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CHEMISTRY

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Paper 4 A Level Structured Questions

May/June 2017

MARK SCHEME

Maximum Mark: 100

Published

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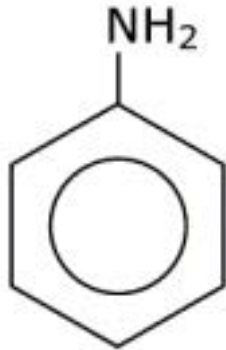
Question	Answer	Marks
1(a)	solubility increases down the group	1
	ΔH_{latt} and ΔH_{hyd} both decrease or ΔH_{latt} and ΔH_{hyd} both become less exothermic / more endothermic	1
	ΔH_{latt} decreases / changes more (than ΔH_{hyd} as OH^- being smaller than M^{2+})	1
	ΔH_{sol} becomes more exothermic / more negative / less endothermic / less positive	1
1(b)(i)	$\Delta H_{\text{r1}} - (538 + 2 \times 230 + 394) = -(1216 + 286)$	1
	$\Delta H_{\text{r1}} - 1392 = -1502$	
	$\Delta H_{\text{r1}} = \mathbf{-110}$	1
1(b)(ii)	let $\Delta H_{\text{f}}(\text{HCO}_3^-(\text{aq})) = y$	1
	$2y - 538 = -1216 - 394 - 286 - 26$ $y = \mathbf{-692}$	1
1(b)(iii)	$\Delta H_{\text{r3}} - 538 - 2(230 + 394) = -538 - 2(692)$ $\Delta H_{\text{r3}} = \mathbf{-136}$	1
1(b)(iv)	ΔH_{r3} will be identical to ΔH_{r4} , / unchanged	1
	as the reaction is the same, or: $2\text{OH}^-(\text{aq}) + 2\text{CO}_2(\text{g}) \longrightarrow 2\text{HCO}_3^-(\text{aq})$ 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 CO₂ 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)	$[H^+] = \sqrt{([HNC]K_a)} = \sqrt{(0.1 \times 1.2 \times 10^{-4})}$ 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 $[OH^-]_{end} = (4 \times 10^{-3} \times 1000) / 50 = 0.08 \text{ mol dm}^{-3}$	1

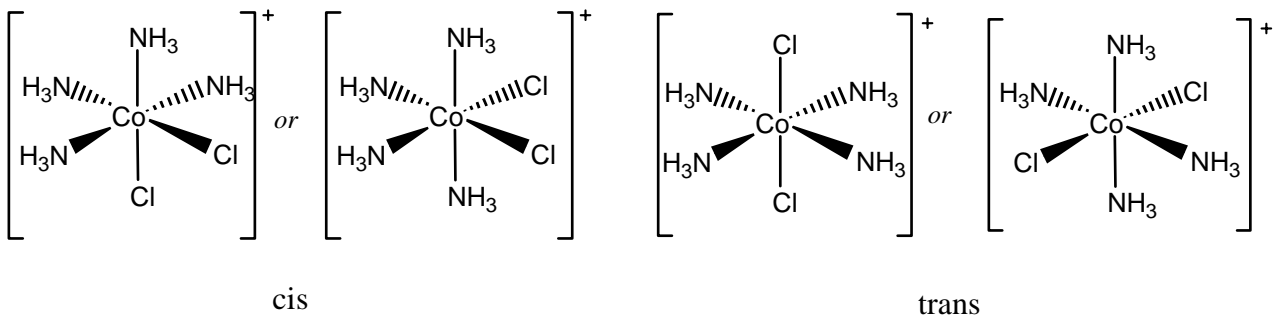
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Question	Answer	Marks
2(c)(ii)	$[H^+] = K_w / [OH^-] = (1 \times 10^{-14}) / 0.08 = 1.25 \times 10^{-13} \text{ mol dm}^{-3}$	1
	so $\text{pH} = -\log(1.25 \times 10^{-13}) = \mathbf{12.9}$	1
2(c)(iii)	curve starts at 2.46 / 2.5	1
	vertical portion (end point) at vol added = 10.0 cm ³	1
	finishes at pH = 12.9	1
2(d)(i)	<i>monodentate</i> : (a species that) forms one dative / coordinate bond	1
	<i>ligand</i> : 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)	$n(\text{BaCO}_3) = 1.66 / 197.3 = 8.4(1) \times 10^{-3} \text{ mol}$	1
2(e)(ii)	$n(\text{RNCO}) = 8.41 \times 10^{-3} \text{ mol}$, so $M_r = 1 / (8.41 \times 10^{-3}) = \mathbf{119}$	1
2(e)(iii)	molecular formula = C ₇ H ₅ NO	1

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

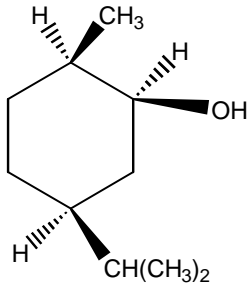
Question	Answer	Marks
3(a)(i)	+3 or Co^{3+}	1
3(a)(ii)	oxidation	1
	ligand displacement / replacement / exchange / substitution	1

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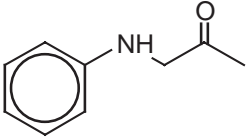
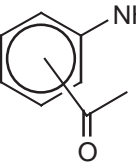
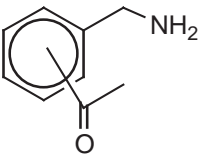
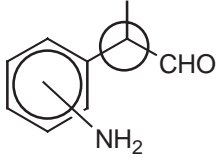
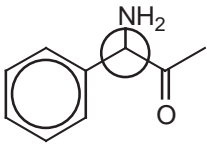
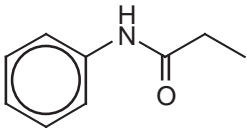
Question	Answer	Marks																
3(a)(iii)	 <p style="text-align: center;">cis trans</p>	1 + 1																
	geometrical or cis-trans	1																
3(b)(i)	The number of bonds / atoms bonded to an atom / ion / species / metal	1																
3(b)(ii)	<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 5%;">C</td> <td style="width: 10%;">6</td> <td style="width: 35%;">[Cr(CN)₆]</td> <td style="width: 50%; text-align: center;">–</td> </tr> <tr> <td>D</td> <td>–</td> <td>[Ni(NH₂CH₂CH₂NH₂)₃]</td> <td style="text-align: center;">2+ / +2</td> </tr> <tr> <td>E</td> <td>4</td> <td>[PtCl₄]</td> <td style="text-align: center;">–</td> </tr> <tr> <td>F</td> <td>3</td> <td>–</td> <td style="text-align: center;">3– / –3</td> </tr> </table>	C	6	[Cr(CN) ₆]	–	D	–	[Ni(NH ₂ CH ₂ CH ₂ NH ₂) ₃]	2+ / +2	E	4	[PtCl ₄]	–	F	3	–	3– / –3	6
C	6	[Cr(CN) ₆]	–															
D	–	[Ni(NH ₂ CH ₂ CH ₂ NH ₂) ₃]	2+ / +2															
E	4	[PtCl ₄]	–															
F	3	–	3– / –3															
3(c)(i)	$K_{\text{stab}(1)} = \frac{[\text{FeSCN}^{2+}]}{([\text{Fe}^{3+}][\text{SCN}^-]} \quad \text{mol}^{-1} \text{ dm}^3$ $K_{\text{stab}(2)} = \frac{[\text{FeCl}_4^-]}{([\text{Fe}^{3+}][\text{Cl}^-]^4)} \quad \text{mol}^{-4} \text{ dm}^{12}$	3																
3(c)(ii)	$K_{\text{eq}(3)} = K_{\text{stab}(1)} / K_{\text{stab}(2)}$	1																
3(c)(iii)	$K_{\text{eq}(3)} = 1750$	1																
	$\text{mol}^3 \text{ dm}^{-9}$	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)	$H_2 + Pt$ or $H_2 + Ni$ + heat or pressure	1

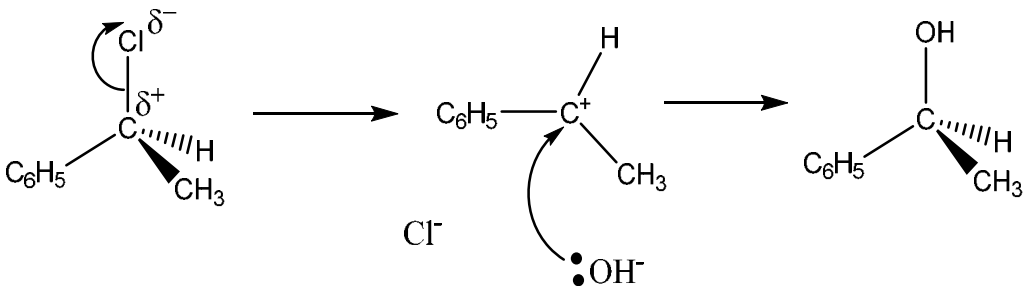
Question	Answer	Marks
4(c)(ii)	 <p>(CH₃)₂CH, CH₃ and OH on the correct ring atoms i.e. structure is correct</p>	1
	all Hs on the same side of the ring	1
	Total:	15

Question	Answer	Marks								
5(a)	<table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>J</th> <th>K</th> <th>L</th> <th>M</th> </tr> </thead> <tbody> <tr> <td>amine methyl ketone</td> <td>aromatic amine aldehyde</td> <td>amine methyl ketone</td> <td>amide</td> </tr> </tbody> </table>	J	K	L	M	amine methyl ketone	aromatic amine aldehyde	amine methyl ketone	amide	
J	K	L	M							
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 ₆ H ₅ NH ₂	1								
	Q is CH ₃ CH ₂ CO ₂ Na	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

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Question	Answer	Marks
6(a)	<p>Any of the three methods possible. Any 4 of the 5 points for each method available for maximum 4 marks.</p> <p>Method 1</p> <ol style="list-style-type: none"> 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 <p>Method 2</p> <ol style="list-style-type: none"> 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 <p>Method 3</p> <ol style="list-style-type: none"> 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 $[\text{RCI}]$ is trebled, so is rate, so order w.r.t. $[\text{RCI}] = 1$	1
	from 1 and 2: when both concentrations are doubled, rate doubles so $[\text{OH}^-]$ has no effect on rate, so order w.r.t. $[\text{OH}^-] = 0$	1
6(b)(ii)	rate = $k[\text{RCI}]$ AND units: $\text{sec}^{-1} \text{ l / s}$	1
6(b)(iii)	relative rate = 2.0	1

Question	Answer	Marks
6(c)(i)	 <p>C-Cl dipole and first curly arrow</p> <p>intermediate cation</p> <p>OH⁻ with lone pair and curly arrow</p>	<p>1</p> <p>1</p> <p>1</p>
6(c)(ii)	<p>Beginning with candidate's mechanism in (c)(i):</p> <p>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</p> <p>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</p>	1

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Question	Answer					Marks
6(d)(i)	δ value	number of H atoms	group	splitting	result with D ₂ O	
	1.4	3	CH₃/methyl	doublet	peak remains	
	2.7	1	OH/hydroxyl/alcohol	singlet	peak disappears	
	4.0	1	CH	quartet	peak remains	
	the three groups are in their correct places wrt the δ values					
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 ₂ O, no other peak disappears					1	
Total:					16	