## MARK SCHEME for the May/June 2012 question paper

## for the guidance of teachers

## 9791 CHEMISTRY

9791/03 Paper 3 (Part B Written), maximum raw mark 100

This mark scheme is published as an aid to teachers and candidates, to indicate the requirements of the examination. It shows the basis on which Examiners were instructed to award marks. It does not indicate the details of the discussions that took place at an Examiners' meeting before marking began, which would have considered the acceptability of alternative answers.

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Qı N	uestion umber	Answer	Max Marks
1	(a) (i)	Different structural forms of the same element (in the same physical state)	[1]
1	(a) (ii)	C–C <u>covalent</u> bond/shared electrons between C atoms in each layer (1) attraction between layers due to delocalised electrons/van der Waal's forces (1) covalent bonds <u>stronger</u> so carbons pulled closer together (1) Do not allow 'intermolecular'	[3]
1	(a) (iii)	Diamond hard due to (equal strength of) covalent bonds in <u>all</u> <u>directions/tetrahedral</u> (1)	
		but graphite soft due to weak (van der Waal's) forces between layers/allowing them to slide over each other (easily) (1) Allow explanation of softness of graphite in terms of air between layers.	
		Diamond doesn't conduct electricity as no mobile charge carriers (1), Graphite conducts due to mobile delocalised electrons between layers (1)	[4]
1	(b)	Carbon (as diamond) is a non–conductor, silicon and/or germanium is/are semi–conductors, tin and/or lead conduct electricity (1) (metals conduct electricity/non–metals are non–conductors) Oxide(s) of carbon are simple covalent/molecular AND Silicon dioxide (and germanium oxide) is giant covalent (1)	
		Oxides of tin and lead have (increasingly) ionic character (1)	[3]
1	(c)	Tin(II) less stable than tin(IV)/lead (IV) less stable than lead(II) (1) Lead(II) more stable than tin(II) (1)	[2]
			[Total: 13]

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Qı N	uestion umber	Answer	Max Marks
2	(a) (i)	$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$	[1]
2	(a) (ii)	$K_{\rm sp} = [{\rm Ba}^{2+}][{\rm SO}_4^{2-}]$	[1]
2	(a) (iii)	$[Ba^{2+}] = [SO_4^{2-}]$ so $K_{sp} = [SO_4^{2-}]^2 = 1.08 \times 10^{-10} (1)$ so $[SO_4^{2-}] = \sqrt{1.08 \times 10^{-10}} = 1.04 \times 10^{-5} (mol dm^{-3}) (1)$	[2]
2	(a) (iv)	$250 \mathrm{mg}\mathrm{dm}^{-3} = 0.250/96 = 2.604 \times 10^{-3} \mathrm{mol}\mathrm{dm}^{-3}$ (1)	
		So: $[SO_4^{2-}]$ in 500 cm <sup>3</sup> after mixing = 2.604 × 10 <sup>-3</sup> × 300/1000 × 1000/500 = 1.563 × 10 <sup>-3</sup> mol dm <sup>-3</sup> (1)	
		so $1.08 \times 10^{-10} = [Ba^{2+}] \times 1.563 \times 10^{-3}$ so $[Ba^{2+}] = 1.08 \times 10^{-10}/1.563 \times 10^{-3} = 6.918 \times 10^{-8} \text{ mol dm}^{-3} = [BaCl_2] \text{ in}$ 500 cm <sup>3</sup> mixture x 5/2 = 1.73 × 10 <sup>-7</sup> mol dm <sup>-3</sup> in original 200 cm <sup>3</sup> sample of BaCl_2 (1)	[3]
2	(b) (i)	Pt (s) (1) Ag <sup>+</sup> (aq) Ag(s) (1) H <sup>+</sup> (aq) = 1 mol dm <sup>-3</sup> (1)	[3]
2	(b) (ii)	[Ag <sup>+</sup> ] will fall so equilibrium Ag <sup>+</sup> + e <sup>-</sup> $\Rightarrow$ Ag moves to left (1) i.e. increase tendency to produce electrons (1)	[2]
2	(b) (iii)	$[Ag^{+}] = 1.8 \times 10^{-2}/2.1 = 8.6 \times 10^{-11} \text{ mol dm}^{-3}(1)$ $E = 0.8 - 0.03 \log (1/(8.6 \times 10^{-11})^{2}(1))$ = (+) 0.196 (1) ALLOW 0.20 V DO NOT ALLOW 0.2 V	[3]
			[Total: 15]

Page 4	Mark Scheme: Teachers' version	Syllabus	Paper
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Question Number	Answers	Max. Mark
3 (a)	1. Adsorption 2. Reaction 3. Desorption	[1]
3 (b) (i)	catalyst in same state as reactants	[1]
3 (b) (ii)	$E_{\text{cell}} = 2.01 - 0.54 = (+)1.47 \text{ V}$	[1]
3 (b)(iii)	$\Delta_{\rm r}G^{\rm e} = -{\rm nF}E^{\rm e} (1)$ = - 2 × 96500 × 1.47 (1) = - 283710 = - 283.7 kJ mol <sup>-1</sup> (1) Allow -284 kJ mol <sup>-1</sup>	[2]
3 (b)(iv)	(Large) negative value indicates favourable reaction/more negative than –60 suggests completion	[1]
3 (b) (v)	High activation energy (1) Repulsion between two negative species (1)	[2]
3 (b) (vi)	$\begin{array}{l} 2Fe^{2^{+}}+S_{2}O_{8}^{2^{-}} \rightarrow 2Fe^{3^{+}}+2SO_{4}^{2^{-}}(1)\\ 2\mathrm{I}^{-}+2Fe^{3^{+}} \rightarrow \mathrm{I}_{2}+2Fe^{2^{+}}\ (1)\\ \text{Reactions can happen in either order (so either $Fe^{2^{+}}$ or $Fe^{3^{+}}$ suitable)\ (1) \end{array}$	[3]
3 (c) (i)	Active site	[1]
3 (c) (ii)	Movement of a <u>pair</u> of electrons (resulting in formation or breaking of a covalent bond)	[1]
3 (c) (iii)	Low pH = high $[H^+]$ (1) so COO <sup>-</sup> in ASP would be protonated (and unable to accept H <sup>+</sup> from HIS) (1)	[2]
3 (c) (iv)	Plot of In[chymotrypsin] vs time being <u>straight</u> (confirms agreement with equation and hence first order kinetics) (1) Use of excess alkali means that [alkali] effectively constant (so doesn't affect rate) (1) Allow reference to constant gradient	[2]
	k = gradient = $\frac{(2.14 \times 10^{-5} - 1.14 \times 10^{-5})}{14000 - 2000}$ (1) = $\frac{1.00 \times 10^{-5}}{12000}$ = 8.33 × 10 <sup>-10</sup> (1) Allow calculation based on substitution into equation given Allow 8.25 - 8.33 × 10 <sup>-10</sup> Ignore units	[2]
		[Total: 19]

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Qı N	uestion umber	Answer	Max. Mark
4	(a)	Two C–O bonds broken and (1) Two C–N bonds formed (1) Both cations 2+ so similar enthalpy of hydration (1)	[max 2]
4	(b)	Positive value for 4.1 indicates feasible reaction/negative for 4.2 indicates unfeasible (1) 4.1 more positive than 4.2 as no. of moles increases (from 2 to 3 while in 4.2 no. of moles remains the same) (1)	[2]
4	(c) (i)	Geometric/cis-trans/E-Z	[1]
4	(c) (ii)	$\begin{bmatrix} OH_{2} \\ H_{2}O \\ OH_{2} \\ H_{3}N \\ OH_{2} \\ Cis \\ (1) \end{bmatrix}^{2+} \begin{bmatrix} OH_{2} \\ H_{3}N \\ OH_{2} \\ OH_{2} \\ OH_{2} \\ OH_{2} \end{bmatrix}^{2+} \begin{bmatrix} OH_{2} \\ H_{3}N \\ OH_{2} \\ OH_{2} \\ OH_{2} \\ OH_{2} \end{bmatrix}^{2+}$	[2]
4	(d) (i)	Optical	[1]
4	(d) (ii)	$\begin{array}{c c} H_2 H_2 N & & \\ N & & NH_2 \\ N & & & NH_2 \\ H_2 H_2 N & & & NH_2 \\ H_2 H_2 N & & & & H_2 \\ (1) & & & & NH_2 \\ (1) & & & & (1) \\ \end{array}$	[2]
			[Total: 10]

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Question Number	Answer	Max. Mark
5 (a)	1° alcohol (1) 2° alcohol (1) secondary/substituted amide (1) carboxylic acid (1) Allow one mark if unqualified 'alcohol' <b>and</b> 'amide' given	[4]
5 (b) (i)	$\begin{array}{ccc} OH & OH \\ & & \\$	[2]
5 (b) (ii)	Na <sup>+</sup> O <sup>-</sup> O <sup>-</sup> Na <sup>+</sup> NH O <sup>-</sup> O <sup>-</sup> Na <sup>+</sup> One mark is for BOTH 'alcoholic' O <sup>-</sup> Na <sup>+</sup> One mark is for 'carboxylic' O <sup>-</sup> Na <sup>+</sup>	[2]
5 (c) (i)	Circle round C attached to $-OH$ , $-CONHCH_2CH_2COOH$ , $-H$ and $-C(CH_3)_2CH_2OH$	[1]
5 (c) (ii)	(+) indicates that this enantiomer <u>rotates</u> plane polarised light clockwise (1) R (= <i>rectus</i> ) indicates that, if chiral centre is orientated such that lowest priority group (H) points away (1) then priority of remaining groups decreases in a clockwise direction $(-OH, -CONHCH_2CH_2COOH, -C(CH_3)_2CH_2OH)$ (1)	[3]
5 (d) (i)	$[H^{+}] = \sqrt{3.98 \times 10^{-5} \times 0.2} = 2.82 \times 10^{-3} \text{ mol dm}^{-3} (1)$ pH = $-\log_{10}[H^{+}] = -\log_{10} 2.82 \times 10^{-3} (1)$ = 2.55 (1)	[3]
5 (d) (ii)	-NHCO or N or O (in pantothenic acid) (1) exerts a –I effect (cf propanoic acid) (1) hence O–H in COOH weakened/COO <sup>–</sup> stabilised so dissociation greater (1)	[3]
5 (e) (i)	Right-hand C in pantothenic acid is carboxylic acid level but in pantothenol is alcohol level (1) Increase in FGL from pantothenol to pantothenic acid corresponds to oxidation (1)	[2]
5 (e) (ii)	CH <sub>3</sub> COOCH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH(OCOCH <sub>3</sub> )CONH(CH <sub>2</sub> ) <sub>3</sub> OCOCH <sub>3</sub>	[1]
5 (e) (iii)	C <sub>9</sub> H <sub>19</sub> NO <sub>4</sub> + 3 CH <sub>3</sub> COC $l$ → C <sub>15</sub> H <sub>25</sub> NO <sub>7</sub> + 3 HC $l$ 1 for species; 1 for balancing	[2]
		[Total: 23]

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Qı N	uestion umber	Answer	Max. Mark
6	(a)	C <sub>11</sub> H <sub>14</sub> O <sub>2</sub>	[1]
6	(b)	Structural/positional	[1]
6	(c)	3-phenylpropylethanoate	[1]
6	(d)	(Isomer 1) Singlet/integral 5 shows 5 Hs on phenyl group (1)	
		Integral 3 as 3Hs shows CH₃ group, (1) triplet as 2Hs on adjacent C (1)	
		3 × Integral 2 as 3 CH <sub>2</sub> groups (1) Quartet indicates 3Hs on adjacent C (1)	
		Only Isomer 1 has $CH_2$ adjacent to $CH_3/CH_3$ adjacent	
		Allow reference to fact that if isomer 2 then would have 2 singlets $\frac{1}{2}$	[6]
6	(e) (i)	$\begin{array}{ccccc} C & H & O \\ \underline{48.6} & \underline{8.11} & \underline{43.2} & (1) \\ \underline{4.05} & \underline{8.11} & \underline{2.70} \\ \underline{2.70} & \underline{2.70} & \underline{2.70} \end{array}$	
		1.50 3.00 1.00 3 6 2 hence $C_3H_6O_2$ (1)	[2]
6	(e) (ii)	From Mass Spec RFM = 74 EFM = 74 EFM = RFM so Empirical Formula = Molecular Formula	[1]
6	(e) (iii)	COOH <sup>+</sup> 1 mark for charge, 1 mark for formula. Allow one mark for '+' if m/z = 45	[2]
6	(e) (iv)	Due to Carbon–13 isotope (1) At approx 1% of abundance of carbon–12 isotope (1)	[2]
6	(f) (i)	C <sub>6</sub> H₅CH₂CH₂OH (1) Broad peak around 3300 cm <sup>-1</sup> indicates O–H group (1)	[2]
6	(f) (ii)	Will also have broad peak around 3300 cm <sup>-1</sup> due to O–H group (1) In addition will have peak around 1500–1900 due to C=O (1)	[2]
			[Total:20]