46th INTERNATIONAL

CHEMISTRY OLYMPIAD

2014

UK Round One

MARK SCHEME

Although we would encourage students to always quote answers to an appropriate number of significant figures, do not penalise students for significant figure errors. Allow where a student's answers differ slightly from the mark scheme due to the use of rounded/non-rounded data from an earlier part of the question.

For answers with missing or incorrect units, penalise one mark for the first occurrence in **each** question and write **UNIT** next to it. Do not penalise for subsequent occurrences in the same question.

Question	1	2	3	4	5	**Total**
Marks Available	9	9	13	18	16	**65**

1. This question is about controlling phosphate levels

(a) **(i)** $La_2(CO_3)_3 + 6HCl \rightarrow 2LaCl_3 + 3H_2O + 3CO_2$ **1**

State symbols not required

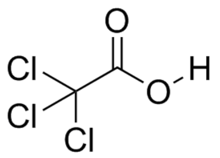
(ii) $La^{3+} + PO_4^{3-} \rightarrow LaPO_4$ **1**

State symbols not required

(b) $2La(NO_3)_3 + 3Na_2CO_3 \rightarrow La_2(CO_3)_3 + 6NaNO_3$ **1**

State symbols not required

(c) **(i)**



1

Do not accept a molecular formula. Accept if O–H bond not drawn out, but all other bonds must be drawn out.

(ii) $La_2O_3 + 6CCl_3CO_2H \rightarrow 2La(CCl_3CO_2)_3 + 3H_2O$ **1**

State symbols not required

(iii) $2La(CCl_3CO_2)_3 + 3H_2O \rightarrow La_2(CO_3)_3 + 6CHCl_3 + 3CO_2$ **1**

State symbols not required

(d) $2LaCl_3 + 6NH_4HCO_3 \rightarrow La_2(CO_3)_3 + 6NH_4Cl + 3CO_2 + 3H_2O$ **1**

State symbols not required

(e) **(i)** Amount of La^{3+} = 1000 mg / 138.91 g mol^{-1} = 7.20 × 10^{-3} mol

Amount of $La_2(CO_3)_3{\cdot}2H_2O$ = 3.60 × 10^{-3} mol

Molar mass of $La_2(CO_3)_3{\cdot}2H_2O$ = (2 × 138.91 + 3 × 12.01 + 11 × 16.00 + 4 × 1.008) g mol^{-1} **1**

= 493.88 g mol^{-1}

Mass of $La_2(CO_3)_3{\cdot}2H_2O$ = 493.88 g mol^{-1} × 3.60 × 10^{-3} mol

= 1780 mg *(or 1.78 g)*

(ii) Amount of La^{3+} = 7.20 × 10^{-3} mol = Amount of PO_4^{3-}

Molar Mass of PO_4^{3-} = (30.97 + 4 × 16.00) g mol^{-1} = 94.97 g mol^{-1}

Mass of PO_4^{3-} removed = 7.20 × 10^{-3} mol × 94.97 g mol^{-1} **1**

= 684 mg *(or 0.684 g)*

Allow ECF when an incorrect amount of La^{3+} from ***(e)(i)*** *has been used correctly in this calculation.*

Question Total 9

2. This question is about a sodium street lamp

(a)		$1s^2, 2s^2, 2p^6, 3s^1$	**1**
(b)		3s	**1**
(c)	**(i)**	Energy = 6.626×10^{-34} J s × 2.998×10^{8} m s^{-1} / 589×10^{-9} m = 3.37×10^{-19} J ($atom^{-1}$)	**1**
	(ii)	Energy per mole = 3.37×10^{-19} J × 6.02×10^{23} mol^{-1} = 2.03×10^{5} J mol^{-1} = 203 kJ mol^{-1} *Allow ECF from **(c)(i)***	**1**
(d)		one [Zero] infinity the constant k	**1**
(e)		Energy change = *I.E.* (nd) − *I.E.* (3p) *Note this answer is negative as energy is given out. Award one mark for the expression:* Energy change = *I.E.* (3p) − *I.E.* (nd)	**2**
(f)	**(i)**	Intercept = 0.00245 nm^{-1} *(Allow values from 0.00243-0.0247 nm^{-1})* *I.E.* (3p) = 6.626×10^{-34} J s × 2.998×10^{8} m s^{-1} × 2.45×10^{6} m^{-1} = 4.87×10^{-19} J ($atom^{-1}$)	**1**
	(ii)	Ionisation energy of sodium = *I.E.* (3p) + ΔE (3s→3p) *I.E.* (3p) = 4.87×10^{-19} J ($atom^{-1}$) × 6.02×10^{23} mol^{-1} = 293 kJ mol^{-1} Ionisation energy of sodium = 293 kJ mol^{-1} + 203 kJ mol^{-1} = 496 kJ mol^{-1} *Allow ECF from (c)(ii) or (f)(i), as long as they have shown that these two quantities must be added together, and both in the units of kJ mol^{-1}*	**1**

Question Total 9

3. This question is about spot cream

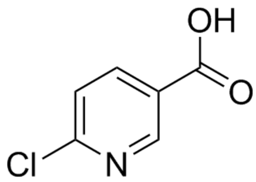
(a) Effective density of tazarotene = 0.90 g cm^{-3} × 0.0005 = 0.00045 g cm^{-3}

= 0.45 g dm^{-3} **1**

Concentration of tazarotene = 0.45 g dm^{-3} / 351.46 g mol^{-1}

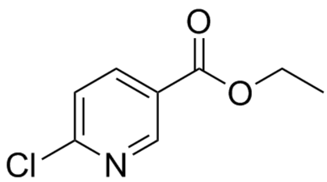
= 0.00128 M *(or 1.28 mM)*

(b)



1

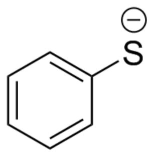
A



1

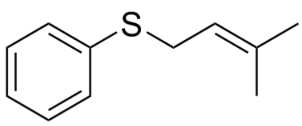
B

(c)



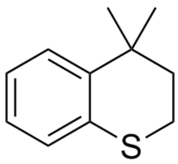
1

$\mathbf{C}^{\ominus}$



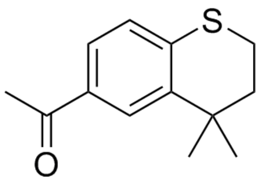
1

D

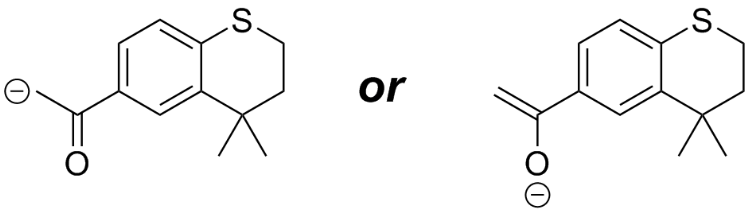


1

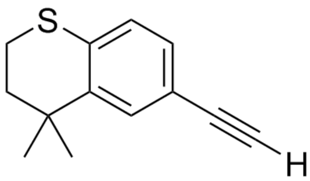
E



F 1



G$^{\ominus}$ 1

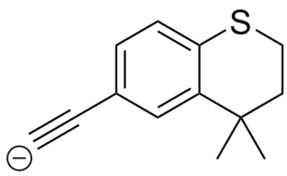


I 1

The alkyne C–H bond does not have to be explicitly drawn in (as in normal skeletal structure drawing).

(d) Oxidation Reduction Addition [Elimination] Substitution **1**

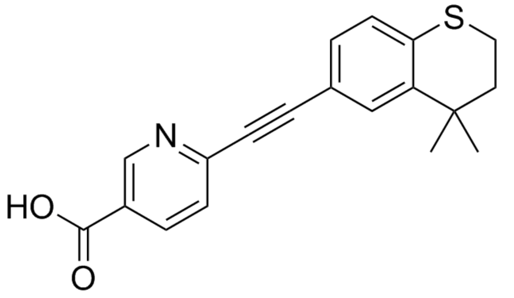
(e)

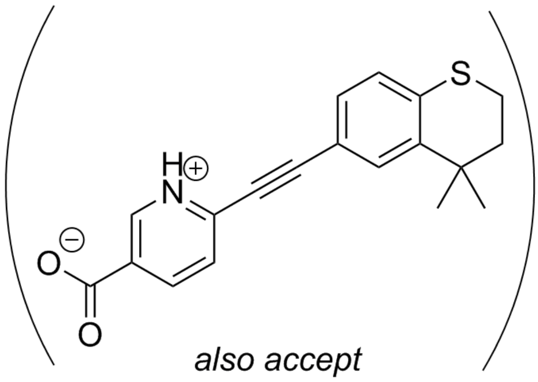


J$^{\ominus}$ **1**

(f) 20 signals **1**

(g)





also accept

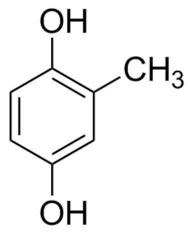
1

Question Total 13

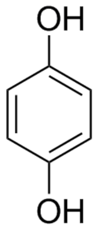
4. This question is about bombardier beetles

(a)	**(i)**	$2H_2O_2 \rightarrow 2H_2O + O_2$ *State symbols not required*	**1**
	(ii)	Oxidation Reduction **[Disproportionation]** Hydrolysis Dehydration	**1**
(b)		Combining $2H_2O_2 \rightarrow 2H_2O + O_2$ and **A** + $\frac{1}{2}O_2 \rightarrow$ **B** + H_2O gives H_2O_2 + **A** $\rightarrow$ **B** + $2H_2O$	**1**
(c)	**(i)**	Amount of energy = specific heat capacity ×temp. change ×mass of water $= 4.18\ J\ g^{-1}\ K^{-1} \times 80\ K \times 1000\ g$ = 334 kJ	**1**
	(ii)	Conc. of H_2O_2 in mixed solution = energy needed per litre / enthalpy change per mole of H_2O_2 $= 334\ kJ\ dm^{-3} / 203\ kJ\ mol^{-1}$ $= 1.65\ mol\ dm^{-3}$ Therefore with equal volumes mixed, conc. of H_2O_2 initially must be double this value = $3.30\ mol\ dm^{-3}$ *Award one mark for the value of 1.65 mol dm^{-3}, and one mark for the realisation of the need to double the concentration. Allow ECF from **(c)(i)**.*	**2**
(d)	**(i)**	6	**1**
	(ii)	3	**1**
(e)		**Peak I** O–H	**1**
		Peak II C–H	**1**
(f)	**(i)**	–OH *(or hydroxyl)*	**1**
	(ii)	$-CH_3$ *(or methyl)*	**1**
(g)		H_1 V H_2 VII H_3 VI *All correct: two marks, two correct: one mark, one correct: half a mark*	**2**

(h)

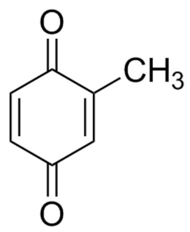


Compound **A** **1**

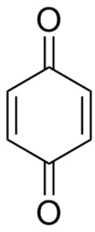


Compound **C** **1**

(i)



Compound **B** **1**



Compound **D** **1**

Question Total 18

5. This question is about fire and ice

(a)		$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ *State symbols not required*	**1**
(b)	**(i)**	Amount of CH_4 = amount of CO_2 = amount of $CaCO_3$ Amount of $CaCO_3$ = 84.73 g / 100.09 g mol^{-1} = 0.847 mol Amount of H_2O = 116.92 g / 18.016 g mol^{-1} = 6.49 mol $(CH_4)_x(H_2O)_y + 2xO_2 \rightarrow xCO_2 + (2x+y)H_2O$ So x = 0.847 mol, and $2x+y$ = 6.49 mol Therefore y = 6.49 − (2 × 0.847) = 4.80 mol Expressing as integers: x = 3, y = 17 *Award one mark for correct calculation of the amount of $CaCO_3$ and H_2O, one mark for correct algebraic expression or equivalent and one mark for final answer. Correct final values score full credit.*	**3**
	(ii)	$(CH_4)_3(H_2O)_{17}$ M_r = 354.40 g mol^{-1}; therefore 2835.18 g mol^{-1} / 354.40 g mol^{-1} = 8 Molecular formula is $(CH_4)_{24}(H_2O)_{136}$	**1**
(c)		Amount of CH_4 = 6.67 × 10^{14} g / 16.04 g mol^{-1} = 4.16 × 10^{13} mol V = nRT/p = 4.16 × 10^{13} mol × 8.31 J K^{-1} mol^{-1} × 254 K / 1.0 × 10^{5} Pa = 8.78 × 10^{11} m^{3}	**1**
(d)	**(i)**	Mass % of methane in methane hydrate = (8 × 16.04) g mol^{-1}/ 957.07 g mol^{-1} = 13.4%	**1**
	(ii)	Mass of Baikal methane hydrate = 6.67 × 10^{14} g / 0.134 = 4.98 × 10^{15} g *Allow ECF from* ***(d)(i)***	**1**
	(iii)	Volume of methane hydrate = 4.98 × 10^{15} g / 0.95 g cm^{-3} = 5.24 × 10^{15} cm^{3} *(or 5.24 × 10^{9} m^{3})* *Allow ECF from* ***(d)(ii)***	**1**
(e)	**(i)**	Unit cell mass = 957.07 g mol^{-1} / 6.02×10^{23} mol^{-1} = 1.59 × 10^{-21} g	**1**
	(ii)	Volume of unit cell = 1.59 × 10^{-21} g / 0.95 g cm^{-3} = 1.67 × 10^{-21} cm^{3} Length of unit cell edge = (1.67 × 10^{-21} cm^{3})$^{1/3}$ = 1.19 × 10^{-7} cm *One mark for correct volume of unit cell. Allow ECF from* ***(e)(i)***	**1**

(iii) Volume of methane in unit cell = $8 \times 4/3 \times \pi \times (0.21 \times 10^{-9}\ m)^3$

$= 3.10 \times 10^{-28}\ m^3$

Volume of water in unit cell = $46 \times 4/3 \times \pi \times (0.14 \times 10^{-9}\ m)^3$ **1**

$= 5.29 \times 10^{-28}\ m^3$

(iv) Percentage of space occupied =

$(3.10 \times 10^{-28} + 5.29 \times 10^{-28})\ m^3 / 1.67 \times 10^{-27}\ m^3$ **1**

= 50%

(f) $\Delta_f H^\ominus\ (CH_4)_8(H_2O)_{46} = 8\Delta_f H^\ominus(CO_2) + 62\Delta_f H^\ominus(H_2O) - \Delta_c H^\ominus\ (CH_4)_8(H_2O)_{46}$

$= (8(-393.5) + 62(-285.8) - (-6690.4))\ kJ\ mol^{-1}$

$= -14177.2\ kJ\ mol^{-1}$

Forming methane hydrate from methane and water has the enthalpy change

$8CH_4 + 46H_2O \rightarrow (CH_4)_8(H_2O)_{46}$ **3**

$\Delta_r H^\ominus = (-14177.2 - 8(-74.8) - 46(-285.8))\ kJ\ mol^{-1} = -432\ kJ\ mol^{-1}$

Final answer scores full marks. One mark for a correct value for $\Delta_f H^\ominus (CH_4)_8(H_2O)_{46}$, one mark for the idea of using two cycles and one mark for correct second cycle calculation. If mistake is made in calculation of $\Delta_f H^\ominus (CH_4)_8(H_2O)_{46}$ but then this answer is used correctly in the second cycle this should be given two marks overall.

Question Total 16

Paper Total 65