51st 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.

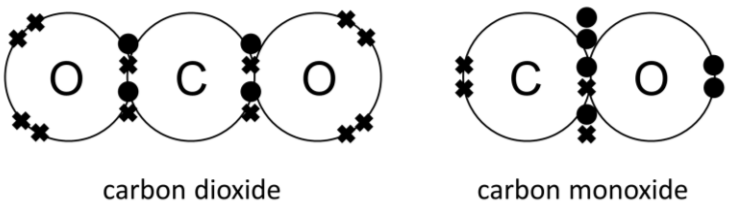
Deduct one mark from answers with missing or incorrect units for the first occurrence in **each** question and write **UNIT** next to it. Do not penalise any further missing or incorrect units in the same question.

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

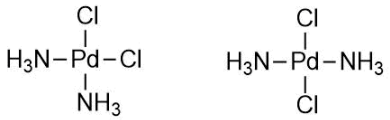
State symbols are not required for balanced equations and students should not be penalised if they are absent.

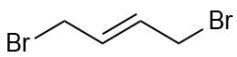
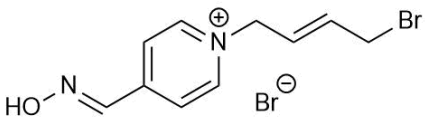
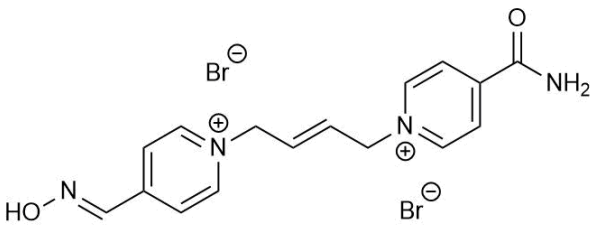
NEW FOR THIS YEAR: Do not award any half marks. One blank tick box has been included per mark available for each part. Please mark by placing a tick in each box if mark is scored.

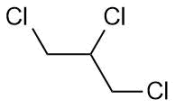
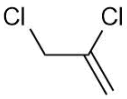
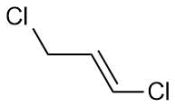
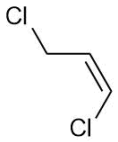
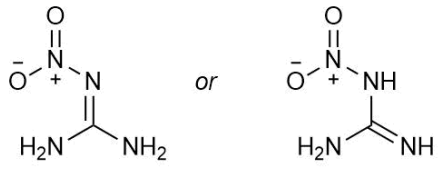
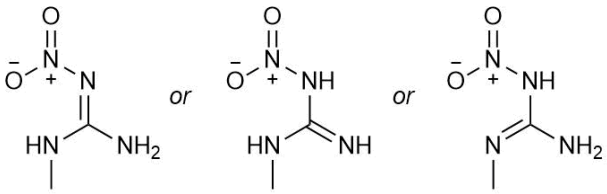
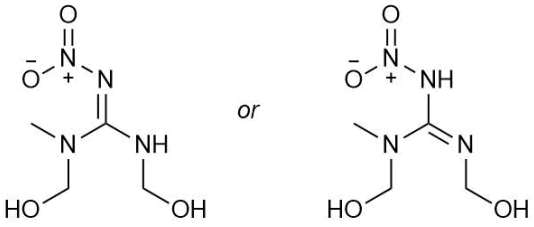
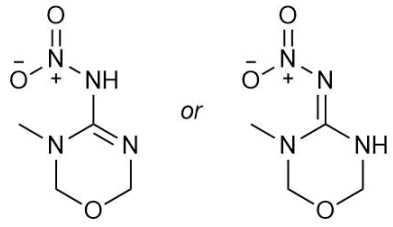
Question	1	2	3	4	5	**Total**
Marks Available	11	18	11	27	13	**80**

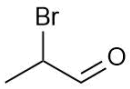
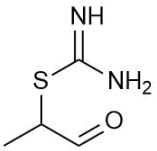
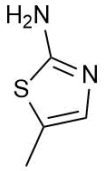
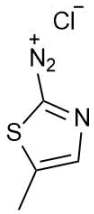
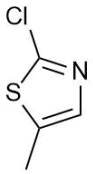
1.	This question is about carbon dioxide	Mark
(a)	(i)  carbon dioxide carbon monoxide *One mark each. Allow any combination of dots and crosses.*	☑ ☑
	(ii) CO_2 = +4 CO = +2 Difference = 2 *Allow −2.*	☑
(b)	(i) $c = k \times p(CO_2)$ 0.099 mol dm^{-3}	☑
	(ii) 1.09 g *ECF answer = (11.01 × answer to part (i)) g*	☑
	(iii) 2.45×10^5 Pa *ECF answer = (2.25×10^5 × answer to part (ii)) Pa*	☑
	(iv) ☑ high pressure and low temperature ☐ high pressure and high temperature ☐ low pressure and low temperature ☐ low pressure and high temperature *No marks if more than one box ticked.*	☑
(c)	Accept values in range 57—63 °C	☑
(d)	CO 33.3 moles H_2O 33.3 moles CO_2 26.7 moles H_2 26.7 moles *All four correct two marks. No partial credit.*	☑ ☑
(e)	enthalpy of reaction = −393.5 kJ mol^{-1} − (−110.5 + −241.1) kJ mol^{-1} = −41.9 kJ mol^{-1} *Do not award mark for positive answer.*	☑
	Total out of 11	**11**

2.	This question is about the industrial separation of precious metals	Mark
(a)	(i) Pd	☑
	(ii) Pt	☑
	(iii) Ir	☑
(b)	(i) $Au + 3HNO_3 + 4HCl \rightarrow HAuCl_4 + 3NO_2 + 3H_2O$ *Must be fully correct for mark.*	☑
	(ii) $Pt + 4HNO_3 + 6HCl \rightarrow H_2PtCl_6 + 4NO_2 + 4H_2O$ *Must be fully correct for mark.*	☑
(c)	$m/z = {}^{197}Au + 4\ {}^{35}Cl = 337$ Prob = $(0.75)^4 = 31.6\%$ $m/z = {}^{197}Au + 3\ {}^{35}Cl + 1\ {}^{37}Cl = 339$ Prob = $(0.75)^3 \times 0.25 \times 4 = 42.2\%$ $m/z = {}^{197}Au + 2\ {}^{35}Cl + 2\ {}^{37}Cl = 341$ Prob = $(0.75)^2 \times (0.25)^2 \times 6 = 21.1\%$ $m/z = {}^{197}Au + 1\ {}^{35}Cl + 3\ {}^{37}Cl = 343$ Prob = $0.75 \times (0.25)^3 \times 4 = 4.7\%$ $m/z = {}^{197}Au + 4\ {}^{37}Cl = 345$ Prob = $(0.25)^4 = 0.4\%$ m/z: 337 | 339 | 341 | 343 | 345 relative intensity: 31.6% | 42.2% | 21.1% | 4.7% | 0.4% (as fractions): $^{81}/_{256}$ | $^{108}/_{256}$ | $^{54}/_{256}$ | $^{12}/_{256}$ | $^{1}/_{256}$ *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.* m/z: 337 | 339 | 341 | 343 | 345 relative intensity: 66.9% | 22.3% | 7.4% | 2.5% | 0.8% (as fractions): $^{81}/_{120}$ | $^{27}/_{120}$ | $^{9}/_{120}$ | $^{3}/_{120}$ | $^{1}/_{120}$	☑ ☑ ☑
(d)	$3FeCl_2 + HAuCl_4 \rightarrow Au + 3FeCl_3 + HCl$ (allow $3Fe^{2+} + Au^{3+} \rightarrow 3Fe^{3+} + Au$) *Must be fully correct for mark.*	☑
(e)	$[PtCl_6][NH_4]_2$ *Allow if written as ions with separate charges. Allow multiples of this formula.*	☑

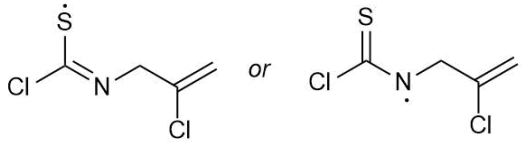
(f)	 *One mark for each correct structure. If three structures drawn maximum mark is one if there is one correct. Four or more structures drawn is no marks.*	☑ ☑
(g)	$H_2PdCl_4 + 4NH_4OH \rightarrow Pd(NH_3)_2Cl_2 + 4H_2O + 2NH_4Cl$ *or* $H_2PdCl_4 + 2NH_4OH \rightarrow Pd(NH_3)_2Cl_2 + 2H_2O + 2HCl$ *or suitable ionic form, eg* $H_2PdCl_4 + 4NH_4OH \rightarrow Pd(NH_3)_2Cl_2 + 4H_2O + 2NH_4^+ 2Cl^-$ *Must be fully correct for mark.*	☑
(h)	(i) $(2N \times I) + 1 = (2 \times 2 \times 1) + 1$ = 5 lines	☑
	(ii) $(2N \times I) + 1 = (2 \times 4 \times 1) + 1$ = 9 lines	☑
	(iii) $(2N \times I) + 1 = (2 \times 4 \times ½) + 1$ = 5 lines	☑
(i)	(i) 1:2:3:2:1	☑
	(ii) 1:4:10:16:19:16:10:4:1	☑
	Total out of 18	**18**

3.	This question is about treating nerve agent poisoning	Mark
(a)	(i) 172.612 g mol^{-1}	☑
	(ii) dosage = 24 hours × 80.0 kg × 3.00 × 10^{-3} mol $hour^{-1}$ kg^{-1} = 5.76 mol mass of PAM = 5.76 mol × 172.612 g mol^{-1} = 994 g *ECF answer = (answer to part (a)(i) × 5.76) g*	☑
(b)	(i) First order	☑
	(ii) Zeroth order	☑
(c)	$K_c = \frac{[\text{AChE-I-PAM}]}{[\text{AChE-I}]\,[\text{PAM}]}$ *Must be fully correct for mark.*	☑
(d)	(i) intercept = 1.58 k_2 = 1/intercept = 0.633 s^{-1}	☑
	(ii) intercept = 1.58; gradient = 6.75 × 10^{-4} K = intercept/gradient = 1.58 / 6.75 × 10^{-4} = 2,340 mol^{-1} dm^3 *No ECF from part (d)(i).*	☑
(e)	 *No mark if drawn as cis isomer.*	☑
(f)	9	☑
(g)	Intermediate **X**  Reactivator **Y**  *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).*	☑ ☑
	Total out of 11	**11**

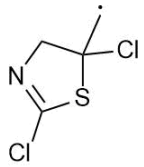
4.	This question is about bees and Brexit	Mark
(a)	$C_8H_{10}ClN_5O_3S$	☑
(b)	**A**  **B**  **B'**  **B''**  *One mark for each correct structure. If **B'** and **B''** are drawn the wrong way around then one mark out of two is scored for **B'** and **B''** combined. No ECF can be applied.*	☑ ☑ ☑ ☑
(c)	$S=C=N^-$ *The correct shape is not required for the mark.*	☑
(d)	$O=N^+=O$ Linear *The shape must be stated as linear or clearly indicated as linear from the diagram for the mark.*	☑
(e)	**E**  **F**  **G**  **H**  *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.*	☑ ☑ ☑ ☑ ☑ ☑

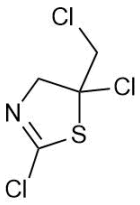
(f)	**I**  **J**  *One mark for **I**, two marks for **J**. No partial credit is given for **J** – structure must be fully correct for the two marks. ECF can be awarded for **J** based on **I** only if **J** is consistent with molecular formula.*	☑ ☑ ☑
(g)	**K**  *No partial credit is given for **K** – structure must be fully correct for the two marks. ECF can be awarded for **K** based on **J** only if **K** is consistent with molecular formula.*	☑ ☑
(h)	**L**  **M**  *Two marks for **L**, one mark for **M**. No partial credit is given for **L** – structure must be fully correct for the two marks. ECF can be awarded for **L** based on **K**. No ECF for **M** as **M** can be worked to backwards from product.*	☑ ☑ ☑

(i) **Intermediate V·**



Intermediate W· **Y**





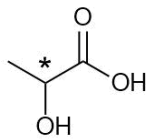
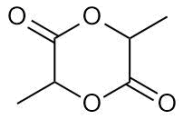
*One mark for **V·**, two marks for **W·** and one mark for **Y**. Position of radical must be clearly indicated with a dot for **V·** and **W·**. No ECF can be awarded as there is sufficient new information about each species.*

(j)

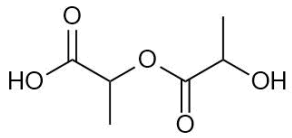
Reagent X	**Chain-carrying radical Z·**
Cl_2	Cl·

One mark each.

Total out of 27 **27**

5.	This question is about a biodegradable plastic	Mark
(a)	 *One mark for structure. One mark for correct marking of chiral centre with asterisk.*	☑ ☑
(b)	☐ addition ☑ condensation ☐ neutralisation ☐ oxidation ☐ reduction *No marks if more than one box ticked.*	☑
(c)	Compound **A**  *No stereochemistry required.*	☑
(d)	amount of KOH = 0.0400 mol dm^{-3} × 0.00681 dm^3 = 2.72 × 10^{-4} mol amount of -COOH residues = 2.72 × 10^{-4} mol = amount of chains average molar mass of chain = total mass / amount of chains average molar mass of chain = 0.1619 g / 2.72 × 10^{-4} mol = 595 g mol^{-1} *Correct answer required for mark. No credit for working only.*	☑
(e)	molar mass of polymer = molar mass of n repeat units + molar mass of H_2O number of repeat units = (595 – 18) g mol^{-1} / 72 g mol^{-1} 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 306 g mol^{-1} = 4* *ECF answer = (answer to part (d) – 18) / 72*	☑ ☑
(f)	one mol of repeat unit reacts with one mole of NaOH mass = 286,000 tonnes × 40 g mol^{-1} / 72 g mol^{-1} = 159,000 tonnes *Correct answer required for mark. No credit for working only.*	☑
(g)	amount of acid = 0.100 mol dm^{-3} × 0.0194 dm^{-3} × 5 = 9.70 × 10^{-3} mol *Correct answer required for mark. No credit for working only.*	☑

(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 mol dm^{-3} × 0.01850 dm^3 = 1.85 × 10^{-3} mol

amount of NaOH in aliquot that had reacted with PLA

= (0.04000 dm^3 × 0.100 mol dm^{-3}) − 1.85 × 10^{-3} mol

= 2.15 × 10^{-3} mol

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

= 1.075 × 10^{-2} mol

amount of repeat unit = 1.075 × 10^{-2} mol *First mark awarded for this*

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

= 1.075 × 10^{-2} mol − 9.7 × 10^{-3} mol = 1.05 × 10^{-3} mol

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

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

amount of monomer = amount of repeat unit – 2 × amount of dimer

= 1.075 × 10^{-2} mol – (2 × 1.05 × 10^{-3} mol) = 8.65 × 10^{-3} mol

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

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

ECF answer: mass of dimer = (162 × (1.075 × 10^{-2} – answer to part (g))) g

ECF answer: mass of lactic acid = (90 × (1.075 × 10^{-2} – 2 × amount of dimer)) g

Answers based on using incorrect value of 8.60 × 10^{-3} mol

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

Total out of 13 **13**