

UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS Pre-U Certificate

MARK SCHEME for the May/June 2010 question paper

for the guidance of teachers

9791 CHEMISTRY

9791/03

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

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Question Number	Expected Answer	Max Marks	Rationale
1 (a) (i)	(A and B) $H^+ + CO_3^{2-} \rightarrow HCO_3^{-}$	1	1/2 for overall equation
(ii)	(C and D) $HCO_3^- + H^+ \rightarrow H_2O + CO_2$	1	1/2 for both non-ionic
(b) (i)	methyl yellow	1	
(ii)	pK_a of indicator matches pH change at equivalence	1	allow pK_a on vertical section of graph owtte
(iii)	from Yellow to Red	1	
(c)	$\begin{array}{l} 18.8 \times 0.200 \ / \ 1000 = 3.76 \times 10^{-3} \ \text{mol of HNO}_3 \\ \text{so amount Na}_2\text{CO}_3 = 3.76 \times 10^{-3} \ / \ 2 = 1.88 \times 10^{-3} \ \text{mol of so conc} = 1.88 \times 10^{-3} \times 1000 \ / \ 20 = 0.094 \ \text{mol dm}^{-3} \\ = 0.094 \times 106 = 9.964 \ \text{g dm}^{-3} \end{array}$	1 1 1	allow 9.96 do not allow 10/10.0 ecf ecf
(d) (i)	$H_2O \rightleftharpoons H^+ + OH^- / 2H_2O \rightleftharpoons H_3O^+ + OH^-$	1	
(ii)	$K_c = [H^+][OH^-]/[H_2O]$ [H ₂ O] const negligible dissociation / equilibrium left	1 1 1	allow water is in large excess
(iii)	$[H^+] = \sqrt{51.3 \times 10^{-14}} = 7.16 \times 10^{-7} \text{ (mol dm}^{-3}\text{)}$ pH = -log 7.16 × 10 ⁻⁷ = 6.15	1 1+1	allow 6.14
(iv)	(endothermic) [H ⁺] higher at higher temperature so equilibrium moves right with increased temperature / increased temperature favours endothermic change	1 1	allow ecf from (d)(iii)

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(e)	5 × 1 / 1000 = 5 × 10 ⁻³ mol of H		1				
	$0.1 \times 1.00 \times 10^{-4} = 1 \times 10^{-5} \text{ mol}$ $1 \times 10^{-5} + 5 \times 10^{-3} \text{ in } 105 \text{ cm}^{3}$ $= 5.01 \times 10^{-3} / 0.105 = 0.0477 \text{ n}$		1				
	pH = -log 0.0477 = 1.32		1	1.32 = 4 m	arks		
	calculation of initial pH = 4.77 after addition of HCl; 0.01 + 5 ×	10 ⁻³ = 0.015 mol	1				
	= $0.015 \times 1000 / 105 = 0.143$ m and $0.01 - 5 \times 10^{-3} = 0.005$ mo	lol dm⁻³ CH₃COOH	1				
	= 0.005 × 1000 / 105 = 0.0476 pH = pK _a – log [acid] / [salt]	mol dm ⁻³ CH ₃ COO ⁻	1				
	= 4.77 – log 0.143 / 0.0476	= 4.17	1	4.17 = 4 m	arks		
			[25]				

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2 (a)) (i)	high temperature and ethanol as solvent	2	one mark for each solvent and third mark for any appropriate mention of temperature
	(ii)	(lower temperature) and water as solvent	1	
(b)	(b) (i) molecule with <u>non-superimposable mirror-image</u> form / molecule with <u>4 different groups</u> attached to the <u>same (C)</u> atom / no plane of symmetry		1	do not allow molecules allow atoms in place of groups
	(ii) equimolar mixture of two enantiomers / optical isomers		1	
	(iii)	<u>stereoisomers</u> that are <u>not enantiomers</u> / non- superimposable mirror images	1	
	(iv)	$\begin{array}{cccc} Br & Br \\ & & \\ H_{3}C & H_{2}CH_{3} & H_{3}C \cdot CH_{2} \\ \end{array} CH_{2}CH_{3} & H_{3}C \cdot CH_{2} \\ \end{array} CH_{3} \\ \end{array}$	2	
(c)) (i)	$HO_{H_3C} \xrightarrow{Br_1}_{CH_2CH_3} \xrightarrow{OH}_{H_3C} \xrightarrow{OH}_{H_1 \text{ for inverted}}_{H_1 \text{ for inverted}}$	4	
	(ii)	S-(+)-butan-2-ol	2	R-(+)- butan-2-ol/S-(-)-butan-2-ol/S-(+)-propan-2-ol all = 1/2

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(d) (i)	RX = 1 st order: Expt 1 to 2 [RX] ×3 = rate ×3 so directly	1	
(ii)	proportional	1	
(iii)	(iii) $OH^- = 1^{st}$ order: Expt 1 to 3 doubling [RX] would double rate to 8.0×10^{-4} so doubling again due to doubling [OH ⁻] so also directly proportional (2) rate = k[RX][OH ⁻] (ecf) (1) $4.0 \times 10^{-4} = k \times 0.050 \times 0.10$ (1) $k = 4.0 \times 10^{-4}/0.005 = 0.08$ (1) dm ³ mol ⁻¹ s ⁻¹ (1)		
(iv)	Br or Br	1	
		[23]	

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3	(a)	(i)	for CO change is from 2 moles of gas to 1 mole gas and 1 mole solid whereas for SiO change is from 2 moles of gas to 2 moles of solid owtte decrease in <u>disorder</u> / <u>randomness</u> is greater with SiO	1 1	
		(ii)	2 moles of solid produce 2 moles of solid owtte very little change in disorder	1 1	
	(b)	(i)	$\Delta_{\rm r}S = \Sigma S_{\rm products} - \Sigma S_{\rm reactants} = (31.1 + 55.3) - (2 \times 50) = -13.4 (J K^{-1} mol^{-1})$	2	+36.4 = 1/2 (not x2) -29.5 = 1/2 (reversed 55.3 and 55)
		(ii)	$\Delta_{\rm r}G^{\circ} = \Delta H - T\Delta S = -126.8 - (298 \times -3.4 / 1000)$ = -122.8 (kJ mol ⁻¹) (-22800 J mol ⁻¹)	2	-118 ecf from 36.4 / -137.6 ecf from -29.5 allow -123 do not allow -122 units not required but must be consistent
	(c)	(i)	$\Delta_{\rm r}G^{\circ} = -\text{RTIn}K_{\rm p} \text{ so } \ln\text{K}_{\rm p} = \Delta_{\rm r}G^{\circ} / -\text{RT}$ = -120.1 × 10 ⁻³ / (-8.31 × 298) = 48.50 so K_{\rm p} = 1.15 × 10^{21}	2	$3.72 \times 10^{21} = 1 / 2$ (used 122.8 from 3(b)(ii)) 1.05 = 1 / 2 (no × 10 ³ ignore units
		(ii)	$\Delta_r G^{\diamond} = 0 = \Delta H - T\Delta S$ so $\Delta H = T\Delta S$ and $T = \Delta H / \Delta S$ = -172500/-175.9 = 980.7 K	2	allow 981 K
		(iii)	activation energy / kinetic barrier too high	1	
				[13]	

		Page 7	Mark Scheme: Teac	hers' versi	on	Syllabus	Paper	
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4 (a)	$\begin{array}{c cccc} Pt & I \\ \underline{40.37} & \underline{52.59} \\ 195 & 127 \\ \underline{0.207} & \underline{0.414} \\ 0.207 & 0.207 \\ 1.00 & 2.00 \\ so \ EF = PtI_2N_2 \end{array}$	$\begin{array}{c} \underline{0.414}\\ 0.207\\ 2.00\\ 5.99 \end{array} \qquad \begin{array}{c} \underline{1.24}\\ 0.207\\ 5.99 \end{array}$	(1) (1) $M_r \text{ so MF} = PtI_2N_2H_6 (1)$ NH_3 (1) and trans (1) I	5	must see li	ink of EFM to RF	=M	
	bond Angle = 9	90°		1	ecf			
(b)	(octahedral) e. (tetrahedral) e.		gle = 90° gle = 109–110°	3		s needed for thi doesn't exist	rd mark	
(c)	lobes of three of results in split of	orbitals directed be of energy levels of	ng cartesian axes etween cartesian axes ⁻ d orbitals orbitals <u>absorbs</u> in visible	1 1 1				
				[13]				

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5	(a)		C ₆ H ₇ NO ₂	1	
	(b)		x = 120° y = 104.5°	2	allow 104 – 105 for y
	(c)		1 = carboxylic Acid Level2 = hydrocarbon Level3 = carboxylic Acid Level	2	three = 2 two = 1
	(d)	(i)	donates pair of electrons to form covalent bond	1 + 1	
		(ii) H $CO_2C_2H_5$ H $CO_2C_2H_5$ H $CO_2C_2H_5$ -C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C			
	(e)		$ \begin{array}{l} \mathbf{Q} = CH_2 = C(CH_2NH_2)CH_2OH \\ \mathbf{R} = CH_3CH_2OH \\ \mathbf{S} = CH_2 = C(CH_2NHOCCH_3)CH_2OCOCH_3 \\ \mathbf{T} = CH_3CH_2OCOCH_3 \\ \mathbf{U} = CH_3CH(CH_2NH_2)CO_2CH_2CH_3 \\ \hline \mathbf{Reactions of } \mathbf{Q} \text{ and } \mathbf{R} \text{ with ethanoyl chloride:} \\ 2:1 \text{ ratio with } \mathbf{Q} \text{ as both } NH_2 \text{ and OH acylated} \\ 1:1 \text{ ratio with } \mathbf{R} \text{ as only one OH group acylated (1)} \\ \hline \text{Reaction with } NH_2 \text{ produces (secondary) amide (+HCl) (1)} \\ \hline \text{Reaction with OH produce ester (+HCl) (1)} \\ \hline \frac{1}{H} \text{ NMR of } \mathbf{T} \text{ :} \\ \text{three signals indicate / due to 3 H environments (1)} \\ \text{triplet } (\mathbf{@} \sim 4.1 \text{ is protons on } CH_3 \text{ adj to } CH_2 (1) \\ \text{quartet } (\mathbf{@} \sim 4.1 \text{ is protons on } CH_3 \text{ on } C=O (1) \\ \hline \frac{1^3C}{1^3C} \text{ NMR of } \mathbf{T} \text{ :} \\ \text{two signals near } 20 = Cs \text{ in the two } CH_3 \text{ groups (1)} \\ \text{signal at } \sim 60 \text{ is } C \text{ in } CH_2 (1) \\ \text{signal at } \sim 170 \text{ is } C \text{ in } C=O (1) \\ \hline \frac{1}{H} \text{ NMR of } \mathbf{U} \text{ :} \\ \text{six signals indicate / due to 6 H environments (1)} \\ \text{disappearing signal due to } \underline{labile \text{ protons on } NH_2 (2) \\ \end{array}$	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	do not allow 'peptide' ¹ H NMR marks are independent of structures drawn except first mark ¹³ C NMR marks are independent of structures drawn
				[26]	