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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 Hydrogen / H (boding)	2
(ii)	octahedral	1
(iii)	$Mg(NO_3)_2.6H_2O \rightarrow Mg(NO_3)_2 + 6H_2O$ $Mg(NO_3)_2 \rightarrow MgO + 2NO_2 + \frac{1}{2}O_2$ *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	4
(iv)	M_r values: $Mg(NO_3)_2.6H_2O$ = 256.3 MgO = 40.3 **or** (loss in molar mass = 256.3 – 40.3 =) 216 percentage loss = 100 × 216 / 256.3 = **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)	$2AgNO_3 \rightarrow 2Ag + 2NO_2 + O_2$	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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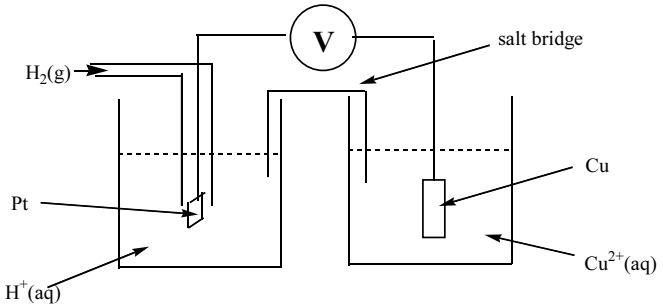
Question	Answer	Marks
(ii)	ethanoic acid (1) is **more acidic** than propanoic acid (2) due to smaller electron-donating (R / alkyl) group / less electron-donating (R / alkyl) group(s) 2-chloropropanoic acid (3) is **more acidic** than propanoic acid (2) due to electron-withdrawing / electronegative (C*l* / chlorine) atom 2-chloropropanoic acid (3) is more acidic than 3¬-chloropropanoic acid (4) since the C*l* / chlorine / electronegative atom is closer to the CO_2^- / acid	3
(c) (i)	 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^+ / HC*l* / H_2SO_4 / any mineral acid M4 Pt **and** one solution at 1 M / 1 mol dm^{-3} OR H_2 at 1 atm	4
(ii)	$E^{\ominus}_{cell}$ = 0.34 (V) **and** (Cu^{2+}) / Cu is the positive electrode	1
d (i)	$K_a = 1.23 \times 10^{-5}$ $[H^+] = \sqrt{(K_a.c)} = \sqrt{(1.23 \times 10^{-5} \times 0.1)} = 1.11 \times 10^{-3}$ mol dm^{-3} pH = **3.0 (2.96)** ecf from $[H^+]$	2

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Question	Answer	Marks
(ii)	E = 0.0 + 0.059log(1.11 × 10^{-3}) OR = –0.17(4)V so new E_{cell} = 0.34 + 0.17 = **0.51V** ecf from **(d)(i)**	2
		[Total: 14]
3 (a) (i)	$(CH_3)_2CHCN$	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: H_2 + Ni *or* LiAlH$_4$	3
(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) which makes the lone pair (on N) more available for donation **or** the lone pair (on N) more available for a proton / H^+	2
(c) (i)	A solution which resists / minimises / roughly maintains changes in pH when (small amounts of) H^+ or OH^- are added	1
(ii)	$CH_3NH_2 + H^+ \rightarrow CH_3NH_3^+$ $CH_3NH_3Cl + OH \rightarrow CH_3NH_2 + H_2O + Cl$	2
		[Total: 10]

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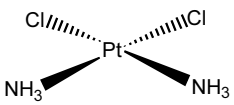
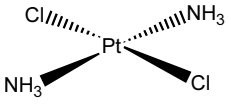
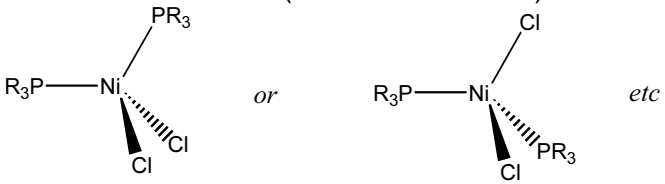
Question	Answer	Marks
4 (a) (i)	 (cis)  (trans)	2
(ii)	***cis*** is (more) **polar** due to both $Cl^{(\delta-)}$ on same side **or** ***cis*** is (more) **polar** as dipoles do not cancel / unsymmetrical **or** **trans** is **non-polar** as it is bond dipoles cancel	1
(iii)	(This can only be *cis*) its mirror image is the same / superimposable **or** the distance between two coordinating nitrogens / oxygens is too small to bond *trans* **or** difficult for the NH_2 and O to change places (since 5-memebered rings can only bridge adjacent positions)	1
(b) (i)	It's not square planar **or** it's tetrahedral	1
(ii)	must be 3D structure (i.e. tetrahedral-like)  *or* *etc*	1
		[Total: 6]

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Question	Answer	Marks
5 (a) (i)	$K_{stab} = \frac{[Cd(CH_3NH_2)_4^{2+}]}{[Cd^{2+}]\,[CH_3NH_2]^4}$ units: $mol^{-4}\,dm^{12}$	2
(ii)	$Cd^{2+} + 4CH_3NH_2 \rightleftharpoons [Cd(CH_3NH_2)_4]^{2+}$ at start: 1×1^{-4} **0** at eqm: 1×10^{-7} **y** **$1 \times 10^{-4} - 1 \times 10^{-7}$** **or 9.99×10^{-5} or 1.0×10^{-4}** $9.99 \times 10^{-5} / (\boldsymbol{y}^4 \times 10^{-7}) = 3.6 \times 10^6$ 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 $[Cd(H_2NCH_2CH_2NH_2)_2]^{2+}$ / equilibrium 2 complex (is more stable) because: *either* K_{stab} is greater or $\Delta G^{\ominus}$ 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  (products)	3
(b) (i)	δ 26 is **C**H3-CO δ 52 is **C**H3-O δ 169 is CH3**CO** δ 167 is phenyl-**C**O 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_3O^+ (to hydrolyse the ester) then add Br_2(aq) / bromine water decolourises/gives white ppt. (with phenol from **B**)	3
		[Total: 8]

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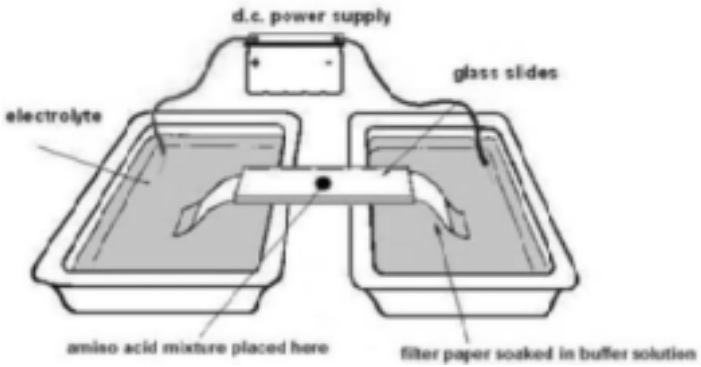
Question	Answer	Marks
7 (a) (i)	*labelled with* M1: DC power supply + and – / battery / cell / + and – sign (on cell / electrodes) with a complete circuit M2: buffer solution / electrolyte labelled M3: (amino acid) mixture / **x** on (filter) paper / gel / agarose  	3
(ii)	direction of movement related 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 $–CH_2COO^-$ (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 $(CH_2)_4NH_3^+$ (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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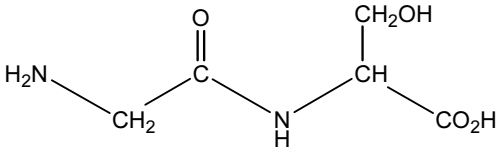
Question	Answer	Marks
(iii)	Tyr + Phe: **pH 12** because Tyr will be $C_6H_5CH_2O^-$ (R-group) moves further / more / faster (to positive electrode than Phe) **or pH12** because Tyr has a charge of 2– but Phe has a charge of 1–	1
(c) (i)	 M1: for –CONH– as shown above M2: for rest of molecule **and** 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) M2: because lattice energy decreases faster than does ΔH_{hyd} M3: ΔH_{sol} / enthalpy of solution becomes more exothermic / less endothermic	3
(b) (i)	Should be the same / similar (enthalpy change), as (both acids) are fully ionised / strong acids	1

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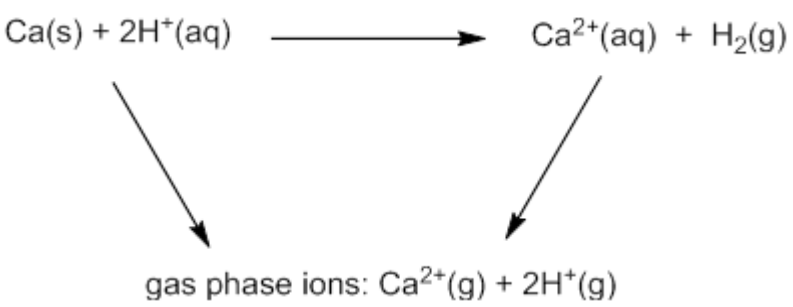
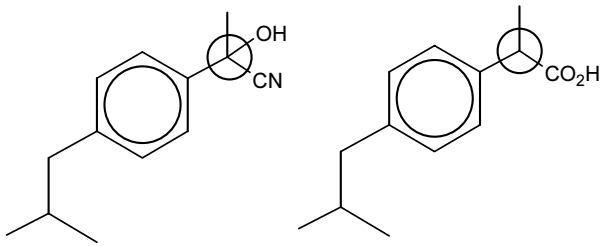
Question	Answer	Marks
(ii)	 $x = \Delta H_{at}(Ca) + IE(1) + IE(2) - 2\Delta H_{hyd}(H^+) + \Delta H_{hyd}(Ca^{2+}) - 2IE(H) - E(H\text{-}H)$ $x = 178 + 590 + 1150 + 2(1090) - 1576 - 2(1310) - 436$ $x = \mathbf{-534}\ kJ\ mol^{-1}$	4
(c)	CH_3CO_2H is incompletely ionised / weak acid / weaker acid enthalpy change of ionisation (of CH_3COOH) is $+2\ kJ\ mol^{-1}$ **or** energy needed to ionise / dissociate (CH_3COOH)	2
		[Total: 10]
9 (a)		1

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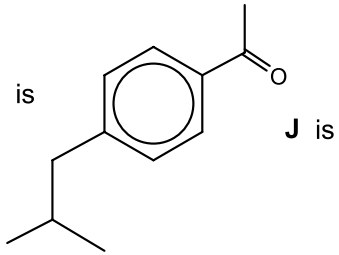
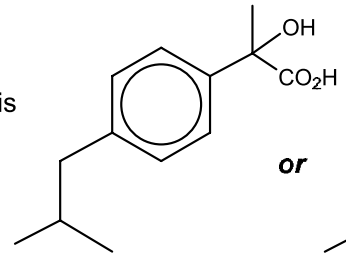
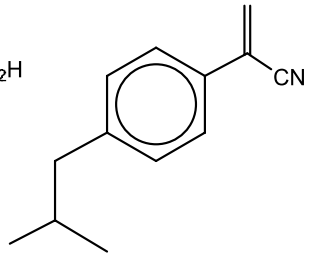
Question	Answer	Marks
(b)	**H** is  **J** is  ***or***  **J1** **J2**	2
(c)	step 1: $(CH_3)_2CHCH_2Cl$ + $AlCl_3$ (+ heat) step 2: CH_3COCl + $AlCl_3$ (+ heat) step 3: HCN + NaCN ***or*** HCN + base ***or*** HCN + CN^- *(steps 4 and 5 could be reversed on J)* ***If J1*** *step 4 then step 5* ***J2*** *step 5 then step 4* step 4: H_3O^+ + heat / aqueous HCl + heat step 5: conc H_2SO_4 + heat / conc H_3PO_4 + heat **or** Al_2O_3 + heat step 6: H_2 + Ni (+ heat)	6
(d)	step 1: electrophilic substitution ***or*** alkylation step 6: reduction / hydrogenation / addition	2
		[Total: 11]

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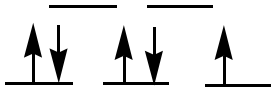
Question	Answer	Marks
10 (a) (i)	Fe is …$3s^2 3p^6 3d^6 4s^2$	1
(ii)		1
(b)	$E^\ominus$ values: Sn^{4+}/Sn^{2+} = +0.15(V); Fe^{3+}/Fe^{2+} = +0.77(V) **or** $E^\ominus_{cell}$ = +0.62 (V) (Sn^{2+} will reduce Fe^{3+}) $Sn^{2+} + 2Fe^{3+} \rightarrow 2Fe^{2+}$	2
(c) (i)	*essential mark* K_{stab} / stability: $[Fe(H_2O)_5F]^{2+} > [Fe(H_2O)_5SCN]^+$ $(> [Fe(H_2O)_6]^{2+})$ *observations* (violet) → deep-red (deep-red) → colourless (violet) → colourless which stays colourless / does not change	4
(ii)	**ligand** displacement / exchange / substitution	1
		[Total: 9]

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