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

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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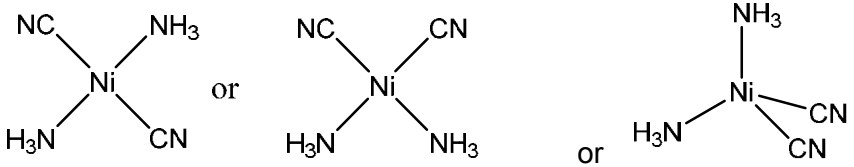
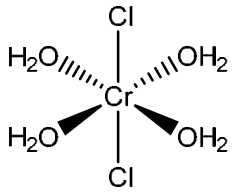
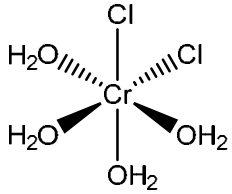
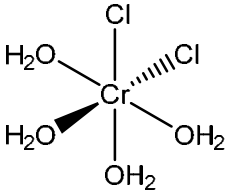
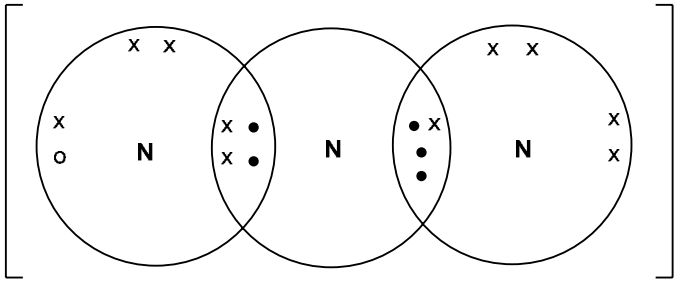
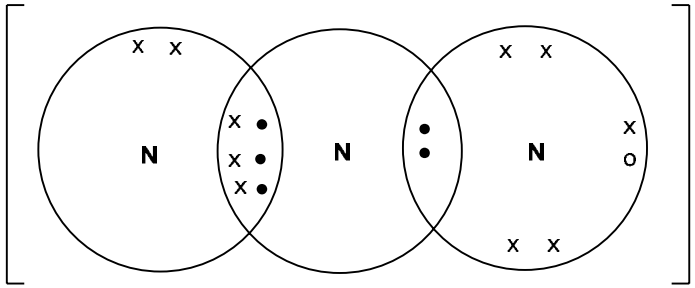
Question	Answer	Marks
1(a)	(an element) forming (one or more stable) **ions** with **incomplete d subshell** [1]	1 **1**
1(b)(i)	<table><tr><td></td><td>co-ordination number</td><td>oxidation number</td></tr><tr><td>$[Ni(CN)_2(NH_3)_2]$</td><td>4</td><td>+2</td></tr><tr><td>$[CrCl_2(H_2O)_4]^+$</td><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**

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

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**

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**

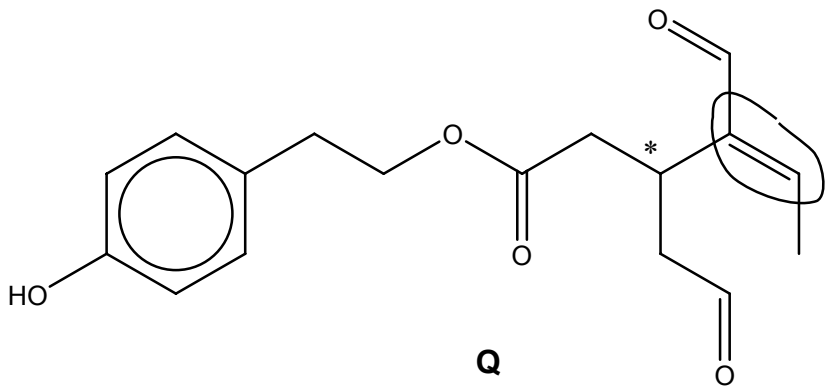
Question	Answer	Mark
3(a)	Fe [Ar] $3d^6 4s^2$ Fe^{3+} [Ar] $3d^5$	1 1 **2**
3(b)(i)	(catalyst is in) the same phase / state as the reactants	1 **1**
3(b)(ii)	$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$	1 **1**
3(b)(iii)	(two) negatively-charged species **repel** each other	1 **1**
3(b)(iv)	Equation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

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**

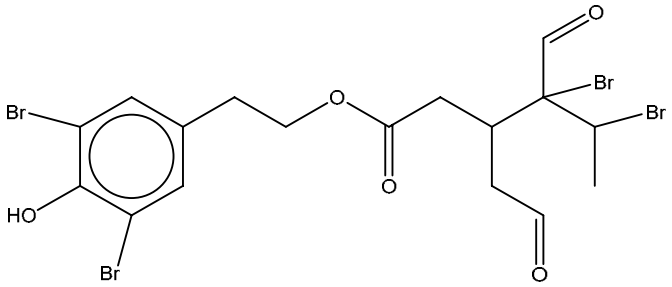
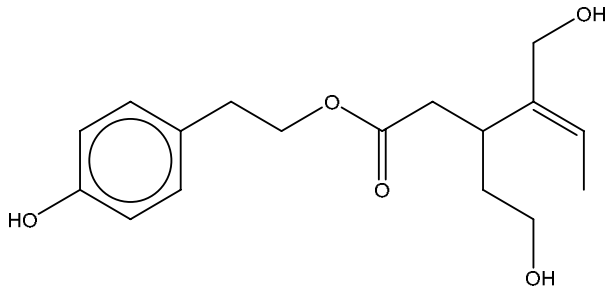
Question	Answer	Marks
4(a)	d orbitals split into lower **and** upper orbitals light / photon absorbed **electron**(s) promoted / excited / jumps up to (higher) (d–) orbital ***or*** **electron**(s) moves / jumps (from lower (d–)) to higher (d–) orbital	1 1 1 **3**
4(b)(i)	$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$ 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**

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**

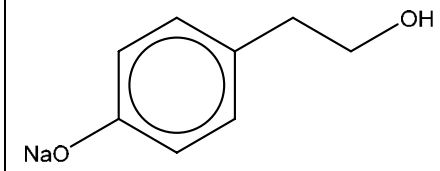
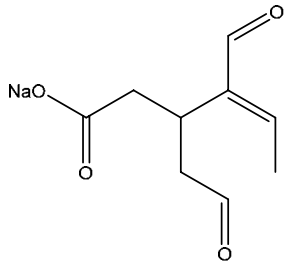
Question	Answer	Marks
5(d)(ii)	$NaOH + HPO_4^{2-} \rightarrow PO_4^{3-} + H_2O + Na^+$ **OR** $OH^- + HPO_4^{2-} \rightarrow PO_4^{3-} + H_2O$ **OR** $H_2O + HPO_4^{2-} \rightarrow PO_4^{3-} + H_3O^+$	1 **1**
	Total:	**10**

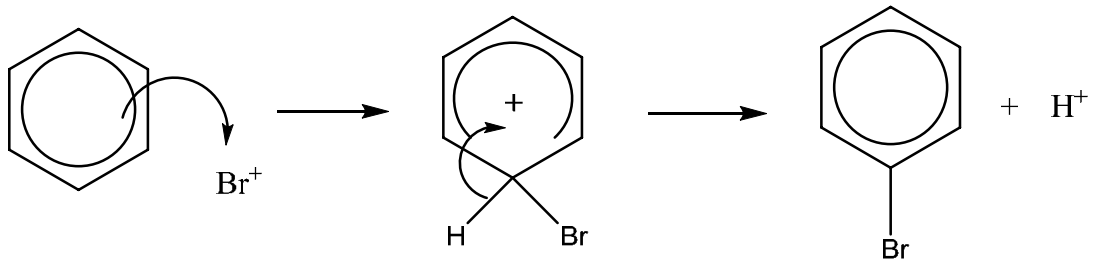
Question	Answer	Marks
6(a)	 **Q**	**1**
6(b)(i)	**ratio** of the **concentration** of a solute in the (two immiscible) solvents / liquids at equilibrium	1 1 **2**
6(b)(ii)	$K_{partition} = (0.06/40)/(0.25–0.06/10)$ or reversed ratio: $K_{partition} = (0.25–0.06/10)/(0.06/40)$ $K_{partition} =$ **0.079**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

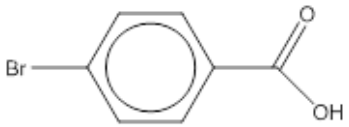
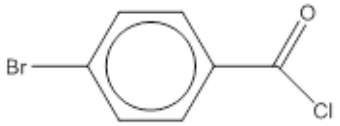
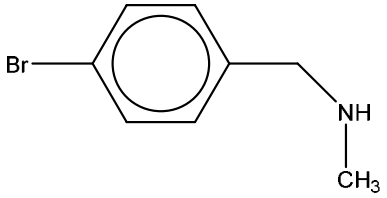
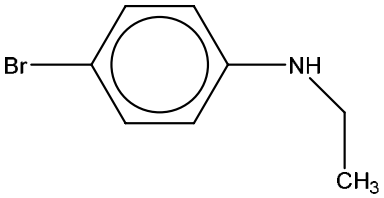
Question	Answer	Marks
6(c)		

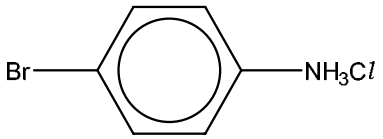
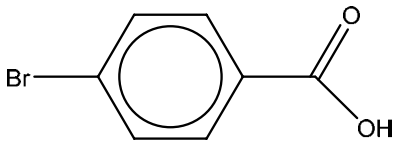
reagent	structure of product(s)	type of reaction
excess $Br_2(aq)$	 addition of bromine to alkene 2×Br substituted in phenol at positions **2** and **6**	(electrophilic) substitution or (electrophilic) addition
$NaBH_4$		reduction (**allow** nucleophilic addition)

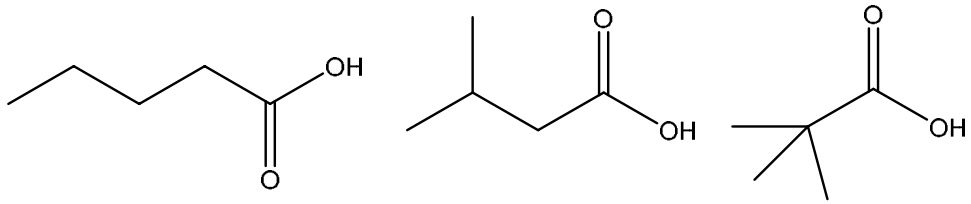
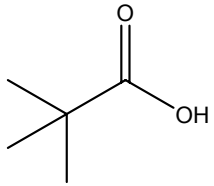
Marks: 1, 1, 1

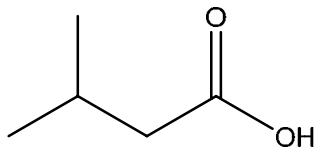
Question	Answer	Marks
	excess hot NaOH(aq)   hydrolysis	1+1
	all three reaction types	1 **6**
6(d)	mixture of (two) **optical / stereo** isomer**s** formed	1 **1**
	Total:	**12**

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**

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**

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**

<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>

<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>