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**CHEMISTRY**

**9701/42**

Paper 4 A Level Structured Questions

**May/June 2016**

MARK SCHEME

Maximum Mark: 100

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**Published**

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

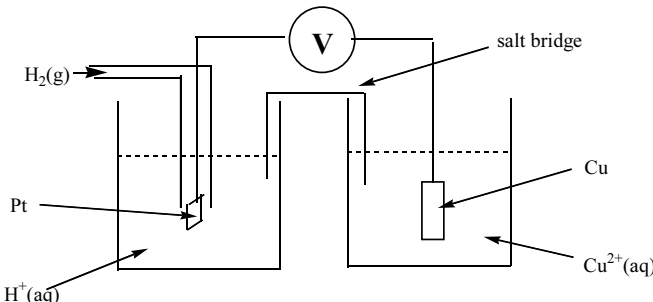
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<b>Question</b>	<b>Answer</b>	<b>Marks</b>
<b>1 (a) (i)</b>	dative (covalent) <i>or</i> coordinate Hydrogen/H (bonding)	2
<b>(ii)</b>	octahedral	1
<b>(iii)</b>	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{Mg}(\text{NO}_3)_2 + 6\text{H}_2\text{O}$ $\text{Mg}(\text{NO}_3)_2 \rightarrow \text{MgO} + 2\text{NO}_2 + \frac{1}{2}\text{O}_2$ <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
<b>(iv)</b>	$M_r$ values: $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} = 256.3$ $\text{MgO} = 40.3$ <b>or</b> (loss in molar mass = $256.3 - 40.3 = 216$ ) percentage loss = $100 \times 216 / 256.3 = \mathbf{84.3 / 84.4\%}$	2
<b>(b)</b>	(cat)-ionic radius / ion size <b>increases</b> (down the group) less polarisation / distortion of nitrate ion / $\text{NO}_3^-$	2
<b>(c)</b>	$2\text{AgNO}_3 \rightarrow 2\text{Ag} + 2\text{NO}_2 + \text{O}_2$	1
		<b>[Total: 12]</b>
<b>2 (a) (i)</b>	(an acid that is) partially / incompletely ionised / dissociated	1
<b>(b) (i)</b>	$\text{p}K_a = -\log K_a$ or $K_a = 10^{-\text{p}K_a}$	1


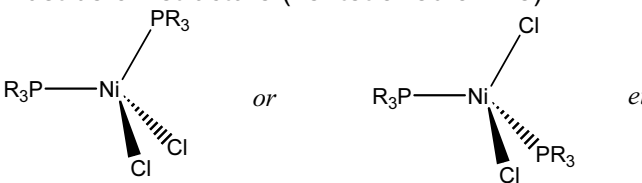
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Question	Answer	Marks
(ii)	<p>ethanoic acid (1) is <b>more acidic</b> than propanoic acid (2) due to smaller electron-donating (R/ alkyl) group/ less electron-donating (R/ alkyl) group(s)</p> <p>2-chloropropanoic acid (3) is <b>more acidic</b> than 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 <math>\text{CO}_2^-</math>/ acid</p>	3
(c) (i)	 <p>M1: voltmeter / V <b>and</b> salt bridge labelled</p> <p>M2: Cu <b>and</b> <math>\text{Cu}^{2+}</math> / <math>\text{CuSO}_4</math> (any soluble Cu(II) salt)</p> <p>M3: <math>\text{H}_2</math> (arrow in) and <math>\text{H}^+</math> / <math>\text{HCl}</math> / <math>\text{H}_2\text{SO}_4</math> / any mineral acid</p> <p>M4 Pt <b>and</b> one solution at 1 M / <math>1 \text{ mol dm}^{-3}</math> OR <math>\text{H}_2</math> at 1 atm</p>	4
(ii)	<p><math>E^\ominus_{\text{cell}} = 0.34 \text{ (V)}</math> <b>and</b> <math>(\text{Cu}^{2+})/\text{Cu}</math> is the positive electrode</p>	1
d (i)	<p><math>K_a = 1.23 \times 10^{-5}</math></p> <p><math>[\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}</math></p> <p>pH = <b>3.0 (2.96)</b> ecf from <math>[\text{H}^+]</math></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: $\text{NH}_3$ (in ethanol) under pressure (+ heat) or heat $\text{NH}_3$ in a sealed tube  reaction 2: KCN/NaCN <b>and</b> heat/reflux (in ethanol)  reaction 3: $\text{H}_2 + \text{Ni}$ or $\text{LiAlH}_4$	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 <b>more basic</b> 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  <b>or</b> the <u>lone pair</u> (on N) more available for a proton/ $\text{H}^+$	2
(c) (i)	A solution which resists/minimises/roughly maintains changes in <u>pH</u> when (small amounts of) $\text{H}^+$ or $\text{OH}^-$ 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><b>cis</b> is (more) <b>polar</b> due to both Cl<sup>(δ-)</sup> on same side  <b>or</b>  <b>cis</b> is (more) <b>polar</b> as dipoles do not cancel / unsymmetrical  <b>or</b>  <b>trans</b> is <b>non-polar</b> 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><b>or</b> the distance between two coordinating nitrogens / oxygens is too small to bond <i>trans</i>  <b>or</b> difficult for the NH<sub>2</sub> and O to change places (since 5-membered rings can only bridge adjacent positions)</p>	1
(b) (i)	It's not square planar <b>or</b> it's tetrahedral	1
(ii)	<p>must be 3D structure (i.e. tetrahedral-like)</p>  <p><i>or</i>                      <i>etc</i></p>	1
		[Total: 6]

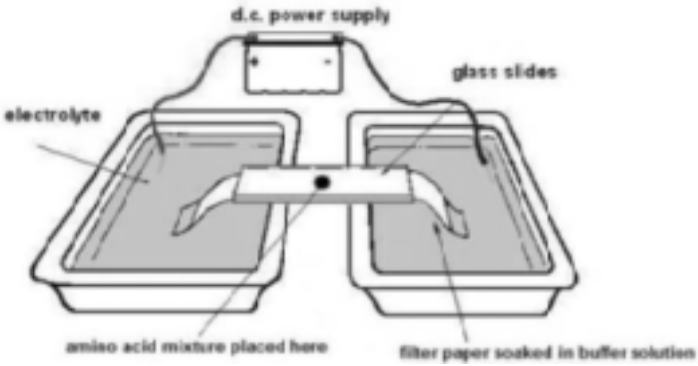
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<b>Question</b>	<b>Answer</b>	<b>Marks</b>
<b>5 (a) (i)</b>	$K_{\text{stab}} = \frac{[\text{Cd}(\text{CH}_3\text{NH}_2)_4^{2+}]}{[\text{Cd}^{2+}][\text{CH}_3\text{NH}_2]^4}$ units: $\text{mol}^{-4} \text{dm}^{12}$	2
<b>(ii)</b>	$\text{Cd}^{2+} + 4\text{CH}_3\text{NH}_2 \rightleftharpoons [\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}$ at start: $1 \times 1^{-4}$ at eqm: $1 \times 10^{-7}$ $y \qquad \qquad \qquad \text{0} \qquad \qquad \qquad 1 \times 10^{-4} - 1 \times 10^{-7}$ $\qquad \qquad \qquad \text{or } 9.99 \times 10^{-5} \text{ or } 1.0 \times 10^{-4}$ $9.99 \times 10^{-5} / (y^4 \times 10^{-7}) = 3.6 \times 10^6$ and $y = \sqrt[4]{(9.99 \times 10^{-5}) / (1 \times 10^{-7} \times 3.6 \times 10^6)} = \mathbf{0.129/0.13}$	2
<b>(b) (i)</b>	(each complex is formed by) making (4 ×) N-Cd bonds and breaking (6 ×) O-Cd bonds <b>or</b> same types of / similar bonds forming / breaking <b>or</b> same number of bonds forming / breaking	1
<b>(ii)</b>	$\Delta S = (\Delta H - \Delta G) / T = (60.7 - 56.5) \times 1000 / 298 = (+)14 / (+)14.1$	1
<b>(iii)</b>	fewer moles (of solutes) are forming (one mole of) the complex (so less loss of disorder) <b>or</b> one en 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
<b>(iv)</b>	The [Cd(H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> ) <sub>2</sub> ] <sup>2+</sup> / equilibrium 2 complex (is more stable) because: <i>either</i> $K_{\text{stab}}$ is greater or $\Delta G^\ominus$ is more negative.	1
		<b>[Total: 8]</b>

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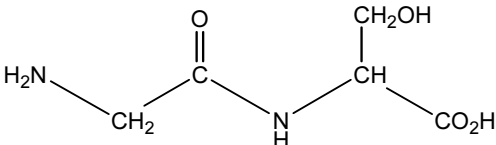
Question	Answer	Marks
6 (a)	<p><i>essential mark</i></p> <p>M1 the reactants/substrate has a <b>shape</b> complementary/<b>specific</b> to <b>active site</b> – can be awarded from a labelled diagram as below <b>or</b> diagrams showing this specificity clearly</p> <p><i>any two of</i></p> <p>M2: reactants/substrate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

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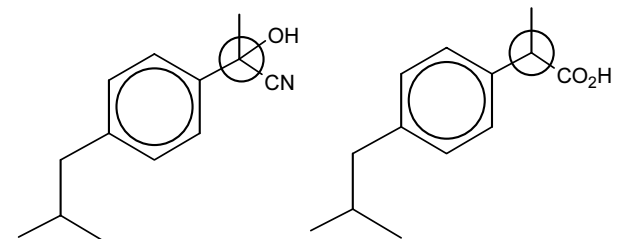
Question	Answer	Marks
7 (a) (i)	<p>labelled with</p> <p>M1: <u>DC</u> power supply + and – / battery / cell / + and – sign (on cell / electrodes) with a complete circuit</p> <p>M2: buffer solution / electrolyte labelled</p> <p>M3: (amino acid) mixture / x on (filter) paper / gel / agarose</p> 	3
(ii)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



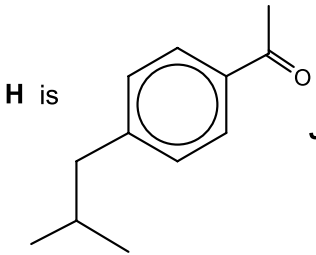
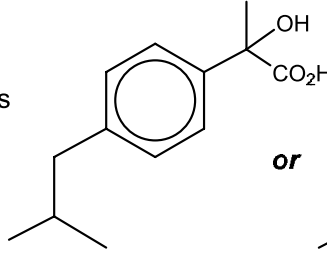
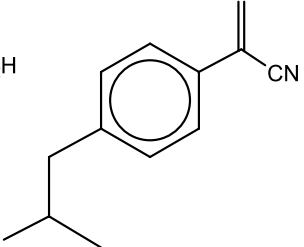
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Question	Answer	Marks
(iii)	Tyr + Phe: <b>pH 12</b> because Tyr will be $\text{C}_6\text{H}_5\text{CH}_2\text{O}^-$ (R-group) moves further / more / faster (to positive electrode than Phe) <b>or pH12</b> because Tyr has a charge of 2- but Phe has a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

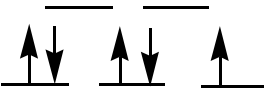
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(ii)	$\text{Ca(s)} + 2\text{H}^+(\text{aq}) \longrightarrow \text{Ca}^{2+}(\text{aq}) + \text{H}_2(\text{g})$  <p>gas phase ions: <math>\text{Ca}^{2+}(\text{g}) + 2\text{H}^+(\text{g})</math></p> $x = \Delta H_{\text{at}}(\text{Ca}) + \text{IE}(1) + \text{IE}(2) - 2\Delta H_{\text{hyd}}(\text{H}^+) + \Delta H_{\text{hyd}}(\text{Ca}^{2+}) - 2\text{IE}(\text{H}) - E(\text{H}-\text{H})$ $x = 178 + 590 + 1150 + 2(1090) - 1576 - 2(1310) - 436$ $x = -534 \text{ kJ mol}^{-1}$	4
(c)	<p><math>\text{CH}_3\text{CO}_2\text{H}</math> is incompletely ionised / weak acid / weaker acid</p> <p>enthalpy change of ionisation (of <math>\text{CH}_3\text{COOH}</math>) is <math>+2 \text{ kJ mol}^{-1}</math></p> <p>or energy needed to ionise / dissociate (<math>\text{CH}_3\text{COOH}</math>)</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><b>J1</b>                      <b>J2</b></p>	2
(c)	<p>step 1: <math>(\text{CH}_3)_2\text{CHCH}_2\text{Cl} + \text{AlCl}_3</math> (+ heat)</p> <p>step 2: <math>\text{CH}_3\text{COCl} + \text{AlCl}_3</math> (+ heat)</p> <p>step 3: <math>\text{HCN} + \text{NaCN}</math> <i>or</i> <math>\text{HCN} + \text{base}</math> <i>or</i> <math>\text{HCN} + \text{CN}^-</math></p> <p><i>(steps 4 and 5 could be reversed on J)</i>  <i><b>If J1</b> step 4 then step 5    <b>J2</b> step 5 then step 4</i></p> <p>step 4: <math>\text{H}_3\text{O}^+</math> + heat/aqueous <math>\text{HCl}</math> + heat</p> <p>step 5: conc <math>\text{H}_2\text{SO}_4</math> + heat/ conc <math>\text{H}_3\text{PO}_4</math> + heat  <i>or</i> <math>\text{Al}_2\text{O}_3</math> + heat</p> <p>step 6: <math>\text{H}_2 + \text{Ni}</math> (+ heat)</p>	6
(d)	<p>step 1: electrophilic substitution <i>or</i> alkylation</p> <p>step 6: reduction / hydrogenation / addition</p>	2
		<b>[Total: 11]</b>

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<b>Question</b>	<b>Answer</b>	<b>Marks</b>
<b>10 (a) (i)</b>	Fe is ...3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>6</sup> 4s <sup>2</sup>	1
<b>(ii)</b>		1
<b>(b)</b>	<p><math>E^\ominus</math> values: Sn<sup>4+</sup>/Sn<sup>2+</sup> = +0.15(V); Fe<sup>3+</sup>/Fe<sup>2+</sup> = +0.77(V)</p> <p><b>or</b></p> <p><math>E^\ominus_{\text{cell}} = +0.62</math> (V)</p> <p>(Sn<sup>2+</sup> will reduce Fe<sup>3+</sup>) Sn<sup>2+</sup> + 2Fe<sup>3+</sup> → 2Fe<sup>2+</sup></p>	2
<b>(c) (i)</b>	<p><i>essential mark</i></p> <p><math>K_{\text{stab}}</math> / stability: [Fe(H<sub>2</sub>O)<sub>5</sub>F]<sup>2+</sup> &gt; [Fe(H<sub>2</sub>O)<sub>5</sub>SCN]<sup>+</sup> (&gt; [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>)</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
<b>(ii)</b>	<b>ligand</b> displacement / exchange / substitution	1
		<b>[Total: 9]</b>