

# 51<sup>st</sup> INTERNATIONAL CHEMISTRY OLYMPIAD

2019

UK Round One

MARK SCHEME

We encourage students to quote answers to an appropriate number of significant figures, but do not penalise students for significant figure errors. Allow marks for answers that differ from the mark scheme due to rounded/non-rounded data used from an earlier part of the question.

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

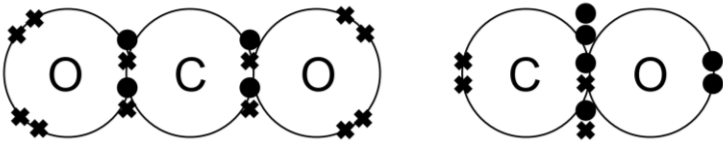
Deduct one mark from answers with missing or incorrect units for the first occurrence in **each** question and write **UNIT** next to it. Do not penalise any further missing or incorrect units in the same question.

Accept organic structures shown in their skeletal form and displayed as formulae if the representation is unambiguous.

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

**NEW FOR THIS YEAR:** Do not award any half marks. One blank tick box has been included per mark available for each part. Please mark by placing a tick in each box if mark is scored.

Question	1	2	3	4	5	Total
Marks Available	11	18	11	27	13	80

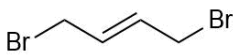
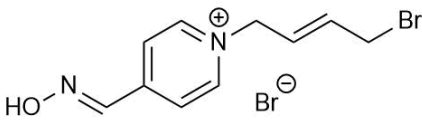
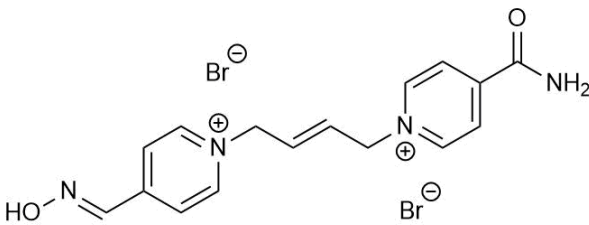
1.	This question is about carbon dioxide	Mark
(a)	<p>(i) </p> <p style="text-align: center;">carbon dioxide                      carbon monoxide</p> <p><i>One mark each. Allow any combination of dots and crosses.</i></p>	<input checked="" type="checkbox"/> <input checked="" type="checkbox"/>
	<p>(ii) <math>\text{CO}_2 = +4</math>    <math>\text{CO} = +2</math>  Difference = 2  <i>Allow -2.</i></p>	<input checked="" type="checkbox"/>
(b)	<p>(i) <math>c = k \times p(\text{CO}_2)</math>  <math>0.099 \text{ mol dm}^{-3}</math></p>	<input checked="" type="checkbox"/>
	<p>(ii) 1.09 g</p> <p><i>ECF answer = (11.01 × answer to part (i)) g</i></p>	<input checked="" type="checkbox"/>
	<p>(iii) <math>2.45 \times 10^5 \text{ Pa}</math></p> <p><i>ECF answer = (2.25 × 10<sup>5</sup> × answer to part (ii)) Pa</i></p>	<input checked="" type="checkbox"/>
	<p>(iv) <input checked="" type="checkbox"/> high pressure and low temperature  <input type="checkbox"/> high pressure and high temperature  <input type="checkbox"/> low pressure and low temperature  <input type="checkbox"/> low pressure and high temperature</p> <p><i>No marks if more than one box ticked.</i></p>	<input checked="" type="checkbox"/>
(c)	<p>Accept values in range 57—63 °C</p>	<input checked="" type="checkbox"/>
(d)	<p>CO 33.3 moles  H<sub>2</sub>O 33.3 moles  CO<sub>2</sub> 26.7 moles  H<sub>2</sub> 26.7 moles</p> <p><i>All four correct two marks. No partial credit.</i></p>	<input checked="" type="checkbox"/> <input checked="" type="checkbox"/>
(e)	<p>enthalpy of reaction = <math>-393.5 \text{ kJ mol}^{-1} - (-110.5 + -241.1) \text{ kJ mol}^{-1}</math>  = <math>-41.9 \text{ kJ mol}^{-1}</math></p> <p><i>Do not award mark for positive answer.</i></p>	<input checked="" type="checkbox"/>

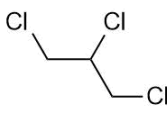
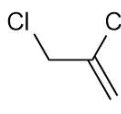
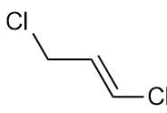
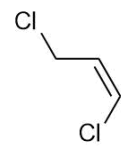
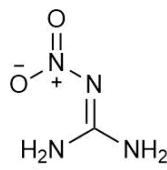
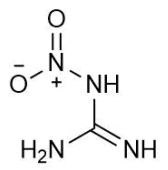
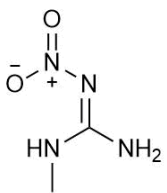
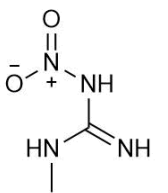
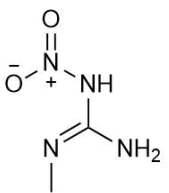
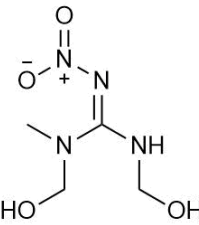
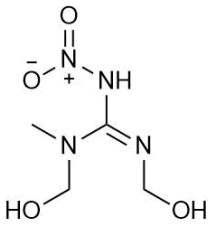
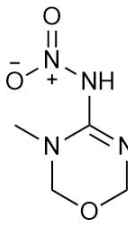
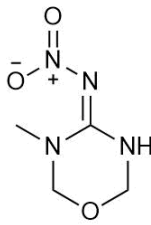
Total out of 11

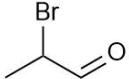
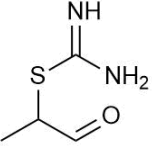
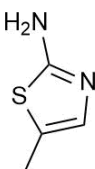
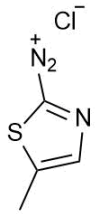
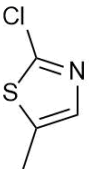
**11**

2.	This question is about the industrial separation of precious metals	Mark																		
(a)	(i) Pd	<input checked="" type="checkbox"/>																		
	(ii) Pt	<input checked="" type="checkbox"/>																		
	(iii) Ir	<input checked="" type="checkbox"/>																		
(b)	(i) $\text{Au} + 3\text{HNO}_3 + 4\text{HCl} \rightarrow \text{HAuCl}_4 + 3\text{NO}_2 + 3\text{H}_2\text{O}$ <i>Must be fully correct for mark.</i>	<input checked="" type="checkbox"/>																		
	(ii) $\text{Pt} + 4\text{HNO}_3 + 6\text{HCl} \rightarrow \text{H}_2\text{PtCl}_6 + 4\text{NO}_2 + 4\text{H}_2\text{O}$ <i>Must be fully correct for mark.</i>	<input checked="" type="checkbox"/>																		
(c)	$m/z = {}^{197}\text{Au} + 4 {}^{35}\text{Cl} = 337$ Prob = $(0.75)^4 = 31.6\%$																			
	$m/z = {}^{197}\text{Au} + 3 {}^{35}\text{Cl} + 1 {}^{37}\text{Cl} = 339$ Prob = $(0.75)^3 \times 0.25 \times 4 = 42.2\%$																			
	$m/z = {}^{197}\text{Au} + 2 {}^{35}\text{Cl} + 2 {}^{37}\text{Cl} = 341$ Prob = $(0.75)^2 \times (0.25)^2 \times 6 = 21.1\%$																			
	$m/z = {}^{197}\text{Au} + 1 {}^{35}\text{Cl} + 3 {}^{37}\text{Cl} = 343$ Prob = $0.75 \times (0.25)^3 \times 4 = 4.7\%$																			
$m/z = {}^{197}\text{Au} + 4 {}^{37}\text{Cl} = 345$ Prob = $(0.25)^4 = 0.4\%$																				
<table border="1" data-bbox="240 952 1370 1064"> <thead> <tr> <th>m/z</th> <th>337</th> <th>339</th> <th>341</th> <th>343</th> <th>345</th> </tr> </thead> <tbody> <tr> <td>relative intensity</td> <td>31.6%</td> <td>42.2%</td> <td>21.1%</td> <td>4.7%</td> <td>0.4%</td> </tr> <tr> <td>(as fractions)</td> <td><math>\frac{81}{256}</math></td> <td><math>\frac{108}{256}</math></td> <td><math>\frac{54}{256}</math></td> <td><math>\frac{12}{256}</math></td> <td><math>\frac{1}{256}</math></td> </tr> </tbody> </table>		m/z	337	339	341	343	345	relative intensity	31.6%	42.2%	21.1%	4.7%	0.4%	(as fractions)	$\frac{81}{256}$	$\frac{108}{256}$	$\frac{54}{256}$	$\frac{12}{256}$	$\frac{1}{256}$	
m/z	337	339	341	343	345															
relative intensity	31.6%	42.2%	21.1%	4.7%	0.4%															
(as fractions)	$\frac{81}{256}$	$\frac{108}{256}$	$\frac{54}{256}$	$\frac{12}{256}$	$\frac{1}{256}$															
<p data-bbox="204 1093 1417 1294"><i>First mark for all m/z correct. First mark not given if one or more m/z incorrect. Second and third mark for all relative intensities correct. Accept if relative intensities quoted as decimals or as fractions or as a whole number ratio. If one relative intensity wrong award second mark but not third. If two or more relative intensities wrong do not award second or third mark. If statistical factors are forgotten, but intensities are all correct otherwise, award second mark but not third. Table without statistical factors shown below.</i></p> <table border="1" data-bbox="248 1323 1361 1453"> <thead> <tr> <th>m/z</th> <th>337</th> <th>339</th> <th>341</th> <th>343</th> <th>345</th> </tr> </thead> <tbody> <tr> <td>relative intensity</td> <td>66.9%</td> <td>22.3%</td> <td>7.4%</td> <td>2.5%</td> <td>0.8%</td> </tr> <tr> <td>(as fractions)</td> <td><math>\frac{81}{120}</math></td> <td><math>\frac{27}{120}</math></td> <td><math>\frac{9}{120}</math></td> <td><math>\frac{3}{120}</math></td> <td><math>\frac{1}{120}</math></td> </tr> </tbody> </table>		m/z	337	339	341	343	345	relative intensity	66.9%	22.3%	7.4%	2.5%	0.8%	(as fractions)	$\frac{81}{120}$	$\frac{27}{120}$	$\frac{9}{120}$	$\frac{3}{120}$	$\frac{1}{120}$	<input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/>
m/z	337	339	341	343	345															
relative intensity	66.9%	22.3%	7.4%	2.5%	0.8%															
(as fractions)	$\frac{81}{120}$	$\frac{27}{120}$	$\frac{9}{120}$	$\frac{3}{120}$	$\frac{1}{120}$															
(d)	$3\text{FeCl}_2 + \text{HAuCl}_4 \rightarrow \text{Au} + 3\text{FeCl}_3 + \text{HCl}$ (allow $3\text{Fe}^{2+} + \text{Au}^{3+} \rightarrow 3\text{Fe}^{3+} + \text{Au}$ ) <i>Must be fully correct for mark.</i>	<input checked="" type="checkbox"/>																		
(e)	$[\text{PtCl}_6][\text{NH}_4]_2$  <i>Allow if written as ions with separate charges. Allow multiples of this formula.</i>	<input checked="" type="checkbox"/>																		

(f)	$\begin{array}{c} \text{Cl} \\   \\ \text{H}_3\text{N}-\text{Pd}-\text{Cl} \\   \\ \text{NH}_3 \end{array} \quad \begin{array}{c} \text{Cl} \\   \\ \text{H}_3\text{N}-\text{Pd}-\text{NH}_3 \\   \\ \text{Cl} \end{array}$ <p>One mark for each correct structure. If three structures drawn maximum mark is one if there is one correct. Four or more structures drawn is no marks.</p>	<input checked="" type="checkbox"/> <input checked="" type="checkbox"/>
(g)	<p><math>\text{H}_2\text{PdCl}_4 + 4\text{NH}_4\text{OH} \rightarrow \text{Pd}(\text{NH}_3)_2\text{Cl}_2 + 4\text{H}_2\text{O} + 2\text{NH}_4\text{Cl}</math>  or <math>\text{H}_2\text{PdCl}_4 + 2\text{NH}_4\text{OH} \rightarrow \text{Pd}(\text{NH}_3)_2\text{Cl}_2 + 2\text{H}_2\text{O} + 2\text{HCl}</math>  or suitable ionic form, eg <math>\text{H}_2\text{PdCl}_4 + 4\text{NH}_4\text{OH} \rightarrow \text{Pd}(\text{NH}_3)_2\text{Cl}_2 + 4\text{H}_2\text{O} + 2\text{NH}_4^+ 2\text{Cl}^-</math></p> <p>Must be fully correct for mark.</p>	<input checked="" type="checkbox"/>
(h)	(i) $(2N \times I) + 1 = (2 \times 2 \times 1) + 1$ = 5 lines	<input checked="" type="checkbox"/>
	(ii) $(2N \times I) + 1 = (2 \times 4 \times 1) + 1$ = 9 lines	<input checked="" type="checkbox"/>
	(iii) $(2N \times I) + 1 = (2 \times 4 \times \frac{1}{2}) + 1$ = 5 lines	<input checked="" type="checkbox"/>
(i)	(i) 1:2:3:2:1	<input checked="" type="checkbox"/>
	(ii) 1:4:10:16:19:16:10:4:1	<input checked="" type="checkbox"/>
<i>Total out of 18</i>		<b>18</b>

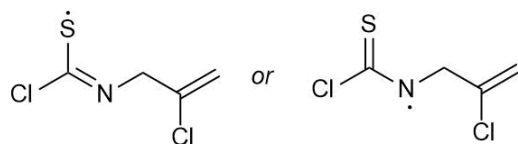
3.	This question is about treating nerve agent poisoning	Mark
(a)	(i) 172.612 g mol <sup>-1</sup> (ii) dosage = 24 hours × 80.0 kg × 3.00 × 10 <sup>-3</sup> mol hour <sup>-1</sup> kg <sup>-1</sup> = 5.76 mol mass of PAM = 5.76 mol × 172.612 g mol <sup>-1</sup> = 994 g  <i>ECF answer = (answer to part (a)(i) × 5.76) g</i>	<input checked="" type="checkbox"/>     <input checked="" type="checkbox"/>
(b)	(i) First order (ii) Zeroth order	<input checked="" type="checkbox"/>  <input checked="" type="checkbox"/>
(c)	$K_c = \frac{[\text{AChE-I-PAM}]}{[\text{AChE-I}][\text{PAM}]}$ <i>Must be fully correct for mark.</i>	<input checked="" type="checkbox"/>
(d)	(i) intercept = 1.58 $k_2 = 1/\text{intercept} = 0.633 \text{ s}^{-1}$ (ii) intercept = 1.58; gradient = 6.75 × 10 <sup>-4</sup> $K = \text{intercept}/\text{gradient} = 1.58 / 6.75 \times 10^{-4} = 2,340 \text{ mol}^{-1} \text{ dm}^3$ <i>No ECF from part (d)(i).</i>	<input checked="" type="checkbox"/>    <input checked="" type="checkbox"/>
(e)	 <i>No mark if drawn as cis isomer.</i>	<input checked="" type="checkbox"/>
(f)	9	<input checked="" type="checkbox"/>
(g)	<div style="display: flex; justify-content: space-around;"> <div style="text-align: center;"> <p>Intermediate X</p>  </div> <div style="text-align: center;"> <p>Reactivator Y</p>  </div> </div> <i>One mark each. Award one mark out of two total if both structures are correct but bromide salts are missing. Allow ECF if cis alkene drawn here AND in part (e).</i>	<input checked="" type="checkbox"/>  <input checked="" type="checkbox"/>
Total out of 11		11

4.	This question is about bees and Brexit	Mark
(a)	$C_8H_{10}ClN_5O_3S$	<input checked="" type="checkbox"/>
(b)	<div style="display: flex; justify-content: space-around; align-items: flex-start;"> <div style="text-align: center;"> <p><b>A</b></p>  </div> <div style="text-align: center;"> <p><b>B</b></p>  </div> </div> <div style="display: flex; justify-content: space-around; align-items: flex-start; margin-top: 20px;"> <div style="text-align: center;"> <p><b>B'</b></p>  </div> <div style="text-align: center;"> <p><b>B''</b></p>  </div> </div> <p><i>One mark for each correct structure. If B' and B'' are drawn the wrong way around then one mark out of two is scored for B' and B'' combined. No ECF can be applied.</i></p>	<input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/>
(c)	$S=C=N^-$ <i>The correct shape is not required for the mark.</i>	<input checked="" type="checkbox"/>
(d)	$O=N^+=O$ Linear <i>The shape must be stated as linear or clearly indicated as linear from the diagram for the mark.</i>	<input checked="" type="checkbox"/>
(e)	<div style="display: flex; justify-content: space-around; align-items: flex-start;"> <div style="text-align: center;"> <p><b>E</b></p>  </div> <div style="text-align: center;"> <p>or</p>  </div> <div style="text-align: center;"> <p>or</p>  </div> <div style="text-align: center;"> <p>or</p>  </div> <div style="text-align: center;"> <p>or</p>  </div> </div> <div style="display: flex; justify-content: space-around; align-items: flex-start; margin-top: 20px;"> <div style="text-align: center;"> <p><b>G</b></p>  </div> <div style="text-align: center;"> <p>or</p>  </div> <div style="text-align: center;"> <p><b>H</b></p>  </div> <div style="text-align: center;"> <p>or</p>  </div> </div> <p><i>One mark for E, two marks for F, two marks for G, and one mark for H. For F and G no partial credit is given – structures must be fully correct for the two marks. ECF can be awarded for F based on E. ECF can be awarded for G based on F only if G is consistent with molecular formula. No ECF for H as H can be worked to backwards from product.</i></p>	<input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/>

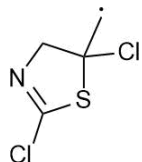
(f)	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> <p><b>I</b></p>  </div> <div style="text-align: center;"> <p><b>J</b></p>  </div> </div> <p>One mark for <b>I</b>, two marks for <b>J</b>. No partial credit is given for <b>J</b> – structure must be fully correct for the two marks. ECF can be awarded for <b>J</b> based on <b>I</b> only if <b>J</b> is consistent with molecular formula.</p>	<input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/>
(g)	<div style="text-align: center;"> <p><b>K</b></p>  </div> <p>No partial credit is given for <b>K</b> – structure must be fully correct for the two marks. ECF can be awarded for <b>K</b> based on <b>J</b> only if <b>K</b> is consistent with molecular formula.</p>	<input checked="" type="checkbox"/> <input checked="" type="checkbox"/>
(h)	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> <p><b>L</b></p>  </div> <div style="text-align: center;"> <p><b>M</b></p>  </div> </div> <p>Two marks for <b>L</b>, one mark for <b>M</b>. No partial credit is given for <b>L</b> – structure must be fully correct for the two marks. ECF can be awarded for <b>L</b> based on <b>K</b>. No ECF for <b>M</b> as <b>M</b> can be worked to backwards from product.</p>	<input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/>

(i)

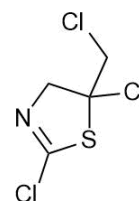
**Intermediate V-**



**Intermediate W-**



**Y**



One mark for **V-**, two marks for **W-** and one mark for **Y**. Position of radical must be clearly indicated with a dot for **V-** and **W-**. No ECF can be awarded as there is sufficient new information about each species.

(j)

**Reagent X**



**Chain-carrying radical Z-**



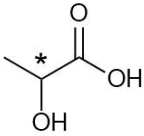
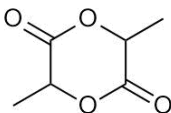
One mark each.



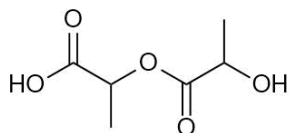
Total out of 27

**27**



5.	This question is about a biodegradable plastic	Mark
(a)	 <p>One mark for structure. One mark for correct marking of chiral centre with asterisk.</p>	<input checked="" type="checkbox"/> <input checked="" type="checkbox"/>
(b)	<input type="checkbox"/> addition <input checked="" type="checkbox"/> condensation <input type="checkbox"/> neutralisation <input type="checkbox"/> oxidation <input type="checkbox"/> reduction <p>No marks if more than one box ticked.</p>	<input checked="" type="checkbox"/>
(c)	<p>Compound A</p>  <p>No stereochemistry required.</p>	<input checked="" type="checkbox"/>
(d)	<p>amount of KOH = <math>0.0400 \text{ mol dm}^{-3} \times 0.00681 \text{ dm}^3 = 2.72 \times 10^{-4} \text{ mol}</math>  amount of -COOH residues = <math>2.72 \times 10^{-4} \text{ mol} = \text{amount of chains}</math>  average molar mass of chain = total mass / amount of chains  average molar mass of chain = <math>0.1619 \text{ g} / 2.72 \times 10^{-4} \text{ mol} = 595 \text{ g mol}^{-1}</math>  Correct answer required for mark. No credit for working only.</p>	<input checked="" type="checkbox"/>
(e)	<p>molar mass of polymer = molar mass of n repeat units + molar mass of H<sub>2</sub>O  number of repeat units = <math>(595 - 18) \text{ g mol}^{-1} / 72 \text{ g mol}^{-1}</math>  number of repeat units = 8  Correct answer scores two marks. One mark can be awarded if working is correct and only one of the following errors has been made: leaving out the factor of -18 for water/getting the value of this factor wrong; OR using an incorrect repeat unit molar mass; OR all values correct but a calculator error has been made. Two or more errors scores no marks.  Answer based on using incorrect value of <math>306 \text{ g mol}^{-1} = 4</math>  ECF answer = (answer to part (d) - 18) / 72</p>	<input checked="" type="checkbox"/> <input checked="" type="checkbox"/>
(f)	<p>one mol of repeat unit reacts with one mole of NaOH  mass = <math>286,000 \text{ tonnes} \times 40 \text{ g mol}^{-1} / 72 \text{ g mol}^{-1} = 159,000 \text{ tonnes}</math>  Correct answer required for mark. No credit for working only.</p>	<input checked="" type="checkbox"/>
(g)	<p>amount of acid = <math>0.100 \text{ mol dm}^{-3} \times 0.0194 \text{ dm}^3 \times 5 = 9.70 \times 10^{-3} \text{ mol}</math>  Correct answer required for mark. No credit for working only.</p>	<input checked="" type="checkbox"/>

(h) Compound **B** (dimer)



*No stereochemistry required.*



(i) mass of dimer = 0.1701 g; mass of lactic acid = 0.7785 g

*Three marks for both masses correct. First mark for calculation of amount of repeat unit. Second mark for mass of dimer. Third mark for mass of lactic acid.*

amount of HCl used =  $0.100 \text{ mol dm}^{-3} \times 0.01850 \text{ dm}^3 = 1.85 \times 10^{-3} \text{ mol}$

amount of NaOH in aliquot that had reacted with PLA

=  $(0.04000 \text{ dm}^3 \times 0.100 \text{ mol dm}^{-3}) - 1.85 \times 10^{-3} \text{ mol}$

=  $2.15 \times 10^{-3} \text{ mol}$

amount of NaOH that had reacted with PLA in stock solution =  $2.15 \times 10^{-3} \text{ mol} \times 5$

=  $1.075 \times 10^{-2} \text{ mol}$

amount of repeat unit =  $1.075 \times 10^{-2} \text{ mol}$  *First mark awarded for this*

amount of dimer = amount of repeat unit – amount of acid needed in part (g)

=  $1.075 \times 10^{-2} \text{ mol} - 9.7 \times 10^{-3} \text{ mol} = 1.05 \times 10^{-3} \text{ mol}$

molar mass of dimer =  $162 \text{ g mol}^{-1}$

mass of dimer =  $162 \text{ g mol}^{-1} \times 1.05 \times 10^{-3} \text{ mol} = 0.1701 \text{ g}$  *Second mark awarded for this*

amount of monomer = amount of repeat unit –  $2 \times$  amount of dimer

=  $1.075 \times 10^{-2} \text{ mol} - (2 \times 1.05 \times 10^{-3} \text{ mol}) = 8.65 \times 10^{-3} \text{ mol}$

molar mass of lactic acid =  $90 \text{ g mol}^{-1}$

mass of lactic acid =  $90 \text{ g mol}^{-1} \times 8.65 \times 10^{-3} \text{ mol} = 0.7785 \text{ g}$  *Third mark awarded for this*

*ECF answer: mass of dimer =  $(162 \times (1.075 \times 10^{-2} - \text{answer to part (g)})) \text{ g}$*

*ECF answer: mass of lactic acid =  $(90 \times (1.075 \times 10^{-2} - 2 \times \text{amount of dimer})) \text{ g}$*

*Answers based on using incorrect value of  $8.60 \times 10^{-3} \text{ mol}$*

*mass of dimer = 0.348 g; mass of lactic acid = 0.581 g*



Total out of 13

**13**