

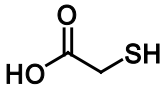
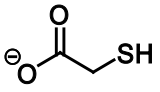
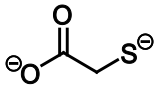
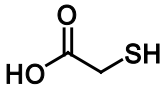
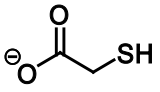
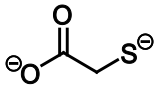
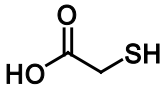
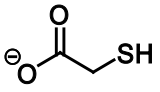
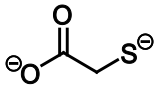
44th INTERNATIONAL CHEMISTRY OLYMPIAD

UK Round 1 - 2012

MARK SCHEME

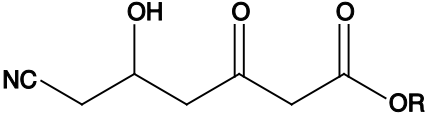
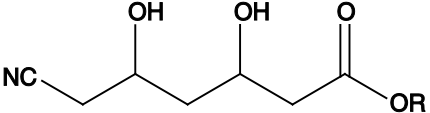
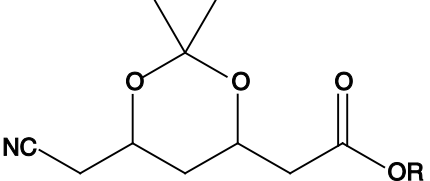
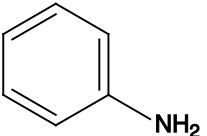
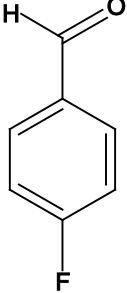
Question	1	2	3	4	5	Total
Mark	9	14	17	23	17	80

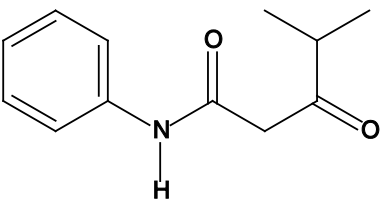
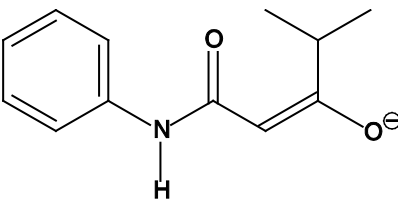
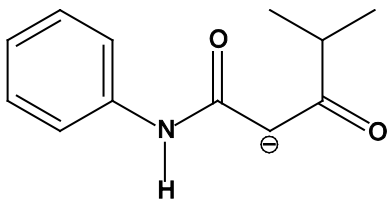
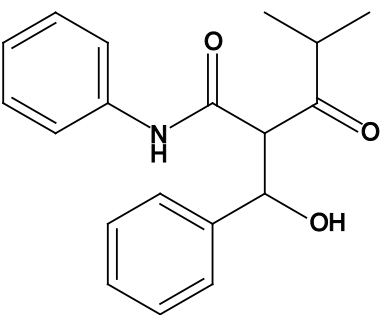
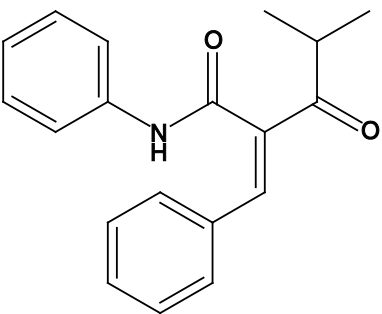
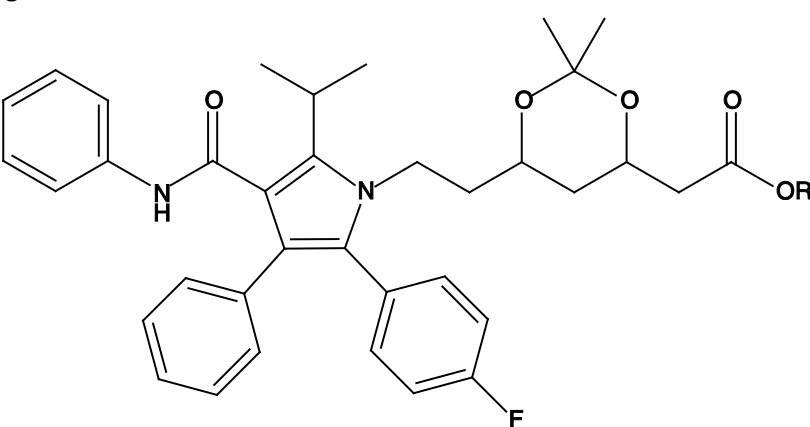
Question 1		Answer	Marks
a)	(i)	Breaking bonds in 8 moles of S_7 (g): $8 \times 7 \times 260.0 \text{ kJ mol}^{-1} = 14560.0 \text{ kJ mol}^{-1}$ Making bonds in 7 moles of S_8 (g): $7 \times 8 \times 263.3 \text{ kJ mol}^{-1} = 14744.8 \text{ kJ mol}^{-1}$ Enthalpy change of reaction = $(14560.0 - 14744.8) \text{ kJ mol}^{-1} = -184.8 \text{ kJ mol}^{-1}$	1
b)	(i)	Amount S_7 = $0.0076 \text{ g} / (7 \times 32.06) \text{ g mol}^{-1} = 3.387 \times 10^{-5} \text{ mol}$ Amount S_8 = $0.9892 \text{ g} / (8 \times 32.06) \text{ g mol}^{-1} = 3.857 \times 10^{-3} \text{ mol}$	1
	(ii)	$K_c = [S_8]^7 / [S_7]^8$	1
	(iii)	Value for K_c $[3.857 \times 10^{-3}]^7 / [3.387 \times 10^{-5}]^8 = 7.34 \times 10^{18}$ (Ignore any units) (allow error carried forward from part b(i))	1
c)	(i)	$\Delta_r H^\ominus(298 \text{ K}) = (-296.8 - (-297.1)) \text{ kJ mol}^{-1} = (+)0.3 \text{ kJ mol}^{-1}$	1
	(ii)	The most stable form is orthorhombic Allow monoclinic if the answer given in c(i) is negative	1
d)		$\begin{array}{c} \text{N}=\text{S}=\text{N} \\ \quad \\ \text{S} \quad \text{S} \\ \quad \\ \text{N}=\text{S}=\text{N} \end{array}$	1
e)		$\begin{array}{c} \text{N}=\text{S}-\text{N} \\ \quad \quad \\ \text{S} \quad \text{S} \\ \quad \quad \\ \text{N}-\text{S}=\text{N} \end{array}$	1
f)		$\left[\text{N}=\text{S}=\text{N}-\text{S} \right]_n \quad \text{or} \quad \left[\text{N}-\text{S}-\text{N}=\text{S} \right]_n$ or either in reverse order	1

		Total for Question 1	9						
Question 2									
		Answer	Marks						
a)	(i)	Amount of S in moles = amount of BaSO ₄ = 0.260 g / (137.34 + 32.06 + 4(16.00)) g mol ⁻¹ = 1.114 mmol % of sulfur by mass = 1.114 mmol × 32.06 g mol ⁻¹ × 100% = 3.57%	1						
	(ii)	Mass of BaSO ₄ (aq) in 2.50 dm ³ = 2.4 mg dm ⁻³ × 2.50 dm ³ = 6.0 mg Total mass of BaSO ₄ in 2.50 dm ³ = 6.0 mg + 260 mg = 266 mg % of sulfur by mass in human hair = (0.266 g / 0.260 g) × 3.57% = 3.65%	1						
b)		Oxidation	1						
c)		<table border="1" style="width: 100%; text-align: center;"> <tr> <td>(i) pH 0</td> <td>(ii) pH 7</td> <td>(iii) pH 14</td> </tr> <tr> <td></td> <td></td> <td></td> </tr> </table>	(i) pH 0	(ii) pH 7	(iii) pH 14				3
(i) pH 0	(ii) pH 7	(iii) pH 14							
									
d)		<p>Via $pK_a = pH - \log_{10} ([A^{2-}]/[HA^-])$ Or via $K_a = [H^+] ([A^{2-}]/[HA^-])$ $10.31 = 9 - \log_{10} ([A^{2-}]/[HA^-])$ $K_a/[H^+] = ([A^{2-}]/[HA^-])$ $\log_{10} ([A^{2-}]/[HA^-]) = -1.31$ $([A^{2-}]/[HA^-]) = (10^{-10.31}/10^{-9})$ $([A^{2-}]/[HA^-]) = 0.049$ $([A^{2-}]/[HA^-]) = 0.049$</p> <p>Then... $[A^{2-}] + [HA^-] = 100\%$ So $[A^{2-}] = 4.67\%$ and therefore $[HA^-] = 95.3\%$</p>	1 1						
e)		Ker-S-S-Ker + 2 RS-H → R-S-S-R + 2 Ker-S-H	1						
f)		Line C	1						
g)		<p>Gradient of graph allowed between 3.83×10^{-3} to $4.16 \times 10^{-3} \text{ min}^{-1}$ <i>k</i> is then calculated by gradient / 0.16 This corresponds to range of acceptable value for the rate constant <i>k</i> Minimum $k = 3.99 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ or $2.40 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$ Maximum $k = 4.34 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ or $2.60 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$ 2 marks for correct value with correct units; 1 mark if correct but units missing / wrong; 1 mark if units correct but value is calculated (correctly) from gradient outside range; 0 marks correct units with incorrect answer.</p>	2						
h)		<p>Gradient of graph allowed between 1.23×10^{-2} to $1.27 \times 10^{-2} \text{ min}^{-1}$ Using <i>k</i> from part (g), concentration is calculated by dividing gradient by <i>k</i>. Concentration = $0.499 \text{ mol dm}^{-3}$ Molar mass of ammonium thioglycolate = $(14.01 + 4 \times 1.008) + (2 \times 12.01 + 2 \times 16.00 + 3 \times 1.008 + 32.06) = 109.146 \text{ g mol}^{-1}$ Amount in one bottle = $0.500 \times 0.499 \times 109.146 = 27.2 \text{ g}$ 2 marks: One of these is for calculating a correct concentration given their <i>k</i> in part (g), and one for a correct mass from their concentration. Any answer close to 27g where the correct method has been used should be given full credit.</p>	2						
Total for Question 2			14						

Question 3			Answer					Marks
a)		Longest-known	Most recently discovered					2
		S	P	O	Ar	Pu		
		All elements in correct order scores 2 marks If the correct order can be achieved by moving one element to any new position in the candidate's answer, award 1 mark						
b)		C ₂ H ₅ OC ₂ H ₅	C ₂ H ₅ OH	HOCH ₂ CH ₂ OH	CH ₃ CHO	C ₄ H ₁₀	H ₂ O	2
		3	4	6	2	1	5	
		All answers correct scores 2 marks If the correct order can be achieved by moving one compound to a new position, award 1 mark						
c)	(i)	FeS ₂ (give 1 mark for FeS)					2	
	(ii)	MgSO ₄ or MgSO ₄ .7H ₂ O					1	
	(iii)	N ₂ O					1	
d)	(i)	Propanone					1	
	(ii)	Methylbenzene					1	
	(iii)	Sodium chlorate(I)					1	
e)		White to yellow					1	
f)	(i)	C					1	
	(ii)	E					1	
	(iii)	B					1	
	(iv)	A					1	
	(v)	D					1	
Total for Question 3						17		

Question 4		Answer	Marks										
a)	B		1										
	C		1										
	D		1										
	E		1										
	F		1										
	G		6										
		<table border="1"> <tbody> <tr> <td>absorption / cm⁻¹</td> <td>~ 3300 (broad)</td> <td>1775</td> <td>2250-2275</td> <td>3374</td> <td>1700-1740</td> </tr> <tr> <td>bond</td> <td>O-H</td> <td>C=O in a small ring</td> <td>C≡N</td> <td>N-H</td> <td>C=O</td> </tr> </tbody> </table>		absorption / cm ⁻¹	~ 3300 (broad)	1775	2250-2275	3374	1700-1740	bond	O-H	C=O in a small ring	C≡N
absorption / cm ⁻¹	~ 3300 (broad)	1775	2250-2275	3374	1700-1740								
bond	O-H	C=O in a small ring	C≡N	N-H	C=O								
One mark for correct structure for G; one mark for each correct entry in table													
b)	Anion I		2										
	2 marks	(1 mark for this alternative)											

Question 4 continued		
	Answer	Marks
c)	<p>J</p> 	3
	<p>K</p> 	
	<p>L</p> 	
d)	<p>Phenylamine</p>  <p>4-fluorobenzaldehyde</p> 	2

Question 4 continued		Answer	Marks
e)	<p>O</p>  <p>P</p>  <p>or</p>  <p>Q</p>  <p>S</p>  <p>(Full credit should be given if phenyl rings are shown as C₆H₅, or Ph)</p>	4	
f)	<p>U</p> 	1	
Total for Question 4			23

Question 5		Answer	Marks																																			
a)	(i)	$C_{132}H_{120}N_2 + 164O_2 \rightarrow 132CO_2 + 60H_2O + 2NO_2$ or $C_{132}H_{120}N_2 + 162O_2 \rightarrow 132CO_2 + 60H_2O + N_2$	1																																			
	(ii)	$M_r = (132 \times 12.01) + (120 \times 1.008) + (2 \times 14.01) = 1734.30$ $\% \text{ of C} = ((132 \times 12.01) / 1734.30) \times 100\% = 91.41 \%$ $\% \text{ of H} = ((120 \times 1.008) / 1734.30) \times 100\% = 6.97\%$ $\% \text{ of N} = ((2 \times 14.01) / 1734.30) \times 100\% = 1.62 \%$	1																																			
b)		<p>Diagram A: Top-right box is empty. Bottom-left arrow points right, bottom-right arrow points left.</p> <p>Diagram B: Top-right box is empty. Bottom-left arrow points left, bottom-right arrow points right.</p> <p>Diagram C: Top-right box is empty. Bottom-left arrow points left, bottom-right arrow points left.</p> <p>Diagram D: Top-right box is empty. Bottom-left arrow points right, bottom-right arrow points right.</p> <p>Diagram E: Top-right box is empty. Bottom-left arrow points right, bottom-right arrow points left.</p> <p>Diagram F: Top-right box is empty. Bottom-left arrow points left, bottom-right arrow points left.</p> <p>If top right box on every car is correctly assigned – 2 marks If top right box on every car is incorrectly assigned – 1 mark (for consistent error) Mark the bottom left and bottom right boxes in the same way</p>	6																																			
c)		"B and F" is awarded 2 marks "B and F; A and C" is awarded one mark Any other answer is awarded no marks	2																																			
d)		A, C and E. Any other answer is awarded no mark	1																																			
e)		<table border="1"> <thead> <tr> <th></th> <th>A</th> <th>B</th> <th>C</th> <th>D</th> <th>E</th> <th>F</th> </tr> </thead> <tbody> <tr> <td>(i) Spin clockwise</td> <td></td> <td>✓</td> <td></td> <td></td> <td></td> <td></td> </tr> <tr> <td>(ii) Spin anti-clockwise</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>✓</td> </tr> <tr> <td>(iii) Remain stationary</td> <td>✓</td> <td></td> <td>✓</td> <td>✓</td> <td></td> <td></td> </tr> <tr> <td>(iv) Move forwards</td> <td></td> <td></td> <td></td> <td></td> <td>✓</td> <td></td> </tr> </tbody> </table> <p>One mark for each car/letter/column Note that if B is marked as 'anti-clockwise' and F is marked as 'clockwise', this combination scores 1 mark for consistent error.</p>		A	B	C	D	E	F	(i) Spin clockwise		✓					(ii) Spin anti-clockwise						✓	(iii) Remain stationary	✓		✓	✓			(iv) Move forwards					✓		6
	A	B	C	D	E	F																																
(i) Spin clockwise		✓																																				
(ii) Spin anti-clockwise						✓																																
(iii) Remain stationary	✓		✓	✓																																		
(iv) Move forwards					✓																																	
Total for Question 5			17																																			

