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**CHEMISTRY**

**9701/42**

Paper 4 A Level Structured Questions

**October/November 2016**

MARK SCHEME

Maximum Mark: 100

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**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.

Mark schemes should be read in conjunction with the question paper and the Principal Examiner Report for Teachers.

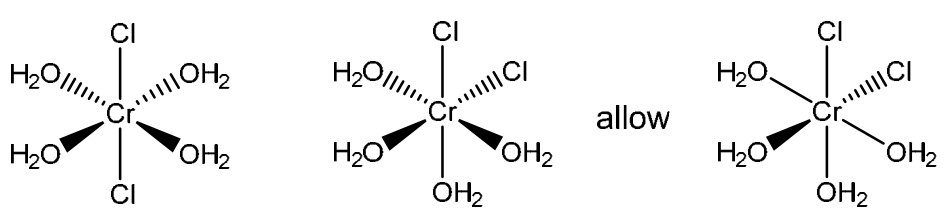
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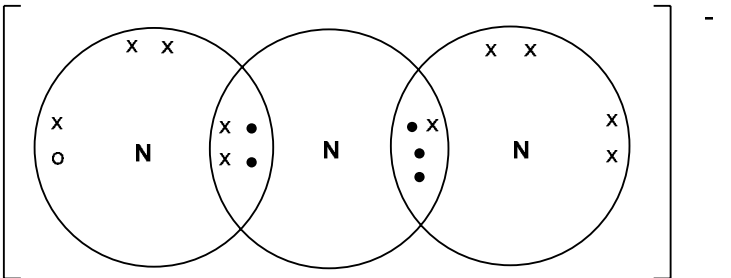
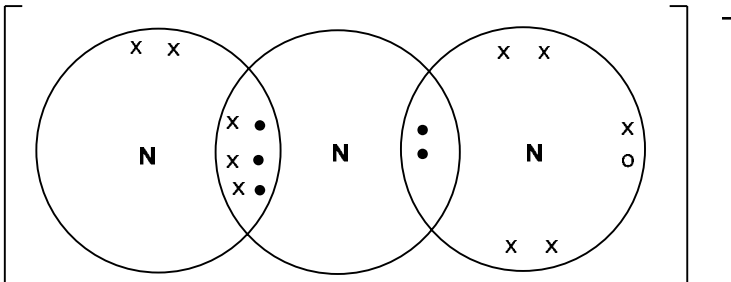
Page 2	Mark Scheme	Syllabus	Paper
	Cambridge International AS/A Level – October/November 2016	9701	42

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

Page 3	Mark Scheme	Syllabus	Paper
	Cambridge International AS/A Level – October/November 2016	9701	42

Question	Answer	Marks
1(d)(ii)	<p>one 3D isomer one correct isomer other isomer correct in 3D</p>  <p>The diagram shows three 3D isomers of the complex [CrCl<sub>2</sub>(OH<sub>2</sub>)<sub>4</sub>].  1. First isomer: Cr center with Cl at top, OH<sub>2</sub> at bottom, H<sub>2</sub>O at top-left (wedge), OH<sub>2</sub> at top-right (dash), H<sub>2</sub>O at bottom-left (wedge), OH<sub>2</sub> at bottom-right (wedge).  2. Second isomer: Cr center with Cl at top, OH<sub>2</sub> at bottom, H<sub>2</sub>O at top-left (wedge), Cl at top-right (dash), H<sub>2</sub>O at bottom-left (wedge), OH<sub>2</sub> at bottom-right (wedge).  3. Third isomer: Cr center with Cl at top, OH<sub>2</sub> at bottom, H<sub>2</sub>O at top-left (wedge), Cl at top-right (dash), H<sub>2</sub>O at bottom-left (wedge), OH<sub>2</sub> at bottom-right (wedge).  The word 'allow' is placed between the second and third isomers.</p>	<p>1 1 1</p> <p><b>3</b></p>
	<b>Total:</b>	<b>12</b>

Page 4	Mark Scheme	Syllabus	Paper
	Cambridge International AS/A Level – October/November 2016	9701	42

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

Page 5	Mark Scheme	Syllabus	Paper
	Cambridge International AS/A Level – October/November 2016	9701	42

Question	Answer	Marks
2(c)(iii)	use of $\Delta H_{f1}$ 494 (kJ mol <sup>-1</sup> ) $\Delta H_f^\circ = +107+494+142-732$ $\Delta H_f^\circ = +11$ (kJ mol <sup>-1</sup> )	1 1 1 <b>3</b>
2(c)(iv)	(ionic) radius / size of Na <sup>+</sup> is smaller (so stronger attraction to azide ion) <b>OR</b> ionic radius increases down the group	1 <b>1</b>
	<b>Total:</b>	<b>11</b>

Question	Answer	Mark
3(a)	Fe [Ar] 3d <sup>6</sup> 4s <sup>2</sup> Fe <sup>3+</sup> [Ar] 3d <sup>5</sup>	1 1 <b>2</b>
3(b)(i)	(catalyst is in) the same phase / state as the reactants	1 <b>1</b>
3(b)(ii)	$\text{S}_2\text{O}_8^{2-} + 2\text{I}^- \rightarrow 2\text{SO}_4^{2-} + \text{I}_2$	1 <b>1</b>
3(b)(iii)	(two) negatively-charged species <b>repel</b> each other	1 <b>1</b>
3(b)(iv)	Equation 1: $2\text{Fe}^{3+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2$ Equation 2: $\text{S}_2\text{O}_8^{2-} + 2\text{Fe}^{2+} \rightarrow 2\text{SO}_4^{2-} + 2\text{Fe}^{3+}$	1 1 <b>2</b>

Page 6	Mark Scheme	Syllabus	Paper
	Cambridge International AS/A Level – October/November 2016	9701	42

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

Page 7	Mark Scheme	Syllabus	Paper
	Cambridge International AS/A Level – October/November 2016	9701	42

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

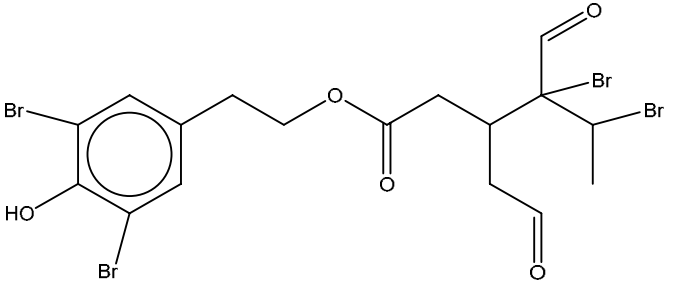
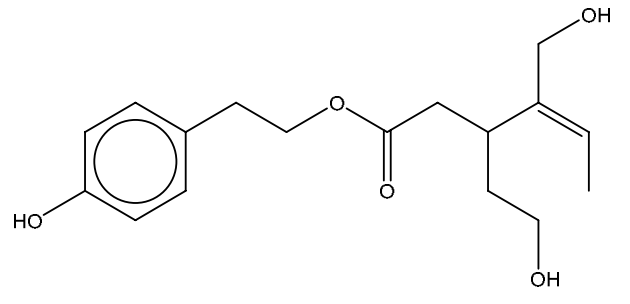
Page 8	Mark Scheme	Syllabus	Paper
	Cambridge International AS/A Level – October/November 2016	9701	42

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

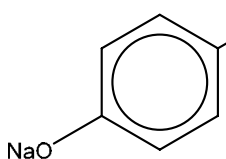
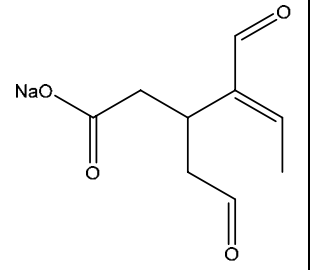


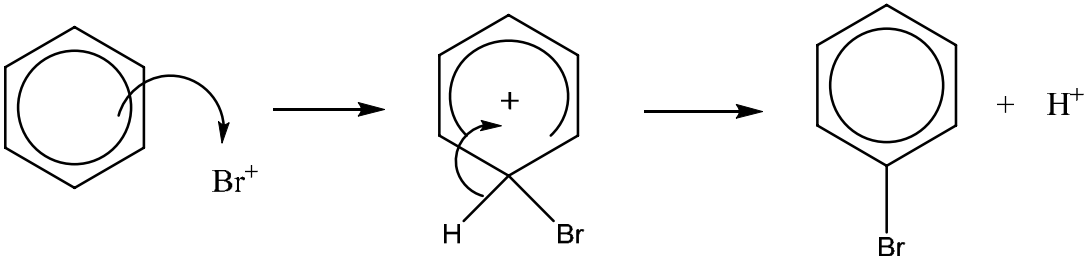


Page 10	Mark Scheme	Syllabus	Paper
	Cambridge International AS/A Level – October/November 2016	9701	42

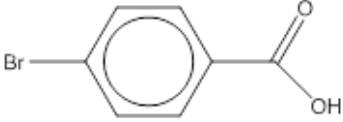
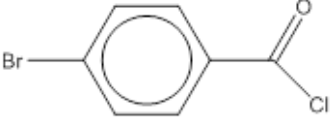

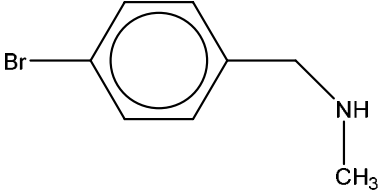
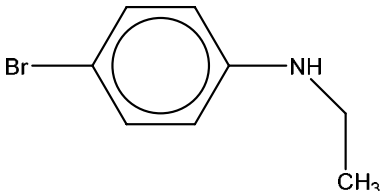
Question	Answer			Marks
6(c)	reagent	structure of product(s)	type of reaction	
	excess $\text{Br}_2(\text{aq})$	 <p>addition of bromine to alkene 2×Br substituted in phenol at positions <b>2</b> and <b>6</b></p>	(electrophilic) substitution  or  (electrophilic) addition	1 1
	$\text{NaBH}_4$		reduction  (allow nucleophilic addition)	1

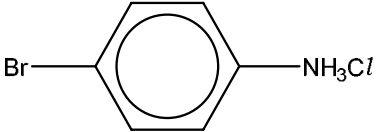
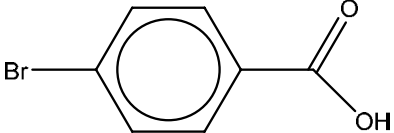
Page 11	Mark Scheme	Syllabus	Paper
	Cambridge International AS/A Level – October/November 2016	9701	42

Question	Answer			Marks
	<div> <div>excess hot NaOH(aq)</div> <div>  </div> </div>	<div>  </div>	<div>hydrolysis</div>	<div>1+1</div> <div>1</div> <div><b>6</b></div>
6(d)	mixture of (two) <b>optical/stereo</b> isomers <u>are</u> formed			<div>1</div> <div><b>1</b></div>
	Total:			<b>12</b>

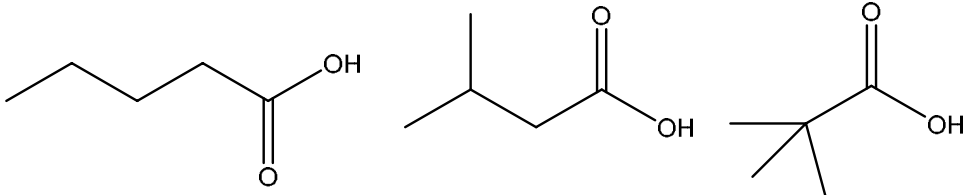
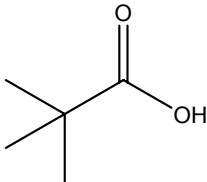
Question	Answer	Marks
7(a)(i)	electrophilic substitution	1 <b>1</b>
7(a)(ii)	$(\text{Br}_2 + \text{A}/\text{Br}_3) \rightarrow \text{Br}^+ + \text{A}/\text{Br}_4^-$  curly arrow from ring system to $\text{Br}^+$ correct intermediate curly arrow from C–H bond into ring and loss of $\text{H}^+$	1 1 1 <b>4</b>
7(b)	<b>both</b> amide	1 <b>1</b>
7(c)(i)	step 1, $\text{A}/\text{Br}_3$ <b>and</b> $\text{CH}_3\text{Br}$ <b>OR</b> other suitable halogen instead of Br step 2, $\text{KMnO}_4$ or potassium manganate(VII) step 3, conc. $\text{H}_2\text{SO}_4$ <b>and</b> conc. $\text{HNO}_3$ step 4. Sn <b>and</b> (conc.) $\text{HCl}$ (heat)	1 1 1 1 <b>4</b>

Page 13	Mark Scheme	Syllabus	Paper
	Cambridge International AS/A Level – October/November 2016	9701	42

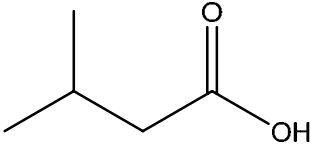
Question	Answer	Marks
7(c)(ii)	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p><b>R</b></p> </div> <div style="text-align: center;">  <p><b>S</b></p> </div> </div> <div style="text-align: center; margin-top: 20px;">  <p><b>T</b></p> </div> <div style="text-align: right; margin-top: 20px;">1 mark for each correct structure</div>	<b>3</b>
7(d)(i)	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  </div> <div style="text-align: center;">  </div> </div> <div style="text-align: right; margin-top: 20px;">1 mark for each correct structure</div>	<b>2</b>
7(d)(ii)	reduction	1 <b>1</b>

Question	Answer	Marks
7(e)(i)	<div style="display: flex; align-items: center; justify-content: space-around;"> <div style="text-align: center;">  <p>(or ionic)</p> </div> <div>CH<sub>3</sub>COOH</div> </div> <p style="text-align: right;">1 mark for each correct structure</p>	<b>2</b>
7(e)(ii)		1 <b>1</b>
7(e)(iii)	(precipitate) compound is less polar / more non-polar / non-ionic resulting in less hydrogen bonding to water	1 <b>1</b>
	<b>Total:</b>	<b>20</b>

Page 15	Mark Scheme	Syllabus	Paper
	Cambridge International AS/A Level – October/November 2016	9701	42

Question	Answer	Marks												
8(a)	$102 \times 0.314 = 32$ ( <b>32.028</b> ) ( $102 - 32 = 70$ ) <b>and</b> $(12 \times 5) + (1 \times 10) = 70$ <b>OR</b> F contains $\text{CO}_2\text{H} = 45$ so $102 - 45 = 57$ so $\text{C}_4\text{H}_9$	1 <b>1</b>												
8(b)(i)	 <p>2 correct = 1 mark 3 correct = 2 marks</p>	<b>2</b>												
8(b)(ii)	2-methyl butanoic acid	1 <b>1</b>												
8(c)(i)		1 <b>1</b>												
8(c)(ii)	<table border="1"> <thead> <tr> <th><math>\delta/\text{ppm}</math></th><th>environment of the carbon atom</th><th>hybridisation of the carbon atom</th></tr> </thead> <tbody> <tr> <td>27</td><td>alkyl / <math>\text{CH}_3</math></td><td><math>\text{sp}^3</math></td></tr> <tr> <td>41</td><td>next to carboxyl / <math>(\text{CH}_3)_3\text{C}</math></td><td><math>\text{sp}^3</math></td></tr> <tr> <td>179</td><td>carboxyl / <math>\text{CO}_2\text{H}</math></td><td><math>\text{sp}^2</math></td></tr> </tbody> </table>	$\delta/\text{ppm}$	environment of the carbon atom	hybridisation of the carbon atom	27	alkyl / $\text{CH}_3$	$\text{sp}^3$	41	next to carboxyl / $(\text{CH}_3)_3\text{C}$	$\text{sp}^3$	179	carboxyl / $\text{CO}_2\text{H}$	$\text{sp}^2$	<b>2</b>
$\delta/\text{ppm}$	environment of the carbon atom	hybridisation of the carbon atom												
27	alkyl / $\text{CH}_3$	$\text{sp}^3$												
41	next to carboxyl / $(\text{CH}_3)_3\text{C}$	$\text{sp}^3$												
179	carboxyl / $\text{CO}_2\text{H}$	$\text{sp}^2$												

Page 16	Mark Scheme	Syllabus	Paper
	Cambridge International AS/A Level – October/November 2016	9701	42

Question	Answer				Marks
8(d)(i)	$\delta/\text{ppm}$	type of proton	number of protons	splitting	4
	0.9	alkane / CH / CH <sub>3</sub>	6	doublet	
	1.6	alkane / CH	1	<b>[multiplet]</b>	
	2.4	alkyl next to C = O / CH <sub>(2)</sub> CO / CH	2	doublet	
	11.5	OH / CO <sub>2</sub> H / carboxylic acid	1	singlet	
8(d)(ii)					1
8(e)	CDCl <sub>3</sub> <b>OR</b> D <sub>2</sub> O, DMSO, CD <sub>2</sub> Cl <sub>2</sub> , CCl <sub>4</sub>				1
	Total				13