
CHEMISTRY

9701/42

Paper 4 A Level Structured Questions

May/June 2017

MARK SCHEME

Maximum Mark: 100

Published

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Mark schemes should be read in conjunction with the question paper and the Principal Examiner Report for Teachers.

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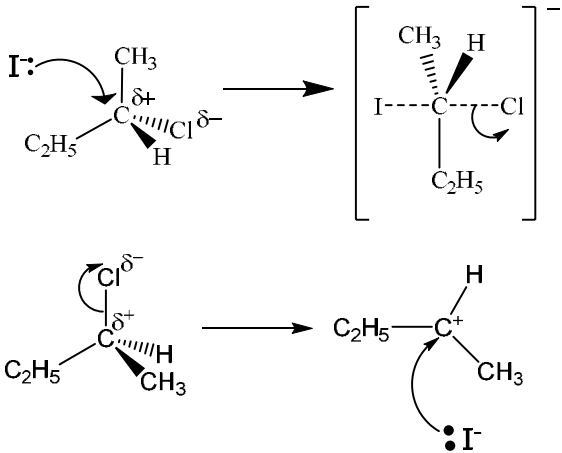
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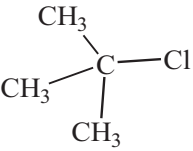
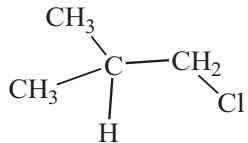
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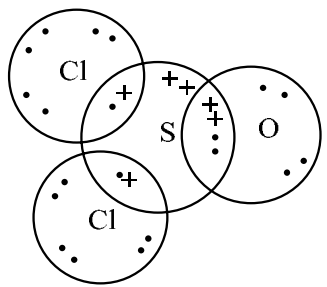
Question	Answer	Marks
1(a)(i)	increases down the group	1
	radius / size of (cat)ion/M ²⁺ increases	1
	less polarisation / distortion of anion / carbonate ion / CO ₃ ²⁻	1
1(a)(ii)	Na ⁺ has smaller ionic charge and larger ionic radii OR the charge density of the Na ⁺ is lower	1
1(b)(i)	2KHCO ₃ —→ K ₂ CO ₃ + CO ₂ + H ₂ O	1
1(b)(ii)	NaHCO ₃ because Na ⁺ is smaller OR charge density Na ⁺ is larger	1
1(c)(i)	LE = $\Delta H_f - 2(\Delta H_{at} + IE) - \frac{1}{2}(\text{O}=\text{O}) - (\text{EA}_1 + \text{EA}_2)$ = $-361 - 2(89) - 2(418) - 496/2 - (-141+798)$ = -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

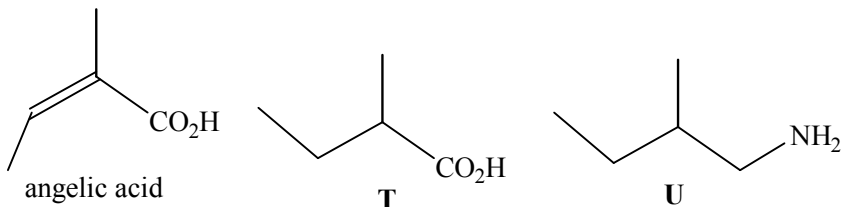
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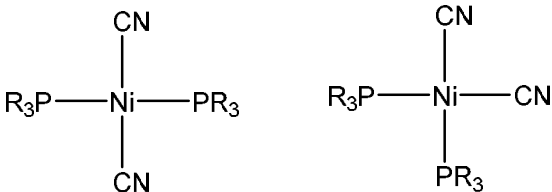
Question	Answer	Marks
2(a)	Add AgNO ₃ Cl ⁻ gives a white ppt and I ⁻ gives a yellow ppt.	1
	Add NH ₃ (aq); ppt dissolves and ppt is insoluble	1
2(b)(i)	conductivity decreases during the reaction, AND number of Na ⁺ / I ⁻ / ions are decreased / used up (from solution)	1
2(b)(ii)	(Equilibrate) solutions at 40 °C / with a water bath (cannot be after mixing) 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]	3 any 3 points
2(c)(i)	[R-Cl]: rate increases by 5 / 3 when concentration increases by 10 / 6 (5 / 3),	1 so order = 1
	[I ⁻]: rate increases by 5 / 3 when concentration increases by 5 / 3,	1 so order = 1
2(c)(ii)	rate = $k[I^-][CH_3CH_2CHClCH_3]$ AND units of $k = dm^3 mol^{-1} s^{-1}$	1
2(c)(iii)	relative rate = 5 / 5.3	1

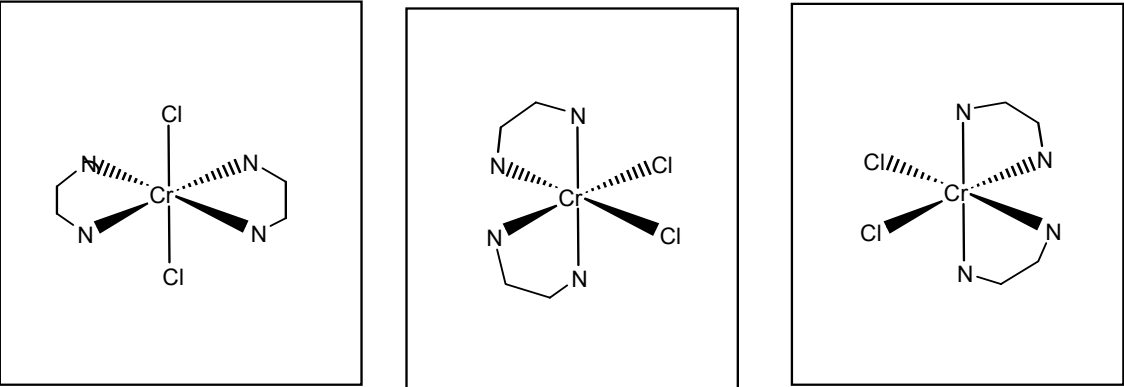
Question	Answer	Marks
2(d)(i)	<p>either S_N1 or S_N2 mechanism</p>  <p>S_N2</p> <p>S_N1</p>	
	C-Cl dipole AND C-Cl curly arrow	1
	intermediate cation OR 5-valent transition state (charge essential)	1
	I ⁻ with lone pair AND other curly arrow	1
2(d)(ii)	<p>If S_N1 in 2(d)(i) mixture of / two optical isomers will be formed, AND the intermediate can be formed by the I⁻ approaching from top or bottom plane</p> <p>If S_N2 in 2(d)(i) one optical isomer AND attack always from fixed direction / opposite side</p>	1

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

Question	Answer	Marks
3(a)		
	four shared pairs: S=O and 2 × S-Cl	1
	all (9) lone pairs	1
3(b)(i)	$\text{NaOH} + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_2\text{O}$	1
	$2\text{NaOH} + \text{SO}_2 \longrightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O}$	1

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 $\text{RCO}_2\text{H} = 2.46 \times 10^{-2} / 3 = 8.2 - 8.3 \times 10^{-3}$ mole	1
3(b)(iv)	$M_r = 1.00 / (8.2 \times 10^{-3}) = 121.95 (=122)$	1
3(b)(v)	$\text{C}_7\text{H}_6\text{O}_2$ OR $\text{C}_6\text{H}_5\text{CO}_2\text{H}$	1
3(c)(i)	LiAlH_4	1
3(c)(ii)	 <p>angelic acid T U</p>	3
3(c)(iii)	angelic acid: geometrical OR cis-trans compound T : optical	1
	Total:	14

Question	Answer	Marks
4(a)(i)	$M_r = 52 + 6 \times 18 + 3 \times 35.5 = 266.5$	1
4(a)(ii)	1.00g = $1 / 266.5$ OR 3.75×10^{-3} moles (of complex in 1g) for A , n=2 AND $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ for B , n=1 AND $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl} \cdot \text{H}_2\text{O}$ for C , n=0; AND $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$	2
4(b)(i)	Geometric(al) / cis-trans	1
4(b)(ii)	 <p style="text-align: center;">isomer 1 isomer 2</p>	1
4(b)(iii)	isomer 2 AND dipoles do not cancel OR CN^- are on the same side of the molecule	1
	Total:	6

Question	Answer	Marks
5(a)(i)	<i>bidentate</i> : (a species that) forms two dative bonds / donates two lone pairs	1
	<i>ligand</i> : a species that uses a lone pair to form a dative bond to a metal atom / metal ion	1
5(a)(ii)		3
5(b)(i)	$K_{\text{stab1}} = [\text{Cu}(\text{NH}_3)_4]^{2+} / [\text{Cu}^{2+}][\text{NH}_3]^4$ $K_{\text{stab2}} = [\text{Cu}(\text{en})_2]^{2+} / [\text{Cu}^{2+}][\text{en}]^2$	1
	$\text{mol}^{-4} \text{ dm}^{12}$ AND $\text{mol}^{-2} \text{ dm}^6$	1
5(b)(ii)	$K_{\text{eq3}} = K_{\text{stab2}} / K_{\text{stab1}}$	1
5(b)(iii)	$K_{\text{eq3}} = K_{\text{stab2}} / K_{\text{stab1}} = 4.4(2) \times 10^6$	1
5(c)(i)	ΔS_{eq1} 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	1
5(c)(ii)	$\Delta G_{\text{eq2}} = -100 - 298 \times 40 / 1000 \text{ OR } \Delta G = \Delta H - T\Delta S$ $= -112 \text{ or } -111.9 \text{ (kJ mol}^{-1}\text{) correct answer [2]}$	2 1 1

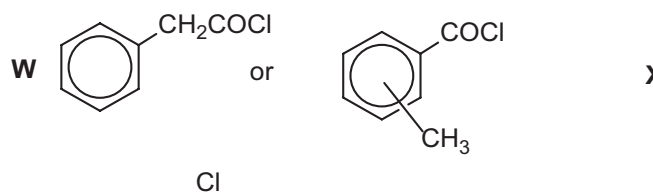
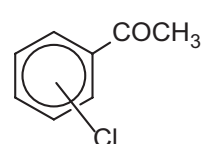
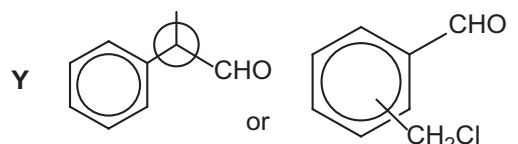
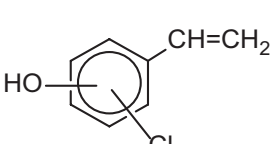
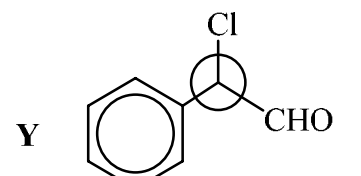
Question	Answer	Marks
5(c)(iii)	Since ($\Delta G_{\text{eq}2}$) is more negative (than $\Delta G_{\text{eq}1}$) AND equilibrium 2 is more feasible	1
5(c)(iv)	$\Delta H_{(3)} = -8 \text{ (kJ mol}^{-1}\text{)}$	1
5(c)(v)	ligand exchange / replacement / substitution / displacement	1
	Total:	17

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)	$\text{NH}_3^+\text{CH}_2\text{CO}_2^- \longrightarrow \text{NH}_2\text{CH}_2\text{CO}_2^- + \text{H}^+$ OR $\text{NH}_3^+\text{CH}_2\text{CO}_2^- + \text{H}_2\text{O} \longrightarrow \text{NH}_2\text{CH}_2\text{CO}_2^- + \text{H}_3\text{O}^+$	1
6(b)(ii)	$K_a = 10^{-9.87} = 1.35 \times 10^{-10}$ $[\text{H}^+] = \sqrt{K_a \cdot c} = 3.67 \times 10^{-6}$	1
	pH = 5.4 (5.43–5.44) min 2sf	1

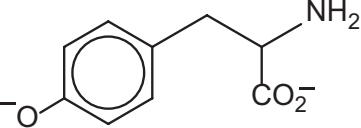
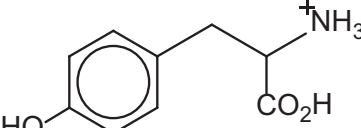
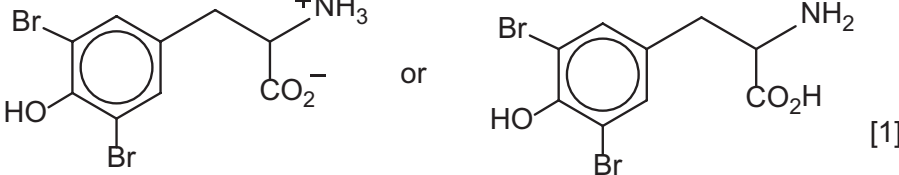
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Question	Answer	Marks
6(b)(iii)	curve starts at 5.4 and continuous	1
	vertical portion (end point) at vol added = 10.0 cm ³	1
	finishes at pH = 12.5 at 20 cm ³ (and does not increase in pH)	1
	Total:	10

Question	Answer				Marks
7(a)	W	X	Y	Z	5
	acyl chloride / COCl	methyl ketone / CH ₃ CO group aryl chloride	aldehyde / CHO chloro(alkane) / RCl	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]					

Question	Answer	Marks
7(b)(i)	<p>W  or </p>	1 + 1
	<p>Y  or </p>	1 + 1
7(b)(ii)	<p>Y </p> <p>OR any chiral atom correctly labelled</p>	1
Total:		10

Question	Answer	Marks
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 $NaOH(aq)$  [2]	1 + 1
	with $HCl(aq)$  [1]	1
	with $Br_2(aq)$  [1]	1
8(b)(i)	P is tyr	1
	tyr is 2- AND it is small / has a small Mr	1

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