AlCl_3$	1
	step 2 HCN + NaCN	1
	step 3 heat in H_3O^+ / heat $H^+(aq)$	1
	step 5 NH_3 under pressure (+ heat) or heat NH_3 in a sealed tube	1
8(a)(iv)	with NaOH(aq)	1 + 1
	-0 CO_2^- [2]	
	with HCl(aq) $+NH_3$ +O	1
	with $Br_2(aq)$ Br CO_2^- or HO CO_2H [1]	1
8(b)(i)	P is tyr	1
	tyr is 2– AND it is small / has a small <i>M</i> r	1

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Question	Answer	
8(b)(ii)	(dipeptide / phe-tyr) 2– is about double the M_r / mass of (phe) 1	1
	OR mass / charge ratios are about the same for each (for dipeptide / phe-tyr and phe)	
	Total:	15