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International
AS & A Level

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Cambridge International Advanced Subsidiary and Advanced Level

CHEMISTRY

9701/42

Paper 4 A Level Structured Questions

October/November 2016

MARK SCHEME

Maximum Mark: 100

Published

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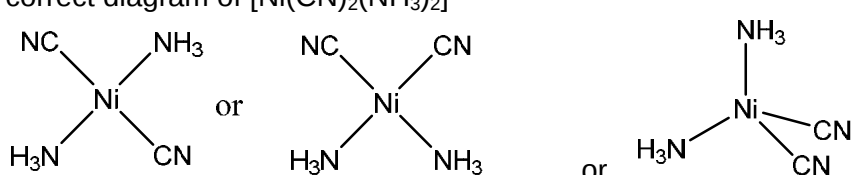
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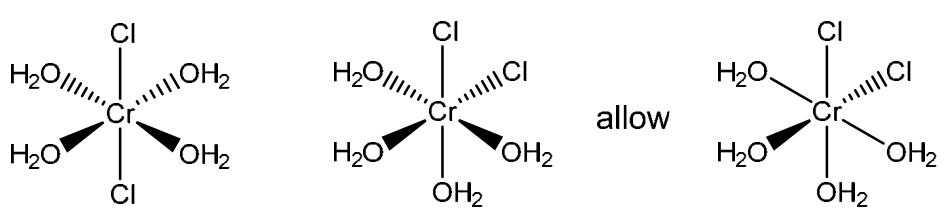
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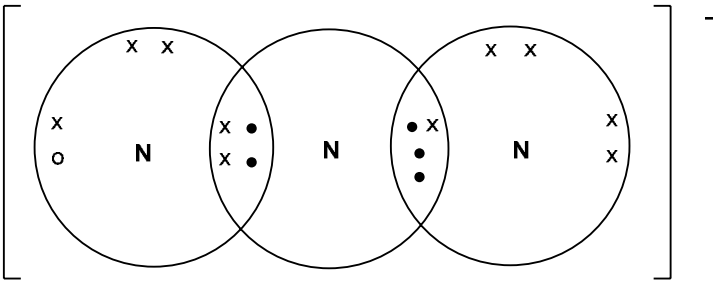
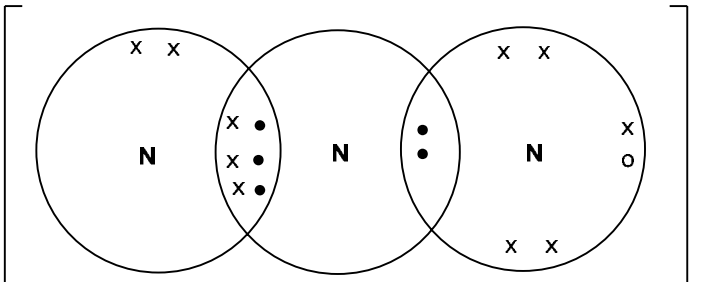
Page 2	Mark Scheme	Syllabus	Paper
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Question	Answer	Marks									
1(a)	(an element) forming (one or more stable) ions with incomplete d subshell [1]	1 1									
1(b)(i)	<table border="1"> <tr> <td></td><td>co-ordination number</td><td>oxidation number</td></tr> <tr> <td>$[\text{Ni}(\text{CN})_2(\text{NH}_3)_2]$</td><td>4</td><td>+2</td></tr> <tr> <td>$[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$</td><td>6</td><td>+3</td></tr> </table>		co-ordination number	oxidation number	$[\text{Ni}(\text{CN})_2(\text{NH}_3)_2]$	4	+2	$[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$	6	+3	2 2
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$[\text{Ni}(\text{CN})_2(\text{NH}_3)_2]$	4	+2									
$[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$	6	+3									
1(b)(ii)	dative (covalent) / co-ordinate	1 1									
1(b)(iii)	correct diagram of $[\text{Ni}(\text{CN})_2(\text{NH}_3)_2]$  square planar or tetrahedral	1 2									
1(c)(i)	(concentrated) hydrochloric acid / soluble chloride ion	1 1									
1(c)(ii)	ligand exchange / substitution	1 1									
1(d)(i)	cis-trans (isomerism) / geometric(al)	1 1									

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Question	Answer	Marks
1(d)(ii)	one 3D isomer one correct isomer other isomer correct in 3D  allow	1 1 1 3
	Total:	12

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Question	Answer	Marks
2(a)	$\text{NaN}_3 \rightarrow \text{Na} + 1.5\text{N}_2$	1 1
2(b)	 all atoms must have 8 outer electrons coding for electrons correct = 16 ($10 \times 5 + 1 \square$) central N must have 8 bonding electrons (inc. 5 • and no non-bonded electrons) allow 	1 1 1 3
2(c)(i)	(energy change) when 1 mole of an (ionic) compound is formed or (energy change) when 1 mole of an <u>ionic</u> solid/lattice/crystal is formed (from) gas (phase) ions / gaseous ions (under standard conditions)	1 1 2
2(c)(ii)	forming an (ionic) bond	1 1

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Question	Answer	Marks
2(c)(iii)	use of ΔH_{i1} 494 (kJ mol ⁻¹) $\Delta H_f^\circ = +107+494+142-732$ $\Delta H_f^\circ = +11$ (kJ mol ⁻¹)	1 1 1 3
2(c)(iv)	(ionic) radius / size of Na ⁺ is smaller (so stronger attraction to azide ion) OR ionic radius increases down the group	1 1
	Total:	11

Question	Answer	Mark
3(a)	Fe [Ar] 3d ⁶ 4s ² Fe ³⁺ [Ar] 3d ⁵	1 1 2
3(b)(i)	(catalyst is in) the same phase / state as the reactants	1 1
3(b)(ii)	$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$	1 1
3(b)(iii)	(two) negatively-charged species repel each other	1 1
3(b)(iv)	Equation 1: $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$ Equation 2: $S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$	1 1 2

Page 6	Mark Scheme	Syllabus	Paper
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Question	Answer	Marks
3(c)(i)	(entropy is a measure / degree of the) disorder of a system / substance	1 1
3(c)(ii)	$\Delta S^\ominus = (2 \times 27) + (3 \times 214) - (90) - (3 \times 198)$ OR $696 - 684$ $\Delta S^\ominus = (+) 12 \text{ (J K}^{-1} \text{ mol}^{-1}\text{)}$	1 1 2
3(c)(iii)	$\Delta G^\ominus = -43.6 - (298 \times 12 / 1000)$ $\Delta G^\ominus = -47.2 \text{ (kJ mol}^{-1}\text{)}$	1 1 2
3(c)(iv)	high E_a and to speed up the rate	1 1
	Total:	13

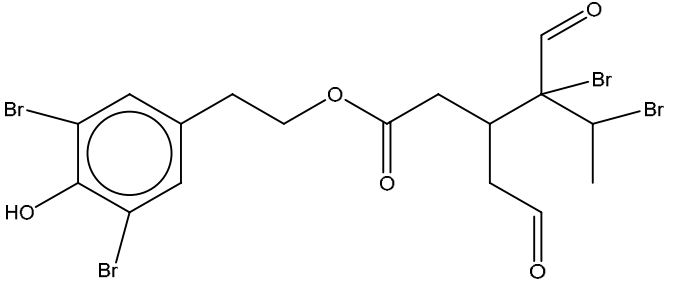
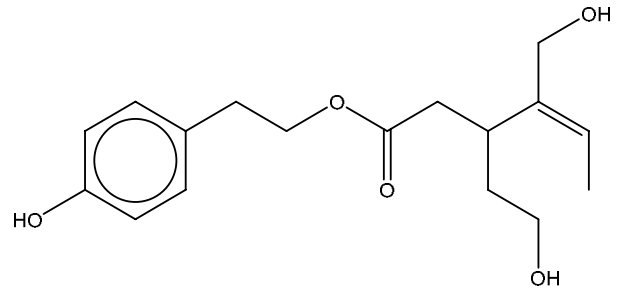
Page 7	Mark Scheme	Syllabus	Paper
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Question	Answer	Marks
4(a)	d orbitals split into lower and upper orbitals light/photon absorbed electron(s) promoted / excited / jumps up to (higher) (d–) orbital or electron(s) moves / jumps (from lower (d–)) to higher (d–) orbital	1 1 1 3
4(b)(i)	$\text{Cu} + 4\text{HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$ or ionic $\text{Cu} + 4\text{H}^+ + 2\text{NO}_3^- \rightarrow \text{Cu}^{2+} + 2\text{NO}_2 + 2\text{H}_2\text{O}$ correct species correct balancing	1 1 2
4(b)(ii)	moles $\text{S}_2\text{O}_3^{2-} = 0.1 \times 22.4 / 1000 = \mathbf{2.24 \times 10^{-3}}$ moles of Cu^{2+} in $25 \text{ cm}^3 = \mathbf{2.24 \times 10^{-3}}$ moles of Cu^{2+} in $250 \text{ cm}^3 = 2.24 \times 10^{-2}$ mass of Cu = $2.24 \times 10^{-2} \times 63.5 = 1.4224 \text{ g}$ % Cu = $1.42 / 1.75 \times 100 = \mathbf{81.1}$ or 81.3%	1 1 1 1 4
	Total:	9

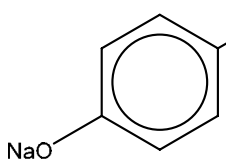
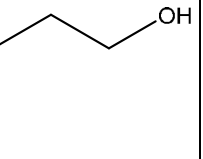
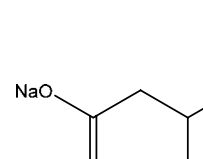
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Question	Answer	Marks
5(a)	$K_a = \frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]}$	1 1
5(b)(i)	a solution that resists changes in pH when small amounts of acid and base / alkali are added	1 1 2
5(b)(ii)	addition of acid: $\text{H}^+ + \text{HPO}_4^{2-} \rightarrow \text{H}_2\text{PO}_4^-$ OR $\text{H}^+ + \text{H}_2\text{PO}_4^- \rightarrow \text{H}_3\text{PO}_4$ addition of base: $\text{HO}^- + \text{H}_2\text{PO}_4^- \rightarrow \text{HPO}_4^{2-} + \text{H}_2\text{O}$ OR $\text{OH}^- + \text{HPO}_4^{2-} \rightarrow \text{H}_2\text{O} + \text{PO}_4^{3-}$	1 1 2
5(c)	$[\text{H}^+] = 10^{-7.4} = 3.98 \times 10^{-8}$ $[\text{HPO}_4^{2-}] / [\text{H}_2\text{PO}_4^-] = K_a / [\text{H}^+]$ $([\text{HPO}_4^{2-}] / [\text{H}_2\text{PO}_4^-]) = 6.31 \times 10^{-8} / 3.98 \times 10^{-8} = \mathbf{1.58-1.6}$	1 1 1 3
5(d)(i)	$\text{HCl} + \text{H}_2\text{PO}_4^- \rightarrow \text{H}_3\text{PO}_4 + \text{Cl}^-$ OR $\text{H}^+ + \text{H}_2\text{PO}_4^- \rightarrow \text{H}_3\text{PO}_4$ OR $\text{H}_2\text{O} + \text{H}_2\text{PO}_4^- \rightarrow \text{H}_3\text{PO}_4 + \text{OH}^-$	1 1

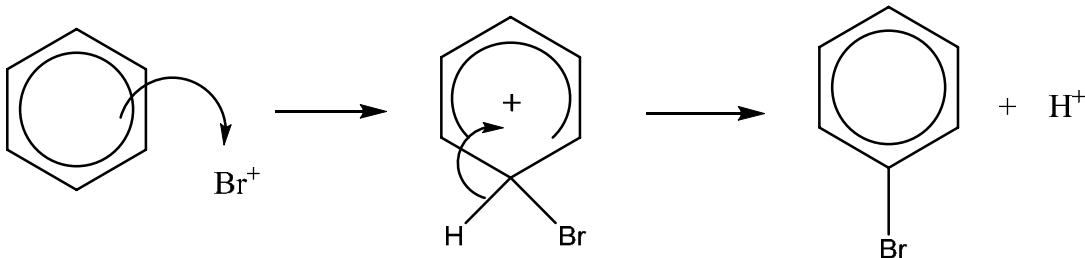
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Question	Answer			Marks
6(c)	reagent	structure of product(s)	type of reaction	
	excess $\text{Br}_2(\text{aq})$	 addition of bromine to alkene 2×Br substituted in phenol at positions 2 and 6	(electrophilic) substitution or (electrophilic) addition	1 1
	NaBH_4		reduction (allow nucleophilic addition)	1

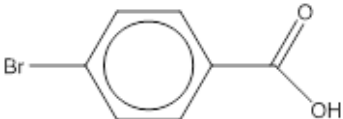
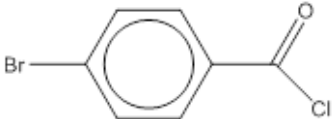
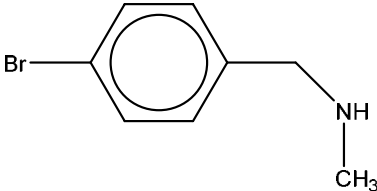
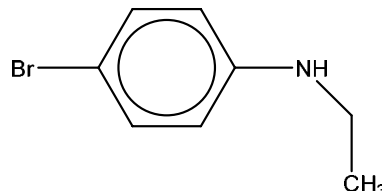
Page 11	Mark Scheme	Syllabus	Paper
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Question	Answer				Marks
	excess hot NaOH(aq) 			hydrolysis	1+1 1 6
6(d)	mixture of (two) optical / stereo isomers <u>are</u> formed				1 1
	Total:				12

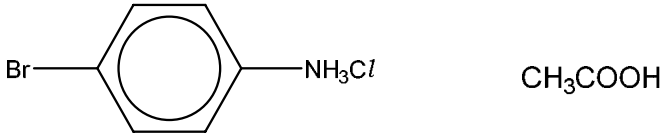
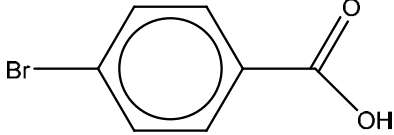
Page 12	Mark Scheme	Syllabus	Paper
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Question	Answer	Marks
7(a)(i)	electrophilic substitution	1 1
7(a)(ii)	$(\text{Br}_2 + \text{A}/\text{Br}_3) \rightarrow \text{Br}^+ + \text{A}/\text{Br}_4^-$  curly arrow from ring system to Br^+ correct intermediate curly arrow from C–H bond into ring and loss of H^+	1 1 1 1 4
7(b)	both amide	1 1
7(c)(i)	step 1, A/Br_3 and CH_3Br OR other suitable halogen instead of Br step 2, KMnO_4 or potassium manganate(VII) step 3, conc. H_2SO_4 and conc. HNO_3 step 4. Sn and (conc.) HCl (heat)	1 1 1 1 4

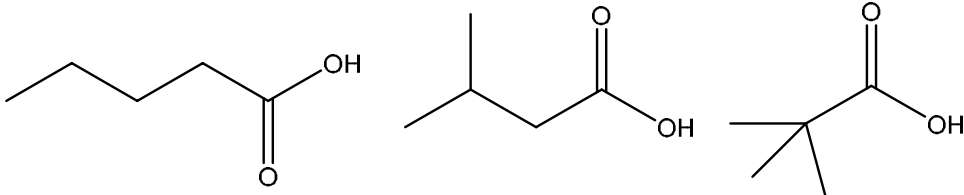
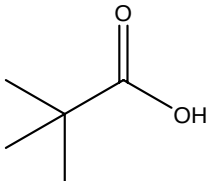
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Question	Answer	Marks
7(c)(ii)	 R  S  T 1 mark for each correct structure	3
7(d)(i)	  1 mark for each correct structure	2
7(d)(ii)	reduction	1 1

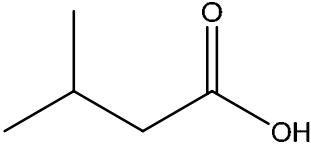
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Question	Answer	Marks
7(e)(i)	 (or ionic) 1 mark for each correct structure	2
7(e)(ii)		1
7(e)(iii)	(precipitate) compound is less polar / more non-polar / non-ionic resulting in less hydrogen bonding to water	1
	Total:	20

Page 15	Mark Scheme	Syllabus	Paper
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Question	Answer	Marks												
8(a)	$102 \times 0.314 = 32$ (32.028) ($102 - 32 = 70$) and $(12 \times 5) + (1 \times 10) = 70$ OR F contains $\text{CO}_2\text{H} = 45$ so $102 - 45 = 57$ so C_4H_9	1 1												
8(b)(i)	 2 correct = 1 mark 3 correct = 2 marks	2												
8(b)(ii)	2-methyl butanoic acid	1 1												
8(c)(i)		1 1												
8(c)(ii)	<table border="1"> <thead> <tr> <th>δ/ppm</th><th>environment of the carbon atom</th><th>hybridisation of the carbon atom</th></tr> </thead> <tbody> <tr> <td>27</td><td>alkyl / CH_3</td><td>sp^3</td></tr> <tr> <td>41</td><td>next to carboxyl / $(\text{CH}_3)_3\text{C}$</td><td>sp^3</td></tr> <tr> <td>179</td><td>carboxyl / CO_2H</td><td>sp^2</td></tr> </tbody> </table>	δ/ppm	environment of the carbon atom	hybridisation of the carbon atom	27	alkyl / CH_3	sp^3	41	next to carboxyl / $(\text{CH}_3)_3\text{C}$	sp^3	179	carboxyl / CO_2H	sp^2	2
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27	alkyl / CH_3	sp^3												
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179	carboxyl / CO_2H	sp^2												

Page 16	Mark Scheme	Syllabus	Paper
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Question	Answer				Marks
8(d)(i)	δ/ppm	type of proton	number of protons	splitting	4
	0.9	alkane / CH / CH ₃	6	doublet	
	1.6	alkane / CH	1	[multiplet]	
	2.4	alkyl next to C = O / CH ₍₂₎ CO / CH	2	doublet	
	11.5	OH / CO ₂ H / carboxylic acid	1	singlet	
8(d)(ii)					1
8(e)	CDCl ₃ OR D ₂ O, DMSO, CD ₂ Cl ₂ , CCl ₄				1
	Total				13