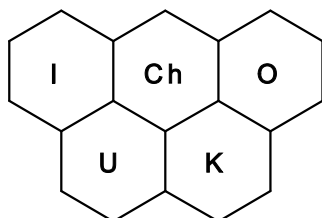




INEOS
THE WORD FOR CHEMICALS



**47th INTERNATIONAL
CHEMISTRY OLYMPIAD
2015
UK Round One
STUDENT QUESTION BOOKLET**

* * * * *

- The time allowed is 2 hours.
- Attempt all 5 questions.
- Write your answers in the special answer booklet.
- In your calculations, please write only the essential steps in the answer booklet.
- Always give the appropriate units and number of significant figures.
- You are provided with a copy of the Periodic Table.
- Do *NOT* write anything in the right hand margin of the answer booklet.
- The marks available for each question are shown below; this may be helpful when dividing your time between questions.

Question	1	2	3	4	5	Total
Marks Available	9	17	20	14	15	75

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

1**18**

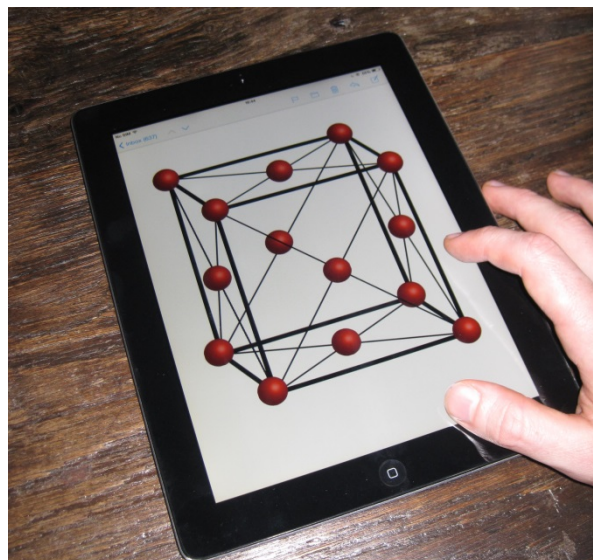
H 1 1.008																	He 2 4.003
Li 3 6.94	Be 4 9.01	symbol atomic number mean atomic mass														F 9 19.00	Ne 10 20.18
Na 11 22.99	Mg 12 24.31															B 5 10.81	C 6 12.01
K 19 39.102	Ca 20 40.08	3	4	5	6	7	8	9	10	11	12	Ga 31 69.72	Ge 32 72.59	As 33 74.92	Se 34 78.96	Br 35 79.904	Kr 36 83.80
Rb 37 85.47	Sr 38 87.62	Y 39 88.91	Zr 40 91.22	Nb 41 92.91	Mo 42 95.94	Tc 43 101.07	Ru 44 102.91	Rh 45 106.4	Pd 46 107.87	Ag 47 107.87	Cd 48 112.40	In 49 114.82	Sn 50 118.69	Sb 51 121.75	Te 52 127.60	I 53 126.90	Xe 54 131.30
Cs 55 132.91	Ba 56 137.34	La* 57 138.91	Hf 72 178.49	Ta 73 180.95	W 74 183.85	Re 75 186.2	Os 76 190.2	Ir 77 192.2	Pt 78 195.09	Au 79 196.97	Hg 80 200.59	Tl 81 204.37	Pb 82 207.2	Bi 83 208.98	Po 84 209	At 85 210	Rn 86 222
Fr 87	Ra 88	Ac+ 89															

*Lanthanides	Ce 58 140.12	Pr 59 140.91	Nd 60 144.24	Pm 61	Sm 62 150.4	Eu 63 151.96	Gd 64 157.25	Tb 65 158.93	Dy 66 162.50	Ho 67 164.93	Er 68 167.26	Tm 69 168.93	Yb 70 173.04	Lu 71 174.97
+Actinides	Th 90 232.01	Pa 91	U 92 238.03	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

1. This question is about the chemistry of touchscreens

In recent years there has been a surge in demand for indium for touchscreen and display equipment. The element is quite rare so its price has rocketed. There are worries that the global supply of the element could run out. Its major use is the electrically conducting transparent glass ITO, indium tin oxide.



- (a) Indium(III) oxide can be obtained by heating indium(III) hydroxide. Write an equation for this reaction.

ITO glass is 90% indium(III) oxide, 10% tin(IV) oxide, by mass. The iPad shown above contains about 27 mg of ITO glass in its touchscreen.

- (b) (i) Calculate the mass of indium present in the ITO glass of the iPad touchscreen.
- (ii) The indium content of ITO glass in touchscreens is taken to be about 700 mg per square metre. Given that the density of ITO glass is about 7.15 g/cm^3 , calculate the thickness of the ITO glass in the touchscreen.

Indium(III) oxide can take the cubic bixbyite crystal structure. The position of the indium ions approximates to the face-centred cubic (FCC) unit cell shown in the illustration above. A unit cell is the simplest repeat unit that contains all the symmetry of the crystal. In the FCC structure the ions are centred on the corners of the cube and the centres of the faces.

- (c) Calculate how many indium ions are actually inside the cube. You will need to consider the fractional occupancy of each ion in the cube.
- (d) The oxide ions occupy positions that are wholly inside the cube. Deduce how many oxide ions are present in the cubic cell shown.
- (e) When indium(III) oxide is heated to $700 \text{ }^\circ\text{C}$ in air, its mass decreases by 11.5%. Work out the formula of the compound produced.
- (f) When indium(III) oxide is heated with ammonia at $630 \text{ }^\circ\text{C}$, the products are water and a semiconductor. Suggest the formula of the semiconductor.

2. This question is about detecting molecules in space

In September 2014, the BBC announced that radio-astronomers had discovered the 'most complex molecule' to date in space. Found in 'Sagittarius-B2(N)' – the largest star-forming region in our Galaxy – this is the first molecule detected with a branched carbon chain. The systematic name for the molecule is 2-methylpropanenitrile. It was found to be approximately 0.4 times as abundant as its straight-chained isomer.

The molecule was detected from the radio signals given out as it dropped from an excited energy level to a lower one.



A nitrile is a molecule in which one of the carbons has a triple bond to nitrogen.

- (a) (i) Draw the structure of 2-methylpropanenitrile.
- (ii) Draw the structure and give the systematic name of another nitrile isomeric with 2-methylpropanenitrile.

Astronomers are now looking for the next series of nitriles with the formula C_5H_9N .

- (b) Draw all the isomeric nitriles with the formula C_5H_9N .

Most of the molecules detected by radio-astronomers in less active regions of space tend to have linear structures. The largest so far detected has the unlikely-looking formula $HC_{11}N$.

- (c) Draw the structure of the linear molecule with the formula $HC_{11}N$.

The signals detected in the radio wave region of the electromagnetic spectrum are due to transitions between rotational energy levels, each of which has a particular energy. Molecules have many rotational energy levels available to them, each level with a different energy being specified by the so-called rotational quantum number, J , which takes integer values from 0 upwards.

The energy (in joules) of the J^{th} rotational energy level, E_J , is given by the formula:

$$E_J = h \times B \times J(J+1)$$

where B = the rotational constant of the molecule (in Hz)
 h = Planck's constant = 6.626×10^{-34} J s.
and light of frequency f (Hz) has energy $h \times f$ (joules)

Two signals have been detected due to $HC_{11}N$. One is due to the transition from rotational energy level ($J = 39$) to ($J = 38$), the other due to the transition from level ($J = 38$) to ($J = 37$).

- (d) Given the signal from ($J = 39$) to ($J = 38$) was observed at 13186.853 MHz, calculate:
- (i) the rotational constant, B , for $HC_{11}N$ (in MHz).
- (ii) the frequency (in MHz) for the transition from level ($J = 38$) to ($J = 37$).

One of the most abundant heteronuclear diatomic molecules detected in space is carbon monoxide formed from ^{12}C and ^{16}O .

- (e) Given the masses of ^{12}C and ^{16}O are 12.00 g mol^{-1} and 16.00 g mol^{-1} respectively, calculate the mass (in kg) of a single atom of each of these elements.

When taking both masses of atoms into account in a diatomic molecule, we use the so-called reduced mass, μ . For a diatomic molecule with masses m_1 and m_2 ,

$$\mu = \frac{m_1 \times m_2}{m_1 + m_2}$$

- (f) Calculate the reduced mass of a molecule of $^{12}\text{C}^{16}\text{O}$.

For a diatomic molecule, the rotational constant (in Hz) is given by the expression:

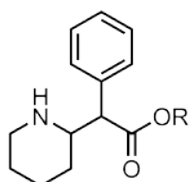
$$B = \frac{h}{8\pi^2\mu r^2}$$

where r is the bond length.

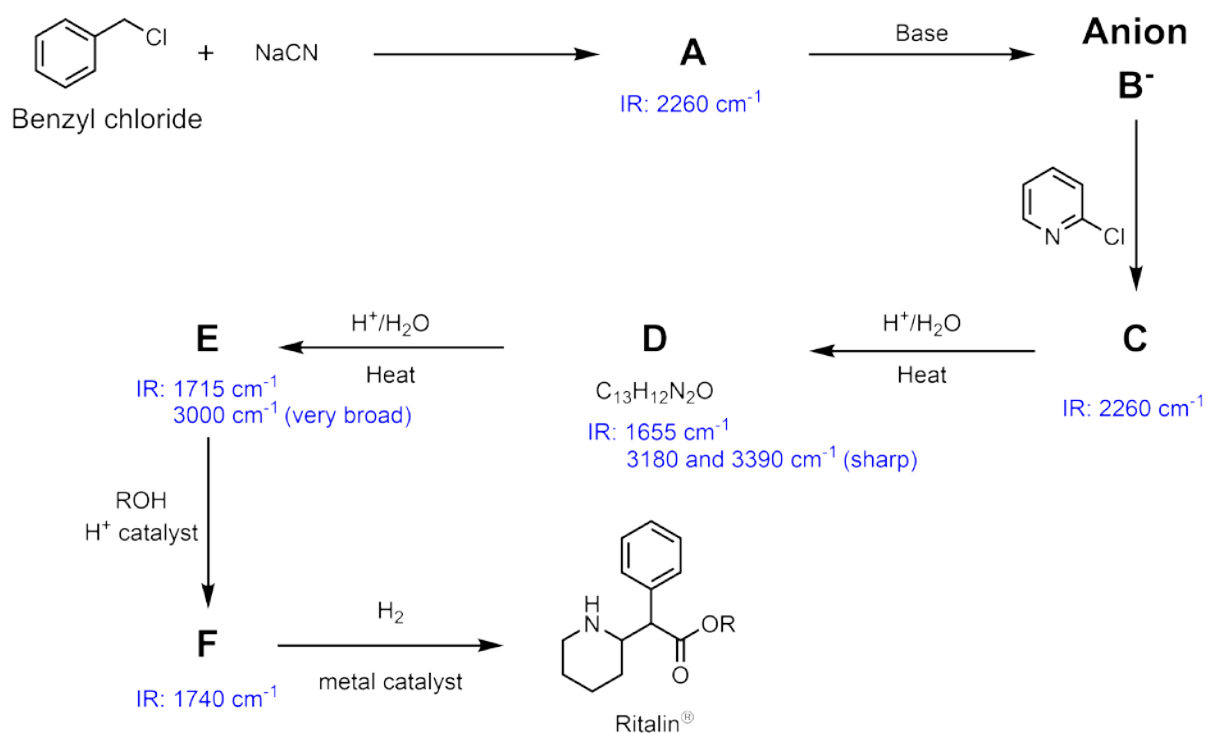
- (g) (i) Given the signal from ($J = 1$) to ($J = 0$) for $^{12}\text{C}^{16}\text{O}$ was observed at 115271.204 MHz , calculate the bond length.
- (ii) A signal thought to be due to $^{12}\text{C}^{16}\text{O}$ was observed at 806651.719 MHz . Given that rotational transitions only take place between adjacent energy levels, determine the transition in $^{12}\text{C}^{16}\text{O}$ consistent with this observation.

3. This question is about the performance-enhancing drug Ritalin[®]

The drug Ritalin[®] has long been used as a treatment for attention-deficit hyperactivity disorder (ADHD). More recently it has been in the news as a possible performance-enhancing drug taken by students studying for exams. The structure of Ritalin is shown below, where R represents a hydrocarbon group.



Ritalin is synthesised according to the scheme below. Some of the characteristic IR stretching frequencies of the intermediates are shown.



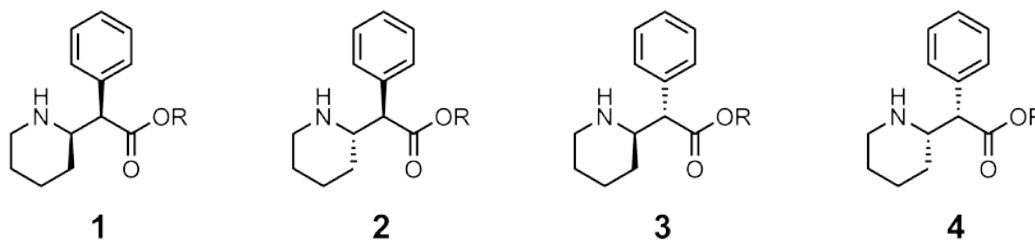
- The synthesis begins with the reaction of benzyl chloride and sodium cyanide to form Compound **A**. Draw the structure of Compound **A**.
- Compound **A** is then deprotonated to form **Anion B⁻**. Draw the structure of **Anion B⁻**.
- Draw the structures of Compounds **C**, **D**, **E** and **F**. For Compound **F** you do not need to worry about the specific identity of R.

Ritalin is present in the tablets as the hydrochloride salt.

- (d) On the structure of Ritalin in the answer booklet, circle the atom that is protonated in the hydrochloride salt (the HCl salt).
- (e) (i) The tablets contain 10.00 mg of the hydrochloride salt which corresponds to 8.647 mg of Ritalin. Using this information calculate the molar mass of Ritalin (include your working).
- (ii) Hence suggest an identity for the hydrocarbon group R.
- (f) For each of the following IR stretching frequencies from this scheme, draw the functional group responsible and indicate with an arrow which of the bonds are vibrating.
- (i) 1655 cm^{-1} (ii) 1715 cm^{-1} (iii) 1740 cm^{-1} (iv) 2260 cm^{-1}
- (v) 3000 cm^{-1} (very broad) (vi) 3180 and 3390 cm^{-1} (sharp)

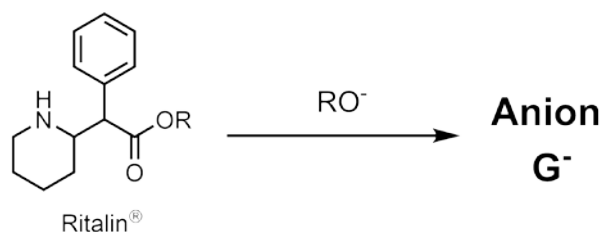
Stereoisomers of a molecule are isomers that have the same connectivity between the atoms but a different three-dimensional arrangement in space. The effectiveness of a drug depends on its three-dimensional shape.

This synthesis leads to the production of a mixture of four stereoisomers of Ritalin, shown below. Some of these isomers are more effective than others.



- (g) By ticking the appropriate box or boxes in the answer booklet, indicate which of these isomers are enantiomers (non-superimposable mirror images).

Some of the less effective stereoisomers can be converted into the more effective ones by deprotonation of Ritalin with the alkoxide base RO^- to give **Anion G⁻** as shown below. Upon reprotonation a different stereoisomer can be formed.



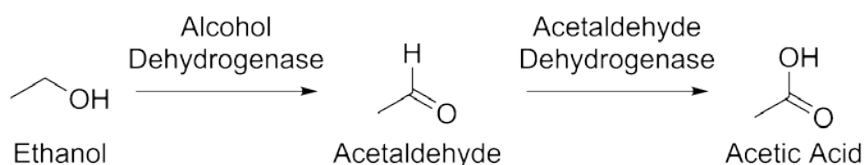
- (h) Draw the structure of **Anion G⁻**.
- (i) By ticking the appropriate box or boxes in the answer booklet, indicate which of these isomers could be interconverted via the intermediary of **Anion G⁻**.

4. This question is about hangovers

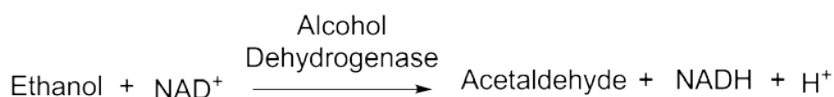
After the consumption of too much alcoholic beverage, people sometimes experience a hangover the following day. There are a variety of causes of a hangover, one of these is the accumulation of the toxic metabolites of ethanol in the body.



In the body, ethanol is first converted into acetaldehyde by the enzyme alcohol dehydrogenase and then into acetic acid by the enzyme acetaldehyde dehydrogenase.



In the first step, ethanol reacts with nicotinamide adenine dinucleotide (NAD⁺) to form acetaldehyde, a compound called NADH and H⁺.



(a) What happens to the NAD⁺ in this reaction? Circle the correct answer.

it is oxidised

it is reduced

it is hydrolysed

it is isomerised

it remains chemically unchanged

In most parts of the UK, the legal drink drive limit is 80 mg of ethanol per 100 ml of blood.

(b) What concentration of ethanol does this correspond to (in mol dm⁻³)? (1 ml = 1 cm³)

After drinking it is not permitted to drive until the concentration of ethanol has fallen below this level. The reaction to remove ethanol involves the initial combination of the ethanol and the alcohol dehydrogenase to form an enzyme-substrate complex, followed by the conversion of this complex into products. The rate of this reaction (the rate of production of acetaldehyde) has a complicated rate law (as shown below).

$$\text{rate} = \frac{k_{\text{cat}}[\text{AD}][\text{C}_2\text{H}_5\text{OH}]}{K_{\text{M}} + [\text{C}_2\text{H}_5\text{OH}]}$$

where [AD] is the concentration of the alcohol dehydrogenase enzyme

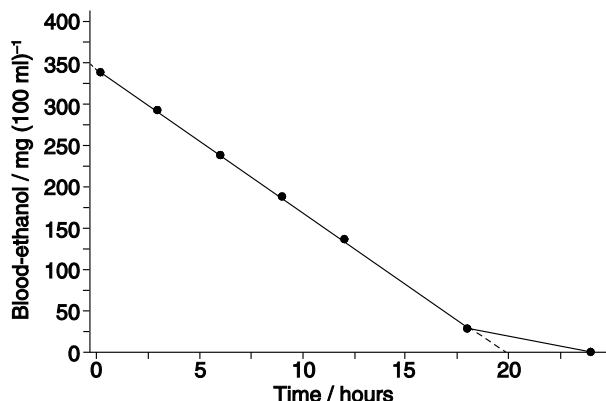
$k_{\text{cat}} = 1.33 \text{ s}^{-1}$ and is the rate constant for the conversion of the enzyme substrate complex to products

$K_{\text{M}} = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$ and is a measure of the ease of dissociation of the enzyme substrate complex back to reactants. It has the units of concentration.

It is often the case that the rate law above simplifies to a much simpler form.

- (c) (i) Write down the simplified form of this rate law when the concentration of ethanol is very much **larger** than the value of K_M .
(ii) Write down the simplified form of this rate law when the concentration of ethanol is very much **smaller** than the value of K_M .
(d) Hence, or otherwise, write down the order of this reaction with respect to ethanol at around or above the UK drink drive limit.

The graph shows how the blood ethanol concentration of someone who has drunk a lot of alcohol varies over time.



- (e) For the majority of the time that this person is sobering up, what is the rate of loss of ethanol?
(i) In $(\text{mg} / 100 \text{ ml}) \text{ h}^{-1}$
(ii) In $\text{mol dm}^{-3} \text{ s}^{-1}$

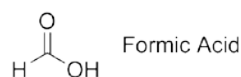
(f) What concentration of alcohol dehydrogenase enzyme does this person have?

- (g) The half-life of this reaction is the time taken for the concentration of ethanol to fall to half of its initial value. From the graph, how does the half-life vary over the majority of the period this person is sobering up?

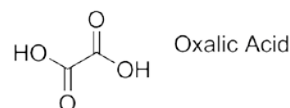
it increases it is constant it decreases it is impossible to determine from the graph

- (h) As well as ethanol, alcohol dehydrogenase will also metabolise other alcohols. The following metabolites are highly toxic. For each of these suggest which highly poisonous alcohol they came from.

(i)



(ii)

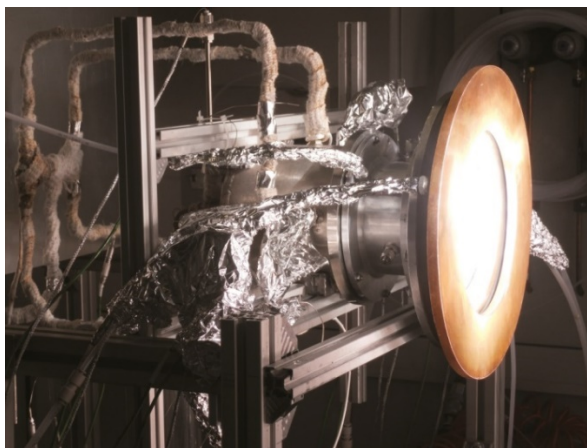


- (i) For one of these poisonous alcohols, alcohol dehydrogenase has a $k_{cat} = 1.10 \text{ s}^{-1}$ and a $K_M = 3.2 \times 10^{-2} \text{ mol dm}^{-3}$. What can be concluded about the metabolism of this alcohol? Tick all that apply.

- The maximum rate of metabolism is faster for ethanol
- The maximum rate of metabolism is faster for the poisonous alcohol
- The maximum rate of metabolism is the same for both
- A higher concentration of ethanol is needed for the reaction to proceed at half of its maximum rate
- A higher concentration of the poisonous alcohol is needed for the reaction to proceed at half of its maximum rate
- The same concentration of ethanol and the poisonous alcohol are needed for the reactions to proceed at half of their maximum rate
- The metabolism of the poisonous alcohol follows a rate law different from that of ethanol

5. This question is about making “green” jet fuel

“Solar-Jet” is a project designed to make aviation fuel from carbon dioxide and water using sunlight as the source of energy. The key to the project is the conversion of carbon dioxide and steam into syngas (a mixture of CO and H₂) with the removal of O₂ as a byproduct. This is achieved using the energy from a solar reactor which focuses and concentrates sunlight.



[In the following question assume the molar volume of a gas is 24.0 dm³ mol⁻¹ at RTP, room temperature and pressure.]

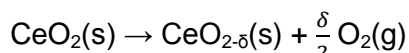
- (a) Write a chemical equation to represent the process of carbon dioxide and steam forming syngas and oxygen.

Syngas can then be used to produce hydrocarbon fuels in a procedure called the Fischer-Tropsch process. In this process the carbon monoxide and hydrogen are catalytically converted into alkanes and water.

- (b) (i) Give the formula for an alkane with n carbon atoms and use this to write a general equation for the Fischer-Tropsch process.
- (ii) Calculate the ideal ratio of carbon monoxide to hydrogen in order to form dodecane ($n = 12$), a major component of jet-fuel.

Solar-Jet uses the following procedure to manufacture syngas and oxygen.

- Step 1.** Cerium(IV) oxide is heated to very high temperatures in the solar reactor which reduces it non-stoichiometrically as shown below:



where δ is a number much smaller than 1 and represents the number of moles of O atoms that are lost to form oxygen molecules.

- Step 2.** The temperature in the solar reactor is lowered, steam and carbon dioxide are passed into the solar reactor and are reduced to syngas. During this process the CeO_{2- δ} is oxidised back to CeO₂.

- (c) (i) Give the overall chemical equation for the reduction of carbon dioxide to carbon monoxide with CeO_{2- δ} .
- (ii) Give the overall chemical equation for the reduction of steam to hydrogen with CeO_{2- δ} .

A laboratory prototype was set up containing 127 g of CeO₂. The prototype was then run under the following experimental conditions:

Step 1. Run time: 26 minutes
Power of the solar radiation: 3.60 kW.
Total volume of oxygen evolved: 367 cm³ at RTP.

Step 2. Run time: 34 minutes
Power of the solar radiation: 0.80 kW.

- (d) (i) Using the information from **Step 1**, calculate the value of δ .
(ii) Predict the volume (at RTP) of syngas produced in **Step 2**.

Under the conditions of the experiment, the actual volume of syngas produced was found to be 747 cm³ at RTP with a H₂ : CO ratio of 1.70:1.

- (e) (i) Calculate the amount (in moles) of hydrogen produced in the experiment.
(ii) Calculate the amount (in moles) of carbon monoxide produced in the experiment.

The crucial factor in deciding whether the process is economically viable, is how efficiently the solar energy is converted into 'usable energy'. This may be defined as:

$$\text{efficiency} = \frac{\text{usable energy of syngas produced}}{\text{total solar energy used}}$$

- (f) Calculate the total amount of solar energy used to produce the syngas.
[Remember 1 W = 1 J s⁻¹.]

The 'usable energy' may be taken to be the energy released when the syngas undergoes complete combustion to form carbon dioxide and water at room temperature and pressure. The standard enthalpy changes of combustion for H₂ and CO are given below.

	CO(g)	H ₂ (g)
Standard enthalpy change of combustion, $\Delta_c H^\ominus$ / kJ mol ⁻¹	-283	-286

- (g) (i) Calculate the energy released (the standard enthalpy change) when the sample of syngas produced from the experiment undergoes complete combustion.
(ii) Calculate the efficiency of the solar-jet reactor for this run.

Petrol typically has lighter alkanes than jet-fuel. The average number of carbon atoms in the petrol is $n = 8$ whereas in jet-fuel it is $n = 12$.

- (h) (i) Given the standard enthalpy changes of combustion ($\Delta_c H^\ominus$) for heptane ($n = 7$) and octane ($n = 8$) are -4816 and -5470 kJ mol⁻¹ respectively, calculate $\Delta_c H^\ominus$ of dodecane ($n = 12$).
(ii) By constructing an appropriate Hess' cycle, calculate the standard enthalpy change for the production of dodecane from syngas.

Acknowledgements & References

References for questions

Q1

The image is from the Royal Society of Chemistry

Q2

The image is from © Shutterstock.

Detection of a branched alkyl molecule in the interstellar medium: iso-propyl cyanide

A. Belloche et al., *Science*, **345**, 1584, 2014.

Detection of HC₁₁N in the cold dust cloud TMC-1

M. B. Bell et al., *The Astrophysical Journal*, **483**, L61-L64, 1997.

Microwave Spectra of Molecules of Astrophysical Interest VII

F. Lovas and P. Krupenie, *Journal of Physical and Chemical Reference Data*, **3**, 245, 1974.

Q3

The image is from Wikipedia.

Q4

The image is from © Shutterstock.

Evidence-based survey of the elimination rates of ethanol from blood with applications in forensic casework

A. W. Jones, *Forensic Science International*, **200**, 1, 2010.

Kinetic Properties of Human Liver Alcohol Dehydrogenase: Oxidation of Alcohols by Class I Isoenzymes


F. W Wagner et al., *Biochemistry*, **22**, 1857, 1983.

Q5

The image is from © ETH Zurich.

Syngas production by simultaneous splitting of water and carbon dioxide via ceria redox reactions in a high-temperature solar reactor

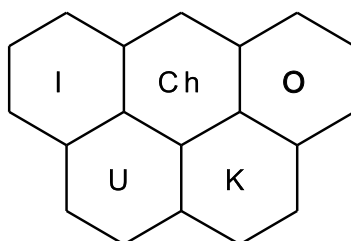
P. Furler et al., *Energy & Environmental Science*, **5**, 6098, 2012.

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**47th INTERNATIONAL
CHEMISTRY OLYMPIAD
2015
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.

In general error carried forward can be applied, we have tried to indicate where this may happen in the mark scheme.

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.

Comments in blue have been added to some questions, these are not required for the marks, but may be of interest in subsequent discussion on the questions.

Question	1	2	3	4	5	Total
Marks Available	9	17	20	14	15	75

1. This question is about the chemistry of touch-screens

- (a) $2\text{In}(\text{OH})_3 \rightarrow \text{In}_2\text{O}_3 + 3\text{H}_2\text{O}$ 1
State symbols not required
- (b) (i) Fraction of indium in In_2O_3 1
 $= (2 \times 114.82) / \{(2 \times 114.82) + (3 \times 16.00)\} = 0.8271$
Mass of In in touchscreen = $0.8271 \times 0.90 \times 27 \text{ mg} = 20.1 \text{ mg}$
- (ii) Volume of ITO touchscreen = $0.027 \text{ g} / 7.15 \text{ g cm}^{-3} = 0.00378 \text{ cm}^3$ 1
Area of ITO touchscreen = $20.1 \text{ mg} / 700 \text{ mg m}^{-2}$
 $= 0.0287 \text{ m}^2$ or 287 cm^2 1
Thickness of ITO touchscreen = $0.00378 \text{ cm}^3 / 287 \text{ cm}^2$ 1
 $= 0.0000132 \text{ cm}$ or $0.132 \mu\text{m}$ or $1.32 \times 10^{-7} \text{ m}$ 1
Correct answer scores full marks. Award 1 mark if area calculated correctly. Allow error carried forward from (b)(i).
- (c) Indium ions in cube = $(8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) = 4$ 1
- (d) Oxide ions in cube = $\frac{3}{2} \times 4 = 6$ 1
They occupy $\frac{3}{4}$ of the tetrahedral holes.
- (e) Molar mass of $\text{In}_2\text{O}_3 = 277.64 \text{ g mol}^{-1}$ 1
The mass decrease corresponds to $0.115 \times 277.64 \text{ g mol}^{-1}$ 1
 $= 31.93 \text{ g mol}^{-1}$ 1
This corresponds to the loss of two oxygen atoms per formula unit, giving In_2O . 1
Correct answer scores 2 marks. Award 1 mark if mass decrease is calculated correctly.
- (f) InN 1
The equation is $\text{In}_2\text{O}_3 + 2\text{NH}_3 \rightarrow 2\text{InN} + 3\text{H}_2\text{O}$ but this is not needed to be given full credit.

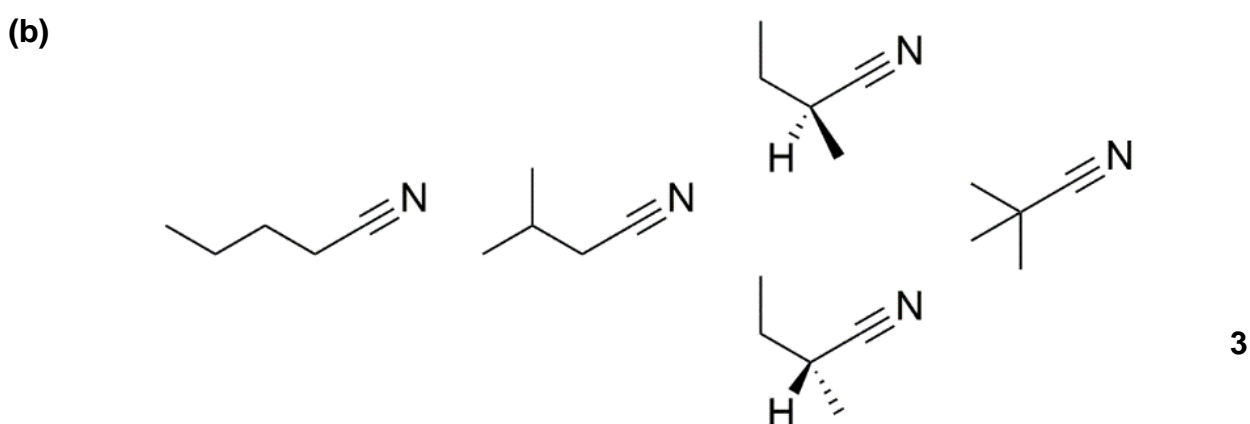
Question Total 9

2. This question is about detecting molecules in space

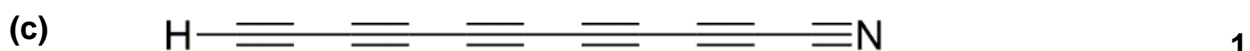


Butanenitrile 1/2

Allow 1-Butanenitrile. 1/2 mark for structure, 1/2 mark for name.



All five structures correct scores 3 marks. Four correct structures scores 2 marks (it is thought that most students will draw only one of the two enantiomers). Three correct structures scores 1 mark. Two correct structures scores 1/2 mark. One correct structure scores 0 marks. Incorrect or duplicated structures should be penalised at minus 1 mark each, down to a minimum of 0 marks.



(d) (i) Energy of transition from $(J+1)^{th}$ level to J^{th} level (an emission)

$$= h \times B \times (J + 1) (J + 2) - h \times B \times J (J + 1)$$

$$= h \times B \times [(J^2 + 3J + 2) - (J^2 + J)]$$

$$= h \times B \times 2(J + 1) = h \times f$$

$$B = f / 2(J + 1)$$

$$B = 13186.853 \text{ MHz} / 2(38 + 1)$$

$$B = 169.0622179 \text{ MHz}$$

2

Correct answer scores full marks. General formula does not have to be derived, but is worth a credit of 1 mark and very useful for remainder of question.

(ii) $h \times f = h \times B \times 2(J + 1)$ (from part (d)(i))

$$f = B \times 2(J + 1)$$

$$f = 169.0622179 \text{ MHz} \times 2(37 + 1)$$

$$f = 12848.72856 \text{ MHz}$$

2

Correct answer scores full marks. General formula does not have to be derived, but is worth a credit of 1 mark. Allow error carried forward from (d)(i). Answer should be answer to (d)(i) multiplied by 76.

(e) Mass of one atom of $^{12}\text{C} = 12.00 \text{ g mol}^{-1} / 6.02 \times 10^{23} \text{ mol}^{-1}$
 $= 1.993 \times 10^{-23} \text{ g} = 1.993 \times 10^{-26} \text{ kg}$

1

Mass of one atom of $^{16}\text{O} = 16.00 \text{ g mol}^{-1} / 6.02 \times 10^{23} \text{ mol}^{-1}$
 $= 2.658 \times 10^{-23} \text{ g} = 2.658 \times 10^{-26} \text{ kg}$

(f) $\mu = 1.993 \times 10^{-26} \text{ kg} \times 2.658 \times 10^{-26} \text{ kg} / (1.993 \times 10^{-26} + 2.658 \times 10^{-26}) \text{ kg}$
 $= 1.139 \times 10^{-26} \text{ kg}$

1

Allow error carried forward from part (e)

(g) (i) $f = B \times 2(J + 1)$

$$f = B \times 2(0 + 1)$$

$$f = 2B$$

$$B = 57,636 \text{ MHz}$$

$$r^2 = \frac{h}{8\pi^2\mu B}$$

$$r^2 = \frac{6.626 \times 10^{-34} \text{ kg m s}^{-2} \text{ s}}{8 \times \pi^2 \times 1.139 \times 10^{-26} \text{ kg} \times 5.7635 \times 10^{10} \text{ s}^{-1}}$$

$$r^2 = 1.2783 \times 10^{-20} \text{ m}^2$$

$$r = 1.13 \times 10^{-10} \text{ m}$$

3

Correct answer scores 3 marks. Statement $f = 2B$ scores 1 mark, correct calculation of B is worth the second mark. The third mark is for the correct answer. Penalise 1 mark for incorrect or missing units, or if out by power(s) of 10 due to mix up with cm/m etc.

(ii) $f = B \times 2(J + 1)$

$$806651.719 \text{ MHz} = 57635 \text{ MHz} \times 2(J + 1)$$

$$2(J + 1) = 14$$

$$(J + 1) = 7$$

$$J = 6$$

Transition is from Level **J = 7** to **J = 6**

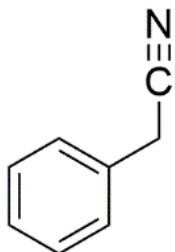
2

Correct answer scores 2 marks. If they have calculated the correct value of J but have labelled the transition the wrong way round i.e. J = 6 to J = 7 then award only 1 mark. If J has not been calculated numerically correctly then 0 marks. Error carried forward is not credited here.

Question Total 17

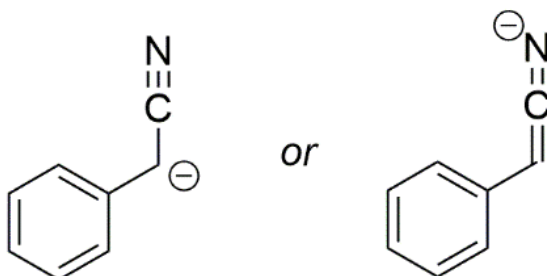
3. This question is about the performance-enhancing drug Ritalin[®]

(a) Compound **A**



1

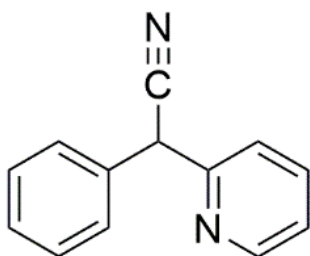
(b) Anion **B⁻**



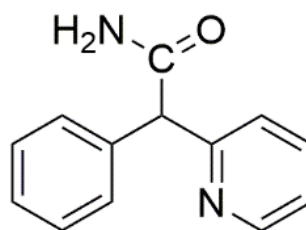
1

Full marks if both are drawn

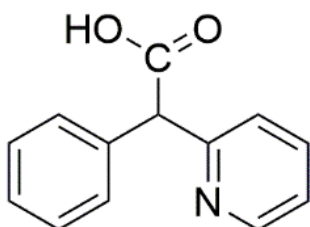
(c) Compound **C**



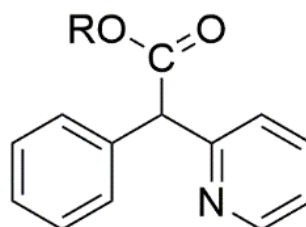
Compound **D**



Compound **E**



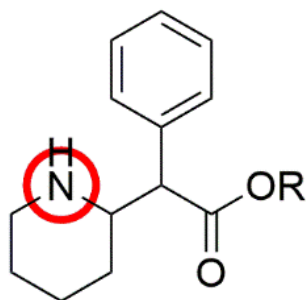
Compound **F**



4

Each correct structure scores 1 mark. If the R group in Compound **F** is drawn in as CH_3 then this is also acceptable.

(d)



1

The nitrogen atom must be the only atom circled.

- (e) (i) Additional molar mass on forming HCl salt = $(1.008 + 35.45) \text{ g mol}^{-1}$
= $36.458 \text{ g mol}^{-1}$

Number of moles of Ritalin must remain constant, therefore the following equation can be set up where M is the molar mass of Ritalin.

$$\frac{10.00}{M + 36.458} = \frac{8.647}{M}$$

$$10.00M = 8.647(M + 36.458)$$

$$10.00M - 8.647M = 315.252$$

$$1.353M = 315.252$$

$$M = 233.00 \text{ g mol}^{-1}$$

3

Working must be shown to get credit. This is because it is possible to work backwards from part (e)(ii) to get the mass. Award 1 mark if the concept of equating moles is shown, award the second mark if the equation above is written explicitly. The final mark is for the correct answer.

- (ii) Molar mass of molecule without R group = 218 g mol^{-1}

$$\text{Molar mass of R group} = (233 - 218) \text{ g mol}^{-1} = 15 \text{ g mol}^{-1}$$

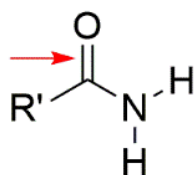
Identity of R group = CH_3 or Methyl or Me

The observant student might notice that the chemical name for Ritalin (Methylphenidate Hydrochloride) on the box in the picture suggests the identity of R, hence it is possible to score credit here even if part (e)(i) is incorrect.

1

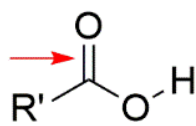
(f)

(i) 1655 cm^{-1}



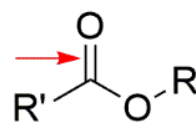
(C=O stretch
in amide)

(ii) 1715 cm^{-1}



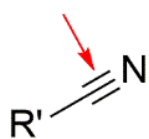
(C=O stretch in
carboxylic acid)

(iii) 1740 cm^{-1}



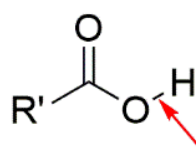
(C=O stretch
in ester)

(iv) 2260 cm^{-1}



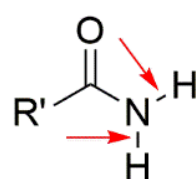
(C \equiv N stretch
in nitrile)

(v) 3000 cm^{-1}
(very broad)



(O-H stretch in
carboxylic acid)

(vi) 3180 and 3390 cm^{-1}
(sharp)



(Symmetric **and**
Asymmetric N-H
stretches in amide)

Must have both arrows

Award $\frac{1}{2}$ mark for each. In each case must be both the correct functional group and have the arrow(s) pointing to the correct bond(s) to obtain the $\frac{1}{2}$ mark. The words in brackets are not needed. In the case of the amide in part (vi) arrows must be drawn to both bonds to obtain the $\frac{1}{2}$ mark.

(g)

Pair of Stereoisomers	Enantiomers	Not Enantiomers
1 and 2		✓
1 and 3		✓
1 and 4	✓	
2 and 3	✓	
2 and 4		✓
3 and 4		✓

All correct 2 marks. For each mistake minus 1 mark, down to a minimum of zero. If both boxes have been ticked for any pair then 0 marks for this part.

3

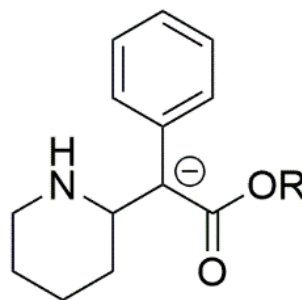
2

(h)

Anion G^-



Worth 2 marks



Worth 1 mark

2

Full marks if both are drawn.

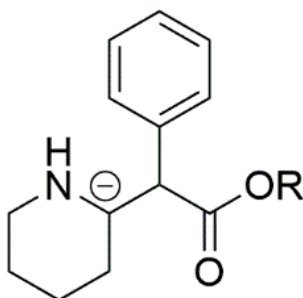
(i)

Pair of Stereoisomers	Intervconverted via Anion G^-	Not Intervconverted via Anion G^-
1 and 2		✓
1 and 3	✓	
1 and 4		✓
2 and 3		✓
2 and 4	✓	
3 and 4		✓

All correct 2 marks. For each mistake minus 1 mark, down to a minimum of 0. If both boxes have been ticked for any pair then 0 marks for this part.

2

If the anion below was drawn in part (h) then error carried forward can be applied here, in which case the correct answers are (1 and 2) and (3 and 4).



Question Total 20

4. This question is about hangovers

- (a) it is oxidised **it is reduced** it is hydrolysed it is isomerised it remains chemically unchanged

1

No marks if more than one answer circled.

- (b) Molar mass of ethanol = $(2 \times 12.01 + 6 \times 1.008 + 16.00) \text{ g mol}^{-1}$
= $46.068 \text{ g mol}^{-1}$

$$\text{Concentration} = 80 \text{ mg} / 100 \text{ cm}^3$$

$$= 800 \text{ mg dm}^{-3} = 0.8 \text{ g dm}^{-3}$$

$$= 0.8 \text{ g dm}^{-3} / 46.068 \text{ g mol}^{-1}$$

$$= 0.017 \text{ mol dm}^{-3} \text{ or } 0.017 \text{ M or } 17 \text{ mM}$$

1

- (c) (i) If $[\text{C}_2\text{H}_5\text{OH}] \gg K_M$, then $K_M + [\text{C}_2\text{H}_5\text{OH}] \approx [\text{C}_2\text{H}_5\text{OH}]$

$$\text{rate} = \frac{k_{\text{cat}}[\text{AD}][\text{C}_2\text{H}_5\text{OH}]}{K_M + [\text{C}_2\text{H}_5\text{OH}]}$$

$$\text{rate} = \frac{k_{\text{cat}}[\text{AD}][\text{C}_2\text{H}_5\text{OH}]}{[\text{C}_2\text{H}_5\text{OH}]}$$

$$\text{rate} = k_{\text{cat}}[\text{AD}]$$

1

- (ii) If $K_M \gg [\text{C}_2\text{H}_5\text{OH}]$, then $K_M + [\text{C}_2\text{H}_5\text{OH}] \approx K_M$

$$\text{rate} = \frac{k_{\text{cat}}[\text{AD}][\text{C}_2\text{H}_5\text{OH}]}{K_M + [\text{C}_2\text{H}_5\text{OH}]}$$

$$\text{rate} = \frac{k_{\text{cat}}[\text{AD}][\text{C}_2\text{H}_5\text{OH}]}{K_M}$$

1

- (d) Zero or 0 or Zeroth Order

At the UK drink drive limit $[\text{C}_2\text{H}_5\text{OH}]$ is much greater than K_M , meaning the case in (c)(i) applies. This is why it is possible to roughly calculate how long it will take someone to 'sober up' as the rate of loss of alcohol is approximately constant.

1

- (e) (i) This is obtained from the gradient of the graph in the period up to 18 h where there is a constant gradient.

$$\text{Gradient} = 17.0 \text{ (mg} / 100 \text{ cm}^3) \text{ h}^{-1}$$

Allow values between 15.5-18.5 (mg / 100 cm³) h⁻¹

1

(ii) From part (b) $80 \text{ mg} / 100 \text{ cm}^3 = 0.0174 \text{ mol dm}^{-3}$
Therefore $1 \text{ mg} / 100 \text{ cm}^3 = 2.175 \times 10^{-4} \text{ mol dm}^{-3}$
 $17 (\text{mg} / 100 \text{ cm}^3) \text{ h}^{-1} = 3.698 \times 10^{-3} \text{ mol dm}^{-3} \text{ h}^{-1}$
 $= 1.03 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$

2

Allow error carried forward from (e)(i). Answer should be 6.04×10^{-8} multiplied by the answer for part (e)(i). Also allow error carried forward from (b) if the same wrong conversion factor has been used.

(f) From part (c)(i) $\text{rate} \approx k_{\text{cat}}[AD]$

$$[AD] = \text{rate} / k_{\text{cat}}$$

$$[AD] = 1.03 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1} / 1.33 \text{ s}^{-1}$$

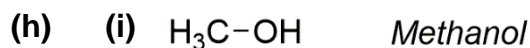
$$[AD] = 7.74 \times 10^{-7} \text{ mol dm}^{-3}$$

1

Allow error carried forward from (e)(ii). Answer should be the answer for part (e)(ii) divided by 1.33.

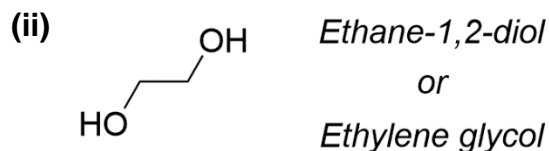
(g) it increases it is constant it decreases it is impossible to determine from the graph

1



1

Structure or name acceptable for 1 mark



1

Structure or name acceptable for 1 mark

(i)

Tick all that apply	
<input checked="" type="checkbox"/>	The maximum rate of metabolism is faster for ethanol
<input type="checkbox"/>	The maximum rate of metabolism is faster for the poisonous alcohol
<input type="checkbox"/>	The maximum rate of metabolism is the same for both
<input type="checkbox"/>	A higher concentration of ethanol is needed for the reaction to proceed at half of its maximum rate
<input checked="" type="checkbox"/>	A higher concentration of the poisonous alcohol is needed for the reaction to proceed at half of its maximum rate
<input type="checkbox"/>	The same concentration of ethanol and the poisonous alcohol are needed for the reactions to proceed at half of their maximum rate
<input type="checkbox"/>	The metabolism of the poisonous alcohol follows a rate law different from that of ethanol

Award 1 mark for each correct tick. If the last box is ticked, minus 1 mark from the overall total for this part. Ticks in other boxes are not negatively marked unless two or three contradictory statements have been ticked, in which case 0 marks are scored for this question. The lowest mark possible for this part is 0.

2

The maximum rate of metabolism occurs at high alcohol concentration when the enzyme is saturated with substrate. In this case $rate \approx k_{cat}[AD]$ and the alcohol with the higher k_{cat} value is metabolised more quickly.

When $K_M = [C_2H_5OH]$ then

$$rate = \frac{k_{cat}[AD]}{2}$$

and the reaction proceeds at half the maximum rate. Therefore alcohols with a high K_M value must be present at higher concentration for the reaction to proceed at half of its maximum rate.

Interestingly, as ethanol is a 'better' substrate for alcohol dehydrogenase than either methanol ($K_M = 3.0 \times 10^{-2} \text{ mol dm}^{-3}$) or ethylene glycol ($K_M = 3.2 \times 10^{-2} \text{ mol dm}^{-3}$), it is often used to treat cases of poisoning with these substances as it is metabolised preferentially by the enzyme.

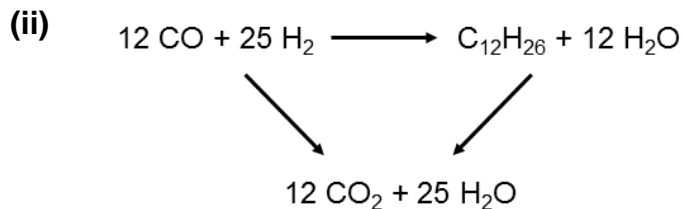
Question Total 14

5. This question is about making “green” jet fuel

- (a) $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 + \text{O}_2$ **1**
State symbols not required
- (b) (i) General formula for an alkane $\text{C}_n\text{H}_{2n+2}$ **1**
 $n \text{CO} + (2n+1) \text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} + n \text{H}_2\text{O}$
State symbols not required
- (ii) $n = 12, 2n+1 = 25$, therefore ratio of $\text{CO}:\text{H}_2 = 12:25$ **1**
- (c) (i) $\text{CeO}_{2-\delta} + \delta \text{CO}_2 \rightarrow \text{CeO}_2 + \delta \text{CO}$ **1**
State symbols not required
- (ii) $\text{CeO}_{2-\delta} + \delta \text{H}_2\text{O} \rightarrow \text{CeO}_2 + \delta \text{H}_2$ **1**
State symbols not required
- (d) (i) Number of moles of O atoms evolved = $2 \times 367 \text{ cm}^3 / 24,000 \text{ cm}^3 \text{ mol}^{-1}$
= 0.0306 mol
Number of moles of $\text{CeO}_2 = 127 \text{ g} / 172.12 \text{ g mol}^{-1}$ **2**
= 0.738 mol of CeO_2
 $\delta = 0.0306 / 0.738 = 0.0414$
Award 1 mark for if the factor of 2 has been forgotten, i.e. 0.0207 scores 1 mark.
- (ii) $2 \times 367 \text{ cm}^3 = 734 \text{ cm}^3$ **1**
- (e) (i) $(1.7/2.7) \times 747 \text{ cm}^3 / 24,000 \text{ cm}^3 = 0.0196 \text{ mol of H}_2$ **1/2**
- (ii) $(1/2.7) \times 747 \text{ cm}^3 / 24,000 \text{ cm}^3 = 0.0115 \text{ mol of CO}$ **1/2**
- (f) $(26 \times 60 \times 3.6 \times 10^3) \text{ J} + (34 \times 60 \times 0.80 \times 10^3) \text{ J} = 7,248 \text{ kJ}$ **1**
- (g) (i) $0.0196 \text{ mol} \times -286 \text{ kJ mol}^{-1} + 0.0115 \text{ mol} \times -283 \text{ kJ mol}^{-1}$
= -8.87 kJ **1**
Accept if magnitude is correct but minus sign is missing. Allow error carried forward from part (e).
- (ii) $8.87 \text{ kJ} / 7248 \text{ kJ} = 0.12\%$ **1**
Allow error carried forward from (f) and/or (g)(i).

(h) (i) From $n=7$ to $n=8$, 654 kJ mol^{-1} more heat energy evolved.
 $\Delta_c H^\ominus$ for $n=12 = -5470 - (4 \times 654 \text{ kJ mol}^{-1}) = -8086 \text{ kJ mol}^{-1}$

1



2

$$\begin{aligned} &= (12 \times -283 \text{ kJ mol}^{-1}) + (25 \times -286 \text{ kJ mol}^{-1}) + 8,086 \text{ kJ mol}^{-1} \\ &= -2,460 \text{ kJ mol}^{-1} \end{aligned}$$

1 mark for correct construction of cycle and attempt at calculation with mathematical error. Allow error carried forward from (h)(i).

Question Total 15

Paper Total 75