The 52nd INTERNATIONAL CHEMISTRY OLYMPIAD 2020

UK Round One

STUDENT QUESTION BOOKLET

* * * * *

- The time allowed is two hours.
- Attempt all six questions.
- Write your answers in the student answer booklet.
- Write only the essential steps of your calculations in the answer booklet.
- Always give the appropriate unit and number of significant figures.
- The final page of this question booklet includes a copy of the periodic table and some useful physical constants and quantities.
- Do NOT write anything in the right-hand margin of the answer booklet.
- The marks available for each question are shown below. These may be helpful when dividing your time between questions.

<table>
<thead>
<tr>
<th>Question</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Marks Available</td>
<td>10</td>
<td>10</td>
<td>17</td>
<td>12</td>
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<td>20</td>
<td>86</td>
</tr>
</tbody>
</table>

Some of the questions will contain material you will not be familiar with. However, you should be able to work through the problems by applying the skills you have learnt as a chemist. There are different ways to approach the tasks – even if you cannot complete certain parts of a question, you may find later parts straightforward.

This resource was downloaded from https://rsc.li/2WmGF2V
1. This question is about calcium carbide

Calcium carbide (CaC₂) is a colourless solid used in the production of ethyne.

Calcium carbide is produced when calcium oxide reacts with carbon, forming calcium carbide and carbon monoxide.

The UK IChO team mascot is pictured with a calcium carbide lamp.

(a) (i) Write an equation for the formation of calcium carbide from calcium oxide.

(ii) Draw a dot and cross diagram of the carbide ion, C₂²⁻.

The German chemist Friedrich Wöhler discovered that calcium carbide reacted with water releasing ethyne gas (C₂H₂) and calcium hydroxide. The ethyne was burnt in miner’s lamps and the head lights of early motor vehicles for the purpose of illumination.

(b) Write an equation for the formation of ethyne from calcium carbide.

An impure sample of calcium carbide of mass 0.752 g was added to 50.0 cm³ of water. After all the calcium carbide had reacted, 20.00 cm³ of the reaction mixture was removed and titrated against 0.250 mol dm⁻³ hydrochloric acid. 34.60 cm³ of hydrochloric acid was required to neutralise the sample. It can be assumed that none of the impurities reacted.

(c) Calculate the percentage purity of the calcium carbide.

The diagram shows the unit cell of calcium carbide. Calcium is positioned at the corners and centre of the unit cell.

Some of the atoms are completely contained within the boundaries of a single unit cell. Only a fraction of atoms centred on corners, edges, or faces are contained within a single unit cell.

(d) By considering the number of fractions of atoms within one unit cell, count the net numbers of calcium and carbon atoms within one unit cell.

The density of calcium carbide is 2.20 g cm⁻³ and the values of x and y are both 3.88 Å.

(e) Calculate the value of z in Å.
2. This question is about hydrogen as a fuel

Carbon dioxide emissions from fossil fuels are a major factor in climate change. Hydrogen is a potential alternative to fossil fuels, providing ‘clean energy’ with only water as a by-product. The UK government is investigating converting the natural gas grid to carry hydrogen instead.

For this question, assume all processes take place at 298 K.

Enthalpy change of formation of CH₄(g), ΔH⦵ᵢᶠ = −74.8 kJ mol⁻¹
Enthalpy change of formation of CO₂(g), ΔH⦵ᵢᶠ = −393.5 kJ mol⁻¹
Enthalpy change of formation of H₂O(l), ΔH⦵ᵢᶠ = −285.8 kJ mol⁻¹
Entropy change of formation of H₂O(l), ΔS⦵ᵢᶠ = −163.0 J K⁻¹ mol⁻¹

One low cost method for producing hydrogen is reforming methane. Though this produces CO₂, this can be easily captured. The reforming process can be represented by the overall reaction:

\[ \text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{CO}_2(\text{g}) + 4\text{H}_2(\text{g}) \]

(a) Calculate the enthalpy change for this reaction.

Electrolysis of water is another method of producing hydrogen. On a large scale, it currently costs more than reforming methane.

In polymer electrolyte membrane electrolysis, protons are transferred through a membrane between the two electrodes. The two half reactions are:

1. \[ 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \]
2. \[ 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) \]

(b) Which of these half reactions occurs at the cathode?
The overall cell reaction is as follows:

\[ 2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g) \]

(c) Calculate the enthalpy change for the overall cell reaction.

Given that \( \Delta G^\circ = -nF E^\circ \) and \( \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \)
where \( n \) = moles of electrons transferred in the overall equation, \( F \) = Faraday constant

(d) Calculate the cell potential, \( E^\circ \), for the overall cell reaction in V.

(If you do not get an answer to this question, use \(-1.13 \text{ V}\) in further calculations)

(e) What is the standard electrode potential for half reaction 1?

To replace natural gas within appliances such as boilers or furnaces, there needs to be a similar amount of heat released per second from burning fuel.

(f) What is the standard enthalpy change of combustion of CH₄?

(If you do not get an answer to this question, use \(-943.2 \text{ kJ mol}^{-1}\) in further calculations)

(g) What is the standard enthalpy change of combustion of H₂?

(If you do not get an answer to this question, use \(-352.8 \text{ kJ mol}^{-1}\) in further calculations)

When fuel gases are supplied under the same pressure, the heat released per second in a burner may be expressed using:

\[ \text{heat released per second} \propto \frac{\text{standard enthalpy change of combustion}}{\sqrt{\text{relative molecular mass}}} \]

(h) What is the ratio of heat released per second in a burner fuelled by hydrogen compared to in the same burner fuelled by methane?

Assume hydrogen and methane are supplied under the same pressure.
3. This question is about sun cream

On 1st January, the Pacific island of Palau imposed a ban on certain sun creams to protect its coral reefs. The ban restricts the use of ten products which are toxic to marine life and are linked to the bleaching of coral. Scientists are particularly concerned with two UV light-absorbing chemicals: oxybenzone and octinoxate.

(a) Which functional groups are present in oxybenzone? Tick the correct answer(s) in the answer booklet.

- ester
- aldehyde
- ketone
- carboxylic acid
- ether
- phenol

Oxybenzone is good at absorbing UV radiation due to the delocalisation of its electrons. This delocalisation of electrons is aided by an intramolecular hydrogen bond in oxybenzone.

(b) On the oxybenzone structure in the answer booklet, circle the two atoms involved in the intramolecular hydrogen bond.

The synthesis of oxybenzone is shown below.

(c) Draw the structures of compounds A, B, C and D.

Octinoxate exists as multiple stereoisomers; only one is shown. Enantiomers are stereoisomers that are non-superimposable mirror images of each other.

(d) (i) Draw a second stereoisomer of octinoxate that is the enantiomer of the one shown.

(ii) Draw a third stereoisomer of octinoxate that is not the enantiomer of the one shown.
In the synthesis of octinoxate, a base-catalysed condensation reaction between two molecules containing C=O groups is used. The product of this reaction is a molecule that contains a C=C and a C=O bond next to each other. This proximity helps to make octinoxate a good absorber of UV light.

\[
\begin{align*}
\text{O} & \quad \text{R}_1 \quad \text{H} \quad \text{R}_2 \\
\text{O} & \quad \text{R}_3 \quad \text{C=O} \quad \text{R}_4
\end{align*}
\]

\[
\xrightarrow{\text{base catalyst}}
\]

\[
\begin{align*}
\text{O} & \quad \text{R}_1 \quad \text{R}_3 \\
\text{O} & \quad \text{R}_2 \quad \text{R}_4 \\
\ &= \quad \text{H}_2\text{O}
\end{align*}
\]

The synthesis of octinoxate begins with the conversion of two molecules of \( \text{E} \) to \( \text{F} \).

\[
\begin{align*}
\text{E} & \quad \text{C}_2\text{H}_6\text{O} \\
\text{E} & \quad \text{C}_2\text{H}_6\text{O}
\end{align*}
\]

\[
\xrightarrow{\text{NaOH}}
\]

\[
\begin{align*}
\text{F} & \quad \text{C}_9\text{H}_{12}\text{O} \\
\ &= \quad \text{H}_2\text{O}
\end{align*}
\]

(e) Draw the structures of compounds \( \text{E} \) and \( \text{F} \). Stereochemistry is not required.

Compound \( \text{F} \) is then converted into octinoxate in three steps. By-products are not shown.

\[
\begin{align*}
\text{F} & \quad \text{H}_2 / \text{Pd} \\
\ &= \quad \text{G}
\end{align*}
\]

\[
\xrightarrow{\text{NaOCH}_3}
\]

\[
\text{H}
\]

(f) Draw the structures of compounds \( \text{G} \) and \( \text{H} \). Stereochemistry is not required.
Upon exposure to UV light, octinoxate forms two types of dimers which are toxic to marine life: truxinates and truxillates. If a single stereoisomer is irradiated with UV light, many different truxinate and truxillate stereoisomers can be formed due to the position of the groups (abbreviated as R or Ar) on the newly formed cyclobutane ring.

\[
\text{truxinate} \\
\text{head to head dimer}
\]

\[
\text{truxillate} \\
\text{head to tail dimer}
\]

(g) What do all the truxinate and truxillate products produced in this reaction have in common? Tick the correct answer(s) in the answer booklet.

- The same molecular formula
- The same melting points
- Rotate plane-polarised light in the same direction

A research group separated the products formed to further understand their toxicological properties. The truxinate dimers can be categorised by the number of substituents on the same face of the cyclobutane ring (either two, three or four). This is shown with wedged and hashed bonds.

<table>
<thead>
<tr>
<th>Substituents on same face</th>
<th>Truxinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Four</td>
<td>![Diagrams of truxinates]</td>
</tr>
<tr>
<td>Three</td>
<td>![Diagrams of truxinates]</td>
</tr>
</tbody>
</table>

(h) (i) In the answer booklet circle to indicate whether each structure has an enantiomer.

(ii) In the answer booklet, draw the structures to complete the 'Two' line(s) in the table. Indicate whether each structure has an enantiomer. For a pair of enantiomers, only draw one of the pair. Not all boxes need to be used.
4. This question is about silicon oxides

Minerals formed from silicon oxides form 90% of the earth’s crust. The most common pure silicon oxide is silicon dioxide. This can be used to make silica gel, packets of which are used to keep items free of moisture.

To make silica gel, solid silicon dioxide must be reacted in 1:2 ratio with sodium carbonate at 1500 °C. This reaction forms salt X and colourless gas Y. The anion of salt X contains only silicon and oxygen and has a tetrahedral structure.

(a) (i) What is the formula of gas Y?
(ii) Draw the structure of the anion in X, clearly indicating its overall charge.
(iii) Write the equation for the reaction to form X.

Reaction of either X or CaSiO₃ with dilute acids forms a gelatinous precipitate of SiO₂·xH₂O. This precipitate is then washed, dried, granulated and put in sachets

(b) Write the equation of the reaction of CaSiO₃ with dilute hydrochloric acid to form SiO₂·11H₂O

Silicates are anions containing only silicon and oxygen which contain only Si–O single bonds. Their structure can be described by joining silica tetrahedra. The pyrosilicate [Si₂O₇]⁶⁻ ion found in Åkermanite (Ca₂Mg[Si₂O₇]) has the structure shown below.

(c) In quartz, how many other tetrahedra is each silica tetrahedron attached to?
(d) Draw the structure of the silicate anion in the following compounds. 3D shape is not required.

(i) The $\text{[Si}_3\text{O}_9\text{]}^{6-}$ ion found in Benitoite, $\text{BaTi}[\text{Si}_3\text{O}_9]$, an extremely rare blue mineral.

(ii) The mineral beryl, $\text{Be}_3\text{Al}_2[\text{Si}_6\text{O}_{18}]$. (Clearly indicate the overall charge)

Talc ($\text{Mg}_3\text{Si}_4\text{H}_2\text{O}_{12}$) is a mineral which contains hydroxide ions in addition to silicates. The hydroxide ions do not interact with the silicate, but instead coordinate to the magnesium cations. The silicate lattice is essentially a 2D sheet that is used as a solid lubricant.

(e) What is the formula and charge of the silicate anion in talc?

Another hydrated silicate mineral, chrysotile ($\text{Mg}_3\text{Si}_2\text{H}_4\text{O}_9$), forms needle-like fibres and is a form of asbestos. Talc is often found contaminated with chrysotile. A mineral sample was analysed and found to contain 20.32% Mg and 28.18% Si by mass.

(f) Assuming the sample contained only talc and chrysotile, determine the molar percentage of each it contained.
5. This question is about colourful compounds

Colourful molecules are found in leaves (β-carotene and chlorophyll), blood (haemoglobin), skin (melanin), and multivitamin supplements. They are all organic compounds with alternating single and double bonds, and we will now explore how this pattern leads to colour.

(a) A simple molecule with alternating single and double bonds is buta-1,3-diene. Draw its skeletal structure.

Buta-1,3-diene is colourless because it does not absorb visible light. It does absorb in the UV at a wavelength, $\lambda$, of 210 nm. This absorption is caused by the electrons in the double bonds moving between different energy levels. The difference between levels is given by:

$$\Delta E = \frac{hc}{\lambda}$$

where $h$ is the Planck constant and $c$ is the speed of light in vacuum. $\Delta E$ is also related to the length of the molecule, $L$, via:

$$\Delta E = \frac{(2n + 1)h^2}{8m_eL^2}$$

where $m_e$ is the mass of the electron and $n$ is the number of double bonds.

(b) (i) Calculate the energy difference, $\Delta E$, for the UV absorption in buta-1,3-diene in J.

(ii) Using this energy difference, calculate the length, $L$, in Å.

Porphine (1) absorbs visible light, forming bright red crystals. Its coordination complexes with metals (2) are also coloured and found in chlorophyll and haemoglobin. It has been determined that the magnesium complex (M = Mg) absorbs at 571.4 nm, and the zinc complex (M = Zn) absorbs at 568.7 nm.

As with buta-1,3-diene, the wavelength is related to the size of the molecule, now via:

$$\lambda = \varepsilon d^2$$

where $d$ is the distance between nitrogen atoms on opposite sides of the ring and $\varepsilon$ is a proportionality constant which is assumed to be the same for 1 and 2. The N–Mg bond length is 2.052 Å.

(c) (i) Calculate the proportionality constant $\varepsilon$ in Å$^{-1}$ to four significant figures.

(ii) Calculate the length of the N–Zn bond in Å to four significant figures.

(iii) Calculate the absorption wavelength of porphine 1 (for which $d = 4.112$ Å) in nm to four significant figures.
Porphycene is an isomer of porphine that has attracted attention as a molecular switch. The hydrogen atoms in porphycene can “hop” across the ring, interconverting between two stable trans-states (T and T*) that are the on/off positions of the switch. There is also an unstable cis-state C. The trans-states can interconvert via the cis-state with rate constant \( k_1 \), or directly with rate constant \( k_2 \).

At high temperatures \( k_1 \gg k_2 \) and so the direct conversion of \( T \rightarrow T^* \) can be ignored. The following rate equation and kinetic data were obtained for the isomerisation.

\[
k_1 = A \exp\left(-\frac{E_a}{RT}\right)
\]

<table>
<thead>
<tr>
<th>( T / K )</th>
<th>( k_1 / s^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>493</td>
<td>3.31 \times 10^{12}</td>
</tr>
<tr>
<td>393</td>
<td>1.32 \times 10^{12}</td>
</tr>
</tbody>
</table>

(d) Under such conditions, calculate the activation energy, \( E_a \), for \( T \rightarrow T^* \) using the Arrhenius law and the above data.

The transformation is much faster at 100 K than expected from the Arrhenius law because the direct conversion of \( T \rightarrow T^* \) now dominates the reaction. This is due to quantum tunnelling. The rate constant \( k_2 \) has a non-Arrhenius temperature dependence

\[
k_2 = \left(\frac{2E_a}{\mu}\right)^{\frac{1}{2}} \frac{\alpha RT}{E_a} \exp\left(-\alpha \left(2 - \frac{\alpha RT}{E_a}\right)\right)
\]

where \( \mu \) is a scaled molar mass with units of \( m^2 \text{ kg mol}^{-1} \) and \( \alpha \) is a dimensionless constant. This expression can be simplified by combining some of the terms together to form new terms \( \beta \) and \( \gamma \).

\[
k_2 = T \left(\frac{\beta}{\gamma}\right)^{\frac{1}{2}} \exp(-2\alpha + \beta T)
\]

(e) Express \( \beta \) and \( \gamma \) in terms of \( \alpha \), \( \mu \), \( E_a \), and \( R \).

The equation can be further rearranged to give

\[
\ln\left(\frac{k_2}{T}\right) = \beta T + i
\]

(f) Use the following data to calculate \( \beta \) in \( K^{-1} \).

<table>
<thead>
<tr>
<th>( T / K )</th>
<th>( k_2 / s^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>83</td>
<td>8.74 \times 10^{10}</td>
</tr>
<tr>
<td>61</td>
<td>6.23 \times 10^{10}</td>
</tr>
</tbody>
</table>

(If you do not get an answer to this question, use \( \beta = 9.456 \times 10^{-4} K^{-1} \) in further calculations)

The value of the constant \( \alpha \) can be shown to be 2.235.

(g) Calculate the activation energy \( E_a \).
6. This question is about anammox and ladderanes

Anammox is an abbreviation for anaerobic ammonium oxidation. Despite being a crucial part of the nitrogen cycle, the bacteria responsible for this process were only identified as recently as 1999. In the membranes of these bacteria an unusual class of lipids were found. These lipids contained several fused cyclobutane rings. Such molecules are called ladderanes due to their resemblance to the rungs of a ladder.

The mechanism of ammonium oxidation is believed to involve several different nitrogen-containing species:

- nitrogen gas
- the ammonium ion
- the nitrite ion (NO$_2^-$)
- hydrazine (NH$_2$NH$_2$)
- hydroxylamine (NH$_2$OH).

(a) (i) Give the oxidation state of the nitrogen atom in nitrogen gas and in the ammonium ion.

(ii) Give the oxidation state of the nitrogen atom in the nitrite ion (NO$_2^-$), hydrazine (NH$_2$NH$_2$), and hydroxylamine (NH$_2$OH).

The reaction takes place over three steps, all of which can be assumed to take place under acidic conditions.

(b) Using your oxidation states from part (a), write equations for the following steps in the cycle.

(i) Step 1: The half-equation for conversion of nitrite to hydroxylamine.

(ii) Step 2: The reaction of the ammonium ion and hydroxylamine to give hydrazine.

(iii) Step 3: The half-equation for the conversion of hydrazine to nitrogen gas.

(c) Hence, write an overall reaction equation for the anammox process.
To further understand the lipids found in these bacteria, a research group synthesised [5]-ladderanoic acid – a key component of such lipids. The synthesis is shown below. Not all by-products are shown.

\[
\begin{align*}
\text{A} & \xrightarrow{\text{LiAlH}_4 (\text{excess})} \text{C}_6\text{H}_{12}\text{O}_2, \\
\text{B} & \xrightarrow{\text{H}_3\text{C}^+\text{Cl}^- (\text{excess})} \xrightarrow{\text{N(C}_2\text{H}_5)_2 \text{ (a base)}} \text{C}_6\text{H}_{16}\text{O}_2\text{S}_2, \\
\text{C} & \xrightarrow{\text{Na}_2\text{S}} \text{ethanol/H}_2\text{O}, \\
\text{D} & \xrightarrow{\text{SO}_2\text{Cl}_2 \text{ pyridine}} \text{O=S}.
\end{align*}
\]

(d) Draw the structures of compounds A – K and by-product X. No stereochemistry is required in any structure.
Acknowledgements & References

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https://www.bbc.co.uk/news/world-asia-50963080

Q4 The image is © Shutterstock

Q5 The image is © Shutterstock
Microcanonical and thermal instanton rate theory for chemical reactions at all temperatures Faraday Discuss., 2016, 195, 49-67. DOI: 10.1039/C6FD00119J

Q6 The image is part of an image of some 15th Century German ladders sourced from Medieval House Book of Wolfegg Castle, Fol. 53v-53v1/via Wikipedia (Public Domain)

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Physical Constants & Formulae

<table>
<thead>
<tr>
<th>Physical Constant</th>
<th>Symbol</th>
<th>Value</th>
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<tbody>
<tr>
<td>Avogadro’s constant</td>
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<tr>
<td>molar gas constant</td>
<td>( R )</td>
<td>( 8.314 \text{ J K}^{-1} \text{ mol}^{-1} )</td>
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<tr>
<td>Faraday constant</td>
<td>( F )</td>
<td>( 96485 \text{ C mol}^{-1} )</td>
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<tr>
<td>Planck constant</td>
<td>( h )</td>
<td>( 6.626 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1} )</td>
</tr>
<tr>
<td>speed of light in vacuum</td>
<td>( c )</td>
<td>( 2.998 \times 10^8 \text{ m s}^{-1} )</td>
</tr>
<tr>
<td>mass of electron</td>
<td>( m_e )</td>
<td>( 9.109 \times 10^{-31} \text{ kg} )</td>
</tr>
</tbody>
</table>

\[ 1 \text{ nm} = 1 \times 10^{-9} \text{ m} \]
\[ 1 \text{ Å} = 1 \times 10^{-10} \text{ m} \]
\[ 0 \degree \text{C} = 273 \text{ K} \]

\[
\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ
\]
\[
\Delta G^\circ = - nFE^\circ
\]
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