Cambridge International AS & A Level

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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**
	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**

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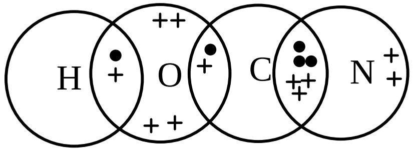
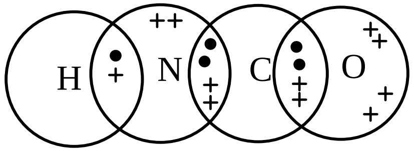
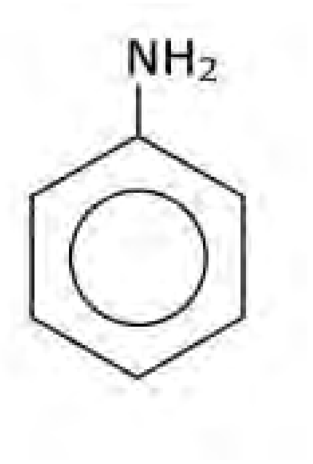
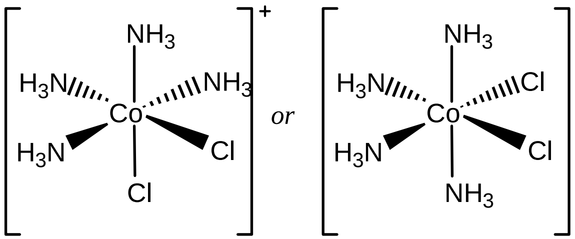
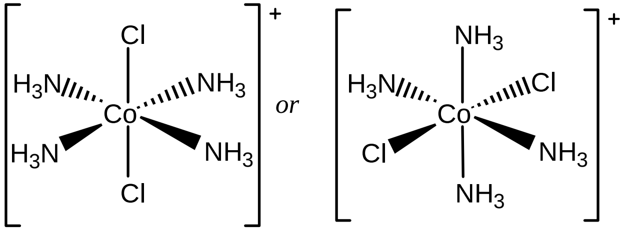
Question	Answer	Marks
1(c)	more **gaseous moles** are being consumed (in reaction 3) **or** more **CO_2 moles** are being consumed (in reaction 3)	**1**
	ΔS is therefore expected to be **more negative/less positive** for reaction 3.	**1**
	Total:	**13**

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  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** 3 – 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**

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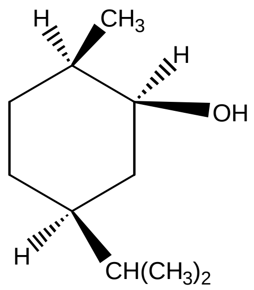
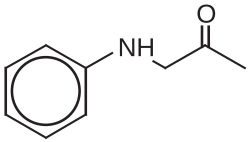
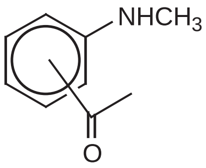
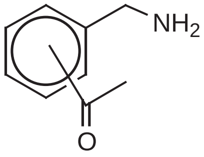
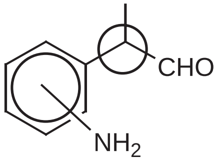
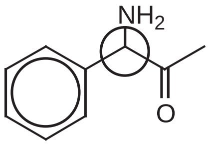
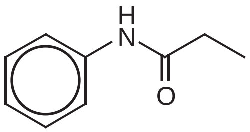
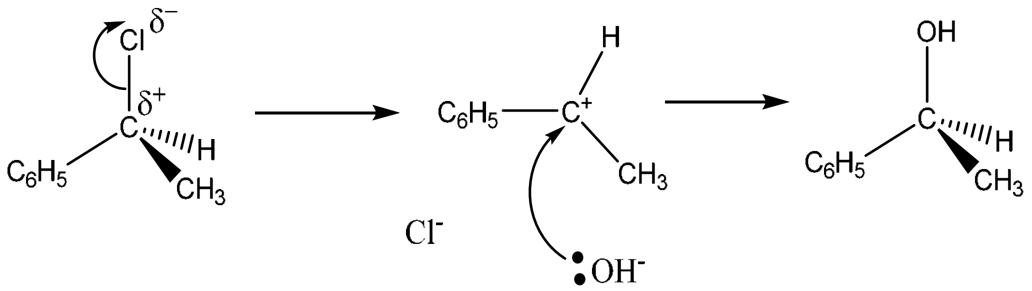
Question	Answer	Marks
4(a)(i)	optical, because it contains a / one chiral C-atom or chiral C-atoms or chiral atom / centre or C* indicated or C with 4 **different** groups	**1**
4(a)(ii)	$C_{10}H_{14}O + 3H_2 \longrightarrow C_{10}H_{20}O$ correct formulae	**1**
	balancing	**1**
4(b)(i)	electrophilic 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**

<table>
<tr><th>Question</th><th>Answer</th><th>Marks</th></tr>
<tr><td>5(a)</td><td><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></td><td></td></tr>
<tr><td></td><td>J and L correct</td><td>1 + 1</td></tr>
<tr><td></td><td>K correct</td><td>1 + 1</td></tr>
<tr><td></td><td>M correct</td><td>1</td></tr>
<tr><td>5(b)(i)</td><td>hydrolysis</td><td>1</td></tr>
<tr><td>5(b)(ii)</td><td>P is $C_6H_5NH_2$</td><td>1</td></tr>
<tr><td></td><td>Q is $CH_3CH_2CO_2Na$</td><td>1</td></tr>
</table>

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 HC*l* 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 HC*l* 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 [RC*l*] is trebled, so is rate, so order w.r.t. [RC*l*] = 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*[RC*l*] 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

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Question	Answer	Marks
6(d)(i)	see table below	
	the three groups are in their correct places wrt the δ values	**1**
	no. of H 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_2O, no other peak disappears	**1**
	Total:	**16**

δ value	number of H atoms	group	splitting	result with D_2O
1.4	**3**	**CH_3 / methyl**	**doublet**	**peak remains**
2.7	**1**	**OH / hydroxyl / alcohol**	**singlet**	**peak disappears**
4.0	**1**	**CH**	**quartet**	**peak remains**

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