41st INTERNATIONAL CHEMISTRY OLYMPIAD

UK Round One - 2009

MARKING SCHEME

Notes

Chemical equations may be given as sensible multiples of those given here. Formulae can be given by any conventional method (i.e. structural or molecular).

State symbols do not need to be included in the chemical equations to obtain the mark(s).

Answers should be given to an appropriate number of significant figures although the marker should only penalise this once.

Total 64 marks.

Question 1			
		Answer	**Marks**
(a)	**i)**	It is aromatic / the bonds in the ring are conjugated / there are alternate single and double bonds in the ring / the electrons in the ring are delocalised / very similar to benzene	1
	ii)	3 peaks	1
	iii)	$C_2H_6N_8 + 7/2\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O + 4\ N_2$ or $2\ C_2H_6N_8 + 7\ O_2 \rightarrow 4\ CO_2 + 6\ H_2O + 8\ N_2$	1
(b)	**i)**	19° or 19.5° or 19°28’	1
	ii)	$C_8N_8O_{16} \rightarrow 8\ CO_2 + 4\ N_2$	1
(c)		$C_6H_7N_3O_{11} + 9/4\ O_2 \rightarrow 6\ CO_2 + 7/2\ H_2O + 3/2\ N_2$ or $4\ C_6H_7N_3O_{11} + 9\ O_2 \rightarrow 24\ CO_2 + 14\ H_2O + 6\ N_2$	2

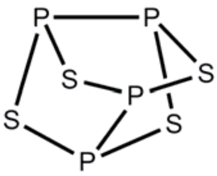
7 marks

Note: Tests are to be taken under controlled conditions. Students must not have access to the information contained in this marking scheme prior to, or during, the test.

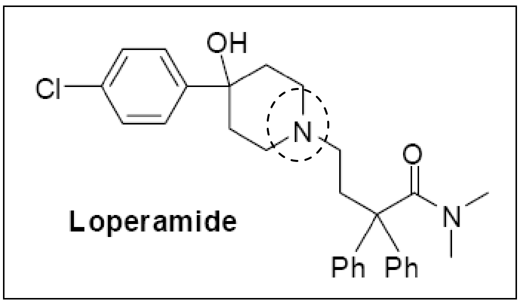
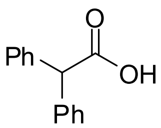
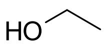
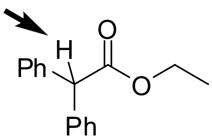
Question 2			
		Answer	**Marks**
(a)	**i)**	Moles = 13000/44.1 = 295	1
	ii)	Mass = 3 x 295 x 44.0 = 38900 g = 38.9 kg (accept 39 kg)	1
	iii)	Heat energy = 2220 x 295 = 655000 kJ = 655 MJ	1
	iv)	1 mol s^{-1} = 2220 kJ s^{-1} = 2220 kW, so 15 kW = 15/2220 mole s^{-1} =15x24000/2220 =162 cm^3 s^{-1}	1
	v)	Still 140 psi (or 9.52 atm)	1
(b)	**i)**	Sensible bonding diagram with all single covalent bonds Accept a bond angle anything between 90^o - 105.5^o	1 1
	ii)	Mass = 295 x 0.02 x 10^{-9} x 62.1 = 0.000000366 g = 0.000366 mg = 3.66 x 10^{-7} g (accept 3.7 or 4.0 x 10^{-7} g)	1
(c)		6000 m^3 CH_4 = 6000 x 10^3 dm^3 = 6000 x 10^3 / 24 moles, so we get 6000 x 10^3 / 24 moles CO_2 = (6000 x 10^3 / 24) X 44 g CO_2 per hour. So in 16 days we get (6000 x 10^3 / 24) X 44 x 24 x 16 = 4224 x 10^6 g = 4224 tonnes (accept 4200 tonnes)	1

9 marks

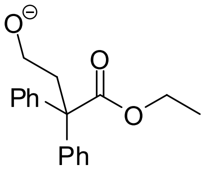
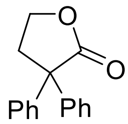
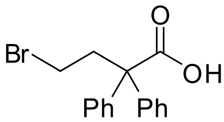
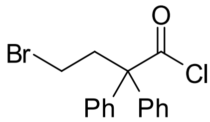
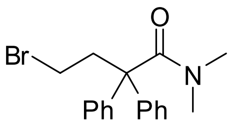
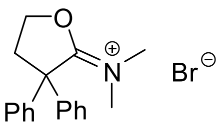
Question 3			
		Answer	**Marks**
(a)	**i)**	$P_4S_3 + 8O_2 \rightarrow P_4O_{10} + 3SO_2$ (accept $2P_2O_5 + 3SO_2$)	1
	ii)	$2KClO_3 \rightarrow 2KCl + 3O_2$	1
	iii)	$3P_4S_3 + 16KClO_3 \rightarrow 3P_4O_{10} + 9SO_2 + 16KCl$ (accept $6P_2O_5$)	1
	iv)	P_4S_3 / $KClO_3$ = 660 / 1961 = 1 / 2.97	1

	v)	$\Delta_r H^{\varnothing} = ((3 \times -2948) + (9 \times -296.8) + (16 \times -436.7)) - ((3 \times -154.0) + (16 \times -397.7))$ $= -11700 \text{ kJ mol}^{-1}$	2
(b)	**i)**	3 peaks	1
	ii)	4 peaks	1
	iii)	3 peaks	1
(c)		 (accept any other reasonable structure, that fits with the data and with elements in correct valencies)	2

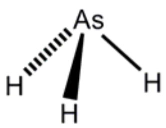
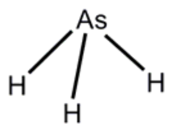
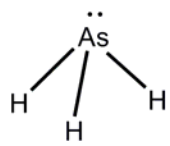
11 marks

Question 4			
		Answer	**Marks**
(a)			1
(b)	**i)**	 carboxylic acid  alcohol	1
	ii)		1

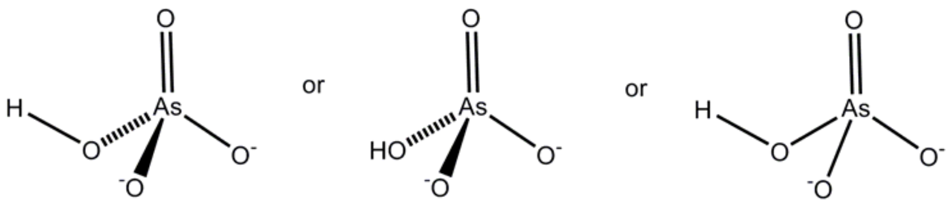
Note: Tests are to be taken under controlled conditions. Students must not have access to the information contained in this marking scheme prior to, or during, the test.

(c)		 anion **C**  cyclic ester **D**	2
(d)		 **E**  **F**	2
(e)	**i)**	 open-chain amide	1
	ii)	 cyclic bromide salt	2

10 marks

Question 5			
		Answer	**Marks**
(a)	**i)**	It must be clear from the structure that arsine is not planar. Structures similar to those shown below would be acceptable:  or  or 	1
	ii)	$4AsH_3 + 3O_2 \rightarrow 4As + 6H_2O$	1
(b)	**i)**	As_2O_3	1
	ii)	$As_2O_3 + 6Zn + 6H_2SO_4 \rightarrow 2AsH_3 + 6ZnSO_4 + 3H_2O$	1
(c)	**i)**	+5 or (V)	1

Note: Tests are to be taken under controlled conditions. Students must not have access to the information contained in this marking scheme prior to, or during, the test.

	ii)	Both the bonding and geometry must be clear, structures such as those shown below would be acceptable: 	1
(d)	**i)**	From the graph the $t_{1/2}$ is 8 mins $k = \ln 2 / t_{1/2}$ therefore k = 0.087 min^{-1} (0.0014 s^{-1} or 0.144 x 10^{-3} s^{-1}) Accept values for $t_{1/2}$ in the region of 7 to 9 mins (k = 0.08 to 0.1 min^{-1}) also accept correct values for k given in s^{-1}.	1
	ii)	$[HAsO_4^{2-}{}_{(aq)}]_t = [HAsO_4^{2-}{}_{(aq)}]_0 \exp^{-(kt)}$ $10 = [HAsO_4^{2-}{}_{(aq)}]_0 \exp^{-(0.09*55)}$ $[HAsO_4^{2-}{}_{(aq)}]_0$ = 1400 μg dm^{-3} For k = 0.08 min^{-1}, $[HAsO_4^{2-}{}_{(aq)}]_0$ = 800 μg dm^{-3} whilst for k = 0.1 min^{-1}, $[HAsO_4^{2-}{}_{(aq)}]_0$ = 2400 μg dm^{-3}. Full marks should be given for values within this range.	2
(e)		$[HAsO_4^{2-}{}_{(aq)}]_{t=0} = [HAsO_4^{2-}{}_{(aq)}]_{eq} + [HAsO_4^{2-}{}_{(adsorbed)}]_{eq}$ Therefore: $K = \frac{[HAsO^{2-}_{4\,(aq)}]_{t=0} - [HAsO^{2-}_{4\,(aq)}]_{eq}}{[HAsO^{2-}_{4\,(aq)}]_{eq}}$ Rearranges to give: $[HAsO^{2-}_{4\,(aq)}]_{eq} = \frac{[HAsO^{2-}_{4\,(aq)}]_{t=0}}{1+K} = \frac{30}{1+186} = 0.16\mu g/dm^3$	2

11 marks

Question 6			
		Answer	**Marks**
(a)	**i)**	–13.6 eV Must have minus sign	1
	ii)	zero	1
	iii)	1300 kJ mol^{-1}	1
(b)		$-495.8 \times 10^3 = -1312 \times 10^3 \times \frac{Z_{eff}{}^2}{3^2}$ Z_{eff} = 1.84 (2 for correct answer; partial credit of 1 if expression is correct)	2

Note: Tests are to be taken under controlled conditions. Students must not have access to the information contained in this marking scheme prior to, or during, the test.

(c)		energy of electron in 2p shell = $-13.6\times\frac{(Z-S)^2}{2^2}$ energy of electron in 1s shell = $-13.6\times\frac{(Z-S)^2}{1^2}$ energy released on transition from 2p to 1s $=\frac{3}{4}\times13.6\times(Z-1)^2=8000$ $(Z-1)=28$ Z = 29 element is copper, Cu	2
(d)	**i)**	energy of electron in 3d shell = $-13.6\times\frac{(Z-S)^2}{3^2}$ energy of electron in 2p shell = $-13.6\times\frac{(Z-S)^2}{2^2}$ energy released on transition from 3d to 2p $=\left(\frac{1}{2^2}-\frac{1}{3^2}\right)\times13.6\times(Z-7.4)^2=10000$ $(Z-7.4)=72.8$ Z = 80 element is mercury, Hg	2
	ii)	HgS (accept other possible mercury sulfide formulae)	1
(e)	**i)**	for **C**, energy released on transition from 2p to 1s $=\frac{3}{4}\times13.6\times(Z-1)^2=10500$ $(Z-1)=32$ Z = 33 element is arsenic, As for **D** energy released on transition from 3d to 2p $=\left(\frac{1}{2^2}-\frac{1}{3^2}\right)\times13.6\times(Z-7.4)^2=10500$ $(Z-7.4)=74.6$ Z = 82 element is lead, Pb	1 1
	ii)	$CuAsHO_3$ (this assumes +2 oxidation state for Cu)	2
(f)		for antimony, Sb, energy released on transition from 2p to 1s $=\frac{3}{4}\times13.6\times(51-1)^2=25500$ eV	1
(g)		Balancing oxidation states: $(2x)+(2\times5)+(7\times-2)=0$ implies x = +2 [formula is $Pb_2Sb_2O_7$]	1

16 marks

Total Marks 64

Note: Tests are to be taken under controlled conditions. Students must not have access to the information contained in this marking scheme prior to, or during, the test.