

## **Cambridge International Examinations**

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	Mark	S
1(a)	(an element) forming (one or more stable) ions with incomplete d subshell [1]	1	1
1(b)(i)	co-ordination number oxidation number		
	[Ni(CN) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ] 4 +2		
	$[CrCl_2(H_2O)_4]^+$ 6 +3		2
1(b)(ii)	dative (covalent)/co-ordinate	1	1
1(b)(iii)	correct diagram of [Ni(CN) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]  NC NH <sub>3</sub> NC CN  Ni Or Ni  NH <sub>3</sub> Or H <sub>3</sub> N  Or CN  Or CN	1	
	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 $ \begin{array}{ccccccccccccccccccccccccccccccccccc$	1 1 1 3
	Total:	12

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Question	Answer	Mar	ks
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    X	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	
2(c)(ii)	forming an (ionic) bond	1	1

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Question	Answer	Mai	·ks
2(c)(iii)	use of $\Delta H_{i1}$ 494 (kJ mol <sup>-1</sup> ) $\Delta H_{f}^{e} = +107 + 494 + 142 - 732$ $\Delta H_{f}^{e} = +11$ (kJ mol <sup>-1</sup> )	1 1 1	3
2(c)(iv)	(ionic) radius / size of Na <sup>+</sup> 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 <sup>6</sup> 4s <sup>2</sup> Fe <sup>3+</sup> [Ar] 3d <sup>5</sup>	1 1 2
3(b)(i)	(catalyst is in) the same phase/state as the reactants	1 <b>1</b>
3(b)(ii)	$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$	1 1
3(b)(iii)	(two) negatively-charged species <b>repel</b> each other	1 <b>1</b>
3(b)(iv)	Equation 1: $2Fe^{3+} + 2I^{-} \rightarrow 2Fe^{2+} + I_{2}$	1
	Equation 2: $S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$	1 <b>2</b>

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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)	$\Delta S^{e-} = (2 \times 27) + (3 \times 214) - (90) - (3 \times 198)$ <b>OR</b> 696 - 684	1
	$\Delta S^{e-} = (+) 12 (J K^{-1} mol^{-1})$	1 <b>2</b>
3(c)(iii)	$\Delta G^{\text{e-}} = -43.6 - (298 \times 12/1000)$	1
	$\Delta G^{\circ} = -47.2 \text{ (kJ mol}^{-1})$	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 <b>and</b> upper orbitals	1
	light/photon absorbed	1
	electron(s) promoted/excited/jumps up to (higher) (d–) orbital or electron(s) moves/jumps (from lower (d–)) to higher (d–) orbital	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	1
	correct balancing	1 2
4(b)(ii)	moles $S_2O_3^{2-} = 0.1 \times 22.4 / 1000 = 2.24 \times 10^{-3}$	1
	moles of $Cu^{2+}$ in $25 \text{ cm}^3 = 2.24 \times 10^{-3}$	1
	moles of $Cu^{2+}$ in $250 \text{ cm}^3 = 2.24 \times 10^{-2}$ mass of $Cu = 2.24 \times 10^{-2} \times 63.5 = 1.4224 \text{ g}$	1
	% Cu = 1.42/1.75×100 = <b>81.1</b> or <b>81.3</b> %	1 4
	Total:	9

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Question	Answer	Mar	ks
5(a)	$K_{a} = \frac{[HPO_{4}^{2-}][H_{3}O^{+}]}{[H_{2}PO_{4}^{-}]}$	1	
			1
5(b)(i)	a solution that resists changes in pH	1	
	when <b>small</b> amounts of acid and base/alkali are added	1	2
5(b)(ii)	addition of acid: $H^+ + HPO_4^{2-} \rightarrow H_2PO_4^-$ <b>OR</b> $H^+ + H_2PO_4^- \rightarrow H_3PO_4$	1	
	addition of base: $HO^- + H_2PO_4^- \rightarrow HPO_4^{2-} + H_2O$ <b>OR</b> $OH^- + HPO_4^{2-} \rightarrow H_2O + PO_4^{3-}$	1	
			2
5(c)	$[H^+] = 10^{-7.4} = 3.98 \times 10^{-8}$	1	
	$[HPO_4^{2-}]/[H_2PO_4^{-}] = K_a/[H^+]$	1	
	$([HPO_4^{2-}]/[H_2PO_4^{-}]) = 6.31 \times 10^{-8}/3.98 \times 10^{-8} = 1.58-1.6$	1	3
5(d)(i)	$HCl + H_2PO_4^- \rightarrow H_3PO_4 + Cl^-$ <b>OR</b> $H^+ + H_2PO_4^- \rightarrow H_3PO_4$		
	<b>OR</b> $H_2O + H_2PO_4^- \rightarrow H_3PO_4 + OH^-$	1	1

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Question	Answer	Marks
5(d)(ii)	NaOH + HPO <sub>4</sub> <sup>2-</sup> $\rightarrow$ PO <sub>4</sub> <sup>3-</sup> + H <sub>2</sub> O + Na <sup>+</sup> <b>OR</b> OH <sup>-</sup> + HPO <sub>4</sub> <sup>2-</sup> $\rightarrow$ PO <sub>4</sub> <sup>3-</sup> + H <sub>2</sub> O	
	<b>OR</b> $H_2O + HPO_4^{2-} \rightarrow PO_4^{3-} + H_3O^+$	1 <b>1</b>
	Total:	10

Question	Answer	Marks
6(a)	HO * O	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)	$K_{\text{partition}} = (0.06/40)/(0.25-0.06/10)$ or reversed ratio: $K_{\text{partition}} = (0.25-0.06/10)/(0.06/40)$ $K_{\text{partition}} = 0.079$ (0.0789) $K_{\text{partition}} = 12.7/13.0$	1 1 2

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Question		Answer		Marks
6(c)	reagent	structure of product(s)	type of reaction	
	excess Br <sub>2</sub> (aq)	addition of bromine to alkene 2×Br substituted in phenol at positions 2 and 6	(electrophilic) substitution or (electrophilic) addition	1 1
	NaBH₄	НО	reduction  (allow nucleophilic addition)	1

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Question	Answer	Marks
	excess hot NaOH(aq)	1+1
	all three reaction types	1 6
6(d)	mixture of (two) optical/stereo isomers formed	1 <b>1</b>
	Total:	12

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Question	Answer	Marks
7(a)(i)	electrophilic substitution	1 1
7(a)(ii)	$(Br_2 + A \mathcal{I}Br_3) \rightarrow Br^+ + A \mathcal{I}Br_4^-$	1
	curly arrow from ring system to Br <sup>+</sup> correct intermediate curly arrow from C–H bond into ring and loss of H <sup>+</sup>	1 1 1
7(b)	both amide	1 1
7(c)(i)	step 1, A/Br <sub>3</sub> and CH <sub>3</sub> Br OR other suitable halogen instead of Br	1
	step 2, KMnO₄ or potassium manganate(VII)	1
	step 3, conc. H <sub>2</sub> SO <sub>4</sub> <b>and</b> conc. HNO <sub>3</sub>	1
	step 4. Sn <b>and</b> (conc.) HCl (heat)	1
		4

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Question	Answer	Marks
7(c)(ii)	Br OH Br Cl	
	Br NH <sub>2</sub> T  1 mark for each correct structure	
	i mark for each correct structure	3
7(d)(i)	$Br$ $NH$ $CH_3$ $CH_3$	
	1 mark for each correct structure	2
7(d)(ii)	reduction	1 1

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Question	Answer		
7(e)(i)	Br——NH <sub>3</sub> C <i>l</i> CH <sub>3</sub> COOH		
	(or ionic)  1 mark for each correct structure	2	
7(e)(ii)	Br—OH	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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Question			Answer		Marks	
8(a)	102 × 0.314 = 32 (32.028) (102–32=70) and $(12 \times 5) + (1 \times 10) = 70$ OR F contains $CO_2H = 45$ so $102-45=57$ so $C_4H_9$					1
8(b)(i)		2 correct = 1 mark 3 correct = 2 marks				
8(b)(ii)	2-methyl butanoic acid					1
8(c)(i)	ОН				1	1
8(c)(ii)	δ/ppm	environment of the carbon atom	hybridisation of the carbon atom			
	27	alkyl / CH₃	sp³			
	41	next to carboxyl/(CH <sub>3</sub> ) <sub>3</sub> <u>C</u>	sp³			
	179	carboxyl / CO₂H	sp <sup>2</sup>			2

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Question	Answer					Marks	
8(d)(i)	δ/ppm	type of proton	number of protons	splitting			
	0.9	alkane/CH/CH <sub>3</sub>	6	doublet			
	1.6	alkane/CH	1	[multiplet]			
	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			4
8(d)(ii)		ОН				1	1
8(e)	CDC l <sub>3</sub>	OR D <sub>2</sub> O, DMSO, CD <sub>2</sub> C <i>l</i> <sub>2</sub> , CC <i>l</i> <sub>4</sub>				1	1
					Total		13