Cambridge International AS & A Level

Cambridge International Examinations
Cambridge International Advanced Subsidiary and Advanced Level

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **May/June 2017**

MARK SCHEME

Maximum Mark: 100

Published

This mark scheme is published as an aid to teachers and candidates, to indicate the requirements of the examination. It shows the basis on which Examiners were instructed to award marks. It does not indicate the details of the discussions that took place at an Examiners' meeting before marking began, which would have considered the acceptability of alternative answers.

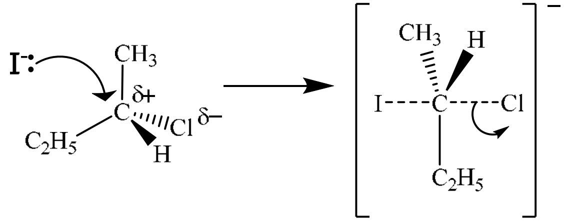
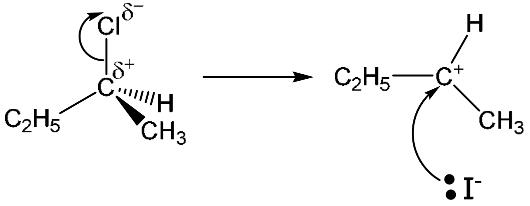
Mark schemes should be read in conjunction with the question paper and the Principal Examiner Report for Teachers.

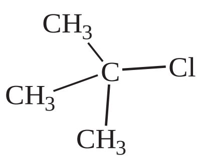
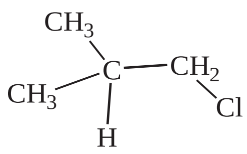
Cambridge will not enter into discussions about these mark schemes.

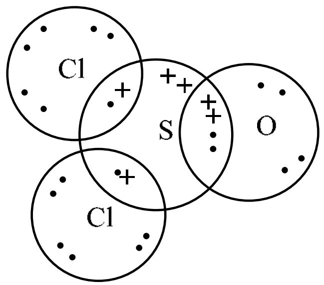
Cambridge is publishing the mark schemes for the May/June 2017 series for most Cambridge IGCSE®, Cambridge International A and AS Level and Cambridge Pre-U components, and some Cambridge O Level components.

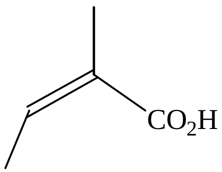
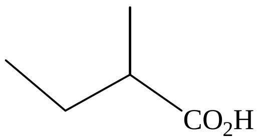
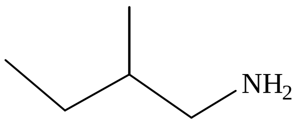
Question	Answer	Marks
1(a)(i)	increases down the group	**1**
	radius / size of (cat)ion/M^{2+} increases	**1**
	less polarisation / distortion of anion / carbonate **ion** / CO_3^{2-}	**1**
1(a)(ii)	Na^+ has smaller ionic charge **and** larger ionic radii OR the **charge density** of the **Na^+** is **lower**	**1**
1(b)(i)	$2KHCO_3 \longrightarrow K_2CO_3 + CO_2 + H_2O$	**1**
1(b)(ii)	$NaHCO_3$ because Na^+ is **smaller** OR charge density Na^+ is **larger**	**1**
1(c)(i)	LE $= \Delta H_f - 2(\Delta H_{at} + IE) - ½(O{=}O) - (EA_1 + EA_2)$ $= -361 - 2(89)$ **–** $2(418) - 496/2 - (-141+798)$ = **–2280** (kJ mol^{-1}) correct answer scores [3]	**3** **1** **1** **1**
1(c)(ii)	LE of Na_2O 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**

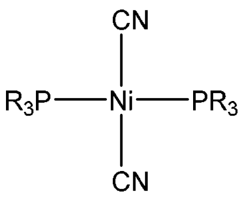
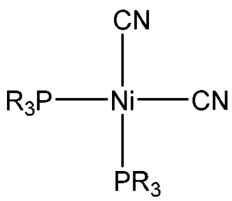
Question	Answer	Marks
2(a)	Add $AgNO_3$ Cl^- gives a white ppt **and** I^- gives a yellow ppt.	**1**
	Add NH_3(aq); ppt dissolves **and** ppt is insoluble	**1**
2(b)(i)	conductivity **decreases** during the reaction, AND number of Na^+ / I^- / **ions** are **decreased** / used up (from solution)	**1**
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] any 3 points	**3**
2(c)(i)	[R-Cl]: 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 = $k[I^-][CH_3CH_2CHClCH_3]$ AND units of k = $dm^3\ mol^{-1}\ s^{-1}$	**1**
2(c)(iii)	relative rate = 5 / 5.3	**1**

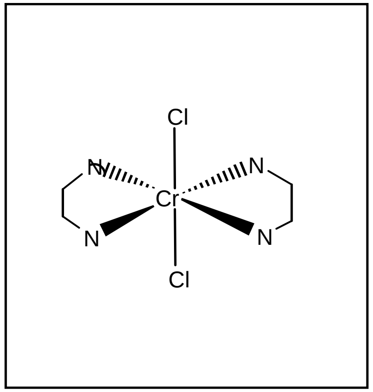
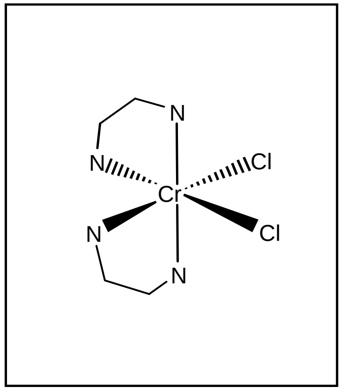
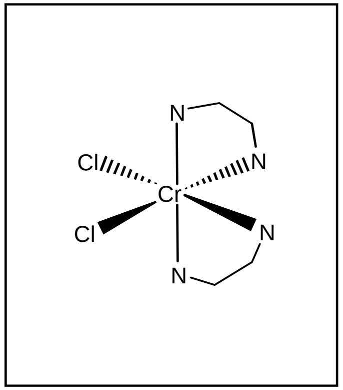
Question	Answer	Marks
2(d)(i)	either S_N1 or S_N2 mechanism S_N2  S_N1 	
	C-C*l* dipole AND C-C*l* curly arrow	**1**
	intermediate cation OR 5-valent transition state (charge essential)	**1**
	I^- with lone pair AND other curly arrow	**1**
2(d)(ii)	If S_N1 in 2(d)(i) **mixture of / two** optical isomers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

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

Question	Answer	Marks
3(a)		
	four shared pairs: S=O and 2 × S-C*l*	**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**

Question	Answer	Marks
3(b)(ii)	moles (at start) = 0.5 × 60 / 1000 = 3×10^{-2} AND moles (at end) = 0.5 × 10.8 / 1000 = 5.4×10^{-3}	**1**
	moles reacted (= (30–5.4) × 10^{-3} =) **2.5×10^{-2}** correct ans. scores [2]	**1**
3(b)(iii)	moles of RCO_2H = 2.46×10^{-2}/3 = 8.2–8.3 × 10^{-3} mole	**1**
3(b)(iv)	M_r = 1.00 / (8.2 × 10^{-3}) = 121.95 (=122)	**1**
3(b)(v)	$C_7H_6O_2$ OR $C_6H_5CO_2H$	**1**
3(c)(i)	$LiAlH_4$	**1**
3(c)(ii)	 angelic acid  **T**  **U**	**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** $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ for **B**, n=1 **AND** $[Cr(H_2O)_5Cl]Cl_2.H_2O$ for **C**, n=0; **AND** $[Cr(H_2O)_6]Cl_3$	**2**
4(b)(i)	Geometric(al) / cis-trans	**1**
4(b)(ii)	 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**

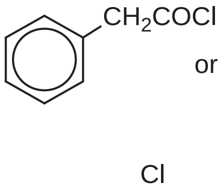
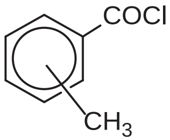
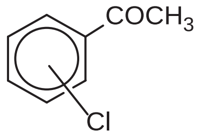
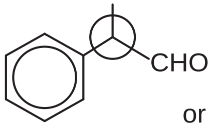
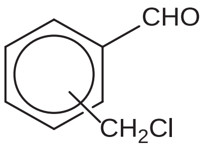
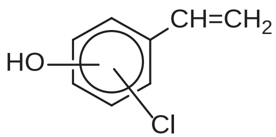
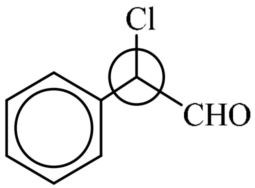
Question	Answer	Marks
5(a)(i)	*bidentate*: (a species that) forms **<u>two</u>** dative bonds / donates **<u>two</u>** lone pairs	**1**
	ligand: a species that uses a **lone pair** to form a **dative** bond to **a metal atom / metal ion**	**1**
5(a)(ii)	   each structure [1] x 3	**3**
5(b)(i)	$K_{stab1} = [Cu(NH_3)_4{}^{2+}]/[Cu^{2+}][NH_3]^4$	**1**
	$K_{stab2} = [Cu(en)_2{}^{2+}]/[Cu^{2+}][en]^2$	**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)	(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)	ΔG_{eq2} = –100 – 298 × 40 / 1000 OR $\Delta G = \Delta H - T\Delta S$ = –112 or –111.9 (kJ mol^{-1}) correct answer [2]	**2** **1** **1**

Question	Answer	Marks
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 (kJ mol^{-1})	**1**
5(c)(v)	**ligand** exchange / replacement / substitution / displacement	**1**
	Total:	**17**

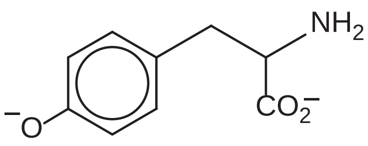
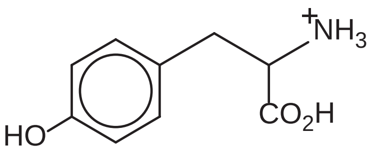
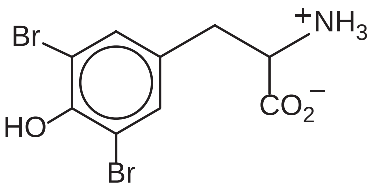
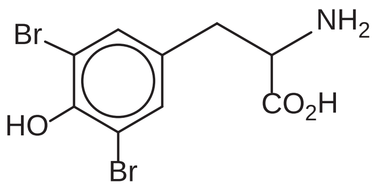
Question	Answer	Marks
6(a)(i)	the lower / smaller the pK_a, the stronger the acid	**1**
6(a)(ii)	$pK_a = -\log(K_a)$ or $pK_a = -\lg(K_a)$ or $K_a = 10^{-pka}$	**1**
6(a)(iii)	(stronger than ethanoic acid because) C*l* is electron-withdrawing	**1**
	and so stabilises the RCO_2^- anion / conjugate base **or** weakens O-H bond (so H^+ is more easily released)	**1**
6(b)(i)	$NH_3^+CH_2CO_2^- \longrightarrow NH_2CH_2CO_2^- + H^+$ OR $NH_3^+CH_2CO_2^- + H_2O \longrightarrow NH_2CH_2CO_2^- + H_3O^+$	**1**
6(b)(ii)	$K_a = 10^{-9.87} = 1.35 \times 10^{-10}$ $[H^+] = \sqrt{(K_a.c)} = 3.67 \times 10^{-6}$	**1**
	pH = **5.4** (5.43–5.44) min 2sf	**1**

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)	<table><tr><th>W</th><th>X</th><th>Y</th><th>Z</th></tr><tr><td>acyl chloride / COC*l*</td><td>methyl ketone / CH3CO group aryl chloride</td><td>aldehyde / CHO chloro(alkane) / RC*l*</td><td>Alkene / C=C phenol / C_6H_5OH aryl chloride</td></tr></table> 0–1 [0]; 2 [1]; 3 [2]; 4 [3]; 5 [4]; 6–8 [5]	**5**

Question	Answer	Marks
7(b)(i)	**W**  or  **X** 	**1 + 1**
	Y  or  **Z** 	**1 + 1**
7(b)(ii)	**Y**  OR any chiral atom correctly labelled	**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)  or  [1]	**1**
8(b)(i)	**P** is tyr	**1**
	tyr is 2– AND it is small / has a small *M*r	**1**

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