Cambridge 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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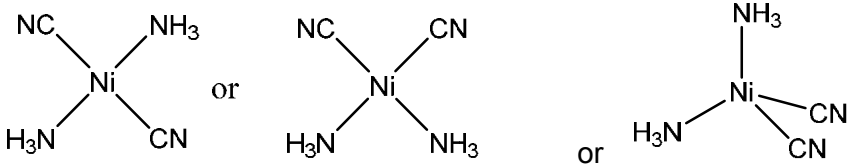
Question	Answer	Marks
1(a)	(an element) forming (one or more stable) **ions** with **incomplete d subshell** [1]	1 **1**
1(b)(i)	<table><tr><td></td><td>co-ordination number</td><td>oxidation number</td></tr><tr><td>$[Ni(CN)_2(NH_3)_2]$</td><td>4</td><td>+2</td></tr><tr><td>$[CrCl_2(H_2O)_4]^+$</td><td>6</td><td>+3</td></tr></table>	**2**
1(b)(ii)	dative (covalent) / co-ordinate	1 **1**
1(b)(iii)	correct diagram of $[Ni(CN)_2(NH_3)_2]$  square planar or tetrahedral	1 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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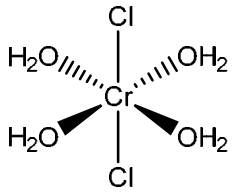
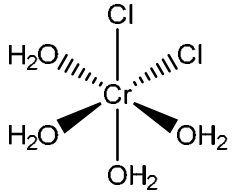
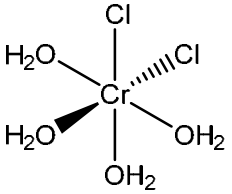
Question	Answer	Marks
1(d)(ii)	one 3D isomer one correct isomer other isomer correct in 3D   allow  	1 1 1 **3**
	Total:	**12**

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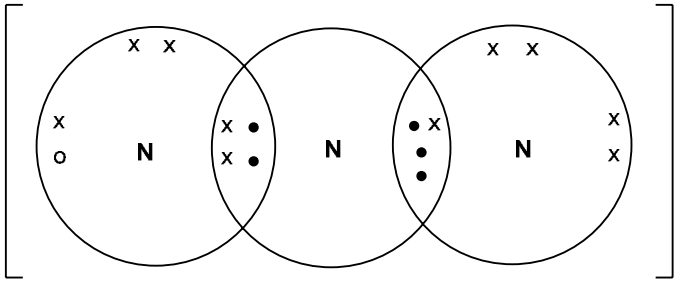
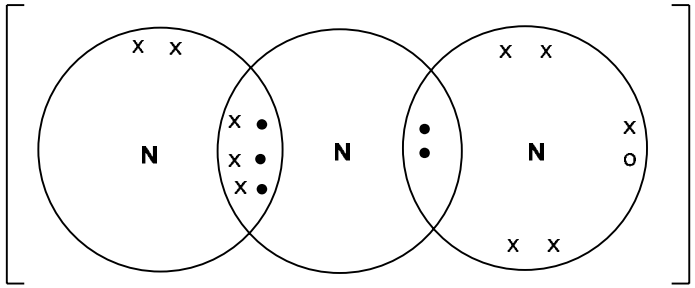
Question	Answer	Marks
2(a)	$NaN_3 \rightarrow Na + 1.5N_2$	1 **1**
2(b)	 - all atoms must have 8 outer electrons coding for electrons correct = 16 (10 × 5 • 1 □) central N must have 8 **bonding** electrons (inc. 5 • and no non-bonded electrons) **allow**  -	1 1 1 **3**
2(c)(i)	(energy change) when **1 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}) ΔH^{e}_{f} = +107+494+142–732 ΔH^{e}_{f} = **+**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**

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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)	$\Delta S^{\ominus} = (2\times27) + (3\times214) - (90) - (3\times198)$ **OR** 696 – 684 $\Delta S^{\ominus} = (+)\,12$ (J K^{-1} mol^{-1})	1 1 **2**
3(c)(iii)	$\Delta G^{\ominus} = -43.6 - (298 \times 12 / 1000)$ $\Delta G^{\ominus} = -47.2$ (kJ mol^{-1})	1 1 **2**
3(c)(iv)	high E_a **and** to speed up the rate	1 **1**
	Total:	**13**

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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)	$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$ or ionic $Cu + 4H^+ + 2NO_3^- \rightarrow Cu^{2+} + 2NO_2 + 2H_2O$ correct species correct balancing	 1 1 **2**
4(b)(ii)	moles $S_2O_3^{2-} = 0.1 \times 22.4 / 1000 =$ **2.24×10^{-3}** moles of Cu^{2+} in 25 cm^3 = **2.24×10^{-3}** moles of Cu^{2+} in 250 cm^3 = = 2.24×10^{-2} mass of Cu = $2.24 \times 10^{-}2 \times 63.5 = 1.4224$ g % Cu = $1.42 / 1.75 \times 100 =$ **81.1** or **81.3**%	1 1 1 1 **4**
	Total:	**9**

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Question	Answer	Marks
5(a)	$K_a = \frac{[HPO_4^{2-}][H_3O^+]}{[H_2PO_4^-]}$	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: $H^+ + HPO_4^{2-} \rightarrow H_2PO_4^-$ **OR** $H^+ + H_2PO_4^- \rightarrow H_3PO_4$ addition of base: $HO^- + H_2PO_4^- \rightarrow HPO_4^{2-} + H_2O$ **OR** $OH^- + HPO_4^{2-} \rightarrow H_2O + PO_4^{3-}$	1 1 **2**
5(c)	$[H^+] = 10^{-7.4} = 3.98 \times 10^{-8}$ $[HPO_4^{2-}] / [H_2PO_4^-] = K_a / [H^+]$ $([HPO_4^{2-}] / [H_2PO_4^-]) = 6.31 \times 10^{-8} / 3.98 \times 10^{-8}$ **= 1.58-1.6**	1 1 1 **3**
5(d)(i)	$HCl + H_2PO_4^- \rightarrow H_3PO_4 + Cl^-$ **OR** $H^+ + H_2PO_4^- \rightarrow H_3PO_4$ **OR** $H_2O + H_2PO_4^- \rightarrow H_3PO_4 + OH^-$	 1 **1**

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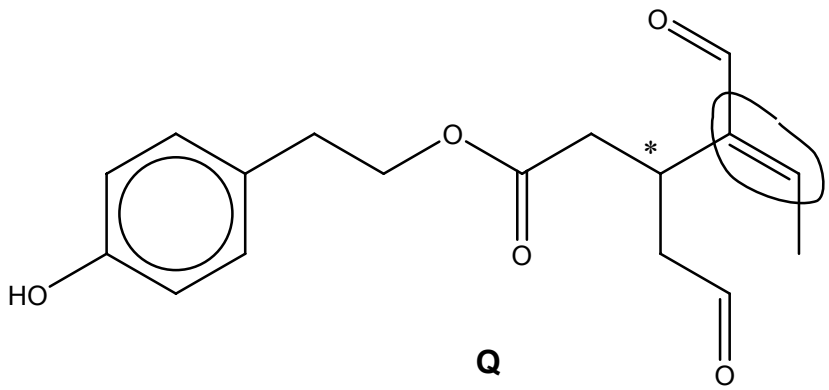
Question	Answer	Marks
5(d)(ii)	$NaOH + HPO_4^{2-} \rightarrow PO_4^{3-} + H_2O + Na^+$ **OR** $OH^- + HPO_4^{2-} \rightarrow PO_4^{3-} + H_2O$ **OR** $H_2O + HPO_4^{2-} \rightarrow PO_4^{3-} + H_3O^+$	1 **1**
	Total:	**10**

Question	Answer	Marks
6(a)	 **Q**	**1**
6(b)(i)	**ratio** of the **concentration** of a solute in the (two immiscible) solvents / liquids at equilibrium	1 1 **2**
6(b)(ii)	$K_{partition} = (0.06/40)/(0.25–0.06/10)$ or reversed ratio: $K_{partition} = (0.25–0.06/10)/(0.06/40)$ $K_{partition} =$ **0.079** (0.0789) $K_{partition} = 12.7/13.0$	1 1 **2**

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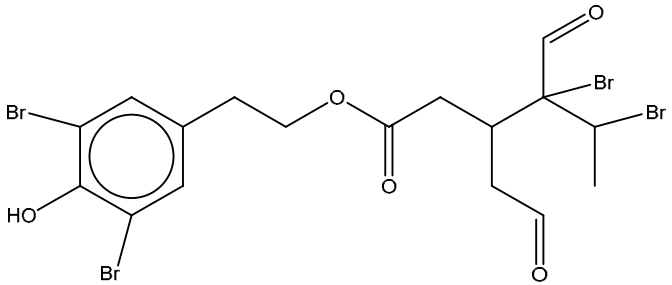
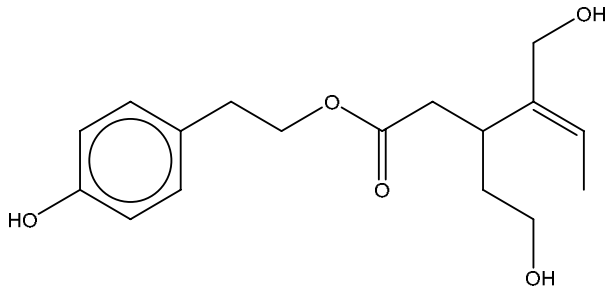
Question	Answer	Marks
6(c)		

reagent	structure of product(s)	type of reaction
excess $Br_2(aq)$	 addition of bromine to alkene 2×Br substituted in phenol at positions **2** and **6**	(electrophilic) substitution or (electrophilic) addition
$NaBH_4$		reduction (**allow** nucleophilic addition)

Marks
1
1
1

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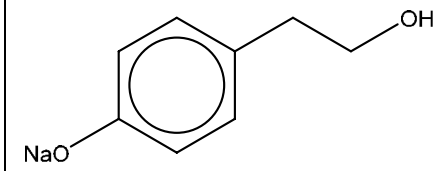
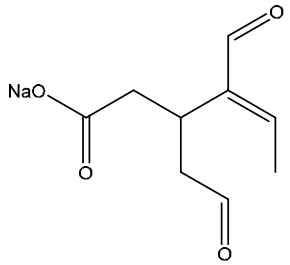
Question	Answer	Marks
	excess hot NaOH(aq)   hydrolysis	1+1
	all three reaction types	1 **6**
6(d)	mixture of (two) **optical / stereo** isomer**s** formed	1 **1**
	Total:	**12**

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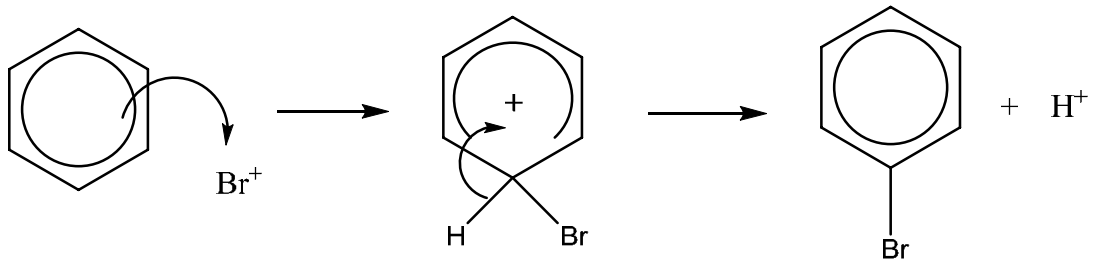
Question	Answer	Marks
7(a)(i)	electrophilic substitution	1 **1**
7(a)(ii)	$(Br_2 + AlBr_3) \rightarrow Br^+ + AlBr_4^-$  curly arrow from ring system to Br^+ correct intermediate curly arrow from C–H bond into ring and loss of H^+	1 1 1 1 **4**
7(b)	**both** amide	1 **1**
7(c)(i)	step 1, $AlBr_3$ **and** 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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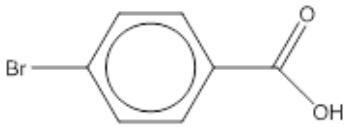
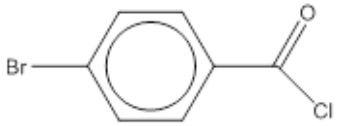
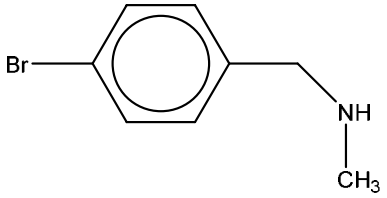
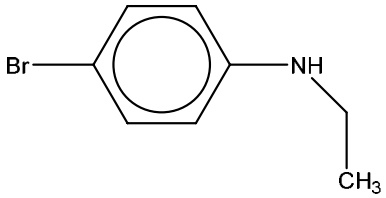
Question	Answer	Marks
7(c)(ii)	 **R**  **S**  **T** 1 mark for each correct structure	**3**
7(d)(i)	  1 mark for each correct structure	**2**
7(d)(ii)	reduction	1 **1**

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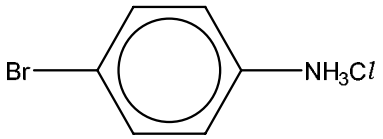
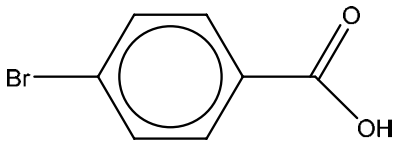
Question	Answer	Marks
7(e)(i)	 CH_3COOH (or ionic) 1 mark for each correct structure	2
7(e)(ii)		1 1
7(e)(iii)	(precipitate) compound is less polar / more non-polar / non-ionic resulting in less hydrogen bonding to water	1 1
	Total:	**20**

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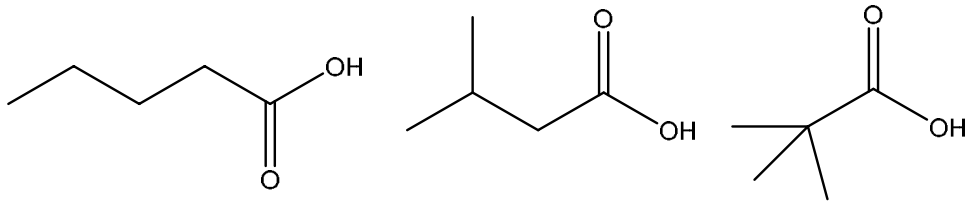
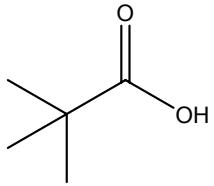
<table>
<tr><th>Question</th><th>Answer</th><th>Marks</th></tr>
<tr><td>8(a)</td><td>102 × 0.314 = 32 (32.028) (102–32=70)
and (12 × 5) + (1 × 10) = 70
OR F contains $CO_2H = 45$ so $102 - 45 = 57$ so C_4H_9</td><td>1
1</td></tr>
<tr><td>8(b)(i)</td><td>
2 correct = 1 mark
3 correct = 2 marks</td><td>2</td></tr>
<tr><td>8(b)(ii)</td><td>2-methyl butanoic acid</td><td>1
1</td></tr>
<tr><td>8(c)(i)</td><td></td><td>1
1</td></tr>
<tr><td>8(c)(ii)</td><td>
<table>
<tr><th>δ/ppm</th><th>environment of the carbon atom</th><th>hybridisation of the carbon atom</th></tr>
<tr><td>27</td><td>alkyl / CH_3</td><td>sp^3</td></tr>
<tr><td>41</td><td>next to carboxyl / $(CH_3)_3\underline{\mathbf{C}}$</td><td>$sp^3$</td></tr>
<tr><td>179</td><td>carboxyl / CO_2H</td><td>sp^2</td></tr>
</table>
</td><td>2</td></tr>
</table>

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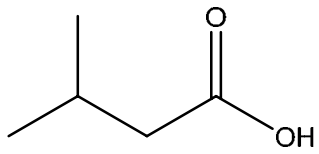
<table>
<tr><th>Question</th><th>Answer</th><th>Marks</th></tr>
<tr><td>8(d)(i)</td><td>
<table>
<tr><th>δ/ppm</th><th>type of proton</th><th>number of protons</th><th>splitting</th></tr>
<tr><td>0.9</td><td>alkane / CH / CH_3</td><td>6</td><td>doublet</td></tr>
<tr><td>1.6</td><td>alkane / CH</td><td>1</td><td>[multiplet]</td></tr>
<tr><td>2.4</td><td>alkyl next to C = O / $CH_{(2)}CO$ / CH</td><td>2</td><td>doublet</td></tr>
<tr><td>11.5</td><td>OH / CO_2H / carboxylic acid</td><td>1</td><td>singlet</td></tr>
</table>
</td><td>4</td></tr>
<tr><td>8(d)(ii)</td><td>
</td><td>1

1</td></tr>
<tr><td>8(e)</td><td>$CDCl_3$ OR D_2O, DMSO, CD_2Cl_2, CCl_4</td><td>1
1</td></tr>
<tr><td></td><td>Total</td><td>13</td></tr>
</table>

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