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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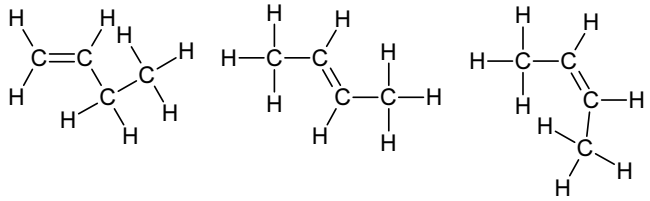
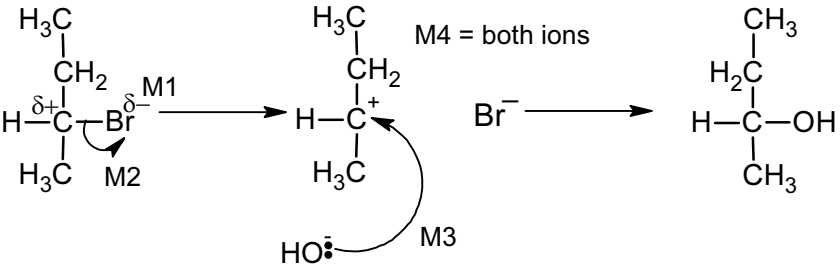
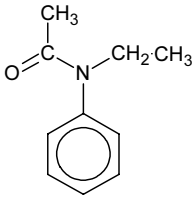
CAMBRIDGE
International Examinations

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 = $CoCl_2.6H_2O$	[1]
	C = $Co(H_2O)_6^{2+}$	[1]
	D = $CoCl_4^{2-}$	[1]
(ii)	Shape = octahedral	[1]
	Bond angles = 90^o	[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]

Question	Marking point	Marks
2 (a)	$2N_2H_4 + N_2O_4 \rightarrow 4H_2O + 3N_2$	[1]
(b)	The enthalpy change when one mole of a compound is formed	[1]
	from its elements under standard conditions	[1]
(c) (i)	$\Delta_r H^{\ominus}_{298} = \Sigma \Delta_f H^{\ominus}_{298}$ products - $\Sigma \Delta_f H^{\ominus}_{298}$ reactants	[1]
	= 2(–393.5) + 4(–241.8) – [83.3 + 2(9.10)]	[1]
	= –1855.7 (kJ mol^{-1})	[1]
(ii)	(Large positive value as) increase in number of moles from 3 to 9 and change from liquids to gases	[1]
	hence (large) increase in disorder	[1]
(iii)	$\Delta_r G^{\ominus}_{298} = \Delta_r H^{\ominus}_{298} - T\Delta_r S^{\ominus}_{298}$ = – 1855.7 – (298 x 0.8441)	[1]
	= – 2107.2 (kJ mol^{-1})	[1]
(d) (i)	M_r UDMH = 60; M_r N_2O_4 = 92	
	1:2 ratio = 60 + 184 = 244	
	Mass of UDMH = 60 kg	[1]
(ii)	60 kg UDMH = 60000/60 = 1000 mol	[1]
	1:9 ratio UDMH:product gases so 9000 mol gas produced	[1]
(iii)	$pV = nRT$, $V = nRT/p$	
	= 9000 × 8.31 × 263/600	[1]
	= 3.28 × 10^2 m^3	[1]
	answer to three significant figures	[1]
(e) (i)	Gradient calculated from graph = – 14194	[1]
	Gradient = $-E_a / R$ i.e. – 14194 = $-E_a$ / 8.31	
	E_a =13778 × 8.31 = 117948 = (+)117.9 kJ mol^{-1}	[1]
(ii)	$[NO_2]$ = 4/2 = 2 mol dm^{-3}	[1]
	Rate = 3.16 × 2^2 = 12.64 mol dm^{-3} s^{-1} (answer plus units)	[1]
(iii)	(Yes) two molecules / moles of NO_2 involved in slow step / rds	[1]
		[Total: 21]

Question	Marking point	Marks
3 (a) (i)	Elimination	[1]
(ii)	Heat (under reflux)	[1]
	Ethanolic / alcoholic	[1]
(iii)	 but-1-ene *trans*-but-2-ene *cis*-but-2-ene (or *E/Z*)	[1][1][1]
(b) (i)	Aqueous	[1]
(ii)		[4]
(iii)	S_N1: Product not optically active + attempt at explanation	[1]
	Planar intermediate	[1]
	Attack from either side	[1]
	Racemate produced	[1]
	S_N2: Inversion of configuration	[1]
(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]

Question	Marking point	Marks
4 (a) (i)	$K_p = \dfrac{p\underline{C}H_3OH}{p\underline{C}O \times p\underline{H}_2^2}$	[1]
(ii)	Amounts: H_2 = 19 mol; CO = 16.5 mol; CH_3OH = 225 mol	[1]
	Mole fractions: H_2 = 0.0729; CO = 0.0633; CH_3OH = 0.864	[1]
(iii)	$K_p = \dfrac{0.864}{0.0633 \times (75 \times 10^3)^2 \times 0.0729^2}$ $= 4.57 \times 10^{-11}$ Allow division by 7500 or 7500000	[1] [1]
(b) (i)	Elevated temperature increases rate in both steps	[1]
	Step 1 endothermic so elevated *T* increases yield	[1]
	Step 2 exothermic so elevated *T* reduces yield so lower *T* than in Step 1 is a compromise between rate and yield	[1]
(ii)	Higher than atmospheric *P* increases rate/moves gases through system	[1]
	Too high in step 1 reduces yield as 2 mol → 4 mol	[1]
	Much higher *P* in Step 2 increases yield as 3 mol → 1 mol	[1]
(c) (i)	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	[1]
(ii)	$3O_2 + 2CH_3OH \rightarrow 4H_2O + 2CO_2$	[1]
	E_{cell} = 1.21 V	[1]
(d) (i)	Shape = square planar Angle = 90°	[1]
(ii)	$Pt(NH_3)_4^{2+} + 2e^- \rightarrow Pt + 4NH_3$	[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 = 5.17×10^{-3} mol	[1]
	Mol Pt deposited = $5.17 \times 10^{-3}/2 = 2.58 \times 10^{-3}$	[1]
	Mass Pt deposited = $2.58 \times 10^{-3} \times 195 = 0.504$ g	[1]
		[Total: 19]

Question Number	Answer	Marks
5 (a)	More energy needed to break bond(s) in benzene	[1]
	due to delocalisation	[1]
5 (b) (i)	Accepts pair of electrons	[1]
(ii)	Reagents conc HNO_3 + conc H_2SO_4	[1]
	Conditions 50 – 60 °C	[1]
	Electrophile NO_2^+	[1]
(c) (i)	NH_2 ring activating / increases charge density of ring	[1]
	due to partial delocalisation of lone pair on N into ring / electron donation of lone pair into ring	[1]
	Ring more susceptible to attack in phenylamine / Br_2 more polarised by ring	[1]
(ii)	$C_6H_5NO_2 + 6[H] \rightarrow C_6H_5NH_2 + 2H_2O$	[1]
(d) (i)	C H N O 73.59/12 8.03/1 8.58/14 9.80/16	
	6.13 8.03 0.613 0.613	[1]
	10 13 1 1 so empirical formula = $C_{10}H_{13}NO$	[1]
	EFM = 163 = RMM so molecular formula = $C_{10}H_{13}NO$	[1]
(ii)		[1]
	Triplet at 1.12 integration 3 = 3 protons of $–CH_3$ of ethyl group split by 2 neighbouring protons	[1]
	Singlet at 1.83 integration *3* = 3 protons of $–CH_3$ attached to C=O – no neighbouring Hs	[1]
	Quadruplet at 3.75 integration 2 = protons of $–CH_2$ split by 3 neighbouring protons	[1]
		[Total: 17]