

## **Cambridge International Examinations**

Cambridge International Advanced Subsidiary and Advanced Level

CHEMISTRY 9701/42

Paper 4 A Level Structured Questions

May/June 2016

MARK SCHEME
Maximum Mark: 100

## **Published**

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Question	Answer	Marks
1 (a) (i)	dative (covalent) or coordinate	2
	Hydrogen/H (boding)	
(ii)	octahedral	1
(iii)	$Mg(NO_3)_2.6H_2O \rightarrow Mg(NO_3)_2 + 6H_2O$ $Mg(NO_3)_2 \rightarrow MgO + 2NO_2 + \frac{1}{2}O_2$	4
	any three of (solid) dissolves/turns to liquid condensation on tube white solid (forms/remains) brown fumes (evolved) gas formed that relights a glowing splint	
(iv)	$M_{\rm r}$ values: Mg(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O = 256.3 MgO = 40.3 or (loss in molar mass = 256.3 – 40.3 =) 216 percentage loss = $100 \times 216/256.3 = 84.3/84.4\%$	2
(b)	(cat)-ionic radius/ion size increases (down the group)	2
	less polarisation/distortion of nitrate ion/NO <sub>3</sub> <sup>-</sup>	
(c)	$2AgNO_3 \rightarrow 2Ag + 2NO_2 + O_2$	1
		[Total: 12]
2 (a) (i)	(an acid that is) partially/incompletely ionised/dissociated	1
(b) (i)	$pK_a = -logK_a$ or $K_a = 10^{-pKa}$	1

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Question	Answer	Marks
(ii)	ethanoic acid (1) is <b>more acidic</b> than propanoic acid (2) due to smaller electron-donating (R/alkyl) group/less electron-donating (R/alkyl) group(s)	3
	2-chloropropanoic acid (3) is <b>more acidic</b> than propanoic acid (2) due to electron-withdrawing/electronegative (C <i>l</i> /chlorine) atom	
	2-chloropropanoic acid (3) is more acidic than $3\neg$ -chloropropanoic acid (4) since the $Cl$ /chlorine/electronegative atom is closer to the $CO_2^-$ /acid	
(c) (i)	H <sub>2</sub> (g)  Pt  Cu  Cu  H <sup>+</sup> (aq)  M1: voltmeter/V and salt bridge labelled  M2: Cu and Cu <sup>2+</sup> /CuSO <sub>4</sub> (any soluble Cu(II) salt)  M3: H <sub>2</sub> (arrow in) and H <sup>+</sup> /HC1/H <sub>2</sub> SO <sub>4</sub> /any mineral acid  M4 Pt and one solution at 1 M/1 mol dm <sup>-3</sup> OR H <sub>2</sub> at 1 atm	4
(ii)	$E_{\text{cell}}^{\text{e}} = 0.34 \text{ (V)}$ and $(\text{Cu}^{2+})/\text{Cu}$ is the positive electrode	1
d (i)	$K_a = 1.23 \times 10^{-5}$ $[H^+] = \sqrt{(K_a.c)} = \sqrt{(1.23 \times 10^{-5} \times 0.1)} = 1.11 \times 10^{-3} \text{mol dm}^{-3}$	2
	pH = <b>3.0 (2.96)</b> ecf from [H <sup>+</sup> ]	

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Question	Answer	Marks
(ii)	$E = 0.0 + 0.059\log(1.11 \times 10^{-3}) \text{ OR } = -0.17(4)\text{V}$	2
	so new $E_{cell} = 0.34 + 0.17 = 0.51V$ ecf from <b>(d)(i)</b>	
		[Total: 14]
3 (a) (i)	(CH <sub>3</sub> ) <sub>2</sub> CHCN	1
(ii)	reaction 1: NH <sub>3</sub> (in ethanol) under pressure (+ heat) or heat NH <sub>3</sub> in a sealed tube	3
	reaction 2: KCN/NaCN and heat/reflux (in ethanol)	
	reaction 3: H <sub>2</sub> + Ni <i>or</i> LiA <i>l</i> H <sub>4</sub>	
(b) (i)	$CH_3CH_2NH_2 + H_2O \rightarrow CH_3CH_2NH_3^+ (+) OH^-$	1
(ii)	ethylamine is <b>more basic</b> than ammonia because of electron-donating (alkyl/ethyl/R) group (in ethylamine)	2
	which makes the lone pair (on N) more available for donation	
	or the lone pair (on N) more available for a proton/H <sup>+</sup>	
(c) (i)	A solution which resists/minimises/roughly maintains changes in <u>pH</u> when (small amounts of) H <sup>+</sup> or OH <sup>-</sup> are added	1
(ii)	$CH_3NH_2 + H^+ \rightarrow CH_3NH_3^+$	2
	$CH_3NH_3Cl + OH \rightarrow CH_3NH_2 + H_2O + Cl$	
		[Total: 10]

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Question	Answer	Marks
4 (a) (i)	CI/////////NH <sub>3</sub> Pt CI	2
	(cis) (trans)	
(ii)	$cis$ is (more) polar due to both $Cl^{(\delta-)}$ on same side or $cis$ is (more) polar as dipoles do not cancel/unsymmetrical or trans is non-polar as it is bond dipoles cancel	1
(iii)	(This can only be <i>cis</i> ) its mirror image is the same/superimposable  or the distance between two coordinating nitrogens/oxygens is too small to bond <i>trans</i> or difficult for the NH <sub>2</sub> and O to change places (since 5-memebered rings can only bridge adjacent positions)	1
(b) (i)	It's not square planar <b>or</b> it's tetrahedral	1
(ii)	must be 3D structure (i.e. tetrahedral-like)  R <sub>3</sub> P—Ni  Or  R <sub>3</sub> P—Ni  CI  etc	1
		[Total: 6]

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Question	Answer	Marks
5 (a) (i)	$K_{\text{stab}} = \frac{[\text{Cd}(\text{CH}_3\text{NH}_2)_4^{2^+}]}{[\text{Cd}^{2^+}][\text{CH}_3\text{NH}_2]^4}$	2
	units: mol <sup>-4</sup> dm <sup>12</sup>	
(ii)	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2
	$9.99 \times 10^{-5} / (\mathbf{y}^4 \times 10^{-7}) = 3.6 \times 10^6$ and $y = \sqrt[4]{(9.99 \times 10^{-5})/(1 \times 10^{-7} \times 3.6 \times 10^6)} = \mathbf{0.129/0.13}$	
(b) (i)	(each complex is formed by) making (4 ×)N-Cd bonds and breaking (6 ×) O-Cd bonds or same types of/similar bonds forming/breaking or same number of bonds forming/breaking	1
(ii)	$\Delta S = (\Delta H - \Delta G)/T = (60.7 - 56.5) \times 1000/298 = (+)14/(+)14.1$	1
(iii)	fewer moles (of solutes) are forming (one mole of) the complex (so less loss of disorder) <b>or</b> one <b>en</b> displaces two H <sub>2</sub> O whereas one CH <sub>3</sub> NH <sub>2</sub> only displaces one H <sub>2</sub> O	1
(iv)	The $[Cd(H_2NCH_2CH_2NH_2)_2]^{2^+}$ / equilibrium 2 complex (is more stable) because: either $K_{\text{stab}}$ is greater or $\Delta G^{\text{e}}$ is more negative.	1
		[Total: 8]

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Question	Answer	Marks
6 (a)	essential mark M1 the reactants/substrate has a <b>shape</b> complementary/ <b>specific</b> to <u>active site</u> – can be awarded from a labelled diagram as below <b>or</b> diagrams showing this specificity clearly  any two of M2: reactants/substrate binds to/fits into the <u>active site</u> of the enzyme M3: (Interaction with site) causes a specific bond to be weakened, (which breaks)	3
	Fig. 6 (products)	
(b) (i)	$\delta$ 26 is <b>C</b> H3-CO $\delta$ 52 is <b>C</b> H3-O $\delta$ 169 is CH3 <b>CO</b> $\delta$ 167 is phenyl- <b>C</b> O  Phenyl ethanoate is <b>B</b> methyl benzoate is <b>A</b> M1 = any two correct $\delta$ linked to phenylethanoate/methyl benzoate  M2 = the rest correct	2
(ii)	heat with $H_3O^+$ (to hydrolyse the ester) then add $Br_2(aq)$ / bromine water decolourises/gives white ppt. (with phenol from <b>B</b> )	3
		[Total: 8]

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Question	Answer	Marks
7 (a) (i)	labelled with M1: DC power supply + and -/battery/cell/+ and - sign (on cell/electrodes) with a complete circuit	3
	M2: buffer solution/electrolyte labelled	
	M3: (amino acid) mixture/x on (filter) paper/gel/agarose	
	electrolyte  amiso acid mixture placed here  filter paper souked in buffer solution	
(ii)	direction of movement related to charge (of amino acids)  distance travelled depends on charge $/M_r$ (of amino acids)	2
(b) (i)	Asp + Val:  pH 12 because Asp will be -CH <sub>2</sub> COO <sup>-</sup> (R-group) moves further (to positive electrode than Val)  or pH 12 Asp more negative so moves further (to positive electrode)  or pH 12 because Asp has a charge of 2– but Val has a charge of 1–  or best at pH 7 because Asp will be negatively charged (anionic) but Val neutral	1
(ii)	Lys + Ser:  pH 2 because Lys will be (CH <sub>2</sub> ) <sub>4</sub> NH <sub>3</sub> <sup>+</sup> (R-group) moves further (to negative electrode than Ser)  or pH 2 Lys more positive so moves further (to negative electrode)  or pH 2 because Lys has a charge of 2+ and Ser has a charge of 1+  or pH 7 because Lys is positively charged (cationic) but Ser neutral/zwitterionic	1

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Question	Answer	Marks
(iii)	Tyr + Phe:  pH 12 because Tyr will be C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> O <sup>-</sup> (R-group) moves further/more/faster (to positive electrode than Phe)  or pH12 because Tyr has a charge of 2– but Phe has a charge of 1–	1
(c) (i)	M1: for -CONH- as shown above  M2: for rest of molecule <b>and</b> correct connectivity of the bonds	2
(ii)	from the IR spectrum  • E is O-H or N-H (allow NH <sub>2</sub> )  • F is C=O  • G is C-O	2
		[Total: 12]
8 (a)	M1: solubility increases (down the group)	3
	M2: because lattice energy decreases faster than does $\Delta \boldsymbol{H}_{\text{hyd}}$	
	M3: $\Delta H_{sol}$ / enthalpy of solution becomes more exothermic/less endothermic	
(b) (i)	Should be the same/similar (enthalpy change), as (both acids) are fully ionised/strong acids	1

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Question	Answer	Marks
(ii)		4
	Ca(s) + 2H <sup>+</sup> (aq) $\longrightarrow$ Ca <sup>2+</sup> (aq) + H <sub>2</sub> (g)	
	gas phase ions: Ca <sup>2+</sup> (g) + 2H <sup>+</sup> (g)	
	$\mathbf{x} = \Delta H_{at}(Ca) + IE(1) + IE(2) - 2\Delta \mathbf{H}_{hyd}(H^{+}) + \Delta \mathbf{H}_{hyd}(Ca^{2+}) - 2IE(H) - E(H-H)$	
	<b>x</b> = 178 + 590 + 1150 + 2(1090) - 1576 - 2(1310) - 436	
	$x = -534 \text{kJ mol}^{-1}$	
(c)	CH₃CO₂H is incompletely ionised/weak acid/weaker acid	2
	enthalpy change of ionisation (of CH₃COOH) is +2 kJ mol <sup>-1</sup>	
	or energy needed to ionise / dissociate (CH₃COOH)	
		[Total: 10]
9 (a)	OH CN CO <sub>2</sub> H	1

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Question	Answer	Marks
(b)	H is OH CO <sub>2</sub> H Or Or J1 J2	2
(c)	step 1: (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> Cl + AlCl <sub>3</sub> (+ heat)	6
	step 2: $CH_3COCl + AlCl_3$ (+ heat)	
	step 3: HCN + NaCN or HCN + base or HCN + CN	
	(steps 4 and 5 could be reversed on J)  If J1 step 4 then step 5 J2 step 5 then step 4	
	step 4: $H_3O^+$ + heat/aqueous $HCl$ + heat	
	step 5: conc H <sub>2</sub> SO <sub>4</sub> + heat/conc H <sub>3</sub> PO <sub>4</sub> + heat or Al <sub>2</sub> O <sub>3</sub> + heat	
	step 6: H <sub>2</sub> + Ni (+ heat)	
(d)	step 1: electrophilic substitution <i>or</i> alkylation	2
	step 6: reduction/hydrogenation/addition	
		[Total: 11]

Page 12	Mark Scheme	Syllabus	Paper
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Question	Answer	Marks
10 (a) (i)	Fe is3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>6</sup> 4s <sup>2</sup>	1
(ii)		1
(b)	$E^{\text{e}}$ values: $\text{Sn}^{4+}/\text{Sn}^{2+} = +0.15(\text{V})$ ; $\text{Fe}^{3+}/\text{Fe}^{2+} = +0.77(\text{V})$ or $E^{\text{e}}_{\text{cell}} = +0.62 \text{ (V)}$	2
	$(\operatorname{Sn}^{2^+} \operatorname{will} \operatorname{reduce} \operatorname{Fe}^{3^+}) \operatorname{Sn}^{2^+} + 2\operatorname{Fe}^{3^+}  o 2\operatorname{Fe}^{2^+}$	
(c) (i)	essential mark $K_{\text{stab}}/\text{stability}$ : $[\text{Fe}(\text{H}_2\text{O})_5\text{F}]^{2^+} > [\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^+$ $(>[\text{Fe}(\text{H}_2\text{O})_6]^{2^+})$	4
	$ \begin{array}{l} \textit{observations} \\ \textit{(violet)} \rightarrow \textit{deep-red} \\ \textit{(deep-red)} \rightarrow \textit{colourless} \end{array} $	
	(violet) → colourless which stays colourless/does not change	
(ii)	<u>ligand</u> displacement/exchange/substitution	1
		[Total: 9]