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Cambridge Pre-U Certificate

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CHEMISTRY (PRINCIPAL)

9791/03

Paper 3 Part B Written

For Examination from 2016

SPECIMEN MARK SCHEME

2 hours 15 minutes

MAXIMUM MARK: 100

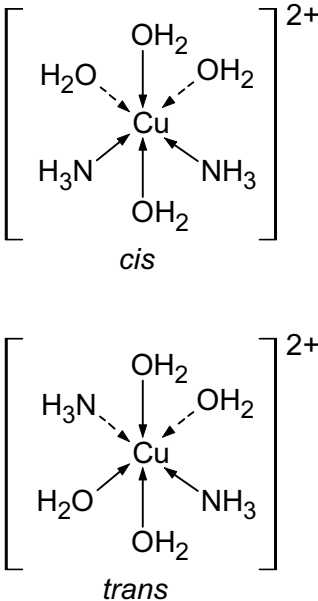
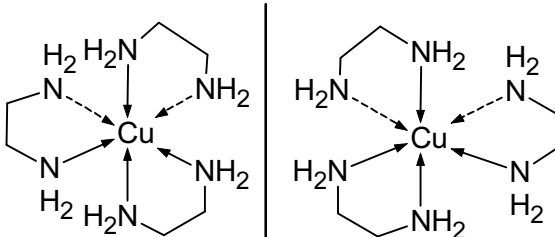
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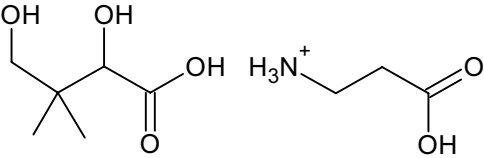
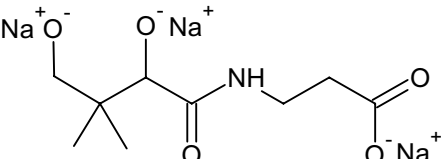
This document consists of 7 printed pages and 1 blank page.

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 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, Graphite conducts due to mobile delocalised electrons between layers (1) (1)	[4]
(b) (i)	<u>2-D/single</u> sheet of carbon atoms in <u>hexagonal rings</u> (1)	[1]
(ii)	<u>weak van der Waals</u> 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) (1) Lead(II) more stable than tin(II) (1)	[2]
		[Total: 12]

Question Number	Answer	Max Marks
2 (a) (i)	$\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$ (1)	[1]
(ii)	$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$ (1)	[1]
(iii)	$[\text{Ba}^{2+}] = [\text{SO}_4^{2-}]$ so $K_{\text{sp}} = [\text{SO}_4^{2-}]^2 = 1.08 \times 10^{-10}$ (1) so $[\text{SO}_4^{2-}] = \sqrt{1.08 \times 10^{-10}} = \underline{1.04 \times 10^{-5}} \text{ (mol dm}^{-3}\text{) (3 sf)}$ (1)	[2]
(iv)	$250 \text{ mg dm}^{-3} = \frac{0.250}{96} = 2.604 \times 10^{-3} \text{ mol dm}^{-3}$ (1) So: $[\text{SO}_4^{2-}]$ in 500 cm^3 after mixing $= 2.604 \times 10^{-3} \times 300/1000 \times \frac{1000}{50}$ $= 1.563 \times 10^{-3} \text{ mol dm}^{-3}$ (1) so $1.08 \times 10^{-10} = [\text{Ba}^{2+}] \times 1.563 \times 10^{-3}$ so $[\text{Ba}^{2+}] = \frac{1.08 \times 10^{-10}}{1.563 \times 10^{-3}} = 6.918 \times 10^{-8} \text{ mol dm}^{-3}$ $= [\text{BaCl}_2]$ in 500 cm^3 mixture $\times 5/2 = \underline{1.73 \times 10^{-7}} \text{ mol dm}^{-3}$ in original 200 cm^3 sample of BaCl_2 (1)	[3]
(b) (i)	Pt (s) (1) $\text{Ag}^+(\text{aq}) \text{Ag}(\text{s})$ (1) $\text{H}^+(\text{aq}) = \underline{1} \text{ mol dm}^{-3}$ (1)	[3]
(ii)	$[\text{Ag}^+]$ will fall so eqm $\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$ moves to left (1) E^\ominus falls (below 0.80V) (1)	[2]
(iii)	$[\text{Ag}^+] = \frac{1.8 \times 10^{-10}}{2.1} = 8.6 \times 10^{-11} \text{ mol dm}^{-3}$ (1) $E = 0.8 - 0.03 \log(1/(8.6 \times 10^{-11})^2)$ (1) $= (+) 0.196$ (1) allow 0.20V do not allow 0.2V	[3]
		[Total: 15]

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)	$E_{\text{cell}}^{\ominus} = 2.01 - 0.54 = (+)1.47 \text{ V}$ (1)	[1]
(iii)	$\Delta_r G^{\ominus} = -nFE^{\ominus}$ $= -2 \times 96500 \times 1.47$ (1) $= -283710 = \underline{-283.7 \text{ kJ mol}^{-1}}$ (1) allow -284 kJ mol^{-1}	[2]
(iv)	(Large) negative value indicates favourable reaction/more -ve than -60 suggests completion (1)	[1]
(v)	High activation energy (1) Repulsion between two negative species (1)	[2]
(vi)	$2\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{Fe}^{3+} + 2\text{SO}_4^{2-}$ (1) $2\text{I}^- + 2\text{Fe}^{3+} \rightarrow \text{I}_2 + 2\text{Fe}^{2+}$ (1) Reactions can happen in either order (owtte) (so either Fe^{2+} or Fe^{3+} suitable) (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 $[\text{H}^+]$ (1) so COO^- in ASP would be protonated (and unable to accept H^+ from HIS) (1)	[2]
(v)	Plot of $\ln[\text{chymotrypsin}]$ 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]
(vi)	$k = \text{gradient} = \frac{2.14 \times 10^{-5} - 1.14 \times 10^{-5}}{14000 - 2000}$ (1) $= \frac{1.00 \times 10^{-5}}{12000} = \underline{8.33 \times 10^{-10}}$ (1) Allow $8.25 - 8.33 \times 10^{-10}$ Ignore units	[2]
		[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 same)	(1) (1) [2]
(c) (i)	Geometric/ <i>cis-trans</i> / <i>E-Z</i>	(1) [1]
(ii)		(1) (1) [2]
(d) (i)	Optical	(1) [1]
(ii)	 <p>Ignore charges</p>	(1) (1) [2]
		[Total: 10]

Question Number	Answer	Max Marks
5 (a)	1° alcohol (1) 2° alcohol (1) Secondary/substituted amide (1) Carboxylic acid (1) Allow one mark if unqualified 'alcohol' and 'amide' given	[4]
(b) (i)	 <p>(1) (1)</p>	[2]
(ii)	 <p>(1) for BOTH 'alcoholic' O⁻Na⁺ (1) for 'carboxylic' O⁻Na⁺</p>	[2]
(c) (i)	Circle round C attached to –OH, –CONHCH ₂ CH ₂ COOH, –H and –C(CH ₃) ₂ CH ₂ OH (1)	[1]
(ii)	(+) indicates that this enantiomer <u>rotates</u> plane polarised light clockwise (1) <i>R</i> (= <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 ₂ CH ₂ COOH, –C(CH ₃) ₂ CH ₂ OH) (1)	[3]
(d) (i)	[H ⁺] = $\sqrt{3.98 \times 10^{-5} \times 0.2} = 2.82 \times 10^{-3} \text{ mol dm}^{-3}$ (1) pH = $-\log_{10}[\text{H}^+] = -\log_{10} 2.82 \times 10^{-3}$ (1) = 2.55 (1)	[3]
(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 ⁻ stabilised so dissociation greater (1)	[3]
(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]
(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 COCl → C ₁₅ H ₂₅ NO ₇ + 3 HCl (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 (1) Quartet indicates 3Hs on adjacent C (1) Only Isomer 1 has CH_2 adjacent to CH_3/CH_3 adjacent to CH_2 (1) Allow reference to fact that if isomer 2 then would have 2 singlets (1)	[6]																												
(e) (i)	<table style="margin-left: auto; margin-right: auto;"> <tr> <td>C</td> <td>H</td> <td>O</td> <td></td> </tr> <tr> <td><u>48.6</u></td> <td><u>8.11</u></td> <td><u>43.2</u></td> <td></td> </tr> <tr> <td>12</td> <td>1</td> <td>16</td> <td></td> </tr> <tr> <td><u>4.05</u></td> <td><u>8.11</u></td> <td><u>2.70</u></td> <td></td> </tr> <tr> <td>2.70</td> <td>2.70</td> <td>2.70</td> <td></td> </tr> <tr> <td>1.50</td> <td>3.00</td> <td>1.00</td> <td></td> </tr> <tr> <td>3</td> <td>6</td> <td>2</td> <td>hence $C_3H_6O_2$</td> </tr> </table> (1) (1)	C	H	O		<u>48.6</u>	<u>8.11</u>	<u>43.2</u>		12	1	16		<u>4.05</u>	<u>8.11</u>	<u>2.70</u>		2.70	2.70	2.70		1.50	3.00	1.00		3	6	2	hence $C_3H_6O_2$	[2]
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(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 (1) At approx 1% of abundance of carbon-12 isotope (1)	[2]																												
(f) (i)	$C_6H_5CH_2CH_2OH$ (1) Broad peak around 3300 cm^{-1} indicates O-H group (1)	[2]																												
(ii)	Will also have very broad peak around $2500\text{--}3300\text{ cm}^{-1}$ due to O-H group (1) In addition will have strong peak around $1640\text{--}1750$ due to C=O (1)	[2]																												
		[Total: 20]																												

