
CHEMISTRY

9701/42

Paper 4 A Level Structured Questions

May/June 2016

MARK SCHEME

Maximum Mark: 100

Published

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Mark schemes should be read in conjunction with the question paper and the Principal Examiner Report for Teachers.

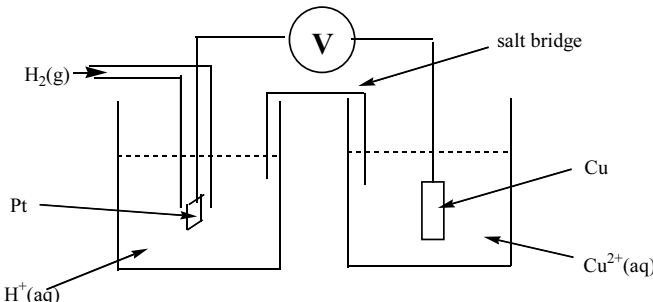
Cambridge will not enter into discussions about these mark schemes.

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Page 2	Mark Scheme	Syllabus	Paper
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Question	Answer	Marks
1 (a) (i)	dative (covalent) <i>or</i> coordinate Hydrogen/H (bonding)	2
(ii)	octahedral	1
(iii)	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{Mg}(\text{NO}_3)_2 + 6\text{H}_2\text{O}$ $\text{Mg}(\text{NO}_3)_2 \rightarrow \text{MgO} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2$ <p><i>any three of</i> (solid) dissolves/turns to liquid condensation on tube <u>white</u> solid (forms/remains) brown fumes (evolved) gas formed that relights a glowing splint</p>	4
(iv)	M_r values: $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} = 256.3$ $\text{MgO} = 40.3$ or (loss in molar mass = $256.3 - 40.3 = 216$) percentage loss = $100 \times 216 / 256.3 = \mathbf{84.3 / 84.4\%}$	2
(b)	(cat)-ionic radius / ion size increases (down the group) less polarisation / distortion of nitrate ion / NO_3^-	2
(c)	$2\text{AgNO}_3 \rightarrow 2\text{Ag} + 2\text{NO}_2 + \text{O}_2$	1
		[Total: 12]
2 (a) (i)	(an acid that is) partially / incompletely ionised / dissociated	1
(b) (i)	$\text{p}K_a = -\log K_a$ or $K_a = 10^{-\text{p}K_a}$	1


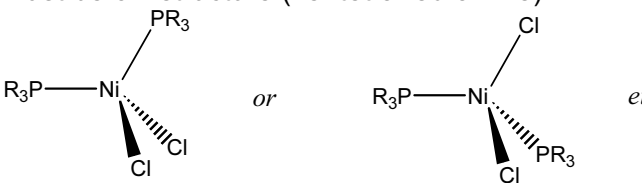
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Question	Answer	Marks
(ii)	<p>ethanoic acid (1) is more acidic than propanoic acid (2) due to smaller electron-donating (R/ alkyl) group/ less electron-donating (R/ alkyl) group(s)</p> <p>2-chloropropanoic acid (3) is more acidic than propanoic acid (2) due to electron-withdrawing/ electronegative (Cl/ chlorine) atom</p> <p>2-chloropropanoic acid (3) is more acidic than 3-chloropropanoic acid (4) since the Cl/ chlorine/ electronegative atom is closer to the CO_2^-/ acid</p>	3
(c) (i)	 <p>M1: voltmeter / V and salt bridge labelled</p> <p>M2: Cu and Cu^{2+} / CuSO_4 (any soluble Cu(II) salt)</p> <p>M3: H_2 (arrow in) and H^+ / HCl / H_2SO_4 / any mineral acid</p> <p>M4 Pt and one solution at 1 M / 1 mol dm^{-3} OR H_2 at 1 atm</p>	4
(ii)	<p>$E^\ominus_{\text{cell}} = 0.34 \text{ (V)}$ and $(\text{Cu}^{2+})/\text{Cu}$ is the positive electrode</p>	1
d (i)	<p>$K_a = 1.23 \times 10^{-5}$</p> <p>$[\text{H}^+] = \sqrt{K_a \cdot c} = \sqrt{(1.23 \times 10^{-5} \times 0.1)} = 1.11 \times 10^{-3} \text{ mol dm}^{-3}$</p> <p>pH = 3.0 (2.96) ecf from $[\text{H}^+]$</p>	2

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Question	Answer	Marks
(ii)	$E = 0.0 + 0.059\log(1.11 \times 10^{-3})$ OR $= -0.17(4)V$ so new $E_{\text{cell}} = 0.34 + 0.17 = \mathbf{0.51V}$ ecf from (d)(i)	2
		[Total: 14]
3 (a) (i)	$(\text{CH}_3)_2\text{CHCN}$	1
(ii)	reaction 1: NH_3 (in ethanol) under pressure (+ heat) or heat NH_3 in a sealed tube reaction 2: KCN/NaCN and heat/reflux (in ethanol) reaction 3: $\text{H}_2 + \text{Ni}$ or LiAlH_4	3
(b) (i)	$\text{CH}_3\text{CH}_2\text{NH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{NH}_3^+ (+) \text{OH}^-$	1
(ii)	ethylamine is more basic than ammonia... because of electron-donating (alkyl/ethyl/R) group (in ethylamine) which makes the <u>lone pair</u> (on N) more available for donation or the <u>lone pair</u> (on N) more available for a proton/ H^+	2
(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)	$\text{CH}_3\text{NH}_2 + \text{H}^+ \rightarrow \text{CH}_3\text{NH}_3^+$ $\text{CH}_3\text{NH}_3\text{Cl} + \text{OH}^- \rightarrow \text{CH}_3\text{NH}_2 + \text{H}_2\text{O} + \text{Cl}^-$	2
		[Total: 10]


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Question	Answer	Marks
4 (a) (i)	 <p>(cis) (trans)</p>	2
(ii)	<p>cis is (more) polar due to both Cl^(δ-) on same side or cis is (more) polar as dipoles do not cancel / unsymmetrical or trans is non-polar as its bond dipoles cancel</p>	1
(iii)	<p>(This can only be <i>cis</i>) its mirror image is the same / superimposable</p> <p>or the distance between two coordinating nitrogens / oxygens is too small to bond <i>trans</i> or difficult for the NH₂ and O to change places (since 5-membered rings can only bridge adjacent positions)</p>	1
(b) (i)	It's not square planar or it's tetrahedral	1
(ii)	<p>must be 3D structure (i.e. tetrahedral-like)</p>  <p><i>etc</i></p>	1
		[Total: 6]

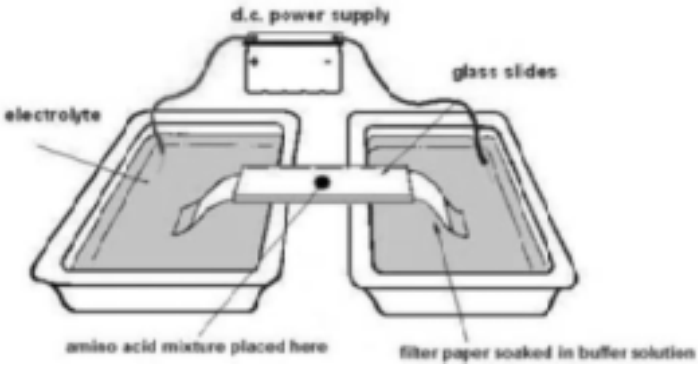
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Question	Answer	Marks
5 (a) (i)	$K_{\text{stab}} = \frac{[\text{Cd}(\text{CH}_3\text{NH}_2)_4^{2+}]}{[\text{Cd}^{2+}][\text{CH}_3\text{NH}_2]^4}$ units: $\text{mol}^{-4} \text{dm}^{12}$	2
(ii)	$\text{Cd}^{2+} + 4\text{CH}_3\text{NH}_2 \rightleftharpoons [\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}$ at start: 1×1^{-4} $\text{at eqm: } 1 \times 10^{-7} \qquad y \qquad \overset{0}{1 \times 10^{-4} - 1 \times 10^{-7}}$ $\text{or } 9.99 \times 10^{-5} \text{ or } 1.0 \times 10^{-4}$ $9.99 \times 10^{-5} / (y^4 \times 10^{-7}) = 3.6 \times 10^6$ and $y = \sqrt[4]{(9.99 \times 10^{-5}) / (1 \times 10^{-7} \times 3.6 \times 10^6)} = 0.129/0.13$	2
(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 en displaces two H_2O whereas one CH_3NH_2 only displaces one H_2O	1
(iv)	The $[\text{Cd}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]^{2+}$ / equilibrium 2 complex (is more stable) because: either K_{stab} is greater or ΔG^\ominus is more negative.	1
		[Total: 8]

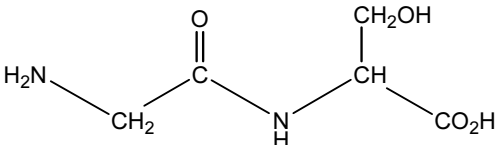
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Question	Answer	Marks
6 (a)	<p><i>essential mark</i></p> <p>M1 the reactants/substrate has a shape complementary/specific to active site – can be awarded from a labelled diagram as below or diagrams showing this specificity clearly</p> <p><i>any two of</i></p> <p>M2: reactants/substrate binds to/fits into the active site of the enzyme</p> <p>M3: (Interaction with site) causes a specific bond to be weakened, (which breaks) or lowers activation energy</p> <p>M4: forms an E-S complex</p> <p>M5: products released from enzyme/active site</p> <p>labelled diagrams</p>  <p style="text-align: right;">(products)</p>	3
(b) (i)	<p>δ 26 is CH₃-CO δ 52 is CH₃-O</p> <p>δ 169 is CH₃CO δ 167 is phenyl-CO</p> <p><u>Phenyl ethanoate</u> is B <u>methyl benzoate</u> is A</p> <p>M1 = any two correct δ linked to phenylethanoate/methyl benzoate</p> <p>M2 = the rest correct</p>	2
(ii)	<p>heat with H₃O⁺ (to hydrolyse the ester)</p> <p>then add Br₂(aq)/bromine water</p> <p>decolourises/gives white ppt. (with phenol from B)</p>	3
		[Total: 8]

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7 (a) (i)	<p>labelled with</p> <p>M1: <u>DC</u> power supply + and – / battery / cell / + and – sign (on cell / electrodes) with a complete circuit</p> <p>M2: buffer solution / electrolyte labelled</p> <p>M3: (amino acid) mixture / x on (filter) paper / gel / agarose</p> 	3
(ii)	<p>direction of movement related to charge (of amino acids)</p> <p>distance travelled depends on charge / M_r (of amino acids)</p>	2
(b) (i)	<p>Asp + Val:</p> <p>pH 12 because Asp will be $-\text{CH}_2\text{COO}^-$ (R-group) moves further (to positive electrode than Val)</p> <p>or pH 12 Asp more negative so moves further (to positive electrode)</p> <p>or pH 12 because Asp has a charge of 2– but Val has a charge of 1–</p> <p>or best at pH 7 because Asp will be negatively charged (anionic) but Val neutral</p>	1
(ii)	<p>Lys + Ser:</p> <p>pH 2 because Lys will be $(\text{CH}_2)_4\text{NH}_3^+$ (R-group) moves further (to negative electrode than Ser)</p> <p>or pH 2 Lys more positive so moves further (to negative electrode)</p> <p>or pH 2 because Lys has a charge of 2+ and Ser has a charge of 1+</p> <p>or pH 7 because Lys is positively charged (cationic) but Ser neutral / zwitterionic</p>	1

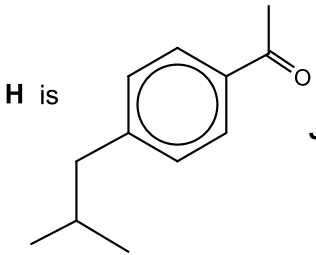
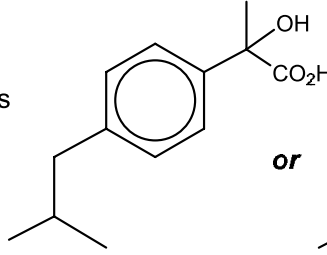
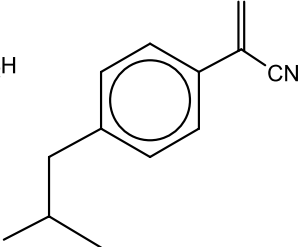
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Question	Answer	Marks
(iii)	Tyr + Phe: pH 12 because Tyr will be $\text{C}_6\text{H}_5\text{CH}_2\text{O}^-$ (R-group) moves further / more / faster (to positive electrode than Phe) or pH12 because Tyr has a charge of 2- but Phe has a charge of 1-	1
(c) (i)	 <p>M1: for $-\text{CONH}-$ as shown above</p> <p>M2: for rest of molecule and correct connectivity of the bonds</p>	2
(ii)	<i>from the IR spectrum</i> <ul style="list-style-type: none"> • E is O-H or N-H (allow NH_2) • F is C=O • G is C-O 	2
		[Total: 12]
8 (a)	<p>M1: solubility increases (down the group)</p> <p>M2: because lattice energy decreases faster than does ΔH_{hyd}</p> <p>M3: ΔH_{sol} / enthalpy of solution becomes more exothermic / less endothermic</p>	3
(b) (i)	Should be the same / similar (enthalpy change), as (both acids) are fully ionised / strong acids	1

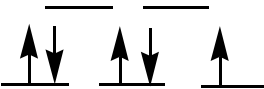
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Question	Answer	Marks
(ii)	$\text{Ca(s)} + 2\text{H}^+(\text{aq}) \longrightarrow \text{Ca}^{2+}(\text{aq}) + \text{H}_2(\text{g})$ <p>gas phase ions: $\text{Ca}^{2+}(\text{g}) + 2\text{H}^+(\text{g})$</p> $x = \Delta H_{\text{at}}(\text{Ca}) + \text{IE}(1) + \text{IE}(2) - 2\Delta H_{\text{hyd}}(\text{H}^+) + \Delta H_{\text{hyd}}(\text{Ca}^{2+}) - 2\text{IE}(\text{H}) - E(\text{H}-\text{H})$ $x = 178 + 590 + 1150 + 2(1090) - 1576 - 2(1310) - 436$ $x = -534 \text{ kJ mol}^{-1}$	4
(c)	<p>$\text{CH}_3\text{CO}_2\text{H}$ is incompletely ionised / weak acid / weaker acid</p> <p>enthalpy change of ionisation (of CH_3COOH) is $+2 \text{ kJ mol}^{-1}$</p> <p>or energy needed to ionise / dissociate (CH_3COOH)</p>	2
		[Total: 10]
9 (a)		1

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Question	Answer	Marks
(b)	<p>H is </p> <p>J is </p> <p><i>or</i> </p> <p>J1 J2</p>	2
(c)	<p>step 1: $(\text{CH}_3)_2\text{CHCH}_2\text{Cl} + \text{AlCl}_3$ (+ heat)</p> <p>step 2: $\text{CH}_3\text{COCl} + \text{AlCl}_3$ (+ heat)</p> <p>step 3: $\text{HCN} + \text{NaCN}$ <i>or</i> $\text{HCN} + \text{base}$ <i>or</i> $\text{HCN} + \text{CN}^-$</p> <p><i>(steps 4 and 5 could be reversed on J)</i> <i>If J1 step 4 then step 5 J2 step 5 then step 4</i></p> <p>step 4: H_3O^+ + heat / aqueous HCl + heat</p> <p>step 5: conc H_2SO_4 + heat / conc H_3PO_4 + heat <i>or</i> Al_2O_3 + heat</p> <p>step 6: $\text{H}_2 + \text{Ni}$ (+ heat)</p>	6
(d)	<p>step 1: electrophilic substitution <i>or</i> alkylation</p> <p>step 6: reduction / hydrogenation / addition</p>	2
		[Total: 11]

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10 (a) (i)	Fe is ...3s ² 3p ⁶ 3d ⁶ 4s ²	1
(ii)		1
(b)	<p>E^\ominus values: $\text{Sn}^{4+}/\text{Sn}^{2+} = +0.15(\text{V})$; $\text{Fe}^{3+}/\text{Fe}^{2+} = +0.77(\text{V})$</p> <p>or</p> <p>$E^\ominus_{\text{cell}} = +0.62(\text{V})$</p> <p>($\text{Sn}^{2+}$ will reduce Fe^{3+}) $\text{Sn}^{2+} + 2\text{Fe}^{3+} \rightarrow 2\text{Fe}^{2+}$</p>	2
(c) (i)	<p><i>essential mark</i></p> <p>K_{stab} / stability: $[\text{Fe}(\text{H}_2\text{O})_5\text{F}]^{2+} > [\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^+$ $(> [\text{Fe}(\text{H}_2\text{O})_6]^{2+})$</p> <p><i>observations</i></p> <p>(violet) → deep-red (deep-red) → colourless</p> <p>(violet) → colourless which stays colourless / does not change</p>	4
(ii)	ligand displacement / exchange / substitution	1
		[Total: 9]