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) $2In(OH)_3 \rightarrow In_2O_3 + 3H_2O$

State symbols not required   **1**

(b) **(i)** Fraction of indium in In_2O_3

= (2 × 114.82) / {(2 × 114.82) + (3 × 16.00)} = 0.8271   **1**

Mass of In in touchscreen = 0.8271 × 0.90 × 27 mg = 20.1 mg

(ii) Volume of ITO touchscreen = 0.027 g / 7.15 g cm^{-3} = 0.00378 cm^3

Area of ITO touchscreen = 20.1 mg / 700 mg m^{-2}

= 0.0287 m^2 or 287 cm^2 **1**

Thickness of ITO touchscreen = 0.00378 cm^3 / 287 cm^2

= 0.0000132 cm or 0.132 µm or 1.32 × 10^{-7} 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 × ⅛) + (6 × ½) = 4   **1**

(d)   Oxide ions in cube = $^3/_2$ × 4 = 6   **1**

They occupy ¾ of the tetrahedral holes.

(e)   Molar mass of In_2O_3 = 277.64 g mol^{-1}

The mass decrease corresponds to 0.115 × 277.64 g mol^{-1}

= 31.93 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 $In_2O_3 + 2NH_3 \rightarrow 2InN + 3H_2O$ but this is not needed to be given full credit.

Question Total 9

2. This question is about detecting molecules in space

(a) **(i)**

1

(ii)

½

Butanenitrile

½

Allow 1-Butanenitrile. ½ mark for structure, ½ mark for name.

(b)

3
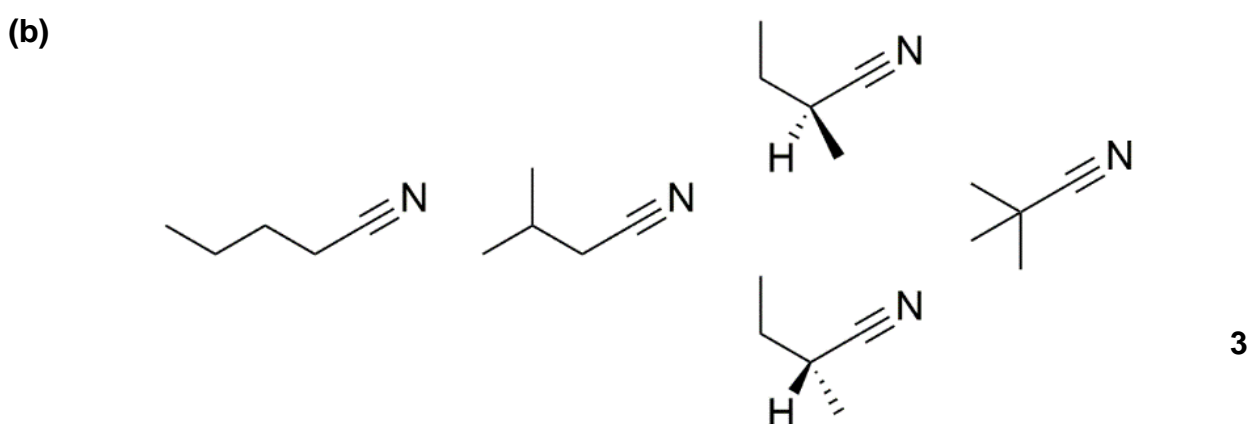
All five structures correct scores 3 marks. Four correct structures scores 2 marks (it is thought that most students will draw only one of the two enantiomers). Three correct structures scores 1 mark. Two correct structures scores ½ mark. One correct structure scores 0 marks. Incorrect or duplicated structures should be penalised at minus 1 mark each, down to a minimum of 0 marks.

(c)

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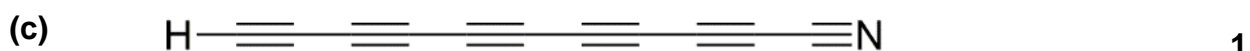
(d) **(i)** *Energy of transition from $(J+1)^{th}$ level to J^{th} level (an emission)*

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

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

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

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

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

$B = 169.0622179 \text{ MHz}$

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))*

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

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

$f = 12848.72856$ 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}C = 12.00 g mol^{-1} / 6.02 × 10^{23} mol^{-1}

= 1.993 × 10^{-23} g = 1.993 × 10^{-26} kg

Mass of one atom of ^{16}O = 16.00 g mol^{-1} / 6.02 × 10^{23} mol^{-1}

= 2.658 × 10^{-23} g = 2.658 × 10^{-26} kg

1

(f) μ = 1.993 × 10^{-26} kg × 2.658 × 10^{-26} kg / (1.993 × 10^{-26} + 2 .658 × 10^{-26}) kg

= 1.139 × 10^{-26} kg

Allow error carried forward from part (e)

1

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

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

$f = 2B$

$B = 57{,}636$ MHz

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

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

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

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

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.

3

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

806651.719 MHz = 57635 MHz × 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.
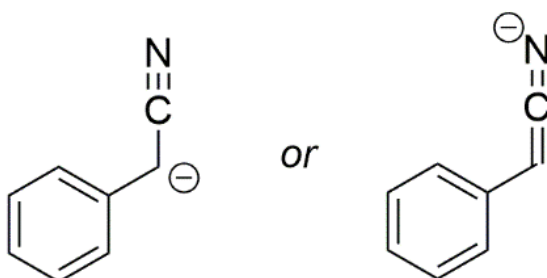
Question Total 17

3. This question is about the performance-enhancing drug Ritalin®
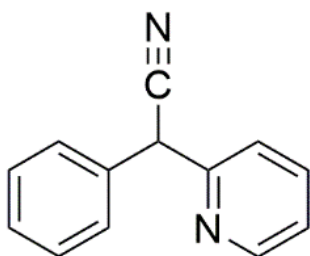
(a) Compound **A**

1

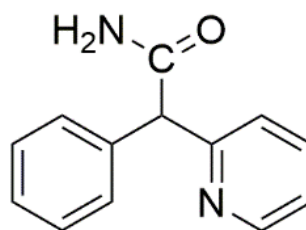**(b)** Anion **B⁻**

or

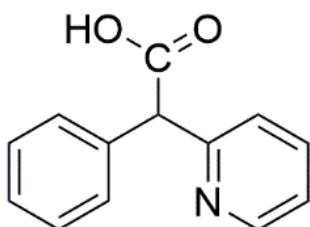*Full marks if both are drawn*

1
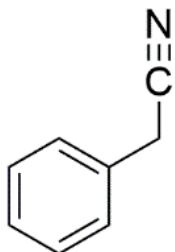
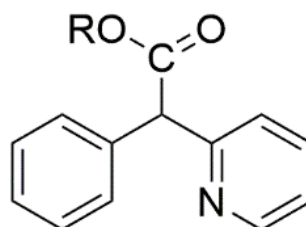**(c)** Compound **C**   Compound **D**

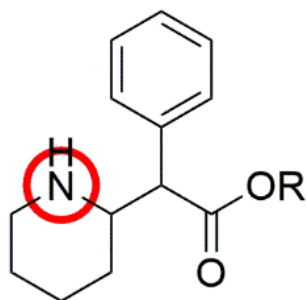Compound **E**   Compound **F**

4

*Each correct structure scores 1 mark. If the R group in Compound **F** is drawn in as CH₃ then this is also acceptable.*

(d)

The nitrogen atom must be the only atom circled.

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

$= 36.458$ 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.

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

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

$$10.00M - 8.647M = 315.252$$

$$1.353M = 315.252$$

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

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}

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

Indentity 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.
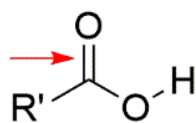
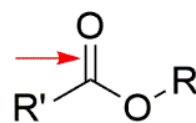1

3

1

(f)

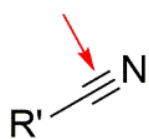(i) 1655 cm^{-1}
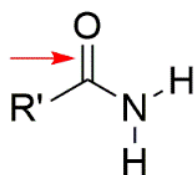
(C=O stretch in amide)

(ii) 1715 cm^{-1}

(C=O stretch in carboxylic acid)

(iii) 1740 cm^{-1}
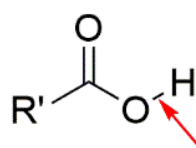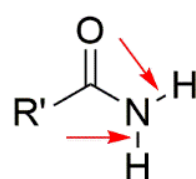

(C=O stretch in ester)

(iv) 2260 cm^{-1}

(C≡O 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

3

Award ½ 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 ½ 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 ½ 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		✓

2

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.

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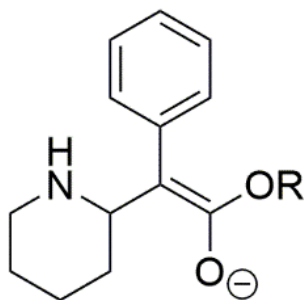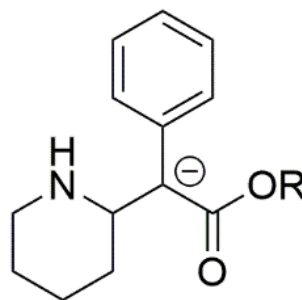
*If the anion below was drawn in part (h) then error carried forward can be applied here, in which case the correct answers are **(1 and 2)** and **(3 and 4)**.*

2
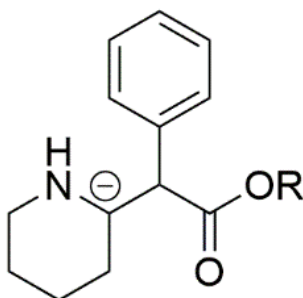
Question Total   20

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 = $(2 \times 12.01 + 6 \times 1.008 + 16.00)$ g mol^{-1}

= 46.068 g mol^{-1}

Concentration = 80 mg / 100 cm^3

= 800 mg dm^{-3} = 0.8 g dm^{-3}

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

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

1

(c) **(i)** If $[C_2H_5OH] \gg K_M$, then $K_M + [C_2H_5OH] \approx [C_2H_5OH]$

$$rate = \frac{k_{cat}[AD][C_2H_5OH]}{K_M + [C_2H_5OH]}$$

$$rate = \frac{k_{cat}[AD][C_2H_5OH]}{[C_2H_5OH]}$$

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

1

(ii) If $K_M \gg [C_2H_5OH]$, then $K_M + [C_2H_5OH] \approx K_M$

$$rate = \frac{k_{cat}[AD][C_2H_5OH]}{K_M + [C_2H_5OH]}$$

$$rate = \frac{k_{cat}[AD][C_2H_5OH]}{K_M}$$

1

(d) Zero *or* 0 *or* Zeroth Order

At the UK drink drive limit $[C_2H_5OH]$ 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.

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

Allow values between 15.5-18.5 (mg / 100 cm^3) h^{-1}

1

(ii) From part (b) 80 mg / 100 cm^3 = 0.0174 mol dm^{-3}

Therefore 1 mg / 100 cm^3 = 2.175 × 10^{-4} mol dm^{-3}

17 (mg / 100 cm^3) h^{-1} = 3.698 × 10^{-3} mol dm^{-3} h^{-1}

= 1.03 × 10^{-6} mol dm^{-3} 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) $rate \approx k_{cat}[AD]$

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

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

$[AD] = 7.74 \times 10^{-7}$ 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

(h) **(i)** H$_3$C−OH   *Methanol*

1

Structure or name acceptable for 1 mark

(ii)   OH   *Ethane-1,2-diol*

HO   *or*

Ethylene glycol

1

Structure or name acceptable for 1 mark

(i)

	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

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 ($K_M = 3.0 \times 10^{-2}$ mol dm^{-3}) or ethylene glycol ($K_M = 3.2 \times 10^{-2}$ mol dm^{-3}), it is often used to treat cases of poisoning with these substances as it is metabolised preferentially by the enzyme.
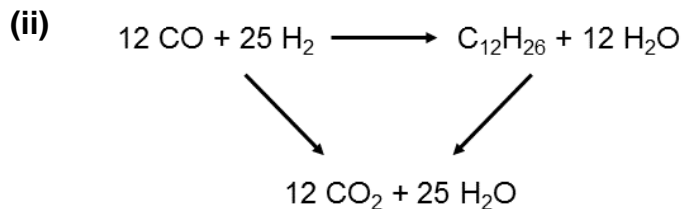
Question Total 14

5. This question is about making "green" jet fuel

(a) $CO_2 + H_2O \rightarrow CO + H_2 + O_2$

State symbols not required   **1**

(b)   **(i)**   General formula for an alkane C_nH_{2n+2}

$n\ CO + (2n+1)\ H_2 \rightarrow C_nH_{2n+2} + n\ H_2O$

State symbols not required   **1**

(ii)   n = 12, 2n+1 = 25, therefore ratio of $CO:H_2$ = 12:25   **1**

(c)   **(i)** $CeO_{2-\delta} + \delta\ CO_2 \rightarrow CeO_2 + \delta\ CO$

State symbols not required   **1**

(ii) $CeO_{2-\delta} + \delta\ H_2O \rightarrow CeO_2 + \delta\ H_2$

State symbols not required   **1**

(d)   **(i)**   Number of moles of O atoms evolved = $2 \times 367\ cm^3/24{,}000\ cm^3\ mol^{-1}$

= 0.0306 mol

Number of moles of CeO_2 = 127 g / 172.12 g mol^{-1}

= 0.738 mol of CeO_2

δ = 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.   **2**

(ii) $2 \times 367\ cm^3 = 734\ cm^3$ **1**

(e)   **(i)** $(1.7/2.7) \times 747\ cm^3/ 24{,}000\ cm^3 = 0.0196$ mol of H_2 **½**

(ii) $(1/2.7) \times 747\ cm^3/ 24{,}000\ cm^3 = 0.0115$ mol of CO   **½**

(f) $(26 \times 60 \times 3.6 \times 10^3)$ J + $(34 \times 60 \times 0.80 \times 10^3)$ J = 7,248 kJ   **1**

(g)   **(i)**   0.0196 mol $\times$ −286 kJ mol^{-1} + 0.0115 mol $\times$ −283 kJ mol^{-1}

= −8.87 kJ

Accept if magnitude is correct but minus sign is missing. Allow error carried forward from part (e).   **1**

(ii)   8.87 kJ / 7248 kJ = 0.12%

Allow error carried forward from (f) and/or (g)(i).   **1**

(h) **(i)** From n=7 to n=8, 654 kJ mol^{-1} more heat energy evolved.

$\Delta_cH^{\ominus}$ for n=12 = −5470 − (4 × 654 kJ mol^{-1}) = −8086 kJ mol^{-1}

1

(ii)

$$12\ CO + 25\ H_2 \longrightarrow C_{12}H_{26} + 12\ H_2O$$

$$12\ CO_2 + 25\ H_2O$$

2

= (12 × −283 kJ mol^{-1}) + (25 x −286 kJ mol^{-1}) + 8,086 kJ mol^{-1}

= −2,460 kJ mol^{-1}

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