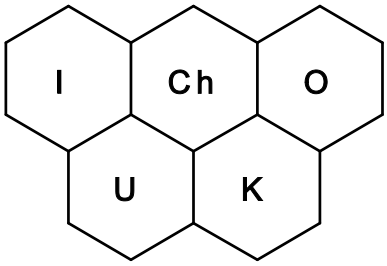
RSC | Advancing the Chemical Sciences

INEOS THE WORD FOR CHEMICALS



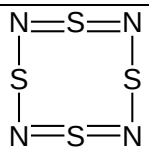
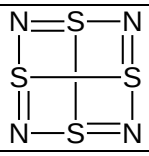
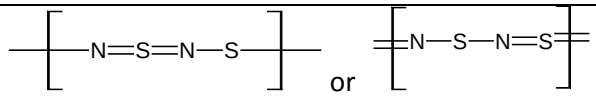
44th INTERNATIONAL CHEMISTRY OLYMPIAD

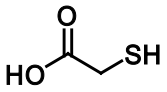
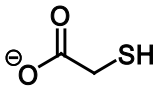
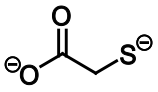
UK Round 1 - 2012

MARK SCHEME

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

Question 1

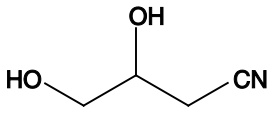
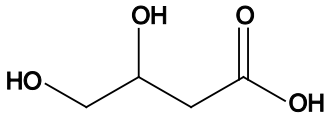
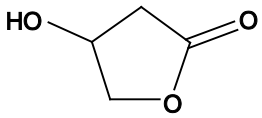
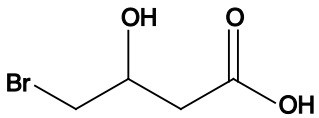
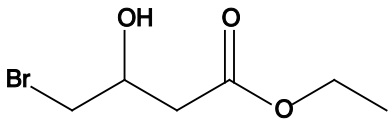
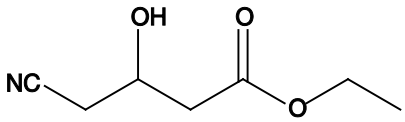
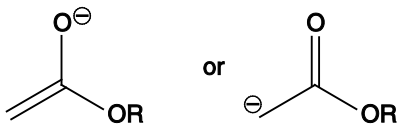
		Answer	Marks
a)	(i)	Breaking bonds in 8 moles of S_7 (g): $8 \times 7 \times 260.0$ kJ mol^{-1} = 14560.0 kJ mol^{-1} Making bonds in 7 moles of S_8 (g): $7 \times 8 \times 263.3$ kJ mol^{-1} = 14744.8 kJ mol^{-1} Enthalpy change of reaction = (14560.0 − 14744.8) kJ mol^{-1} = −184.8 kJ mol^{-1}	1
b)	(i)	**Amount S_7** = 0.0076 g / (7 × 32.06) g mol^{-1} = 3.387×10^{-5} mol **Amount S_8** = 0.9892 g / (8 × 32.06) g mol^{-1} = 3.857×10^{-3} 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)	$\Delta_r H^{\ominus}(298\ K)$ = (−296.8 − (−297.1)) kJ mol^{-1} = (+)0.3 kJ mol^{-1}	1
	(ii)	**The most stable form is** orthorhombic Allow monoclinic if the answer given in c(i) is negative	1
d)			1
e)			1
f)		 or either in reverse order	1

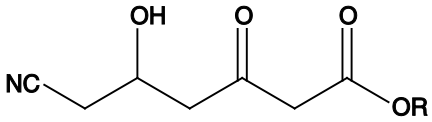
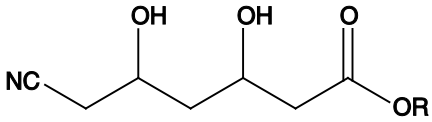
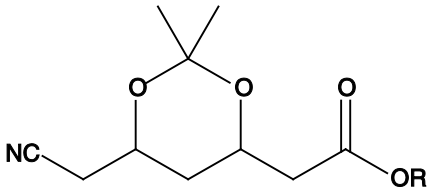
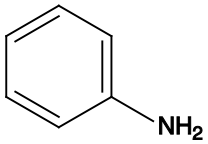
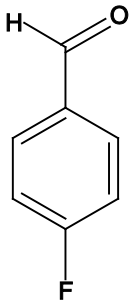
		Total for Question 1	**9**
Question 2			
		Answer	**Marks**
a)	**(i)**	Amount of S in moles = amount of $BaSO_4$ = 0.260 g / (137.34 + 32.06 + 4(16.00)) g mol^{-1} = 1.114 mmol % of sulfur by mass = 1.114 mmol × 32.06 g mol^{-1} × 100% = 3.57%	**1**
	(ii)	Mass of $BaSO_4$ (aq) in 2.50 dm^3 = 2.4 mg dm^{-3} × 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)		**(i)** pH 0  **(ii)** pH 7  **(iii)** pH 14 	**3**
d)		Via $pK_a = pH - \log_{10}([A^{2-}]/[HA^-])$ $10.31 = 9 - \log_{10}([A^{2-}]/[HA^-])$ $\log_{10}([A^{2-}]/[HA^-]) = -1.31$ $([A^{2-}]/[HA^-]) = 0.049$ Or via $K_a = [H^+]([A^{2-}]/[HA^-])$ $K_a/[H^+] = ([A^{2-}]/[HA^-])$ $([A^{2-}]/[HA^-]) = (10^{-10.31}/10^{-9})$ $([A^{2-}]/[HA^-]) = 0.049$ Then… $[A^{2-}] + [HA^-] = 100\ \%$ So $[A^{2-}] = 4.67\ \%$ and therefore $[HA^-] = 95.3\ \%$	**1** **1**
e)		Ker-S-S-Ker + 2 RS-H → R-S-S-R + 2 Ker-S-H	**1**
f)		Line C	**1**
g)		Gradient of graph allowed between 3.83×10^{-3} to 4.16×10^{-3} min^{-1} *k* is then calculated by gradient / 0.16 This corresponds to range of acceptable value for the rate constant *k* Minimum $k = 3.99 \times 10^{-4}$ mol^{-1} dm^3 s^{-1} or 2.40×10^{-2} mol^{-1} dm^3 min^{-1} Maximum $k = 4.34 \times 10^{-4}$ mol^{-1} dm^3 s^{-1} or 2.60×10^{-2} mol^{-1} dm^3 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.	**2**
h)		Gradient of graph allowed between 1.23×10^{-2} to 1.27×10^{-2} min^{-1} Using *k* from part (g), concentration is calculated by dividing gradient by *k.* Concentration = 0.499 mol dm^{-3} Molar mass of ammonium thioglycolate = (14.01 + 4 × 1.008) + (2 × 12.01 + 2 × 16.00 + 3 × 1.008 + 32.06) = 109.146 g mol^{-1} Amount in one bottle = 0.500 × 0.499 × 109.146 = 27.2 g **2 marks:** One of these is for calculating a correct concentration given their k 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.	**2**
		Total for Question 2	**14**

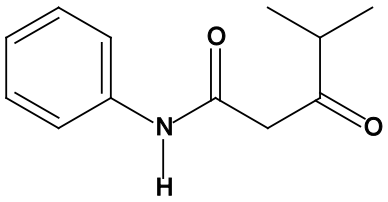
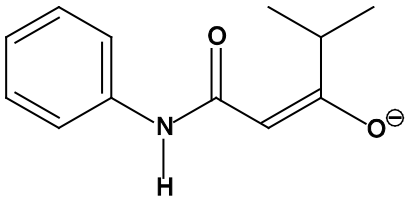
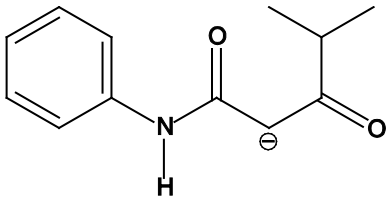
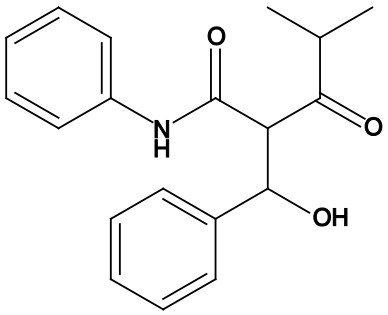
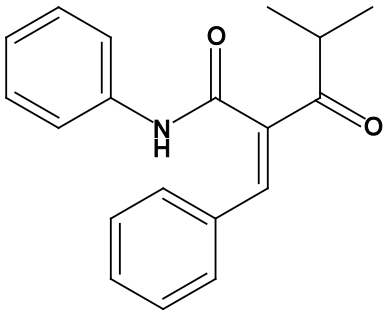
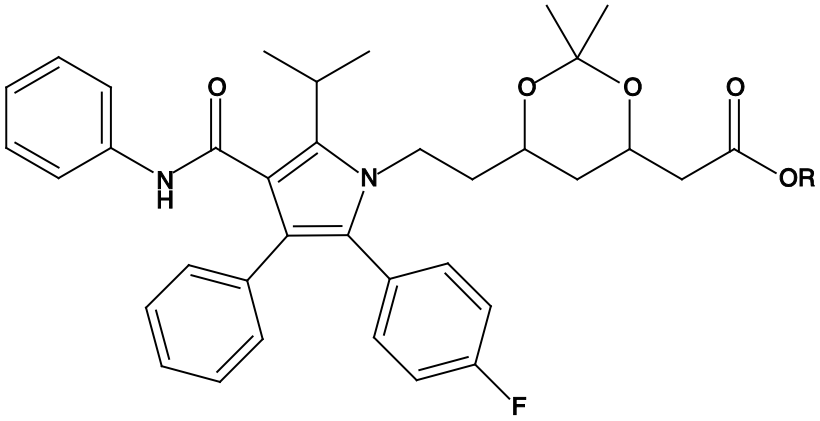
Question 3

		Answer	Marks
a)		Longest-known → Most recently discovered 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	**2**
b)		$C_2H_5OC_2H_5$ | C_2H_5OH | $HOCH_2CH_2OH$ | CH_3CHO | C_4H_{10} | H_2O 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	**2**
c)	**(i)**	FeS_2 (give 1 mark for FeS)	**2**
	(ii)	$MgSO_4$ or $MgSO_4.7H_2O$	**1**
	(iii)	N_2O	**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**

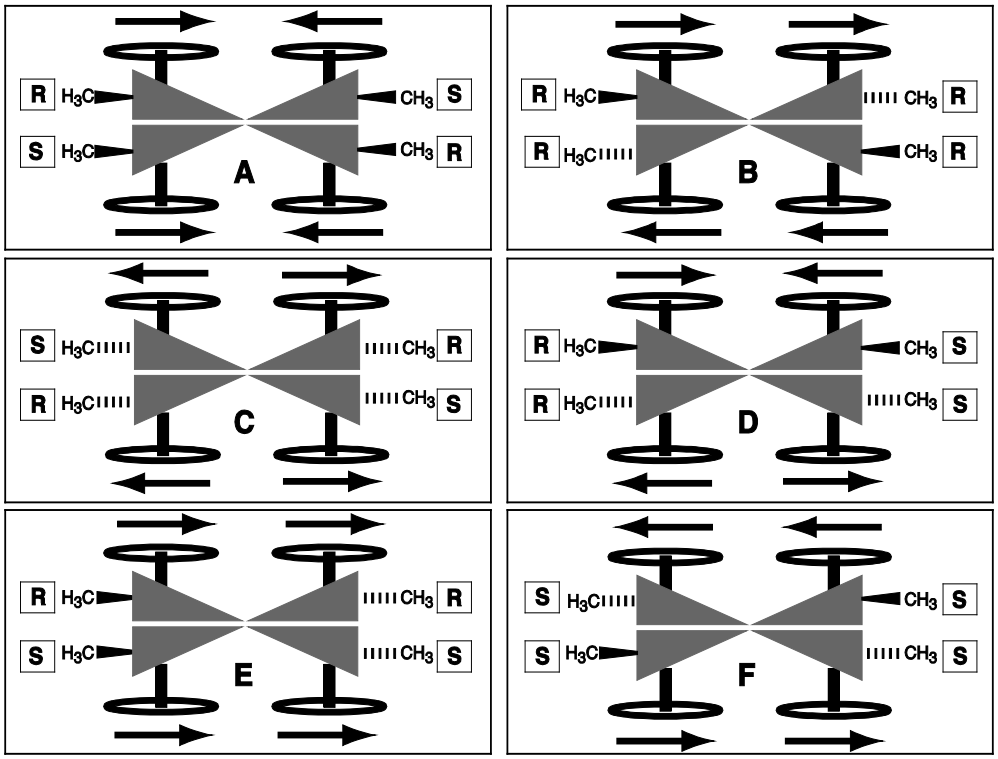
Question 4

		Answer	Marks
a)		**B**  	**1**
		C  	**1**
		D  	**1**
		E  	**1**
		F  	**1**
		G  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	**6**
b)		Anion I  2 marks (1 mark for this alternative)	**2**

Question 4 continued			
		Answer	**Marks**
c)		**J**  	**3**
		K  	
		L  	
d)		**Phenylamine**  **4-fluorobenzaldehyde**  	**2**

Question 4 continued			
		Answer	**Marks**
e)		**O**  **P**  or  **Q**  **S**  (Full credit should be given if phenyl rings are shown as C_6H_5, or Ph)	**4**
f)		**U** 	**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)	$M_r = (132 \times 12.01) + (120 \times 1.008) + (2 \times 14.01) = 1734.30$ % of C = ((132 × 12.01) / 1734.30) × 100% = 91.41 % % of H = ((120 × 1.008) / 1734.30) × 100% = 6.97% % of N = ((2 x 14.01) / 1734.30) × 100% = 1.62 %	**1**
b)		 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	**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><tr><th></th><th>A</th><th>B</th><th>C</th><th>D</th><th>E</th><th>F</th></tr><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></table> 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.	**6**
		Total for Question 5	**17**