

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 ₃) ₂ .6H ₂ 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 ₃ ⁻	
(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)	$pK_a = -\log K_a$ or $K_a = 10^{-pKa}$	1

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Question	Answer	Marks
(ii)	ethanoic acid (1) is more acidic 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 more acidic than propanoic acid (2) due to electron-withdrawing/electronegative (C <i>l</i> /chlorine) atom	
	2-chloropropanoic acid (3) is more acidic than 3¬-chloropropanoic acid (4) since the C1/chlorine/electronegative atom is closer to the CO ₂ ¬/acid	
(c) (i)	H ₂ (g) Pt Cu Cu H ⁺ (aq) M1: voltmeter/V and salt bridge labelled M2: Cu and Cu ²⁺ /CuSO ₄ (any soluble Cu(II) salt) M3: H ₂ (arrow in) and H ⁺ /HC1/H ₂ SO ₄ /any mineral acid M4 Pt and one solution at 1 M/1 mol dm ⁻³ OR H ₂ at 1 atm	4
(ii)	$E_{\text{cell}}^{\text{e}} = 0.34 \text{ (V)}$ and $(Cu^{2+})/Cu$ is the positive electrode	1
d (i)	$K_{\rm a} = 1.23 \times 10^{-5}$ $[{\rm H^+}] = \sqrt{({\rm K_a.c})} = \sqrt{(1.23 \times 10^{-5} \times 0.1)} = 1.11 \times 10^{-3} {\rm mol dm^{-3}}$	2
	pH = 3.0 (2.96) ecf from [H ⁺]	

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Que	estion	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 (d)(i)	
			[Total: 14]
3 (a	a) (i)	(CH ₃) ₂ CHCN	1
	(ii)	reaction 1: NH ₃ (in ethanol) under pressure (+ heat) or heat NH ₃ in a sealed tube	3
		reaction 2: KCN/NaCN and heat/reflux (in ethanol)	
		reaction 3: H ₂ + Ni <i>or</i> LiA <i>l</i> H ₄	
(k	b) (i)	$CH_3CH_2NH_2 + H_2O \rightarrow CH_3CH_2NH_3^+ (+) OH^-$	1
	(ii)	ethylamine is more basic 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 ⁺	
(0	c) (i)	A solution which resists/minimises/roughly maintains changes in <u>pH</u> when (small amounts of) H ⁺ or OH ⁻ 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/// _{I/I} CI// _{I/I} CI// _{I/I} CI// _{I/I} NH ₃	2
	NH ₃ NH ₃ CI	
	(cis) (trans)	
(ii)	$m{cis}$ is (more) polar due to both $\mathrm{Cl}^{(\delta-)}$ on same side $m{or}$	1
	cis is (more) polar as dipoles do not cancel/unsymmetrical	
	or trans is non-polar as it is bond dipoles cancel	
(iii)	(This can only be <i>cis</i>) its mirror image is the same/superimposable	1
	 or the distance between two coordinating nitrogens/oxygens is too small to bond trans or difficult for the NH₂ and O to change places (since 5-memebered rings can only bridge adjacent positions) 	
(b) (i)	It's not square planar or it's tetrahedral	1
(ii)	must be 3D structure (i.e. tetrahedral-like) R ₃ P—Ni or R ₃ P—Ni etc CI CI CI CI CI CI CI CI CI PR ₃	1
		[Total: 6]

Page 6	Mark Scheme	Syllabus	Paper
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Question	Answer	Marks
5 (a) (i)	$K_{\text{stab}} = \frac{[Cd(CH_3NH_2)_4^{2+}]}{[Cd^{2+}][CH_3NH_2]^4}$	2
	units: mol ⁻⁴ dm ¹²	
(ii)	$Cd^{2^{+}} + 4CH_{3}NH_{2} \rightleftharpoons [Cd(CH_{3}NH_{2})_{4}]^{2^{+}}$ at start: 1×1^{-4}	2
	and $y = \sqrt[4]{(9.99 \times 10^{-5})/(1 \times 10^{-7} \times 3.6 \times 10^{6})} = 0.129/0.13$	
(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) or one <i>en</i> displaces two H ₂ O whereas one CH ₃ NH ₂ only displaces one H ₂ O	1
(iv)	The $[Cd(H_2NCH_2CH_2NH_2)_2]^{2^+}$ / equilibrium 2 complex (is more stable) because: either K_{stab} is greater or ΔG^{e} is more negative.	1
		[Total: 8]

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Question	Answer	Marks
6 (a)	essential mark M1 the reactants/substrate has a shape complementary/specific to active site — can be awarded from a labelled diagram as below or diagrams showing this specificity clearly any two of M2: reactants/substrate binds to/fits into the active site of the enzyme M3: (Interaction with site) causes a specific bond to be weakened, (which breaks) or lowers activation energy M4: forms an E-S complex M5: products released from enzyme/active site labelled diagrams	3
	(products)	
(b) (i)	δ 26 is CH 3-CO δ 52 is CH 3-O δ 169 is CH3 CO δ 167 is phenyl- CO Phenyl ethanoate is B methyl benzoate is A M1 = any two correct δ linked to phenylethanoate/methyl benzoate M2 = the rest correct	2
(ii)	heat with H ₃ O ⁺ (to hydrolyse the ester)	3
	then add Br ₂ (aq)/bromine water decolourises/gives white ppt. (with phenol from B)	
		[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 soaked in buffer solution	
(ii)	direction of movement related to charge (of amino acids)	2
(b) (i)	distance travelled depends on charge / M _r (of amino acids) Asp + Val: pH 12 because Asp will be -CH ₂ COO ⁻ (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 ₂) ₄ NH ₃ ⁺ (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 ₆ H ₅ CH ₂ O ⁻ (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 and correct connectivity of the bonds	2
(ii)	from the IR spectrum • E is O-H or N-H (allow NH ₂) • 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 $\Delta \pmb{H}_{\text{hyd}}$	
	$M3:\Delta H_{sol}$ / 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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Ques	stion	Answer	Marks
	(ii)	Ca(s) + 2H ⁺ (aq) \longrightarrow Ca ²⁺ (aq) + H ₂ (g)	4
		gas phase ions: Ca ²⁺ (g) + 2H ⁺ (g)	
		$\mathbf{x} = \Delta H_{at}(Ca) + IE(1) + IE(2) - 2\Delta H_{hyd}(H^{+}) + \Delta H_{hyd}(Ca^{2+}) - 2IE(H) - E(H-H)$	
		x = 178 + 590 + 1150 + 2(1090) - 1576 - 2(1310) - 436	
		$x = -534 \mathrm{kJ} \mathrm{mol}^{-1}$	
(c))	CH ₃ CO ₂ H is incompletely ionised/weak acid/weaker acid	2
		enthalpy change of ionisation (of CH ₃ COOH) is +2 kJ mol ⁻¹	
		or energy needed to ionise/dissociate (CH ₃ COOH)	
			[Total: 10]
9 (a))	OH CN CO ₂ H	1

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Question	Answer	Marks
(b)	H is OH CO ₂ H Or J1 J2	2
(c)	step 1: $(CH_3)_2CHCH_2Cl + AlCl_3$ (+ heat) step 2: $CH_3COCl + AlCl_3$ (+ heat)	6
	step 3: HCN + NaCN <i>or</i> HCN + base <i>or</i> 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 ₃ O ⁺ + heat/aqueous HC <i>l</i> + heat	
	step 5: conc H_2SO_4 + heat/conc H_3PO_4 + heat or Al_2O_3 + heat	
	step 6: H ₂ + 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 ² 3p ⁶ 3d ⁶ 4s ²	1
(ii)		1
(b)	E^{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)	ligand displacement/exchange/substitution	1
		[Total: 9]