50^{th} INTERNATIONAL

CHEMISTRY OLYMPIAD

2018

UK Round One

MARK SCHEME

Although we would encourage students always to 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.

In general, 'error carried forward' (referred to as ECF) can be applied. We have tried to indicate where this may happen in the mark scheme.

In calculation questions, the correct numerical answer with units scores full marks. Partial marks can be awarded for intermediate steps where the answer is given in acceptable alternative units to those in the mark scheme (e.g. m^3 instead of dm^3).

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.

Organic structures are shown in their skeletal form, but also accept displayed formulae as long as the representation is unambiguous. Benzene rings may be drawn with localised or delocalised bonding.

State symbols are not required for balanced equations and students should not be penalised if they are absent. Multiples of equations are allowed.

Question	1	2	3	4	5	**Total**
Marks Available	10	12	21	25	13	**81**

1. This question is about the application of some lithium compounds

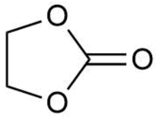
(a) (i) +4 ½

(ii) +3 ½

(b) **D** At the cathode, which is the graphite electrode. **1**

Note: The electrode which is the anode (graphite) when the battery is being discharged becomes the cathode when the battery is being charged. Li metal is formed by the reduction of Li^+ ions, which must happen on the cathode, which is the electrode based on graphite.

(c) **1**



(d) $4Li + {}^{3}/_{2}O_2 \rightarrow Li_2O + Li_2O_2$ *or* **1**

$8Li + 3O_2 \rightarrow 2Li_2O + 2Li_2O_2$

Multiples allowed. No partial credit.

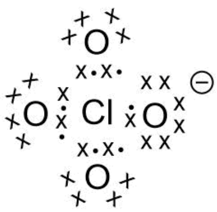
(e) $2Li_2O_2 + 2CO_2 \rightarrow O_2 + 2Li_2CO_3$ *or* **1**

$Li_2O_2 + CO_2 \rightarrow ½O_2 + Li_2CO_3$

No partial credit.

(f) (i) $LiClO_4$ **1**

(ii) **1**



All electrons on oxygens must be shown. Dots and cross can be alternate way around. The extra electron can be marked with a different symbol.

*No ECF if formula for **(f)(i)** is incorrect.*

(iii) Tetrahedral ½

*No ECF if formula for **(f)(i)** is incorrect.*

(iv) $LiClO_4 \rightarrow 2O_2 + LiCl$ ½

*No ECF if formula for **(f)(i)** is incorrect.*

(g) Two moles of oxygen are produced by the decomposition of 1 mole of **A**.

Two moles of oxygen have a volume of 48.0 dm^3. ½

1 mole of **A** has a mass of 106.39 g, therefore

Volume = (106.39 g) / (2.42 g cm^{-3}) = 43.96 cm^3 ½

Therefore, the oxygen to volume ratio is 48000 cm^3 / 43.96 cm^3 = 1090 **1**

Note: The oxygen to volume ratio must have no units. If units are given for the ratio the maximum mark is 1. If a different amount of compound is used for this calculation then the part marks should be awarded in the same way as here.

Question total 10

2. This question is about making ammonia

(a) $Li^+ + e^- \rightarrow Li$ ½

$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$ ½

Multiples allowed. Equation must be fully correct to score the ½ mark.

(b) (i) = (2 × −268 kJ mol^{-1}) + 15.8 kJ mol^{-1} + (4 × 15.0 kJ mol^{-1}) − (4 × −446 kJ mol^{-1})

= +1,320 kJ mol^{-1} **1**

Do not penalise if positive sign is absent, however, zero marks if negative.

(ii) = (4 × 63.7 J K^{-1} mol^{-1}) + (2 × 224 J K^{-1} mol^{-1}) + 236 J K^{-1} mol^{-1} − (4 × 128 J K^{-1} mol^{-1})

= +427 J K^{-1} mol^{-1} **1**

Do not penalise if positive sign is absent, however, zero marks if negative.

(iii) = $\Delta H^\ominus - T\Delta S^\ominus$

= 1,320 kJ mol^{-1} − (750 K × 427 J K^{-1} mol^{-1} × 10^{-3} kJ J^{-1})

= +1,004 kJ mol^{-1}

*Do not penalise if positive sign is absent, however, zero marks if negative. ECF allowed from part **(b)(i)** and **(b)(ii)**:* **1**

*ECF Answer = **(b)(i)** – (0.75 × **(b)(ii)**)*

(c) = $\Delta G^\ominus$ / (n × F)

= –1,004 kJ mol^{-1} × 10^3 J kJ^{-1}/ (4 × 9.65 × 10^4 C mol^{-1}) = −2.60 V ½

*ECF Answer = −(**(b)(iii)** × 2.59 × 10^{-3})*

Therefore, a potential of +**3.20 V** should be applied. ½

*ECF Answer = (**(b)(iii)** × 2.59 × 10^{-3}) + 0.60*

½ mark for correct calculation of −2.60 V (negative sign required) and ½ mark for adding 0.60 V to the absolute value of $E^\ominus_{cell}$ students have obtained.

(d) $6Li + N_2 \rightarrow 2Li_3N$ ½

$Li_3N + 3H_2O \rightarrow NH_3 + 3LiOH$ ½

Ratio Li:NH_3 is 3:1 **1**

½ mark for each correct equation. 1 mark for the correct ratio.

No ECF from incorrect equations.

(e) Q = 0.2 A × 1000 s = 200 C

Amount of e^- = 200 C / 9.65 × 10^4 C mol^{-1} = 0.00207 mol **1**

Amount of Li = 88.5% × 0.00207 mol = 0.00183 mol ½

Mass of Li = 0.00183 × 6.94 g mol^{-1} = 0.0127 g ½

1 mark for correct calculation of charge and correct use of Faraday's constant, ½ mark for calculation of amount of lithium from amount of electrons and ½ mark for correct numerical answer.

(f) Amount of NH_3 = amount of Li × $^1/_3$ = 0.00183 mol × $^1/_3$ = 6.11 × 10^{-4} mol ½

Volume of NH_3 = 6.11 × 10^{-4} mol × 24000 cm^3 mol^{-1} = 14.7 cm^3 ½

*ECF Answer = 3458 × **(e)** / **(d)***

ECF Answer scores 1 mark.

(g) Mass of NH_3 required for UK farm = 130 acres × 0.077 tonnes $acre^{-1}$ = 10.01 tonnes ½

Amount of NH_3 = 10.01 × 10^6 g / 17.034 g mol^{-1} = 5.88 × 10^5 mol ½

Amount of Li = 5.88 × 10^5 mol × 3 = 1.76 × 10^6 mol ½

Mass of Li = 1.76 × 10^6 mol × 6.94 g mol^{-1} = 1.22 × 10^7 g = 12.2 tonnes ½

*ECF Answer = 4.08 × 10^6 × **(d)***

Question Total 12

3. **This question is about the use of enriched uranium**

(a) Amount of U in 1 pound = 0.45 kg × 10^3 g kg^{-1} / 235.0439 g mol^{-1} = 1.91 mol

Energy released from 1 pound = 8.0 × 4.184 × 10^{12} J = 3.35 × 10^{13} J

Energy released in kJ mol^{-1} = 3.35 × 10^{13} J / 1.91

= 1.8 × 10^{10} kJ mol^{-1} **1**

(b) (i) Relative Atomic Mass = $m_{235}\,x + m_{238}\,(1 - x)$

$$x = \frac{238.0289\text{-}238.0507}{235.0439\text{-}238.0507} = 0.00725$$

% abundance of ^{235}U = 0.725% **1**

*If percentage of ^{238}U is calculated first but incorrectly, allow ECF for percentage of ^{235}U, where ECF answer = 100% − **(b)(ii)***

(ii) % abundance of ^{238}U = 100 − 0.725 = 99.275% **1**

*ECF answer = 100% − **(b)(i)***

(c) **B** Fluorine has only one naturally occurring isotope. **1**

(d) No. **1**

Whilst the individual U–F bonds are polar, the octahedral shape of UF_6 means that these cancel out.

(e) % heavier = (238 − 235) / (235 + 6 × 19) × 100 = 0.860% **1**

(f) (i) $UF_6 + H_2 \rightarrow UF_4 + 2HF$ **1**

(ii) $UF_4 + 2Mg \rightarrow U + 2MgF_2$ **1**

(g) (i) +6, +5, (+5) **1**

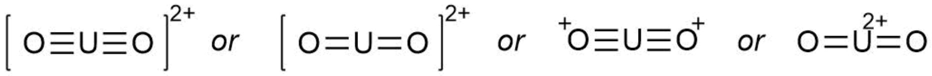
Duplication of +5 oxidation state not required. Do not penalise lack of a + sign. Allow use of Roman numerals.

(ii) +4, +6, (+6) **1**

Duplication of +6 oxidation state not required. Do not penalise lack of a + sign. Allow use of Roman numerals.

(h) (i) Compound **R**

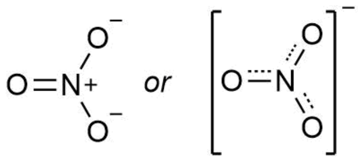
Structure of cation



1

Accept if dative bonds drawn from oxygen to uranium. The charges drawn must add up to an overall charge of +2.

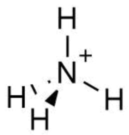
Structure of anion **1**



Accept if a dative bond drawn from nitrogen to oxygen. No credit for any structure where nitrogen has more than four discrete bonds. The charges drawn must add up to an overall charge of −1.

(ii) Compound **T**

Structure of cation



1

Shape does not have to be drawn in three dimensions as students were told the shape in the question. There are two ammoniums per formula unit but it does not matter whether students draw one or two here. Charge must be indicated. Accept if dative bond drawn from nitrogen to hydrogen.

Formula of anionic part

$U_2O_7^{2-}$ **1**

Please note that we did not ask for students to draw the structure here because this is not a simple molecular anion like dichromate. If they have attempted to draw a structure which has this formula then mark as correct.

(iii) Compound **X** UO_2 **1**

Compound **Z** UF_4 **1**

(i) (i) $^{235}U \rightarrow {}^{231}Th + \alpha$ **½**

(ii) $^{238}U \rightarrow {}^{234}Th + \alpha$ **½**

(j) (i) Half-life = 0.704×10^9 years ½

Range allowed: 0.604×10^9 years to 0.804×10^9 years

(ii) Half-life = 4.47×10^9 years ½

Range allowed: 4.07×10^9 years to 4.87×10^9 years

(k) From $\lambda = \frac{ln\,2}{t_{½}}$ and answers in part **(j)**

$\lambda_{235} = 9.85 \times 10^{-10}$ years^{-1} ½

$\lambda_{238} = 1.55 \times 10^{-10}$ years^{-1} ½

$$\frac{N_{235}}{N_{238}} = e^{-(\lambda_{235}-\lambda_{238})t}$$

as the N_0 values for both isotopes are the same and so cancel out

$\frac{N_{235}}{N_{238}}$ from part **(b)** = 0.725 / 99.275 1

$$t = \frac{ln\left(\frac{0.725}{99.275}\right)}{-(9.85 - 1.55) \times 10^{-10}} = 5.92 \times 10^9 \text{ years}$$ 1

½ mark for each correct λ calculation, 1 mark for correct $\frac{N_{235}}{N_{238}}$ calculations and 1 mark for answer.

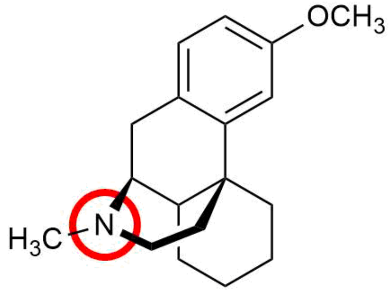
*For ECF from part **(b)** and **(j)** use:*

$$Age = \frac{ln\left(\frac{^{238}U \text{ percentage abundance}}{^{235}U \text{ percentage abundance}}\right)}{\left(\frac{ln\,2}{t_{½}{}^{235}U} - \frac{ln\,2}{t_{½}{}^{238}U}\right)} = \frac{ln\left(\frac{(\mathbf{b})(\mathbf{ii})}{(\mathbf{b})(\mathbf{i})}\right)}{\left(\frac{ln\,2}{(\mathbf{j})(\mathbf{i})} - \frac{ln\,2}{(\mathbf{j})(\mathbf{ii})}\right)}$$

Question Total 21

4. This question is about cough suppressants

(a)



1

Note: The hydrogen at the central ring junction which is drawn later in the question to indicate the stereochemistry has been omitted here to avoid confusing students.

(b) Molecular formula of dextromethorphan = $C_{18}H_{25}NO$ 1

Molecular formula of hydrobromide monohydrate salt = $C_{18}H_{25}NO + H_2O + HBr$

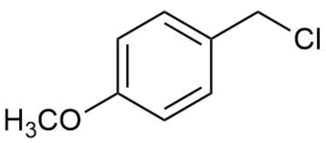
$= C_{18}H_{28}BrNO_2$

Molar mass = $[(18 \times 12.01) + (28 \times 1.008) + 79.904 + 14.01 + (2 \times 16.00)]\ g\ mol^{-1}$

$= 370.318\ g\ mol^{-1}$ 1

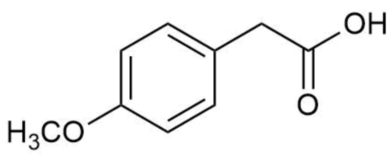
1 mark for correct determination of molecular formula of dextromethorphan, 1 mark for final answer.

(c) **Compound A**



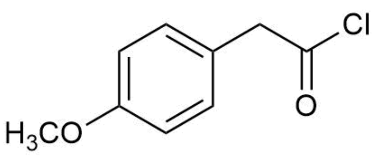
1 mark

Compound B



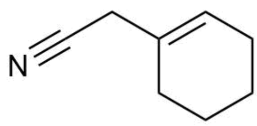
1 mark 2

Compound C



1 mark

Compound D

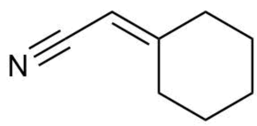


3

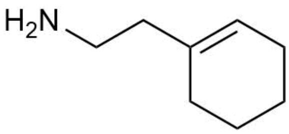
2 marks

Nitrile group does not have to be drawn out.

The following incorrect isomer scores 1 mark.



Compound E



1 mark

No credit awarded if alkene is in wrong position.

Gas X

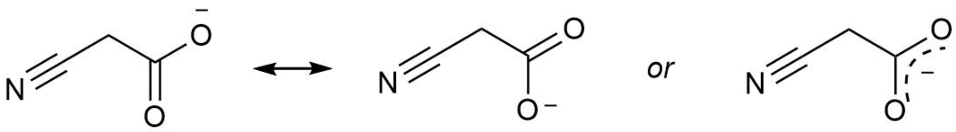
$O=C=O$ **2**

1 mark

Accept if structure is not drawn out or carbon dioxide is written in words.

*ECF can be awarded for compounds **B** and **C** only. It cannot be awarded for the others because there is a known compound to work forward from or back from. An example where ECF could be used for compound **B** or **C** is in the case of a small error such as an extra CH_2 in the chain.This should of course be penalised when it first occurs (in compound **A** for example), but ECF can be awarded if the rest of the chemistry in **B** and/or **C** is correct after the initial mistake.*

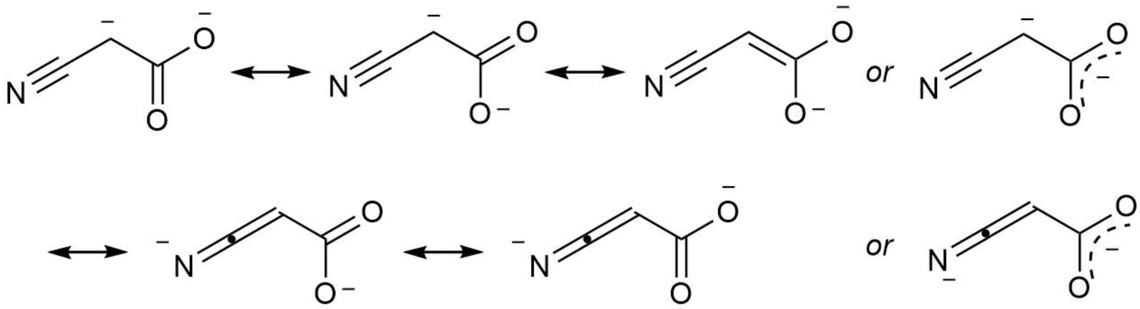
(d) (i) **Anion Z^-**



1

Only one correct form is required to score the mark.

(ii) **Dianion Z^{2-}**



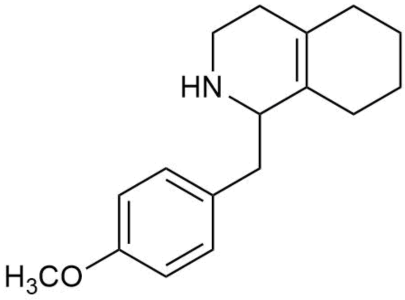
1

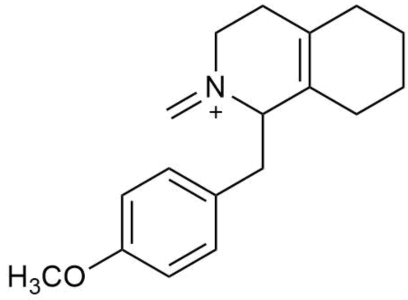
Only one correct form is required to score the mark.

(e) 9 and 13 **1**

½ mark each

(f) **Compound H** **Cation I$^+$**



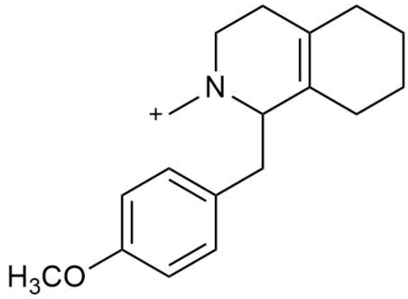


3

1 mark *2 marks*

No credit if the incorrect double bond is reduced.

Also accept for 2 marks



*ECF can be awarded if a trivial mistake in Compound **H** (such as an extra CH_2) is repeated here.*

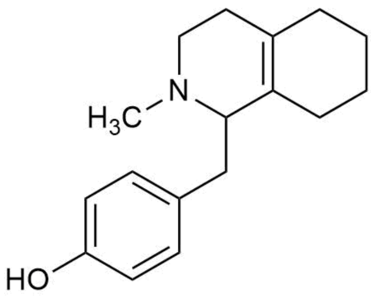
(g) 4 and 13 **1**

4 and 15 **1**

One mark to be awarded for each complete pair. If the pair is not correct then no partial credit can be scored (e.g. 4 and 7 does not score any credit). If three pairs are written down the maximum score is 1 mark if there is at least one correct pair. If four or more pairs are written down then the score is zero.

*When discussing with students afterwards please point out that it is the symmetry present in the benzene ring that means that there are two possible pairs of carbon atoms that can become connected. It is NOT the case that connecting one pair makes isomer M_1 and the other one M_2. Which of compound M_1 or M_2 is formed depends on which face of the alkene in intermediate **K** is protonated to make carbocation L^+ (protonation on one face gives M_1 and protonation on the other face gives M_2).*

(h) **Intermediate K** **Liquid Y**



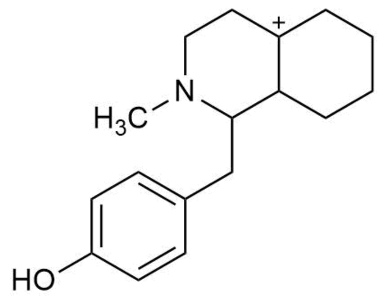
H_3C-OH **2**

1 mark

1 mark

Accept if not drawn out as a structural formula or methanol is written in words.

Carbocation L^+

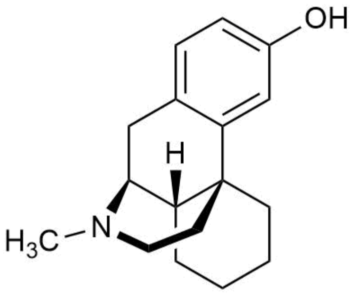


2

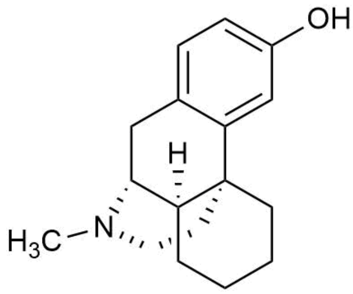
*If positive charge is not in correct position then no marks can be awarded. ECF can be awarded if an error in intermediate **K** (such as not removing the methyl group, or removing the methyl group on the nitrogen rather than the oxygen) is also present here.*

When going through this paper with students afterwards you should draw an analogy to the more familiar Friedel–Crafts alkylation reactions which proceed via similar carbocations reacting with electron-rich benzene rings.

(i) **Compound M_1** **Compound M_2**



1 mark



1 mark

2

*Compounds **M_1** and **M_2** can be either way around. The stereochemistry of the bond to nitrogen and the bond to carbon must be clearly shown for the mark in each case These two substituents must be shown to be above the plane of the rings in one isomer and below the plane of the rings in the other isomer. The stereochemistry of the hydrogen does not need to be shown, but if shown must be correct or half a mark should be deducted in each structure. A structure where one of the carbon/nitrogen substituents is up and the other is down scores no marks.*

*ECF can be awarded if an error in intermediate **K** (such as not removing the methyl group, or removing the methyl group on the nitrogen rather than the oxygen) is also present here.*

Type of isomers: **Enantiomers** **1**

Allow 'optical isomers'. Award ½ mark for 'stereoisomers' (as whilst this is true we can be more specific here as the two compounds are enantiomers).

Question Total 25

5. This question is about the 'inert' gas helium

(a) Volume of atmosphere = 4.2×10^9 km^3 = 4.2×10^{18} m^3

Mass of He in atmosphere = 0.916 mg m^{-3} × 4.2×10^{18} m^3

= 3.85×10^{18} mg = 3.85×10^{15} g

Moles He = 3.85×10^{15} g / 4.003 g mol^{-1} = 9.61×10^{14} mol **1**

(b) Radius of balloon = 14 cm = 1.4 dm

Volume = $^4/_3 \times \pi \times (1.4\ \text{dm})^3$ = 11.5 dm^3 **1**

Moles in one balloon = 11.5 dm^3 / 24 dm^3 mol^{-1} = 0.479 mol

Number of balloons = 9.61×10^{14} mol / 0.479 mol = 2.01×10^{15} balloons **1**

*ECF answer = **(a)** / 0.479*

Alternatively students may calculate the volume of He in the atmosphere (2.31×10^{16} dm^3) and then divide this by the volume of one balloon.

(c) 4 He **1**

8 Na **1**

(d) Na_2He *or* $HeNa_2$ **1**

*No ECF from part **(c)**. We do not believe this is a double penalty as the high unit cell symmetry should lead students to expect a simple ratio of the two elements.*

(e) Molar mass of unit cell = (4 × 4.003 g mol^{-1} + 8 × 22.99 g mol^{-1}) = 199.9 g mol^{-1}

Mass of unit cell = 199.9 g mol^{-1} / 6.02×10^{23} mol^{-1} = 3.32×10^{-22} g **1**

Volume of unit cell = $(3.95 \times 10^{-10}\ \text{m})^3$ = 6.16×10^{-29} m^3 **1**

Density of **X** = 3.32×10^{-22} g / 6.16×10^{-29} m^3 = 5.39×10^6 g m^{-3} = 5.39 g cm^{-3} **1**

*Allow ECF from part **(c)** for different numbers of atoms in the unit cell.*

(f) **A** A metallic solid

B A covalent solid

C An ionic solid ✓ **1**

If more than one of the above is ticked then zero as this is a contradiction.

D A conductor

E An insulator ✓

If more than one of the above is ticked then zero as this is a contradiction. **1**

(g) $HeNa_2 \rightarrow He + 2Na$ **1**

*Allow ECF from part **(d)**.*

(h) Graph crosses zero axis at 160 GPa. Allow range 155–165 GPa **1**

Question Total 13