

#### **Cambridge International Examinations**

Cambridge International Advanced Subsidiary and Advanced Level

CHEMISTRY 9701/41

Paper 4 A Level Structured Questions

May/June 2017

MARK SCHEME
Maximum Mark: 100

#### **Published**

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Question	Answer	Marks
1(a)	solubility increases down the group	1
	$\Delta H_{\text{latt}}$ and $\Delta H_{\text{hyd}}$ both <b>decrease</b> or $\Delta H_{\text{latt}}$ and $\Delta H_{\text{hyd}}$ both become less exothermic / more endothermic	1
	$\Delta H_{\text{latt}}$ decreases / changes more (than $\Delta H_{\text{hyd}}$ as OH <sup>-</sup> being smaller than M <sup>2+</sup> )	1
	$\Delta H_{\rm sol}$ becomes more exothermic / more negative / less endothermic / less positive	1
1(b)(i)	$\Delta H_{r1} - (538 + 2x230 + 394) = -(1216 + 286)$	1
	$\Delta H_{\rm r1} - 1392 = -1502$	
	$\Delta H_{\rm r1} = -110$	1
1(b)(ii)	$let \Delta H_f(HCO_3^-(aq)) = y$	1
	2y - 538 = -1216 - 394 - 286 - 26	
	y = <b>-692</b>	1
1(b)(iii)	$\Delta H_{r3} - 538 - 2(230 + 394) = -538 - 2(692)$	1
	$\Delta H_{\rm r3} = -136$	
1(b)(iv)	$\Delta H_{r3}$ will be identical to $\Delta H_{r4}$ , / unchanged	1
	as the reaction is the same, or:	1
	$2OH^{-}(aq) + 2CO_{2}(g) \longrightarrow 2HCO_{3}^{-}(aq) \text{ or}$	
	metal ions stay in solution/metal ions are unchanged / are spectators	

May/June 2017

Question	Answer	Marks
1(c)	more <b>gaseous moles</b> are being consumed (in reaction 3) or more CO₂ moles are being consumed (in reaction 3)	1
	$\Delta S$ is therefore expected to be <b>more negative/less positive</b> for reaction 3.	1
	Total:	13

Question	Answer	Marks
2(a)(i)	$\begin{array}{c c} & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} \begin{array}{c} & & \\ & \\ \end{array} \begin{array}{c} & \\ \end{array} \begin{array}{c} & \\ \\ \end{array} \begin{array}{c} &$	1 + 1
	16 electrons on each diagram	1
2(a)(ii)	HNC = 115–125° AND NCO = 180°	1
2(a)(iii)	cyanic acid, because it's a stronger / higher bond enthalpy / triple / C≡N / more electrons involved bond	1
2(b)(i)	$[H^{+}] = \sqrt{([HNCO]K_a)} = \sqrt{(0.1 \times 1.2 \times 10^{-4})} \text{ or } 3.46 \times 10^{-3}$	1
	$pH = log [H^{+}] = 2.5 (2.46)$	1
2(b)(ii)	$Na_2CO_3 + 2(NH_2)_2CO \longrightarrow 2NaNCO + CO_2 + 2NH_3 + H_2O$	1
2(c)(i)	$(n(OH^{-}) \text{ at start} = (2 \times 0.1 \times 30) / 1000 = 6 \times 10^{-3} \text{ mol})$ $(n(OH^{-}) \text{ reacted} = (0.1 \times 20) / 1000 = 2 \times 10^{-3} \text{ mol})$ $n(OH^{-}) \text{ remaining} = (6-2) \times 10^{-3} = 4 \times 10^{-3} \text{ mol}, (in 50 \text{ cm}^{3})$	1
	so $[OH^{-}]_{end} = (4 \times 10^{-3} \times 1000) / 50 = 0.08 \text{ mol dm}^{-3}$	1

Question	Answer	Marks
2(c)(ii)	$[H^{+}] = K_w / [OH^{-}] = (1 \times 10^{-14}) / 0.08 = 1.25 \times 10^{-13} \text{ mol dm}^{-3}$	1
	so pH = $-\log(1.25 \times 10^{-13})$ = <b>12.9</b>	1
2(c)(iii)	curve starts at 2.46 / 2.5	1
	vertical portion (end point) at vol added = 10.0 cm <sup>3</sup>	1
	finishes at pH = 12.9	1
2(d)(i)	monodentate: (a species that) forms one dative / coordinate bond	1
	ligand: a species that uses a lone pair of electrons to form a dative / coordinate bond to a metal atom / metal ion	1
2(d)(ii)	[Ag(NCO) <sub>2</sub> ] <sup>-</sup> or [Ag(OCN) <sub>2</sub> ] <sup>-</sup> correct formula	1
	correct charge	1
2(e)(i)	$n(BaCO_3) = 1.66 / 197.3 = 8.4(1) \times 10^{-3} \text{ mol}$	1
2(e)(ii)	$n(RNCO) = 8.41 \times 10^{-3} \text{ mol, so } M_r = 1/(8.41 \times 10^{-3}) = 119$	1
2(e)(iii)	molecular formula = C <sub>7</sub> H <sub>5</sub> NO	1

9701/41

# Cambridge International AS/A Level – Mark Scheme **PUBLISHED**

Question	Answer	Marks
2(e)(iv)	NH <sub>2</sub>	1
	Total:	23

Question	Answer	Marks
3(a)(i)	+3 or Co <sup>3+</sup>	1
3(a)(ii)	oxidation	1
	ligand displacement / replacement / exchange / substitution	1

© UCLES 2017 Page 5 of 12

Question	Answer	Marks
3(a)(iii)	$\begin{bmatrix} H_3N/I_{II} & NH_3 \\ H_3N/I_{II} & Or \\ CI & NH_3 \end{bmatrix}^+ \begin{bmatrix} H_3N/I_{II} & Or \\ H_3N/I_{II} & Or \\ H_3N/I_{II} & Or \\ CI & NH_3 \end{bmatrix}^+ \begin{bmatrix} NH_3 \\ H_3N/I_{II} & Or \\ NH_3 \end{bmatrix}^+ $ $cis $ $trans$	1+1
	geometrical or cis-trans	1
3(b)(i)	The number of bonds / atoms bonded to an atom / ion / species / metal	1
3(b)(ii)	<b>C</b> 6 [Cr(CN) <sub>6</sub> ] –	6
	<b>D</b> – $[Ni(NH_2CH_2CH_2NH_2)_3]$ 2+/+2	
	<b>E</b> 4 [PtC4] –	
	F 3 - 3-/-3	
3(c)(i)	$K_{\text{stab}(1)} = [\text{FeSCN}^{2+}]/([\text{Fe}^{3+}][\text{SCN}^{-}])$ mol <sup>-1</sup> dm <sup>3</sup>	3
	$K_{\text{stab}(2)} = [\text{FeC } l_{4}^{-}]/([\text{Fe}^{3+}][\text{C} l_{1}^{-}]^{4})$ mol <sup>-4</sup> dm <sup>12</sup>	
3(c)(ii)	$K_{eq(3)} = K_{stab(1)} / K_{stab(2)}$	1
3(c)(iii)	$K_{eq(3)} = 1750$	1
	$mol^3 dm^{-9}$	1
	Total:	19

Question	Answer	Marks
4(a)(i)	optical, because it contains a / one chiral C-atom or chiral C-atoms or chiral atom / centre or C* indicated or C with 4 <b>different</b> groups	1
4(a)(ii)	$C_{10}H_{14}O + 3H_2 \longrightarrow C_{10}H_{20}O$ correct formulae	1
	balancing	1
4(b)(i)	electrophilic substitution	1
4(b)(ii)	step 3 reduction	1
	step 5 substitution / hydrolysis	1
4(b)(iii)	step 1 (CH <sub>3</sub> ) <sub>2</sub> CHC <i>l</i> + A <i>l</i> C <i>l</i> <sub>3</sub> / A <i>l</i> Br <sub>3</sub> / FeC <i>l</i> <sub>3</sub> / FeBr <sub>3</sub>	1+1
	step 2 $HNO_3 + H_2SO_4$ conc (T < 55 °C)	1
	step 3 Sn + HC1	1
	step 4 HNO <sub>2</sub> (or NaNO <sub>2</sub> + HCl) (at T < 10 °C)	1
	the two temperatures for steps 2 and 4	1
4(c)(i)	H <sub>2</sub> + Pt or H <sub>2</sub> + Ni + heat or pressure	1

Question	Answer	Marks
4(c)(ii)	HILL CH <sub>3</sub> OH  CH(CH <sub>3</sub> ) <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> CH, CH <sub>3</sub> and OH on the correct ring atoms i.e. structure is correct	1
	all Hs on the same side of the ring	1
	Total:	15

Question	Answer					Marks	
5(a)		J	К	L	М		
		amine methyl ketone	aromatic amine aldehyde	amine methyl ketone	amide		
	J and L correct						1+1
	K correct						1+1
	M correct						1
5(b)(i)	hydrolysis						1
5(b)(ii)	P is C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>						1
	Q is CH <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> N	Na					1

Question	Answer	Marks
5(c)	J is $O$	1
	K is CHO	1
	L is $0$	1
	$\mathbf{M}$ is	1
	K&L only: two chiral atoms shown	1
5(d)	<b>W</b> is C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> Na	1
	Total:	14

#### May/June 2017

Question	Answer	Marks
6(a)	Any of the three methods possible. Any 4 of the 5 points for each method available for maximum 4 marks.  Method 1  1 Ensure both solutions ( <b>A</b> and <b>B</b> ) at 40 °C before mixing  2 mix known volumes of <b>A</b> and <b>B</b> and start the clock  3 at known time take out a sample / <b>X</b> and add it to ice-cold solvent  4 titrate against HCl  5 repeat at time at known time intervals  Method 2  1 Ensure both solutions ( <b>A</b> and <b>B</b> ) at 40 °C before mixing  2 mix known volumes of <b>A</b> and <b>B</b> and start the clock  3 at known time pour into ice-cold solvent or pour ice-cold solvent in  4 titrate against HCl  5 repeat with different concentrations of either A or B, or repeat using different times  Method 3  1 Ensure both solutions ( <b>A</b> and <b>B</b> ) at 40 °C before mixing  2 mix known volumes of <b>A</b> and <b>B</b> and start the clock and add pH meter  3 at a known time  4 record the pH	4
6(b)(i)	5 repeat pH readings at known time intervals  from 1 and 3: when [RCl] is trebled, so is rate, so order w.r.t. [RCl] = 1	1
	from 1 and 2: when both concentrations are doubled, rate doubles so [OH <sup>-</sup> ] has no effect on rate, so order w.r.t.[OH <sup>-</sup> ] = 0	1
6(b)(ii)	rate = $k[RCl]$ AND units: $sec^{-1} 1/s$	1
6(b)(iii)	relative rate = 2.0	1

© UCLES 2017 Page 10 of 12

Question	Answer				
6(c)(i)	$\begin{array}{c} C_{1} \\ C_{6} \\ C_{7} \\ C_{1} \\ C_{1} \\ C_{1} \\ C_{1} \\ C_{1} \\ C_{1} \\ C_{2} \\ C_{3} \\ C_{1} \\ C_{1} \\ C_{2} \\ C_{3} \\ C_{3} \\ C_{4} \\ C_{1} \\ C_{1} \\ C_{2} \\ C_{3} \\ C_{4} \\ C_{1} \\ C_{2} \\ C_{3} \\ C_{4} \\ C_{1} \\ C_{2} \\ C_{3} \\ C_{4} \\ C_{5} \\ C_{5} \\ C_{6} \\ C_{7} \\ C_{7} \\ C_{8} \\ C_{1} \\ C_{1} \\ C_{2} \\ C_{3} \\ C_{4} \\ C_{5} \\ C_{5} \\ C_{5} \\ C_{6} \\ C_{7} \\ C_{7} \\ C_{8} \\ C_{7} \\ C_{8} \\ C_{7} \\ C_{8} \\$	1			
	intermediate cation	1			
	OH <sup>-</sup> with lone pair and curly arrow	1			
6(c)(ii)	Beginning with candidate's mechanism in (c)(i):  If S <sub>N</sub> 1: racemate / mixture of / two optical isomers will be formed, because: the intermediate is planar / has a plane of symmetry / OH <sup>-</sup> can approach from top or bottom or from any direction  If S <sub>N</sub> 2: one optical isomer because attack always from fixed direction / from same side / the "configuration" always inverts / there is an asymmetric transition state	1			

Question	Answer							
6(d)(i)		δ value	number of H atoms	group	splitting	result with D <sub>2</sub> O		
		1.4	3	CH₃ / methyl	doublet	peak remains		
		2.7	1	OH / hydroxyl / alcohol	singlet	peak disappears		
		4.0	1	СН	quartet	peak remains		
	the three groups are in their correct places wrt the $\delta$ values							1
	no. of H atom	atoms for each peak agrees with group column						1
splitting patterns doublet, singlet and quartet are assigned to correct groups								1
	peak identified as OH disappears with D <sub>2</sub> O, no other peak disappears							1
							Total:	16