Cambridge International AS & A Level

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CHEMISTRY **9701/43**

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.

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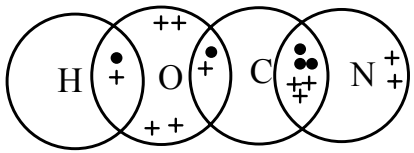
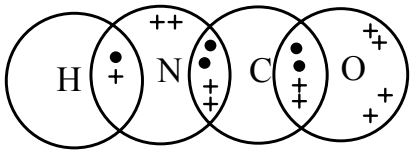
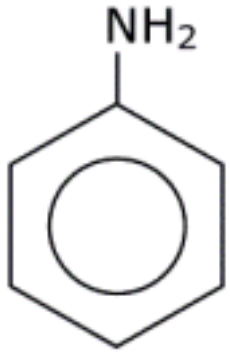
Question	Answer	Marks
1(a)	solubility increases down the group	**1**
	ΔH_{latt} and ΔH_{hyd} both **decrease** **or** ΔH_{latt} and ΔH_{hyd} both become less exothermic / more endothermic	**1**
	ΔH_{latt} decreases / changes more (than ΔH_{hyd} as OH^- being smaller than M^{2+})	**1**
	ΔH_{sol} becomes more exothermic / more negative / less endothermic / less positive	**1**
1(b)(i)	ΔH_{r1} – (538 + 2x230 + 394) = –(1216 + 286) ΔH_{r1} – 1392 = –1502	**1**
	ΔH_{r1} = **–110**	**1**
1(b)(ii)	let $\Delta H_f(HCO_3^-(aq))$ = y 2y – 538 = –1216 – 394 – 286 – 26	**1**
	y = **–692**	**1**
1(b)(iii)	ΔH_{r3} –538 – 2(230 + 394) = –538 – 2(692) ΔH_{r3} = **–136**	**1**
1(b)(iv)	ΔH_{r3} will be identical to ΔH_{r4}, / unchanged	**1**
	as the reaction is the same, or: $2OH^-(aq) + 2CO_2(g) \longrightarrow 2HCO_3^-(aq)$ or metal ions stay in solution/metal ions are unchanged / are spectators	**1**

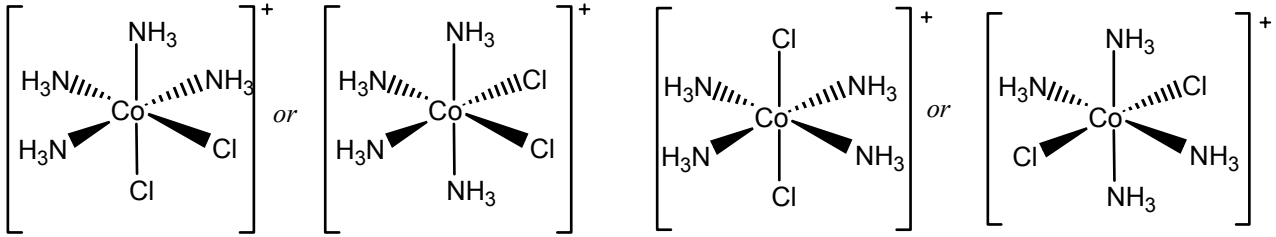
Question	Answer	Marks
1(c)	more **gaseous moles** are being consumed (in reaction 3) **or** more **CO_2 moles** are being consumed (in reaction 3)	**1**
	ΔS is therefore expected to be **more negative/less positive** for reaction 3.	**1**
	Total:	**13**

Question	Answer	Marks
2(a)(i)	 	**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)	$[H^+] = \sqrt{([HNCO]K_a)} = \sqrt{(0.1 \times 1.2 \times 10^{-4})}$ or 3.46×10^{-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)	($n(OH^-)$ at start = $(2 \times 0.1 \times 30) / 1000 = 6 \times 10^{-3}$ mol) ($n(OH^-)$ reacted = $(0.1 \times 20) / 1000 = 2 \times 10^{-3}$ mol) $n(OH^-)$ remaining = $(6–2) \times 10^{-3} = 4 \times 10^{-3}$ mol, (in 50 cm^3)	**1**
	so $[OH^-]_{end} = (4 \times 10^{-3} \times 1000) / 50$ = **0.08 mol dm^{-3}**	**1**

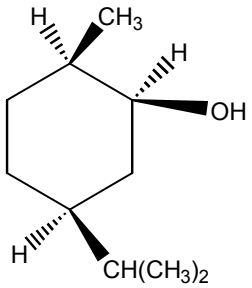
Question	Answer	Marks
2(c)(ii)	$[H^+] = K_w / [OH^-] = (1 \times 10^{-14}) / 0.08 = 1.25 \times 10^{-13}$ mol dm^{-3}	**1**
	so pH = $-\log(1.25 \times 10^{-13})$ = **12.9**	**1**
2(c)(iii)	curve starts at 2.46 / 2.5	**1**
	vertical portion (end point) at vol added = 10.0 cm^3	**1**
	finishes at pH = 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)	$[Ag(NCO)_2]^-$ or $[Ag(OCN)_2]^-$ correct formula	**1**
	correct charge	**1**
2(e)(i)	n($BaCO_3$) =1.66 / 197.3 = 8.4(1) $\times 10^{-3}$ mol	**1**
2(e)(ii)	n(RNCO) = 8.41 $\times 10^{-3}$ mol, so M_r = 1 / (8.41 $\times 10^{-3}$) = **119**	**1**
2(e)(iii)	molecular formula = C_7H_5NO	**1**

Question	Answer	Marks
2(e)(iv)		**1**
	Total:	**23**

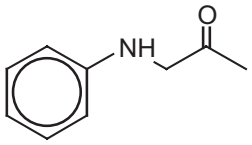
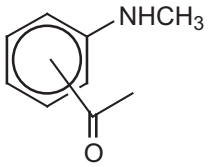
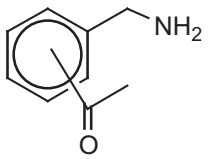
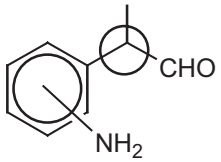
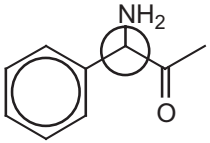
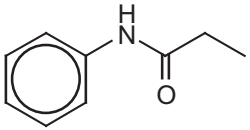
Question	Answer	Marks
3(a)(i)	+3 or Co^{3+}	**1**
3(a)(ii)	oxidation	**1**
	ligand displacement / replacement / exchange / substitution	**1**

Question	Answer	Marks
3(a)(iii)	 cis *or* 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)	**C** 6 $[Cr(CN)_6]$ – **D** – $[Ni(NH_2CH_2CH_2NH_2)_3]$ 2+/+2 **E** 4 $[PtCl_4]$ – **F** 6 – 3–/–3	**6**
3(c)(i)	$K_{stab(1)} = [FeSCN^{2+}]/([Fe^{3+}][SCN^-])$ $mol^{-1}\ dm^3$ $K_{stab(2)} = [FeCl_4^-]/([Fe^{3+}][Cl^-]^4)$ $mol^{-4}\ dm^{12}$	**3**
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**

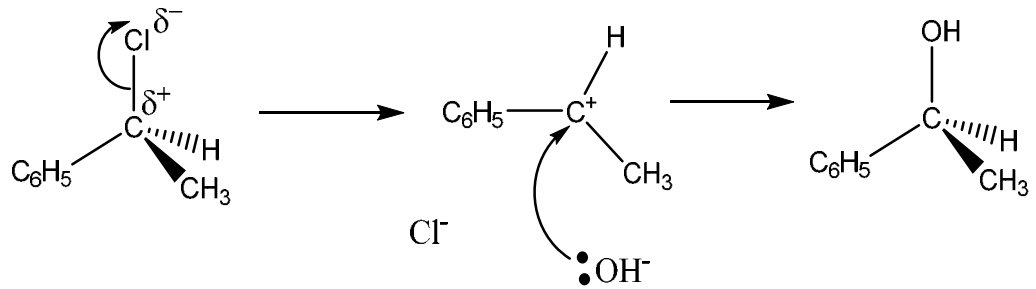
Question	Answer	Marks
4(a)(i)	optical, because it contains a / one chiral C-atom or chiral C-atoms or chiral atom / centre or C* indicated or C with 4 **different** groups	**1**
4(a)(ii)	$C_{10}H_{14}O + 3H_2 \longrightarrow C_{10}H_{20}O$ correct formulae	**1**
	balancing	**1**
4(b)(i)	electrophilic substitution	**1**
4(b)(ii)	step 3 reduction	**1**
	step 5 substitution / hydrolysis	**1**
4(b)(iii)	step 1 $(CH_3)_2CHCl + AlCl_3 / AlBr_3 / FeCl_3 / FeBr_3$	**1 + 1**
	step 2 $HNO_3 + H_2SO_4$ conc (T < 55 °C)	**1**
	step 3 Sn + HCl	**1**
	step 4 HNO_2 (*or* $NaNO_2$ + HCl) (at T < 10 °C)	**1**
	the two temperatures for steps 2 and 4	**1**
4(c)(i)	$\mathbf{H_2}$ + Pt or $\mathbf{H_2}$ + Ni + heat or pressure	**1**

Question	Answer	Marks
4(c)(ii)	 $(CH_3)_2CH$, CH_3 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)	<table><tr><th>J</th><th>K</th><th>L</th><th>M</th></tr><tr><td>amine methyl ketone</td><td>aromatic amine aldehyde</td><td>amine methyl ketone</td><td>amide</td></tr></table>	
	J and L correct	**1 + 1**
	K correct	**1 + 1**
	M correct	**1**
5(b)(i)	hydrolysis	**1**
5(b)(ii)	**P** is $C_6H_5NH_2$	**1**
	Q is $CH_3CH_2CO_2Na$	**1**

Question	Answer	Marks
5(c)	**J** is  *or*  *or* 	**1**
	K is 	**1**
	L is 	**1**
	M is 	**1**
	K&L only: two chiral atoms shown	**1**
5(d)	**W** is $C_6H_5CO_2Na$	**1**
	Total:	**14**

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 (**A** and **B)** at 40 °C before mixing 2 mix known volumes of **A** and **B** and start the clock 3 at known time take out a sample / **X** 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 (**A** and **B)** at 40 °C before mixing 2 mix known volumes of **A** and **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 (**A** and **B)** at 40 °C before mixing 2 mix known volumes of **A** and **B** and start the clock and add pH meter 3 at a known time . . . . 4 . . . . record the pH 5 repeat pH readings at known time intervals	**4**
6(b)(i)	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^-] has no effect on rate, so order w.r.t.[OH^-] = 0	**1**
6(b)(ii)	rate = k[RCl] AND units: sec^{-1} 1 / s	**1**
6(b)(iii)	relative rate = 2.0	**1**

Question	Answer	Marks
6(c)(i)	 C-Cl dipole and first curly arrow	**1**
	intermediate cation	**1**
	OH^- with lone pair and curly arrow	**1**
6(c)(ii)	Beginning with candidate's mechanism in (c)(i): **If S_N1:** racemate / mixture of / two optical isomers will be formed, because: the intermediate is planar / has a plane of symmetry / OH^- can approach from top or bottom or from any direction **If S_N2:** one optical isomer because attack always from fixed direction / from same side / the "configuration" always inverts / there is an asymmetric transition state	**1**

<table>
<tr><th>Question</th><th>Answer</th><th>Marks</th></tr>
<tr><td rowspan="5">6(d)(i)</td><td>
<table>
<tr><th>δ value</th><th>number of H atoms</th><th>group</th><th>splitting</th><th>result with D_2O</th></tr>
<tr><td>1.4</td><td>3</td><td>CH_3 / methyl</td><td>doublet</td><td>peak remains</td></tr>
<tr><td>2.7</td><td>1</td><td>OH / hydroxyl / alcohol</td><td>singlet</td><td>peak disappears</td></tr>
<tr><td>4.0</td><td>1</td><td>CH</td><td>quartet</td><td>peak remains</td></tr>
</table>
</td><td></td></tr>
<tr><td>the three groups are in their correct places wrt the δ values</td><td>1</td></tr>
<tr><td>no. of H atoms for each peak agrees with group column</td><td>1</td></tr>
<tr><td>splitting patterns doublet, singlet and quartet are assigned to correct groups</td><td>1</td></tr>
<tr><td>peak identified as OH disappears with D_2O, no other peak disappears</td><td>1</td></tr>
<tr><td></td><td>Total:</td><td>16</td></tr>
</table>