

Cambridge International Examinations Cambridge Pre-U Certificate

CHEMISTRY (PRINCIPAL)

Paper 3 Part B Written SPECIMEN MARK SCHEME 9791/03 For Examination from 2016

2 hours 15 minutes

MAXIMUM MARK: 100

The syllabus is approved for use in England, Wales and Northern Ireland as a Cambridge International Level 3 Pre-U Certificate.

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	Question Number		Answer		Max Marks
1	(a)	(i)	Different structural forms of the same element (in the same physical state)	(1)	[1]
		(ii)	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) Allow explanation of softness of graphite in terms of air between layers	(1)	
			Diamond doesn't conduct electricity as no mobile charge carriers, Graphite conducts due to mobile delocalised electrons between	(1)	
			layers	(1)	[4]
	(b)	(i)	<u>2-D/single</u> sheet of carbon atoms in <u>hexagonal rings</u>	(1)	[1]
		(ii)	weak van der Waals forces between graphene sheets in graphite	(1)	[1]
	(c)		Carbon (as diamond) is a non-conductor, silicon and/or germanium is/are semi-conductors, tin and/or lead conduct electricity (metals conduct electricity/non-metals are non-conductors)	(1)	
			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]
	(d)		Tin(II) less stable than tin(IV)/lead (IV) less stable than lead(II) Lead(II) more stable than tin(II)	(1) (1)	[2]
					[Total: 12]

	Question Number		Answer		Max Marks
2	(a)	(i)	$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$	(1)	[1]
		(ii)	$K_{\rm sp} = [{\rm Ba}^{2+}][{\rm SO}_4^{2-}]$	(1)	[1]
		(iii)	$[Ba^{2^+}] = [SO_4^{2^-}] \text{ so } K_{sp} = [SO_4^{2^-}]^2 = 1.08 \times 10^{-10}$ so $[SO_4^{2^-}] = \sqrt{1.08} \times 10^{-10} = \underline{1.04 \times 10^{-5}} \pmod{\text{m}^{-3}} (3 \text{ sf})$	(1) (1)	[2]
		(iv)	$250 \mathrm{mg}\mathrm{dm}^{-3} = \frac{0.250}{96} = 2.604 \times 10^{-3} \mathrm{mol}\mathrm{dm}^{-3}$	(1)	
			So: $[SO_4^{2^-}]$ in 500 cm ³ after mixing = 2.604 × 10 ⁻³ × 300/1000 × $\frac{1000}{50}$ = 1.563 × 10 ⁻³ mol dm ⁻³ so 1.08 × 10 ⁻¹⁰ = $[Ba^{2^+}]$ × 1.563 × 10 ⁻³ so $[Ba^{2^+}] = \frac{1.08 \times 10^{-10}}{1.563 \times 10^{-3}} = 6.918 \times 10^{-8} \text{ mol dm}^{-3}$	(1)	
			= [BaC l_2] in 500 cm ³ mixture × 5/2 = 1.73×10^{-7} mol dm ⁻³ in original 200 cm ³ sample of BaC l_2	(1)	[3]
	(b)	(i)	Pt (s) Ag⁺(aq) Ag(s) H⁺(aq) = <u>1</u> mol dm ⁻³	(1) (1) (1)	[3]
		(ii)	[Ag ⁺] will fall so eqm Ag ⁺ + e ⁻ \rightleftharpoons Ag moves to left E^{\ominus} falls (below 0.80V)	(1) (1)	[2]
		(iii)	$[Ag^{+}] = \frac{1.8 \times 10^{-10}}{2.1} = 8.6 \times 10^{-11} \text{ mol dm}^{-3}$ $E = 0.8 - 0.03 \log(1/(8.6 \times 10^{-11})^{2})$ = (+) 0.196 allow 0.20 V do not allow 0.2 V	(1) (1) (1)	[3]
					[Total: 15]

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	Question Number		Answer		Max Marks
3	(a)		1. Adsorption 2. Reaction 3. Desorption	(1)	[1]
	(b)	(i)	catalyst in same state as reactants	(1)	[1]
		(ii)	$E_{\text{cell}}^{\ominus}$ = 2.01 – 0.54 = (+)1.47 V	(1)	[1]
		(iii)	$\Delta_{\rm r}G^{\ominus} = -{\rm nF}E^{\ominus}$ = -2 × 96500 × 1.47 = -283710 = <u>-283.7</u> kJ mol ⁻¹ allow -284 kJ mol ⁻¹	(1) (1)	[2]
		(iv)	(Large) negative value indicates favourable reaction/more –ve than –60 suggests completion	(1)	[1]
		(v)	High activation energy Repulsion between two negative species	(1) (1)	[2]
		(vi)	$\begin{array}{l} 2Fe^{2^{+}}+S_2O_8^{2^{-}} \rightarrow 2Fe^{3^{+}}+2SO_4^{2^{-}}\\ 2I^-+2Fe^{3^{+}} \rightarrow I_2+2Fe^{2^{+}}\\ \text{Reactions can happen in either order (owtte) (so either $Fe^{2^{+}}$ or $Fe^{3^{+}}$ suitable) \end{array}$	(1) (1) (1)	[3]
	(c)	(i)	Active site	(1)	[1]
		(ii)	Movement of a <u>pair</u> of electrons (resulting in formation or breaking of a covalent bond)	(1)	[1]
		(iii)	Lewis base	(1)	[1]
		(iv)	Low pH = high [H ⁺] so COO ^{$-^-$} in ASP would be protonated (and unable to accept H ⁺ from HIS)	(1) (1)	[2]
		(v)	Plot of In[chymotrypsin] vs time being <u>straight</u> (confirms agreement with equation and hence first order kinetics) Use of excess alkali means that [alkali] effectively constant (so doesn't affect rate) Allow reference to constant gradient	(1) (1)	[2]
		(vi)	$k = \text{gradient} = \frac{2.14 \times 10^{-5} - 1.14 \times 10^{-5}}{14000 - 2000}$ $= \frac{1.00 \times 10^{-5}}{12000} = \frac{8.33 \times 10^{-10}}{12000}$	(1) (1)	[2]
			Allow $8.25 - 8.33 \times 10^{-10}$ Ignore units		[Total: 20]

Question Number	Answer		Max Marks
4 (a)	Two C-O bonds broken and Two C-N bonds formed Both cations 2+ so similar enthalpy of hydration	(1) (1) (1)	[max 2]
(b)	Positive value for reaction with 'en' indicates feasible reaction/negative for reaction with NH ₃ indicates unfeasible Reaction with 'en' more positive than with NH ₃ as no. of moles increases (from 2 to 3 while with NH ₃ no. of moles remains the	(1)	
	same)	(1)	[2]
(c) (i)	Geometric/cis-trans/E–Z	(1)	[1]
	$\begin{bmatrix} OH_2 \\ H_2O \\ H_3N \\ OH_2 \\ Cis \end{bmatrix}^{2+}$	(1)	[2]
	L 2 1 trans	(1)	[2]
(d) (i)	Optical	(1)	[1]
(ii)	$\begin{array}{c c} H_2 H_2 N & & \\ N & & NH_2 \\ \hline N & & Cu \\ H_2 H_2 N & & NH_2 \\ H_2 H_2 N & & NH_2 \\ \hline H_2 N & & NH_2 \\ \hline H_2 N & & NH_2 \\ \hline H_2 N & & H_2 \\ \hline H_2 N$	(1) (1)	[2]
			[Total: 10]

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

Question Number	Answer		Max Marks
6 (a)	C ₁₁ H ₁₄ O ₂	(1)	[1]
(b)	Structural/positional	(1)	[1]
(c)	3-phenylpropylethanoate	(1)	[1]
(d)	(Isomer 1) Singlet/integral 5 shows 5 Hs on phenyl group	(1)	
	Integral 3 as 3Hs shows CH_3 group, triplet as 2Hs on adjacent C	(1) (1)	
	$3 \times$ Integral 2 as 3 CH ₂ groups Quartet indicates 3Hs on adjacent C	(1) (1)	
	Only Isomer 1 has CH_2 adjacent to CH_3/CH_3 adjacent to CH_2 Allow reference to fact that if isomer 2 then would have 2 singlets	(1)	[6]
(e) (i)	$\begin{array}{cccccc} C & H & O \\ \underline{48.6} & \underline{8.11} & \underline{43.2} \\ 12 & 1 & 16 \\ \underline{4.05} & \underline{8.11} & \underline{2.70} \\ 2.70 & 2.70 & 2.70 \end{array}$	(1)	
	1.50 3.00 1.00 3 6 2 hence C ₃ H ₆ O ₂	(1)	[2]
(ii)	From Mass Spec RFM = 74 EFM = 74 EFM = RFM so Empirical Formula = Molecular Formula	(1)	[1]
(iii)	COOH ⁺ (1) for charge; (1) for formula Allow one mark for '+' if m/z = 45		[2]
(iv)	Due to carbon–13 isotope At approx 1% of abundance of carbon–12 isotope	(1) (1)	[2]
(f) (i)	$C_6H_5CH_2CH_2OH$ Broad peak around 3300 cm ⁻¹ indicates O–H group	(1) (1)	[2]
(ii)	Will also have very broad peak around 2500–3300 cm ⁻¹ due to O–H group In addition will have strong peak around 1640–1750 due to C=O	(1) (1)	[2]
			[Total: 20]

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