CAMBRIDGE INTERNATIONAL EXAMINATIONS

Cambridge International Advanced Level

MARK SCHEME for the October/November 2014 series

9701 CHEMISTRY

9701/42 Paper 4 (A2 Structured Questions), 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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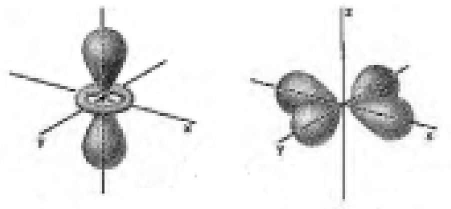
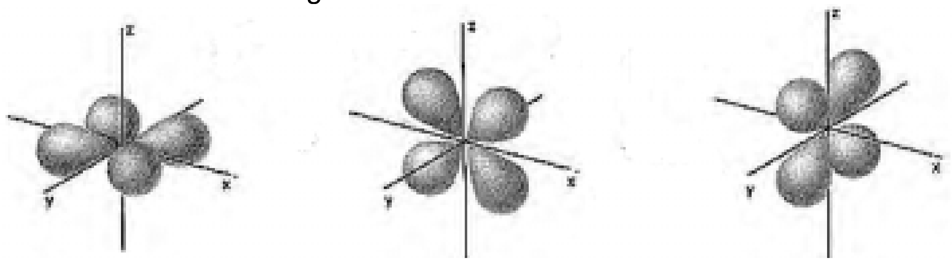
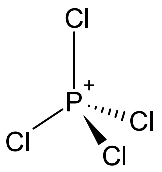
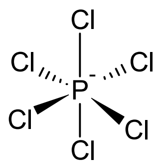
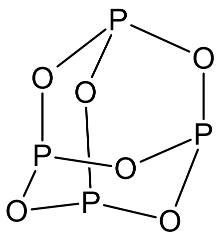
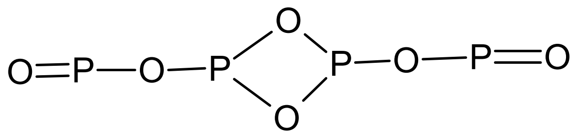
CAMBRIDGE
International Examinations

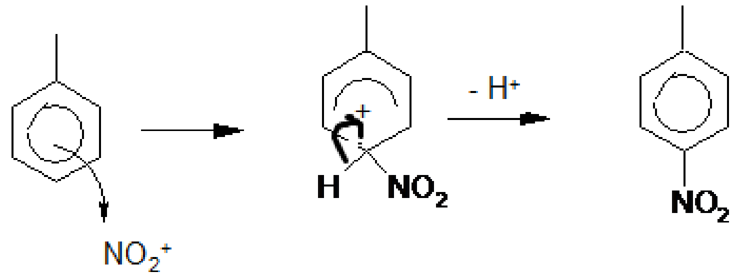
Question	Marking point	Marks	Marks total
1 (a) (i)	[NO] 2^{nd} order **and** the concentration is ×2, rate × 4 [O_2] 1^{st} order **and** evidence of using expt 1 & 2 when the concentration is ×2, rate doubles	1 1	
(ii)	(0.00408 × 27) rate = **<u>0.11</u>** (mol dm^{-3} s^{-1}) to **2sf**	1	
(iii)	(Rate =) k [O_2][NO]^2	1	
(iv)	k = 332(.03125) mol^{-2} dm^6 s^{-1}	1 1	[6]
(b) (i)	labelled axes *x*-axis: energy (KE) and *y*-axis: molecules or particles two curves: starts origin; not touching *x*-axis again; no levelling out; curves only intersecting once curves labelled and T2 is to the right and lower max than T1	1 1 1	
(ii)	rate increases **and** energy of the particles increases more particles have E_a	1 1	[5]
(c)	1 mole of F_2 and 1 mole NO reacting in the **slow** step a balanced mechanism consistent with overall equation e.g. F_2 + NO → NOF + F **OR** F_2 + NO → NOF_2 NO + F → NOF NO + NOF_2 → 2NOF	1 1	[2]
Total			[13]

<table>
<tr><td>2 (a)</td><td>
<table>
<tr><td></td><td colspan="5">3d</td><td>4s</td></tr>
<tr><td>(Ni)</td><td>↑↓</td><td>↑↓</td><td>↑↓</td><td>↑</td><td>↑</td><td>↑↓</td></tr>
<tr><td>(Ni^{2+})</td><td>↑↓</td><td>↑↓</td><td>↑↓</td><td>↑</td><td>↑</td><td></td></tr>
</table>
</td><td>1
1</td><td>[2]</td></tr>
<tr><td>(b) (i)</td><td>degenerate</td><td>1</td><td></td></tr>
<tr><td>(ii)</td><td>2 upper orbitals and 3 lower orbitals</td><td>1</td><td></td></tr>
<tr><td>(iii)</td><td>correct upper orbital diagram

correct lower orbital diagram
</td><td>1
1</td><td>[4]</td></tr>
<tr><td>(c)</td><td>electron(s) move from lower to upper level
absorb (red/blue) light/photon
complementary colour (green) is seen
OR green light is transmitted</td><td>1
1
1</td><td>[3]</td></tr>
</table>

(d)	**A** $Ni(OH)_2$ **OR** $Ni(OH)_2(H_2O)_4$ **B** $[Ni(NH_3)_6]^{2+}$ **OR** $[Ni(NH_3)_n(H_2O)_{6-n}]^{2+}$ **OR** $[Ni(NH_3)_n(H_2O)_{4-n}]^{2+}$ $Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2$ **OR** $[Ni(H_2O)_6]^{2+} + 2OH^- \rightarrow Ni(OH)_2 + 6H_2O$ **OR** $[Ni(H_2O)_6]^{2+} + 2NH_3 \rightarrow Ni(OH)_2 + 4H_2O + 2NH_4^+$ **OR** $[Ni(H_2O)_6]^{2+} + 2OH^- \rightarrow Ni(OH)_2(H_2O)_4 + 2H_2O$ $Ni(OH)_2 + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+-} + 2OH^-$ **OR** $Ni(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+-} + 6H_2O$	1 1 1 1	 [4]
Total			[13]

3 (a) (i)	101 = $P^{35}Cl^{35}Cl$ 103 = $P^{35}Cl^{37}Cl$ 105 = $P^{37}Cl^{37}Cl$	**1** **1** **1**	
(ii)	9:6:1	**1**	**[4]**
(b) (i)	PCl_5 5 bonding pairs around P	**1**	
(ii)	 	**1** **1**	**[3]**
(c) (i)	 P_4O_6 structure where each P has three P-O bonds and each O has two P-O bonds e.g. 	**1**	
(ii)	(molecule/ion/species) that **donates** a lone pair of electrons (to a central transition metal atom or ion)	**1**	**[2]**
(d) (i)	$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$	**1**	

(ii)	$[Ca^{2+}]$ = 3 × 2.50 × 10^{-6} = 7.50 × 10^{-6} mol dm^{-3} $[PO_4^{3-}]$ = 2 × 2.50 × 10^{-6} = 5.00 × 10^{-6} mol dm^{-3} = $(7.50 \times 10^{-6})^3(5.00 \times 10^{-6})^2$ = **1.05(1.1) × 10^{-26}** mol^5dm^{-15}	1 1 1	[4]
(e) (i)	(enthalpy change) when **1 mole** of an **ionic compound** is **formed** from its **gaseous ions**	1 1	
(ii)	Mg^{2+} has a smaller (ionic) radii than Ca^{2+} **OR** Mg^{2+} is smaller than Ca^{2+}	1	[3]
Total			**[16]**
4 (a) (i)	$2H_2SO_4 + HNO_3 \rightarrow 2HSO_4^- + NO_2^+ + H_3O^+$ **OR** $H_2SO_4 + HNO_3 \rightarrow HSO_4^- + NO_2^+ + H_2O$	1	

(ii)	**any three** of • curly arrow from inside the benzene ring to NO_2^+ group • intermediate – **penalise** NO_2 connectivity ***or*** missing methyl group (once) • curly arrow from C-H bond into ring • product + H^+ (or as diagram $-H^+$) **allow** 2- and 3-substituted nitromethylbenzene)  	3	[4]
(b) (i)	acidity of $ClCH_2CO_2H > CH_3CO_2H$ **AND** ($ClCH_2CO_2H$) as an electronegative/electron withdrawing Cl	1	
(ii)	acidity of phenol $> CH_3CH_2OH$ **AND** electrons on oxygen (on phenol) delocalised into ring **OR** benzene ring withdraws electrons from oxygen	1	
	stronger acid linked to weakening O-H bond/anion being stabilised	1	[3]

Page 8	Mark Scheme	Syllabus	Paper
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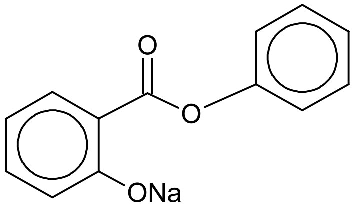
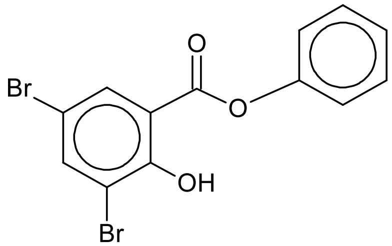
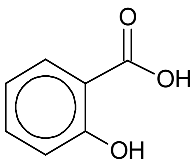
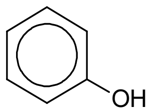
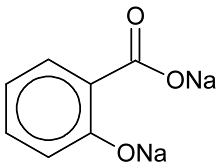
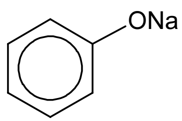
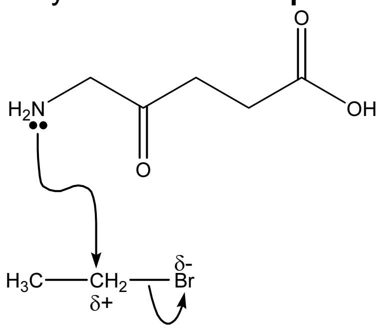
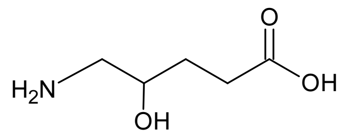
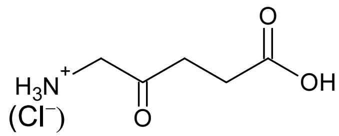
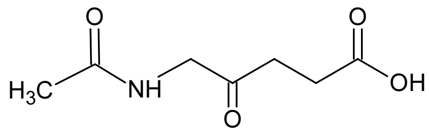
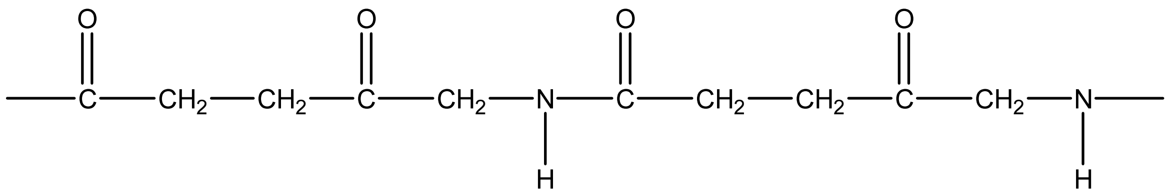
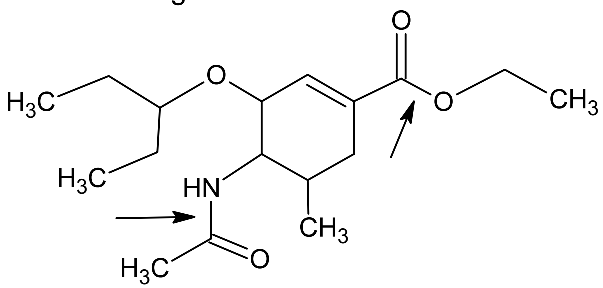
(c)

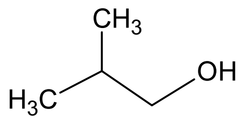
Na	 (or ionic)	redox/reduction
Br_2		(electrophilic) substitution
NaOH	 and  [1] or ionic  	hydrolysis/ acid-base/

1 mark for each correct structure	**4**	
for reaction types, 2 correct = 1 mark, 3 correct = 2 marks	**2**	**[6]**

Total			**13**
5 (a)	$CH_3CH_2COCl > CH_3CH_2CH_2Cl > C_6H_5Cl$ **any two** *of:* • C-C*l* bond strength is weakest in CH_3CH_2COCl ora • In C_6H_5Cl (no hydrolysis) C-C*l* bond is part of delocalised system **OR** p-orbital on C*l* overlaps with π system **OR** electrons from C*l* overlap with π system • CH_3CH_2COCl carbon in C-C*l* bond is more electron deficient since it is also attached to an oxygen atom ora	**1** **1+1**	**[3]**
(b)	ketone, amine, carboxylic acid two correct 1 mark, all three 2	**2**	**[2]**
(c) (i)	dipole on C-Br curly arrow breaking C-Br bond curly arrow from **lone pair** on N to carbon in C-Br bond 	**1** **1** **1**	
(ii)	nucleophilic substitution	**1**	
(iii)	HBr or hydrogen bromide	**1**	**[5]**

(d)	Y =  W =  X =  each structure 1 mark	3	[3]
(e)	 correct displayed amide formula correct polyamide with two repeat units	 1 1	 [2]
Total			**15**
6 (a)	• (move in different directions) some amino acids have a different charge • (move at different speeds) some amino acids have a different size/different charge • (some amino acids do not move at all) some amino acids exist as a zwitterions/have no net(overall) charge/neutral/both NH_2/COOH are charged in amino acids	1 1 1	 [3]
(b) (i)	mobile – solvent ***or*** water stationary – alumina/silica (supported on glass/plastic/Al)	1 1	
(ii)	by adsorption	1	[3]

(c)	**any three** of: (all can be awarded from a clear, labelled diagram) • (base pairing) A to T **OR** C to G • H-bonds between bases • two/double stranded/chains • anti-parallel strands • (general structure) sugar-phosphate backbone **OR** BASE-SUGAR-PHOSPHATE bonded in a diagram	3	[3]
(d)	van der Waals' forces lost (in val) H-bonding gained (in ser)	1 1	[2]
Total			**11**
7 (a)	amide group circled **OR** indicated as diagram ester group circled **OR** indicated as diagram 	1 1	[2]
(b)	lower doses of the drug required **OR** improved activity of the drug **OR** reduced side effects	1	[1]

(c)	decreases enzyme activity **OR** decreases rate at which product is formed binds with the enzyme's active site **OR** has a complementary shape to active site **OR** similar shape to substrate (competitive inhibition can be overcome by) increasing [substrate] **OR** increasing substrate concentration	1 1 1	[3]
(d)	**energy** source/carrier **OR** releases energy when hydrolysed	1	[1]
Total			7
8 (a)	M:M+1 = 100/(1.1 x n) 20.4/0.9 = 100/(1.1 x n) x =4	1 1	
(ii)	$C_4H_{10}O$	1	[3]
(b) (i)	2-methylpropan-1-ol **OR** correct structure  	1	
(ii)	0.9-1.0 is (2 x)CH_3R/CH_3/RCH multiplet/1.8 is CHR/R_3CH singlet/2.5 is OH 3.4 is CH_2O/CH_3O	1 1 1 1	
(iii)	doublet 1H/one proton on adjacent carbon	1 1	

(iv)	OH peak or one peak disappears OH proton is labile ***or*** exchanges for D of D_2O ***or*** as an equation e.g. D_2O + OH → DOH + OD as a minimum	**1** **1**	**[9]**
Total			**12**
			100