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

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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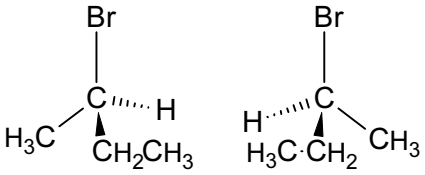
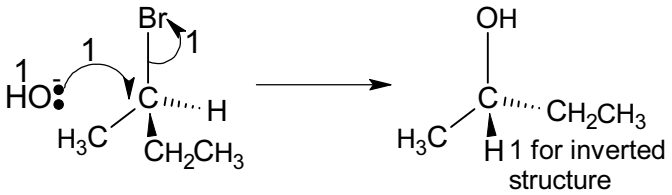
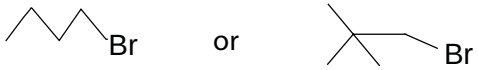
UNIVERSITY of CAMBRIDGE
International Examinations

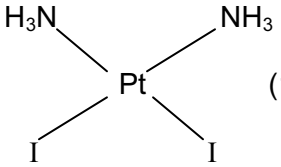
Question Number	Expected Answer	Max Marks	Rationale
1 (a) (i)	(A and B) $H^+ + CO_3^{2-} \rightarrow HCO_3^-$	1	1/2 for overall equation
(ii)	(C and D) $HCO_3^- + H^+ \rightarrow H_2O + CO_2$	1	1/2 for both non-ionic
(b) (i)	methyl yellow	1	
(ii)	pK_a of indicator matches pH change at equivalence	1	allow pK_a on vertical section of graph owtte
(iii)	from Yellow to Red	1	
(c)	$18.8 \times 0.200 / 1000 = 3.76 \times 10^{-3}$ mol of HNO_3 so amount $Na_2CO_3 = 3.76 \times 10^{-3} / 2 = 1.88 \times 10^{-3}$ mol so conc $= 1.88 \times 10^{-3} \times 1000 / 20 = 0.094$ mol dm^{-3} $= 0.094 \times 106 = 9.964$ g dm^{-3}	 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)	$K_c = [H^+][OH^-]/[H_2O]$ $[H_2O]$ const negligible dissociation / equilibrium left	1 1 1	 allow water is in large excess
(iii)	$[H^+] = \sqrt{51.3 \times 10^{-14}} = 7.16 \times 10^{-7}$ (mol dm^{-3}) pH = –log $7.16 \times 10^{-7} = 6.15$	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)**

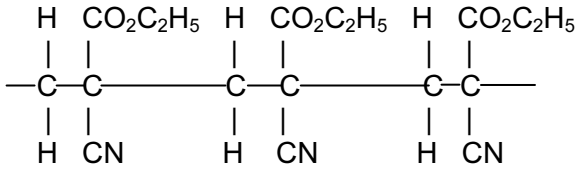
(e)	$5 \times 1 / 1000 = 5 \times 10^{-3}$ mol of H^+	1	
	$0.1 \times 1.00 \times 10^{-4} = 1 \times 10^{-5}$ mol of HCl in soln	1	
	$1 \times 10^{-5} + 5 \times 10^{-3}$ in 105 cm^3 $= 5.01 \times 10^{-3} / 0.105 = 0.0477$ mol dm^{-3}	1	
	pH = -log 0.0477 = 1.32	1	1.32 = 4 marks
	calculation of initial pH = 4.77	1	
	after addition of HCl; $0.01 + 5 \times 10^{-3} = 0.015$ mol $= 0.015 \times 1000 / 105 = 0.143$ mol dm^{-3} CH_3COOH	1	
	and $0.01 – 5 \times 10^{-3} = 0.005$ mol $= 0.005 \times 1000 / 105 = 0.0476$ mol dm^{-3} CH_3COO^-	1	
	pH = pK_a – log [acid] / [salt] = 4.77 – log 0.143 / 0.0476 = 4.17	1	4.17 = 4 marks
		[25]	

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) (i)	molecule with non-superimposable mirror-image form / molecule with 4 different groups attached to the same (C) 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)	stereoisomers that are not enantiomers / non-superimposable mirror images	1	
(iv)		2	
(c) (i)		4	
(ii)	S-(+)-butan-2-ol	2	R-(+)- butan-2-ol/S-(-)-butan-2-ol/S-(+)-propan-2-ol all = 1/2

(d) (i)	RX = 1st order: Expt 1 to 2 [RX] ×3 = rate ×3 so directly	1	
(ii)	proportional	1	
(iii)	OH^- = 1st 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)	6	
(iv)		1	
		[23]	

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)	$\Delta_r S = \Sigma S_{products} - \Sigma S_{reactants} = (31.1 + 55.3) - (2 \times 50)$ $= -13.4$ (J K^{-1} mol^{-1})	2	+36.4 = 1/2 (not x2) -29.5 = 1/2 (reversed 55.3 and 55)
(ii)	$\Delta_r G^{\ominus} = \Delta H - T\Delta S = -126.8 - (298 \times -3.4 / 1000)$ $= -122.8$ (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)	$\Delta_r G^{\ominus} = -RT\ln K_p$ so $\ln K_p = \Delta_r G^{\ominus} / -RT$ $= -120.1 \times 10^{-3} / (-8.31 \times 298) = 48.50$ so $K_p = 1.15 \times 10^{21}$	2	$3.72 \times 10^{21} = 1 / 2$ (used 122.8 from **3(b)(ii)**) $1.05 = 1 / 2$ (no $\times 10^3$ ignore units
(ii)	$\Delta_r G^{\ominus} = 0 = \Delta H - T\Delta S$ 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]	

4 (a)	Pt I N H 40.37/195 52.59/127 5.80/14 1.24/1 (1) 0.207/0.207 0.414/0.207 0.414/0.207 1.24/0.207 (1) 1.00 2.00 2.00 5.99 so EF = $PtI_2N_2H_6$ EFM = 483 = M_r so MF = $PtI_2N_2H_6$ (1)  (1) and trans (1)	5	must see link of EFM to RFM
	bond Angle = 90°	1	ecf
(b)	(octahedral) e.g. $Co(H_2O)_6^{2+}$ angle = 90° (tetrahedral) e.g. $CoCl_4^{2-}$ angle = 109–110°	3	both angles needed for third mark NB $CoCl_4^-$ doesn't exist
(c)	lobes of two orbitals directed along cartesian axes lobes of three orbitals directed between cartesian axes results in split of energy levels of d orbitals promotion of electrons between orbitals <u>absorbs</u> in visible region	1 1 1 1	
		[13]	

5	**(a)**	$C_6H_7NO_2$	1	
	(b)	**x** = 120° **y** = 104.5°	2	allow 104 – 105 for **y**
	(c)	**1** = carboxylic Acid Level **2** = hydrocarbon Level **3** = carboxylic Acid Level	2	three = 2 two = 1
	(d) **(i)**	donates pair of electrons to form covalent bond	1 + 1	
	(ii)		2	
	(e)	**Q** = $CH_2=C(CH_2NH_2)CH_2OH$ **R** = CH_3CH_2OH **S** = $CH_2=C(CH_2NHOCCH_3)CH_2OCOCH_3$ **T** = $CH_3CH_2OCOCH_3$ **U** = $CH_3CH(CH_2NH_2)CO_2CH_2CH_3$ Reactions of **Q** and **R** with ethanoyl chloride: 2:1 ratio with **Q** as both NH_2 and OH acylated/ 1:1 ratio with **R** as only one OH group acylated (1) Reaction with NH_2 produces (secondary) amide (+HCl) (1) Reaction with OH produce ester (+HCl) (1) ^{1}H NMR of **T**: three signals indicate / due to 3 H environments (1) triplet @ ~1.3 is protons on CH_3 adj to CH_2 (1) quartet @ ~ 4.1 is protons on CH_2 (adj to CH_3) (1) singlet @ ~ 2.0 is protons on CH_3 on C=O (1) ^{13}C NMR of **T**: two signals near 20 = Cs in the two CH_3 groups (1) signal at ~ 60 is C in CH_2 (1) signal at ~170 is C in C=O (1) ^{1}H NMR of **U**: six signals indicate / due to 6 H environments (1) disappearing signal due to labile protons on NH_2 (2)	1 1 1 1 1 1 1 1 max 3 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]	