

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

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

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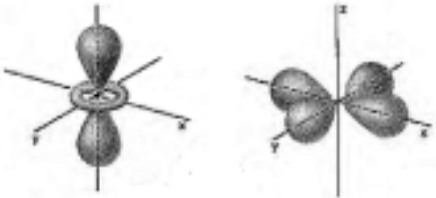
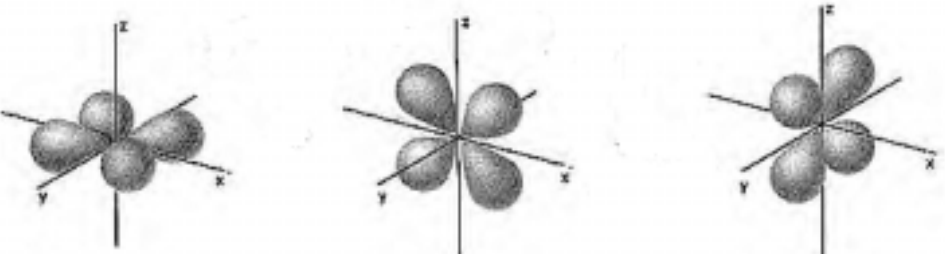
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Question	Marking point	Marks	Marks total
1 (a) (i)	[NO] 2 nd order and the concentration is ×2, rate × 4	1	
	[O ₂] 1 st order and evidence of using expt 1 & 2 when the concentration is ×2, rate doubles	1	
(ii)	(0.00408 × 27) rate = 0.11 (mol dm ⁻³ s ⁻¹) to 2sf	1	
(iii)	(Rate =) $k [\text{O}_2][\text{NO}]^2$	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	1	
	a balanced mechanism consistent with overall equation e.g. $\text{F}_2 + \text{NO} \rightarrow \text{NOF} + \text{F}$ OR $\text{F}_2 + \text{NO} \rightarrow \text{NOF}_2$ $\text{NO} + \text{F} \rightarrow \text{NOF}$ $\text{NO} + \text{NOF}_2 \rightarrow 2\text{NOF}$	1	[2]
Total			[13]

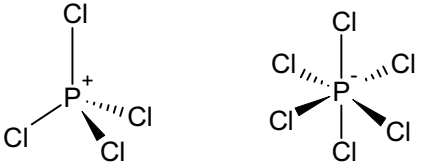
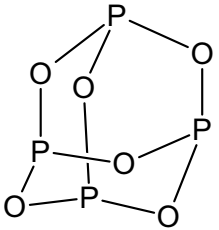
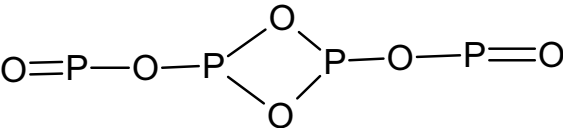
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2 (a)	<table style="margin-left: auto; margin-right: auto;"> <tr> <td></td> <td colspan="5" style="text-align: center;">3d</td> <td></td> <td style="text-align: center;">4s</td> </tr> <tr> <td>(Ni)</td> <td style="text-align: center;">↑↓</td> <td style="text-align: center;">↑↓</td> <td style="text-align: center;">↑↓</td> <td style="text-align: center;">↑</td> <td style="text-align: center;">↑</td> <td></td> <td style="text-align: center;">↑↓</td> </tr> <tr> <td>(Ni²⁺)</td> <td style="text-align: center;">↑↓</td> <td style="text-align: center;">↑↓</td> <td style="text-align: center;">↑↓</td> <td style="text-align: center;">↑</td> <td style="text-align: center;">↑</td> <td></td> <td></td> </tr> </table>		3d						4s	(Ni)	↑↓	↑↓	↑↓	↑	↑		↑↓	(Ni ²⁺)	↑↓	↑↓	↑↓	↑	↑			1 1	[2]
	3d						4s																				
(Ni)	↑↓	↑↓	↑↓	↑	↑		↑↓																				
(Ni ²⁺)	↑↓	↑↓	↑↓	↑	↑																						
(b) (i)	degenerate	1																									
(ii)	2 upper orbitals and 3 lower orbitals	1																									
(iii)	<p>correct upper orbital diagram</p>  <p>correct lower orbital diagram</p> 	1 1	[4]																								
(c)	<p>electron(s) move from lower to upper level</p> <p>absorb (red/blue) light/photon</p> <p>complementary colour (green) is seen OR green light is transmitted</p>	1 1 1	[3]																								

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(d)	A Ni(OH)_2 OR $\text{Ni(OH)}_2(\text{H}_2\text{O})_4$	1	
	B $[\text{Ni}(\text{NH}_3)_6]^{2+}$ OR $[\text{Ni}(\text{NH}_3)_n(\text{H}_2\text{O})_{6-n}]^{2+}$ OR $[\text{Ni}(\text{NH}_3)_n(\text{H}_2\text{O})_{4-n}]^{2+}$	1	
	$\text{Ni}^{2+} + 2\text{OH}^- \rightarrow \text{Ni(OH)}_2$ OR $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} + 2\text{OH}^- \rightarrow \text{Ni(OH)}_2 + 6\text{H}_2\text{O}$ OR $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} + 2\text{NH}_3 \rightarrow \text{Ni(OH)}_2 + 4\text{H}_2\text{O} + 2\text{NH}_4^+$ OR $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} + 2\text{OH}^- \rightarrow \text{Ni(OH)}_2(\text{H}_2\text{O})_4 + 2\text{H}_2\text{O}$	1	
	$\text{Ni(OH)}_2 + 6\text{NH}_3 \rightarrow [\text{Ni}(\text{NH}_3)_6]^{2+} + 2\text{OH}^-$ OR $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} + 6\text{NH}_3 \rightarrow [\text{Ni}(\text{NH}_3)_6]^{2+} + 6\text{H}_2\text{O}$	1	[4]
Total			[13]

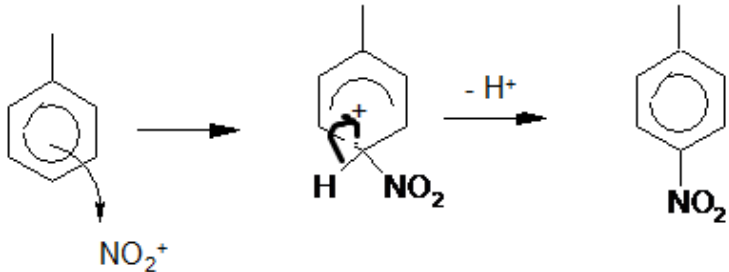
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3 (a) (i)	$101 = \text{P}^{35}\text{Cl}^{35}\text{Cl}$ $103 = \text{P}^{35}\text{Cl}^{37}\text{Cl}$ $105 = \text{P}^{37}\text{Cl}^{37}\text{Cl}$	1 1 1	
(ii)	9:6:1	1	[4]
(b) (i)	PCl_5 5 bonding pairs around P	1	
(ii)		1 1	[3]
(c) (i)	 P_4O_6 structure 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)	$K_{\text{sp}} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$	1	

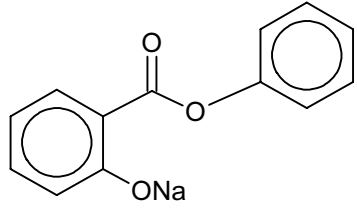
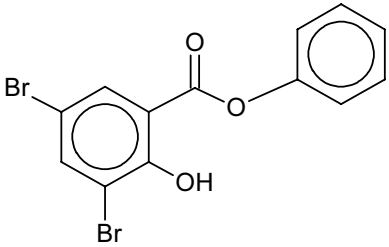
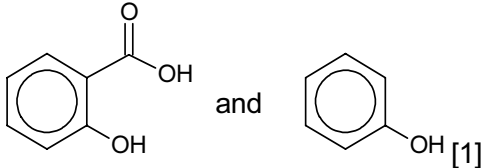
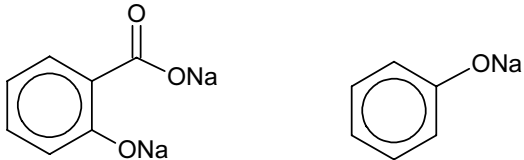
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(ii)	$[Ca^{2+}] = 3 \times 2.50 \times 10^{-6} = 7.50 \times 10^{-6} \text{ mol dm}^{-3}$ $[PO_4^{3-}] = 2 \times 2.50 \times 10^{-6} = 5.00 \times 10^{-6} \text{ mol dm}^{-3}$ $= (7.50 \times 10^{-6})^3 (5.00 \times 10^{-6})^2$ $= \mathbf{1.05(1.1)} \times \mathbf{10^{-26}}$ $\text{mol}^5 \text{dm}^{-15}$	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	

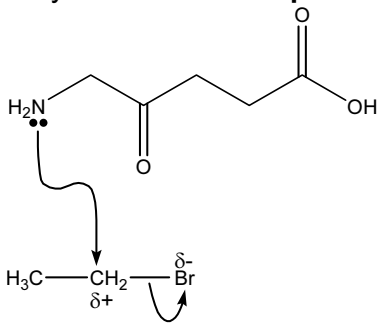
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<p>(ii)</p>	<p>any three of</p> <ul style="list-style-type: none"> • curly arrow from inside the benzene ring to NO_2^+ group • intermediate – penalise NO_2 connectivity or missing methyl group (once) • curly arrow from C-H bond into ring • product + H^+ (or as diagram $-\text{H}^+$) <p>allow 2- and 3-substituted nitromethylbenzene)</p> 	<p>3</p>	<p>[4]</p>
<p>(b) (i)</p>	<p>acidity of $\text{ClCH}_2\text{CO}_2\text{H} > \text{CH}_3\text{CO}_2\text{H}$ AND ($\text{ClCH}_2\text{CO}_2\text{H}$) as an electronegative/electron withdrawing Cl</p>	<p>1</p>	
<p>(ii)</p>	<p>acidity of phenol $> \text{CH}_3\text{CH}_2\text{OH}$ AND electrons on oxygen (on phenol) delocalised into ring OR benzene ring withdraws electrons from oxygen stronger acid linked to weakening O-H bond/anion being stabilised</p>	<p>1</p>	<p>[3]</p>

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

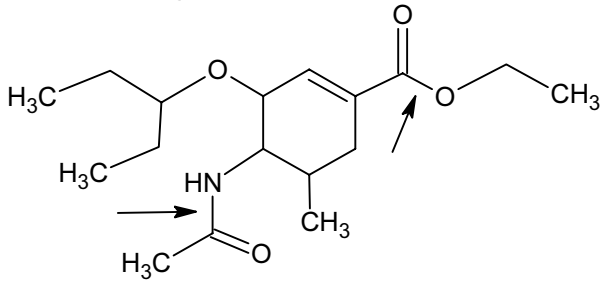
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Total			13
5 (a)	$\text{CH}_3\text{CH}_2\text{COCl} > \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} > \text{C}_6\text{H}_5\text{Cl}$ any two of: <ul style="list-style-type: none"> C-Cl bond strength is weakest in $\text{CH}_3\text{CH}_2\text{COCl}$ ora In $\text{C}_6\text{H}_5\text{Cl}$ (no hydrolysis) C-Cl bond is part of delocalised system OR p-orbital on Cl overlaps with π system OR electrons from Cl overlap with π system $\text{CH}_3\text{CH}_2\text{COCl}$ carbon in C-Cl 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]

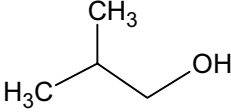
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(d)	<p>Y = </p> <p>W = </p> <p>X = </p> <p>each structure 1 mark</p>	3	[3]
(e)	<p></p> <p>correct displayed amide formula correct polyamide with two repeat units</p>	1 1	[2]
Total			15
6 (a)	<ul style="list-style-type: none"> • (move in different directions) 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 NH₂/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]

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(c)	<p>any three of: (all can be awarded from a clear, labelled diagram)</p> <ul style="list-style-type: none"> • (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)	<p>van der Waals' forces lost (in val) H-bonding gained (in ser)</p>	1 1	[2]
Total			11
7 (a)	<p>amide group circled OR indicated as diagram ester group circled OR indicated as diagram</p> 	1 1	[2]
(b)	<p>lower doses of the drug required OR improved activity of the drug OR reduced side effects</p>	1	[1]

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(c)	decreases enzyme activity OR decreases rate at which product is formed	1	
	binds with the enzyme's active site OR has a complementary shape to active site OR similar shape to substrate	1	
	(competitive inhibition can be overcome by) increasing [substrate] OR increasing substrate concentration	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 ₄ H ₁₀ O	1	[3]
(b) (i)	2-methylpropan-1-ol OR correct structure 	1	
(ii)	0.9-1.0 is (2 x)CH ₃ R/CH ₃ /RCH	1	
	multiplet/1.8 is CHR/R ₃ CH	1	
	singlet/2.5 is OH	1	
	3.4 is CH ₂ O/CH ₃ O	1	
(iii)	doublet 1H/one proton on adjacent carbon	1	
		1	

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(iv)	OH peak or one peak disappears	1	[9]
	OH proton is labile or exchanges for D of D ₂ O or as an equation e.g. D ₂ O + OH → DOH + OD as a minimum	1	
Total			12
			100