

CAMBRIDGE INTERNATIONAL EXAMINATIONS

Pre-U Certificate

MARK SCHEME for the May/June 2013 series

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.

Mark schemes should be read in conjunction with the question paper and the Principal Examiner Report for Teachers.

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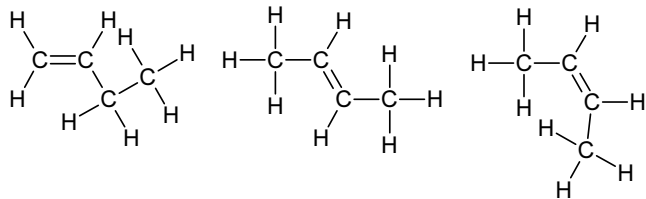
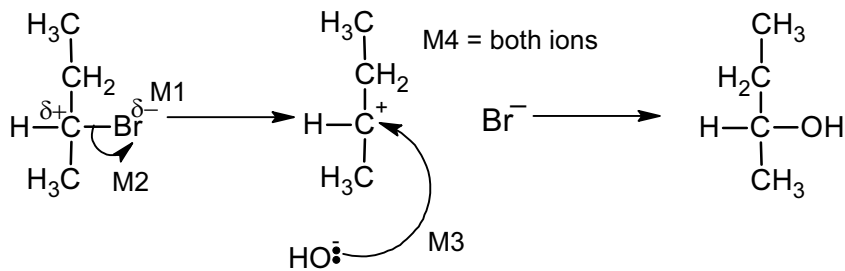
Page 2	Mark Scheme	Syllabus	Paper
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Question	Marking point	Marks
1 (a)	They are in the section of the PT that corresponds to the d-subshells filling	[1]
(b) (i)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$	[1]
(ii)	no ions formed with incomplete d-subshell / orbital	[1]
(c) (i)	(Period 3) general increase due to <u>increasing nuclear charge</u> with (approx) <u>constant shielding</u>	[1]
	Decrease between groups 2 and 3 due to increased shielding of full s-subshell / higher energy of p subshell	[1]
	Decrease between groups 5 and 6 due to repulsion from previous p-orbital electron	[1]
(ii)	(Relative constancy across first transition series as) <u>increasing shielding</u> due to filling of an inner shell	[1]
	(Extra) shielding effect not (quite) enough to (completely) cancel effect of increasing nuclear charge	[1]
(d) (i)	CCP = cubic close-packed	[1]
(ii)	HCP = ABAB	[1]
	CCP = ABC	[1]
(e) (i)	(Simplest) repeating unit of the lattice	[1]
	that displays the full symmetry of the crystal	[1]
(ii)	MCl as filling half the holes gives 1:1 ratio	[1]
	Ratio of anions:tetrahedral holes is 1:2	[1]
(f) (i)	$A = CoCl_2$	[1]
	$B = CoCl_2 \cdot 6H_2O$	[1]
	$C = Co(H_2O)_6^{2+}$	[1]
	$D = CoCl_4^{2-}$	[1]
(ii)	Shape = octahedral	[1]
	Bond angles = 90°	[1]
(iii)	$Co(H_2O)_6^{2+} + 4Cl^- \rightleftharpoons CoCl_4^{2-} + 6H_2O$	[1]
(iv)	(Change from hexa to tetra-coordinate due to) large(r) size of Cl^- (cf H_2O)	[1]
		[Total: 23]

Page 3	Mark Scheme	Syllabus	Paper
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Question	Marking point	Marks
2 (a)	$2\text{N}_2\text{H}_4 + \text{N}_2\text{O}_4 \rightarrow 4\text{H}_2\text{O} + 3\text{N}_2$	[1]
(b)	The enthalpy change when one mole of a compound is formed from its elements under standard conditions	[1] [1]
(c) (i)	$\Delta_r H^\ominus_{298} = \sum \Delta_f H^\ominus_{298} \text{ products} - \sum \Delta_f H^\ominus_{298} \text{ reactants}$ $= 2(-393.5) + 4(-241.8) - [83.3 + 2(9.10)]$ $= -1855.7 \text{ (kJ mol}^{-1}\text{)}$	[1] [1] [1]
(ii)	(Large positive value as) increase in number of moles from 3 to 9 and change from liquids to gases hence (large) increase in disorder	[1] [1]
(iii)	$\Delta_r G^\ominus_{298} = \Delta_r H^\ominus_{298} - T\Delta_r S^\ominus_{298}$ $= -1855.7 - (298 \times 0.8441)$ $= -2107.2 \text{ (kJ mol}^{-1}\text{)}$	[1] [1]
(d) (i)	$M_r \text{ UDMH} = 60; M_r \text{ N}_2\text{O}_4 = 92$ 1:2 ratio = $60 + 184 = 244$ Mass of UDMH = 60 kg	[1]
(ii)	60 kg UDMH = $60000/60 = 1000 \text{ mol}$ 1:9 ratio UDMH:product gases so 9000 mol gas produced	[1] [1]
(iii)	$pV = nRT, V = nRT/p$ $= 9000 \times 8.31 \times 263/600$ $= 3.28 \times 10^2 \text{ m}^3$ answer to three significant figures	[1] [1] [1]
(e) (i)	Gradient calculated from graph = -14194 Gradient = $-E_a / R$ i.e. $-14194 = -E_a / 8.31$ $E_a = 13778 \times 8.31 = 117948 = (+)117.9 \text{ kJ mol}^{-1}$	[1] [1]
(ii)	$[\text{NO}_2] = 4/2 = 2 \text{ mol dm}^{-3}$ Rate = $3.16 \times 2^2 = 12.64 \text{ mol dm}^{-3} \text{ s}^{-1}$ (answer plus units)	[1] [1]
(iii)	(Yes) two molecules / moles of NO_2 involved in slow step / rds	[1]
		[Total: 21]

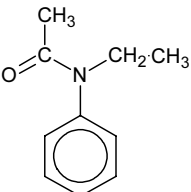
Page 4	Mark Scheme	Syllabus	Paper
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Question	Marking point	Marks
3 (a) (i)	Elimination	[1]
(ii)	Heat (under reflux)	[1]
	Ethanol / alcoholic	[1]
(iii)	 <p>but-1-ene trans-but-2-ene cis-but-2-ene (or E/Z)</p>	[1][1][1]
(b) (i)	Aqueous	[1]
(ii)		[4]
(iii)	<p>S_N1: Product not optically active + attempt at explanation [1]</p> <p>Planar intermediate [1]</p> <p>Attack from either side [1]</p> <p>Racemate produced [1]</p> <p>S_N2: Inversion of configuration [1]</p>	
(iv)	(R) – (–) – butan-2-ol	[1]
(c)	2-bromo-2-methylpropane/2-methyl-2-bromopropane [1]	
	Intermediate carbocation stabilised / more likely to form [1]	
	+I / electron releasing effect of three alkyl / methyl groups OR Steric effect prevents S_N2 [1]	
	due to size of methyl groups	
[Total: 20]		

Page 5	Mark Scheme	Syllabus	Paper
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Question	Marking point	Marks
4 (a) (i)	$K_p = \frac{p_{\text{CH}_3\text{OH}}}{p_{\text{CO}} \times p_{\text{H}_2}^2}$	[1]
(ii)	Amounts: $\text{H}_2 = 19 \text{ mol}$; $\text{CO} = 16.5 \text{ mol}$; $\text{CH}_3\text{OH} = 225 \text{ mol}$ Mole fractions: $\text{H}_2 = 0.0729$; $\text{CO} = 0.0633$; $\text{CH}_3\text{OH} = 0.864$	[1] [1]
(iii)	$K_p = \frac{0.864}{0.0633 \times (75 \times 10^3)^2 \times 0.0729^2}$ $= 4.57 \times 10^{-11}$ Allow division by 7500 or 7500000	[1] [1]
(b) (i)	Elevated temperature increases rate in both steps Step 1 endothermic so elevated T increases yield Step 2 exothermic so elevated T reduces yield so lower T than in Step 1 is a compromise between rate and yield	[1] [1] [1]
(ii)	Higher than atmospheric P increases rate/moves gases through system Too high in step 1 reduces yield as $2 \text{ mol} \rightarrow 4 \text{ mol}$ Much higher P in Step 2 increases yield as $3 \text{ mol} \rightarrow 1 \text{ mol}$	[1] [1] [1]
(c) (i)	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	[1]
(ii)	$3\text{O}_2 + 2\text{CH}_3\text{OH} \rightarrow 4\text{H}_2\text{O} + 2\text{CO}_2$ $E_{\text{cell}} = 1.21 \text{ V}$	[1] [1]
(d) (i)	Shape = square planar Angle = 90°	[1]
(ii)	$\text{Pt}(\text{NH}_3)_4^{2+} + 2\text{e}^- \rightarrow \text{Pt} + 4\text{NH}_3$	[1]
(e)	$Q = I \times t = 3.5 \times 10^{-3} \times 25 \times 95 \times 60 = 498.75$ Mol of electrons = $498.75/96500 = 5.17 \times 10^{-3} \text{ mol}$ Mol Pt deposited = $5.17 \times 10^{-3}/2 = 2.58 \times 10^{-3}$ Mass Pt deposited = $2.58 \times 10^{-3} \times 195 = 0.504 \text{ g}$	[1] [1] [1]
[Total: 19]		

Page 6	Mark Scheme	Syllabus	Paper
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Question Number	Answer	Marks																									
5 (a)	More energy needed to break bond(s) in benzene due to delocalisation	[1] [1]																									
5 (b) (i)	Accepts pair of electrons	[1]																									
(ii)	Reagents conc HNO ₃ + conc H ₂ SO ₄ Conditions 50 – 60 °C Electrophile NO ₂ ⁺	[1] [1] [1]																									
(c) (i)	NH ₂ ring activating / increases charge density of ring due to partial delocalisation of lone pair on N into ring / electron donation of lone pair into ring Ring more susceptible to attack in phenylamine / Br ₂ more polarised by ring	[1] [1] [1]																									
(ii)	C ₆ H ₅ NO ₂ + 6[H] → C ₆ H ₅ NH ₂ + 2H ₂ O	[1]																									
(d) (i)	<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="text-align: center;">C</td> <td style="text-align: center;">H</td> <td style="text-align: center;">N</td> <td style="text-align: center;">O</td> <td></td> </tr> <tr> <td style="text-align: center;"><u>73.59</u></td> <td style="text-align: center;"><u>8.03</u></td> <td style="text-align: center;"><u>8.58</u></td> <td style="text-align: center;"><u>9.80</u></td> <td></td> </tr> <tr> <td style="text-align: center;">12</td> <td style="text-align: center;">1</td> <td style="text-align: center;">14</td> <td style="text-align: center;">16</td> <td></td> </tr> <tr> <td style="text-align: center;">6.13</td> <td style="text-align: center;">8.03</td> <td style="text-align: center;">0.613</td> <td style="text-align: center;">0.613</td> <td></td> </tr> <tr> <td style="text-align: center;">10</td> <td style="text-align: center;">13</td> <td style="text-align: center;">1</td> <td style="text-align: center;">1</td> <td style="text-align: left;">so empirical formula = C₁₀H₁₃NO</td> </tr> </table> <p>EFM = 163 = RMM so molecular formula = C₁₀H₁₃NO</p>	C	H	N	O		<u>73.59</u>	<u>8.03</u>	<u>8.58</u>	<u>9.80</u>		12	1	14	16		6.13	8.03	0.613	0.613		10	13	1	1	so empirical formula = C ₁₀ H ₁₃ NO	[1] [1] [1]
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(ii)	 <p><i>Triplet</i> at 1.12 integration 3 = 3 protons of –CH₃ of ethyl group split by 2 neighbouring protons</p> <p><i>Singlet</i> at 1.83 integration 3 = 3 protons of –CH₃ attached to C=O – no neighbouring Hs</p> <p><i>Quadruplet</i> at 3.75 integration 2 = protons of –CH₂ split by 3 neighbouring protons</p>	[1] [1] [1] [1]																									
[Total: 17]																											