

**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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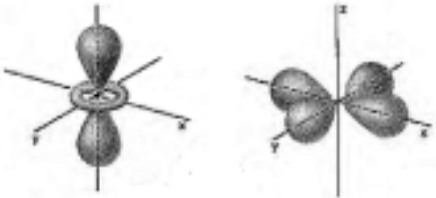
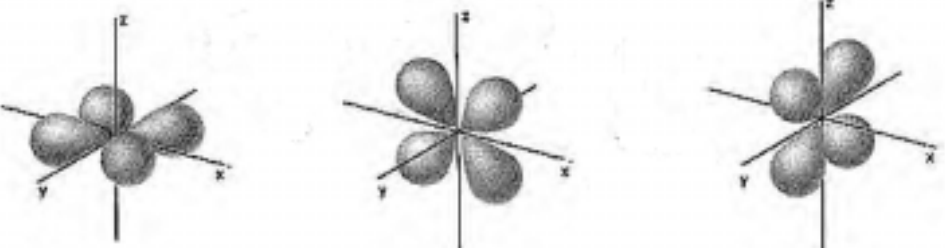
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Question	Marking point	Marks	Marks total
<b>1 (a) (i)</b>	[NO] 2 <sup>nd</sup> order <b>and</b> the concentration is ×2, rate × 4	1	
	[O <sub>2</sub> ] 1 <sup>st</sup> order <b>and</b> evidence of using expt 1 & 2 when the concentration is ×2, rate doubles	1	
<b>(ii)</b>	(0.00408 × 27) rate = <b>0.11</b> (mol dm <sup>-3</sup> s <sup>-1</sup> ) to <b>2sf</b>	1	
<b>(iii)</b>	(Rate =) $k [\text{O}_2][\text{NO}]^2$	1	
<b>(iv)</b>	$k = 332(.03125)$ mol <sup>-2</sup> dm <sup>6</sup> s <sup>-1</sup>	1 1	[6]
<b>(b) (i)</b>	labelled axes x-axis: energy (KE) and y-axis: molecules or particles	1	
	two curves: starts origin; not touching x-axis again; no levelling out; curves only intersecting once	1	
	curves labelled and T2 is to the right and lower max than T1	1	
<b>(ii)</b>	rate increases <b>and</b> energy of the particles increases	1	
	more particles have $E_a$	1	[5]
<b>(c)</b>	1 mole of F <sub>2</sub> and 1 mole NO reacting in the <b>slow</b> step	1	
	a balanced mechanism consistent with overall equation  e.g. $\text{F}_2 + \text{NO} \rightarrow \text{NOF} + \text{F}$ <b>OR</b> $\text{F}_2 + \text{NO} \rightarrow \text{NOF}_2$ $\text{NO} + \text{F} \rightarrow \text{NOF}$ $\text{NO} + \text{NOF}_2 \rightarrow 2\text{NOF}$	1	[2]
<b>Total</b>			[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>(Ni<sup>2+</sup>)</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 <sup>2+</sup> )	↑↓	↑↓	↑↓	↑	↑			1 1	[2]
	3d						4s																				
(Ni)	↑↓	↑↓	↑↓	↑	↑		↑↓																				
(Ni <sup>2+</sup> )	↑↓	↑↓	↑↓	↑	↑																						
(b) (i)	degenerate	1																									
(ii)	2 upper orbitals <b>and</b> 3 lower orbitals	1																									
(iii)	<p><b>correct upper</b> orbital diagram</p> <div style="text-align: center;">  </div> <p><b>correct lower</b> orbital diagram</p> <div style="text-align: center;">  </div>	1  1	[4]																								
(c)	<p><b>electron(s)</b> move from lower to upper level</p> <p><b>absorb</b> (red/blue) light/photon</p> <p>complementary colour (green) is seen <b>OR</b> green light is transmitted</p>	1 1 1	[3]																								

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

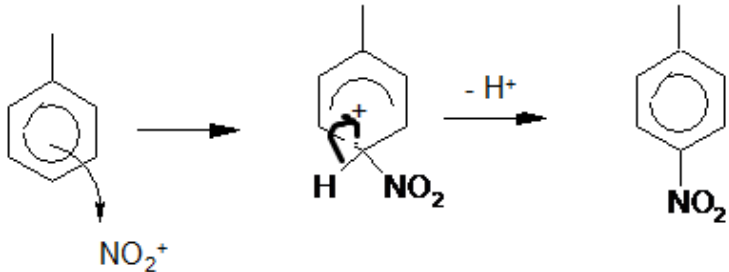
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3	(a) (i)	$101 = \text{P}^{35}\text{Cl}^{35}\text{Cl}$ $103 = \text{P}^{35}\text{Cl}^{37}\text{Cl}$ $105 = \text{P}^{37}\text{Cl}^{37}\text{Cl}$	1 1 1	
	(ii)	9:6:1	1	[4]
	(b) (i)	$\text{PCl}_5$ 5 bonding pairs around P	1	
	(ii)		1 1	[3]
	(c) (i)	<p><math>\text{P}_4\text{O}_6</math> structure where each P has three P-O bonds and each O has two P-O bonds e.g.</p>	1	
	(ii)	(molecule/ion/species) that <b>donates</b> 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	

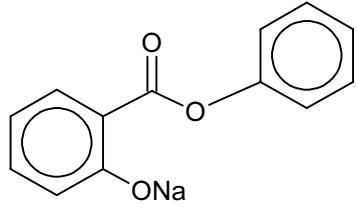
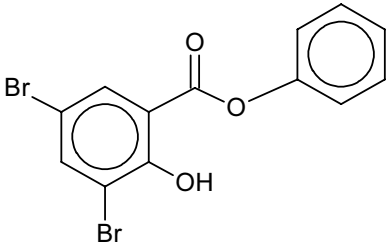
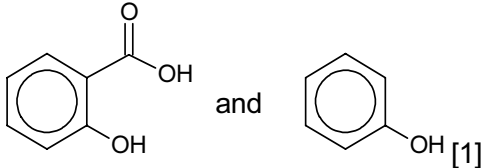
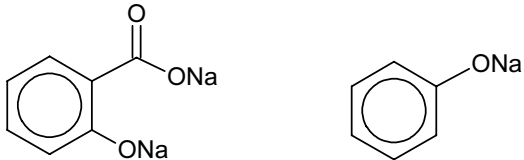
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<b>(ii)</b>	$[Ca^{2+}] = 3 \times 2.50 \times 10^{-6} = 7.50 \times 10^{-6} \text{ mol dm}^{-3}$ $[PO_4^{3-}] = 2 \times 2.50 \times 10^{-6} = 5.00 \times 10^{-6} \text{ mol dm}^{-3}$  $= (7.50 \times 10^{-6})^3 (5.00 \times 10^{-6})^2$ $= \mathbf{1.05(1.1)}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

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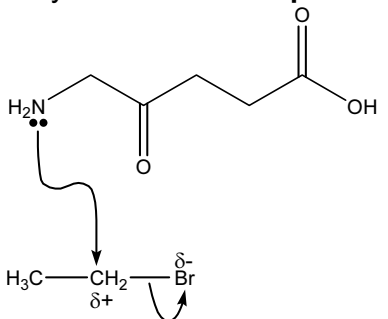
<p>(ii)</p>	<p><b>any three of</b></p> <ul style="list-style-type: none"> <li>• curly arrow from inside the benzene ring to <math>\text{NO}_2^+</math> group</li> <li>• intermediate – <b>penalise</b> <math>\text{NO}_2</math> connectivity <b>or</b> missing methyl group (once)</li> <li>• curly arrow from C-H bond into ring</li> <li>• product + <math>\text{H}^+</math> (or as diagram <math>-\text{H}^+</math>)</li> </ul> <p><b>allow</b> 2- and 3-substituted nitromethylbenzene)</p> 	<p>3</p>	<p>[4]</p>
<p>(b) (i)</p> <p>(ii)</p>	<p>acidity of <math>\text{ClCH}_2\text{CO}_2\text{H} &gt; \text{CH}_3\text{CO}_2\text{H}</math> <b>AND</b> (<math>\text{ClCH}_2\text{CO}_2\text{H}</math>) as an electronegative/electron withdrawing <math>\text{Cl}</math></p> <p>acidity of phenol <math>&gt; \text{CH}_3\text{CH}_2\text{OH}</math> <b>AND</b> electrons on oxygen (on phenol) delocalised into ring  <b>OR</b> benzene ring withdraws electrons from oxygen  stronger acid linked to weakening O-H bond/anion being stabilised</p>	<p>1</p> <p>1</p> <p>1</p>	<p>[3]</p>

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(c)	Na	 (or ionic)	redox/reduction		
	Br <sub>2</sub>		(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]



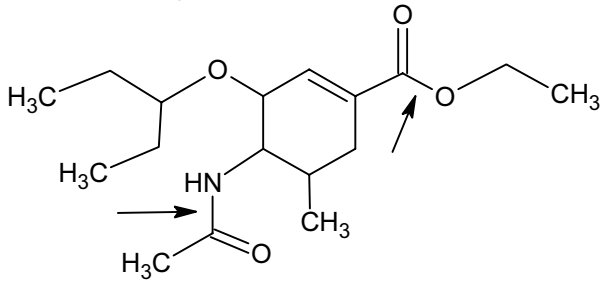
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<b>Total</b>			<b>13</b>
<b>5 (a)</b>	$\text{CH}_3\text{CH}_2\text{COCl} > \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} > \text{C}_6\text{H}_5\text{Cl}$ <b>any two of:</b> <ul style="list-style-type: none"> <li>C-Cl bond strength is weakest in <math>\text{CH}_3\text{CH}_2\text{COCl}</math> ora</li> <li>In <math>\text{C}_6\text{H}_5\text{Cl}</math> (no hydrolysis) C-Cl bond is part of delocalised system <b>OR</b> p-orbital on Cl overlaps with <math>\pi</math> system <b>OR</b> electrons from Cl overlap with <math>\pi</math> system</li> <li><math>\text{CH}_3\text{CH}_2\text{COCl}</math> carbon in C-Cl bond is more electron deficient since it is also attached to an oxygen atom ora</li> </ul>	1   1+1	<b>[3]</b>
<b>(b)</b>	ketone, amine, carboxylic acid two correct 1 mark, all three 2	2	<b>[2]</b>
<b>(c) (i)</b>	dipole on C-Br curly arrow breaking C-Br bond curly arrow from <b>lone pair</b> on N to carbon in C-Br bond 	1 1 1	
<b>(ii)</b>	nucleophilic substitution	1	
<b>(iii)</b>	HBr or hydrogen bromide	1	<b>[5]</b>

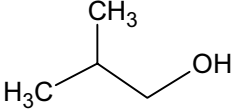
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(d)	<p>Y = </p> <p>W = </p> <p>X = </p> <p>each structure 1 mark</p>	3	[3]
(e)	<p></p> <p>correct displayed amide formula correct polyamide with two repeat units</p>	1 1	[2]
<b>Total</b>			<b>15</b>
6 (a)	<ul style="list-style-type: none"> <li>• (move in different directions) some amino acids have a different charge</li> <li>• (move at different speeds) some amino acids have a different size/different charge</li> <li>• (some amino acids do not move at all) some amino acids exist as a zwitterions/have no net(overall) charge/neutral/both NH<sub>2</sub>/COOH are charged in amino acids</li> </ul>	1 1 1	[3]
(b) (i)	mobile – solvent <b>or</b> water stationary – alumina/silica (supported on glass/plastic/Al)	1 1	
(ii)	by adsorption	1	[3]

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(c)	<p><b>any three</b> of: (all can be awarded from a clear, labelled diagram)</p> <ul style="list-style-type: none"> <li>• (base pairing) A to T <b>OR</b> C to G</li> <li>• H-bonds between bases</li> <li>• two/double stranded/chains</li> <li>• anti-parallel strands</li> <li>• (general structure) sugar-phosphate backbone <b>OR</b> BASE-SUGAR-PHOSPHATE bonded in a diagram</li> </ul>	3	[3]
(d)	<p>van der Waals' forces lost (in val) H-bonding gained (in ser)</p>	1 1	[2]
<b>Total</b>			<b>11</b>
7 (a)	<p>amide group circled <b>OR</b> indicated as diagram ester group circled <b>OR</b> indicated as diagram</p> 	1 1	[2]
(b)	<p>lower doses of the drug required <b>OR</b> improved activity of the drug <b>OR</b> reduced side effects</p>	1	[1]

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(c)	decreases enzyme activity <b>OR</b> decreases rate at which product is formed	1	
	binds with the enzyme's active site <b>OR</b> has a complementary shape to active site <b>OR</b> similar shape to substrate	1	
	(competitive inhibition can be overcome by) increasing [substrate] <b>OR</b> increasing substrate concentration	1	[3]
(d)	<b>energy</b> source/carrier <b>OR</b> releases energy when hydrolysed	1	[1]
<b>Total</b>			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 <sub>4</sub> H <sub>10</sub> O	1	[3]
(b) (i)	2-methylpropan-1-ol <b>OR</b> correct structure 	1	
(ii)	0.9-1.0 is (2 x)CH <sub>3</sub> R/CH <sub>3</sub> /RCH	1	
	multiplet/1.8 is CHR/R <sub>3</sub> CH	1	
	singlet/2.5 is OH	1	
	3.4 is CH <sub>2</sub> O/CH <sub>3</sub> 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 <i>or</i> exchanges for D of D <sub>2</sub> O <i>or</i> as an equation e.g. D <sub>2</sub> O + OH → DOH + OD as a minimum	1	
<b>Total</b>			<b>12</b>
			<b>100</b>