

Examiners' Report

June 2023

International Advanced Level Chemistry WCH14 01

Introduction

The paper was accessible to most candidates and provided the full range of marks. Some candidates scored very high marks and were well prepared for the examination, showing excellent learning and teaching has taken place. Many candidates had a sound knowledge of the specification and could demonstrate this in their explanations and descriptions. However, a small minority of candidates found the questions challenging and needed to express their understanding of Chemistry more clearly. The calculations were generally well attempted with the main errors being in the substitution of data correctly into the equations. There were no reports of candidates running out of time and the majority of candidates provided responses to the last question, indicating that the paper was not unduly long. The mean mark for the paper was 51.

Section A

The mean mark for the multiple choice questions was 12.

The questions that candidates found easiest were Q01 (K_c expression of a homogeneous equilibrium), Q03 (K_p units), Q05 (racemic isomers) and Q13(a) (choosing appropriate indicators). Over 70% of candidates achieved these marks.

Q07 was the question that candidates found the most difficult (rate equation for a multistep reaction) with only 30% of candidates gaining this mark. The other multiple choice questions that were more challenging were Q09(a) (number of curly arrows in a mechanism), Q12 (hydrolysis of a polyester with hydroxide) and Q04(a) (axes on an HPLC chromatogram).

Question 17 (a)

Q17(a) was a simple selection of the correct value from the Born-Haber cycle. 86% of candidates achieved this mark though almost all of the values on the cycle were given as answers, and a small minority of candidates tried to do a calculation. Units were not required and so were not penalised.

Question 17 (b)

Two marks were available for this question, and over three quarters of candidates gained both. Common errors included omitting the negative sign, forgetting that two chloride ions were involved (despite this being shown in the cycle), incorrectly transcribed numbers and arithmetical errors. Most candidates included units although these were not required. Incorrect units negated M2.

This is an example of a common incorrect answer.

(b) Calculate the enthalpy change of formation for calcium chloride.

$$\begin{aligned} -\Delta H_f [\text{CaCl}_2] + 178 + 590 + 1145 + 2 \times 122 & \quad (2) \\ + 2 \times -349 - 2558 & = 0 \\ -\Delta H_f [\text{CaCl}_2] - 1099 & = 0 \\ \Delta H_f [\text{CaCl}_2] & = 1099 \text{ kJ mol}^{-1} \text{ (Ans)} \end{aligned}$$



ResultsPlus
Examiner Comments

The candidate gains the first mark for a correct expression but no credit for their answer.



ResultsPlus
Examiner Tip

Remember that the enthalpy of formation for stable substances will be negative (as shown on the cycle).

A fully correct answer.

(b) Calculate the enthalpy change of formation for calcium chloride.

$$178 + 590 + 1145 + (2 \times 122) + (2 \times -349) - 2258 \quad (2)$$
$$\Delta H_f = -799 \text{ kJ mol}^{-1}$$



ResultsPlus
Examiner Comments

The candidate has shown their calculation and the correct answer to 3 significant figures with the correct sign.



ResultsPlus
Examiner Tip

It is good practice to always show your workings and to check that your units match the information in the question.

Question 17 (c)

Four marks were available for this question and the mark scheme is similar to that used in previous series. Candidates made a good attempt at their response but the mean mark was 2, with many candidates not attempting M1 (that CaCl_2 is mainly ionic) and some losing M3 for confusion over the iodide ions – as shown in the example below. Some candidates lost M3 for references to molecules, or confusion over which ion was bigger or had the greatest charge density. There were also a small minority of candidates who confused polarisability with the ions ability to polarise, stating incorrectly that the iodide could polarise the calcium ion more than the chloride.

This response highlights some common errors for this question.

(c) Some energy data are shown.

Compound	Theoretical lattice energy / kJ mol^{-1}	Experimental lattice energy / kJ mol^{-1}
CaCl_2	-2223	-2258
CaI_2	-1905	-2074

Explain why the difference between the theoretical and the experimental values for lattice energy is very much greater for calcium iodide than for calcium chloride.

(4)

Calcium ~~the~~ Iodide has some degree of covalency as the atomic radius of iodide ions is much greater than it is for chloride ions. Hence the iodide ion is easily and strongly polarised by the Ca^{2+} ions and its electron cloud is easily ~~pulled to~~ easily distorted making the bond require more lattice energy than theoretical lattice energy.



M2 is awarded for the degree of covalency in calcium iodide and M4 for the distortion of the iodide ion. Calcium chloride's bonding is not mentioned so no M1 and M3 is not gained for "atomic radius of iodide ions".



Check your use of atomic radius and ionic radius when answering bonding questions.

An example of a fully correct response.

(c) Some energy data are shown.

Compound	Theoretical lattice energy / kJ mol^{-1}	Experimental lattice energy / kJ mol^{-1}
CaCl_2	-2223	-2258
CaI_2	-1905	-2074

Explain why the difference between the theoretical and the experimental values for lattice energy is very much greater for calcium iodide than for calcium chloride.

(4)

I^- ions are larger than Cl^- ions so they are polarised by the Ca^{2+} ions more easily. So there is greater covalent character in CaI_2 compared with CaCl_2 which is almost completely ionic. So there is greater difference between the theoretical and experimental lattice energies for CaI_2 than CaCl_2 .



ResultsPlus
Examiner Comments

Marks are awarded in the order M3, M4, M2 and M1. The answer is succinct and clear. The final sentence ensures the question has been fully answered by using the data.



ResultsPlus
Examiner Tip

The answer lines should allow you to completely answer the question even if you have large handwriting. If you find you are writing more then you may have misunderstood the question.

Question 17 (d)

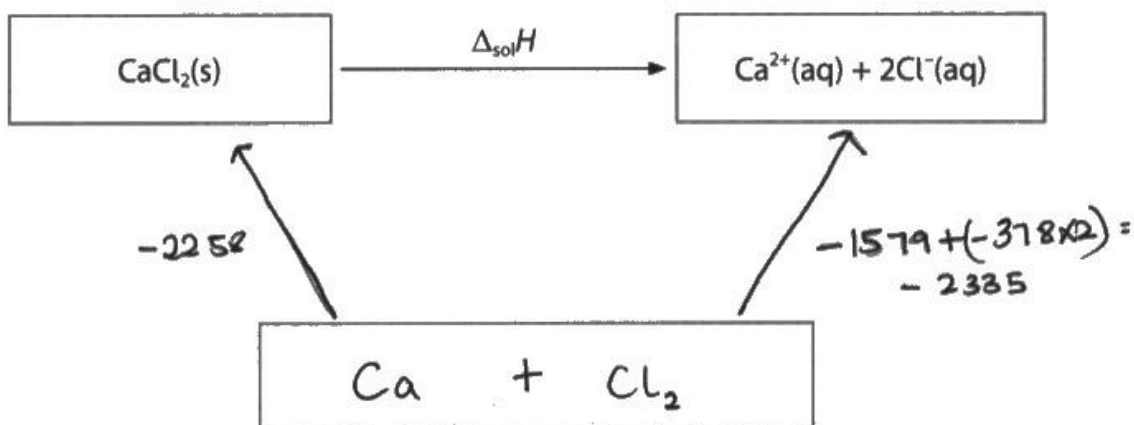
The completion on the cycle in this question was supposed to make the topic more accessible than drawing the full cycle. Over 40% of candidates gained all 4 marks with a few common errors highlighted below.

This candidate only gained 1 mark for the cycle. Q17(d)(ii) is fully correct for 2 marks.

(d) Calcium chloride is soluble in water.

(i) Complete the energy cycle including labelled arrows.

(2)



(ii) Calculate the enthalpy change of solution, $\Delta_{\text{sol}}H$, for calcium chloride using the data given and the completed energy cycle in (d)(i).

(2)

Data	Energy change / kJ mol^{-1}
LE ($\text{CaCl}_2(\text{s})$)	-2258
$\Delta_{\text{hyd}}H (\text{Ca}^{2+}(\text{g}))$	-1579
$\Delta_{\text{hyd}}H (\text{Cl}^{-}(\text{g}))$	-378

$$\Delta_{\text{sol}} H = +2258 - 2335 = -77 \text{ kJ mol}^{-1}$$



Labelling the arrows with the data from the table was allowed and the mark for the arrows was awarded. Some candidates either put heads on both ends of the arrows or had the arrows pointing in the wrong direction so lost M1.

Unfortunately, the candidate has not used the gaseous ions in the box so cannot gain M2. Omission of the state symbols was a common error, even when the correct ions were included.



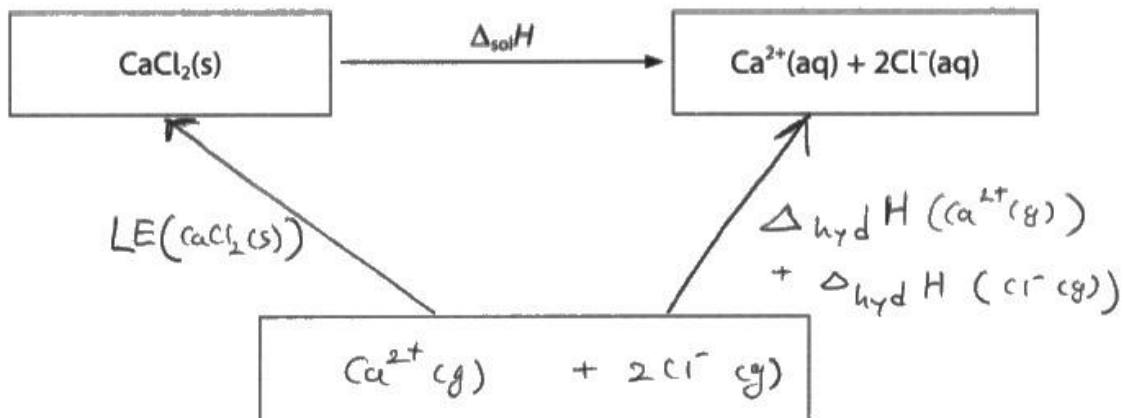
Remember state symbols are important in all energy cycles.

Full marks are awarded for the cycle but the candidate only achieves 1 mark for Q17(d)(ii).

(d) Calcium chloride is soluble in water.

(i) Complete the energy cycle including labelled arrows.

(2)



(ii) Calculate the enthalpy change of solution, $\Delta_{\text{sol}}H$, for calcium chloride using the data given and the completed energy cycle in (d)(i).

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$\Delta_{\text{hyd}}H (\text{Ca}^{2+}(\text{g}))$	-1579
$\Delta_{\text{hyd}}H (\text{Cl}^{-}(\text{g}))$	-378

$$\Delta_{\text{sol}}H = -LE(\text{CaCl}_2(\text{s})) + \Delta_{\text{hyd}}H(\text{Ca}^{2+}(\text{g})) + \Delta_{\text{hyd}}H(\text{Cl}^{-}(\text{g}))$$

$$= -(-2258) + (-1579) + (-378)$$

$$= +301 \text{ kJ mol}^{-1} \text{ (Ans.)}$$



The labelled arrows are pointing in the correct direction and are appropriately labelled for M1. The ions are correct and have gaseous state symbols for M2.

In Q17(d)(ii) the candidate has not doubled the value for the hydration of the chloride ion so does not gain M1. They have correctly calculated the answer to their expression so gain M2 as a transferred error (TE).



Ensure your calculations match the stoichiometry of your balanced equations.

Question 18 (a)(i-ii)

Q18(a)(i) proved far more challenging to candidates than anticipated, with many drawing a straight line of best fit rather than the anticipated curve. Only 44% of candidates gained both marks here and there was no transferred error from one part to another. There were quite a number of candidates who drew a straight line and then commented that the points did not fit on their best fit line.

No credit for the graph here but the explanation gains a mark.

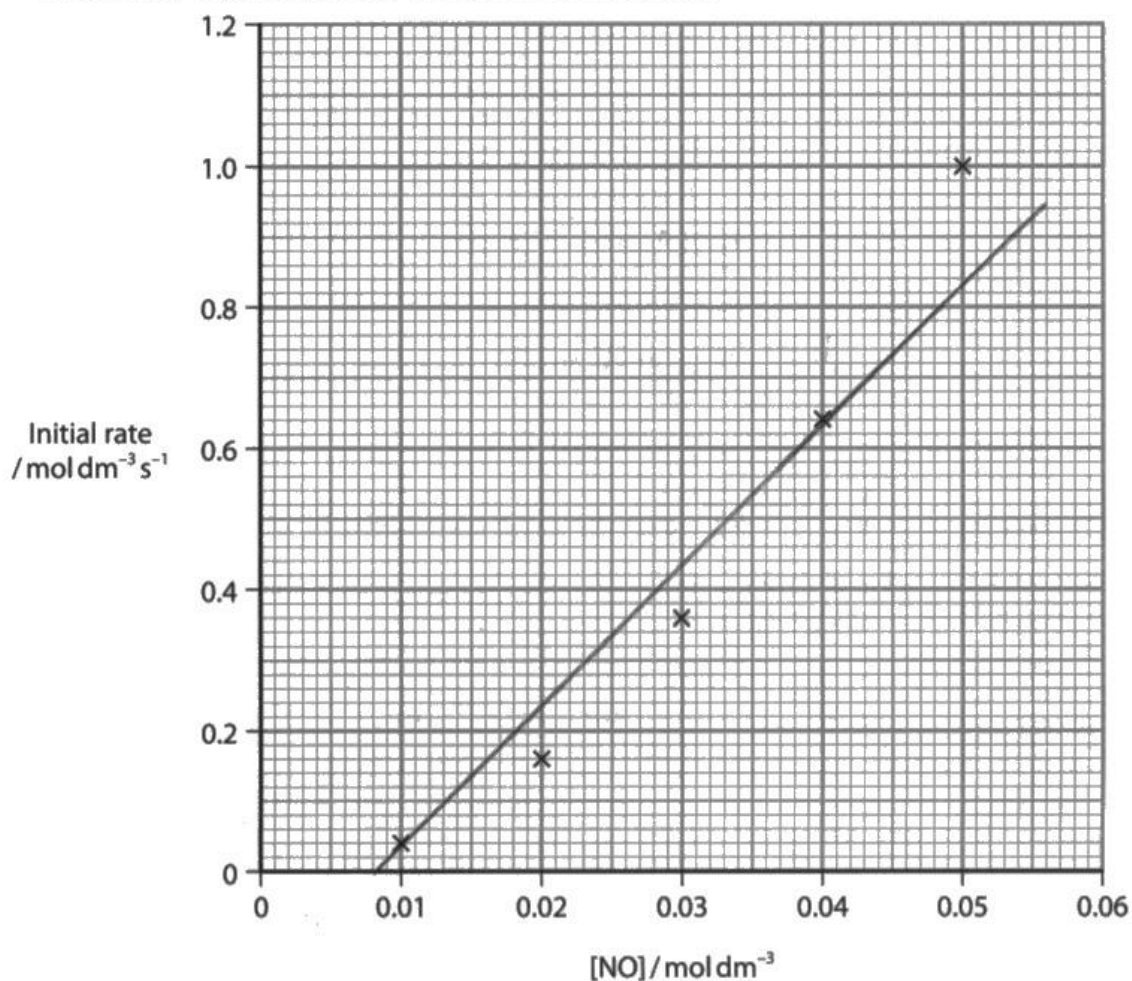
18 This question is about the reaction between nitrogen monoxide and oxygen.



(a) The results of a series of kinetics experiments are shown.

Experiment	Initial [NO] / mol dm ⁻³	Initial [O ₂] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	0.010	0.050	0.040
2	0.020	0.050	0.160
3	0.030	0.050	0.360
4	0.040	0.050	0.641
5	0.050	0.050	1.001
6	0.020	0.025	0.080

The data for experiments 1–5 were plotted on a graph.



(i) Draw a best-fit line on the graph.

- (ii) State how the graph shows that the reaction is **not** first order with respect to nitrogen monoxide.

(1)

Because the graph shows an exponential growth rather than a directly proportional growth



A straight line cannot score the mark for Q18(a)(i) as the mark scheme requires a smooth curve. Any extrapolation beyond the points was ignored.

The reference to direct proportionality allows the mark to be scored for M2, though references to exponential graphs were ignored.



Ensure your lines of best fit pass through as many points on the graph as possible.

This response did not score.

- (ii) State how the graph shows that the reaction is **not** first order with respect to nitrogen monoxide.

(1)

The line is not passing through the origin.



Both first and second order rate graphs should pass through the origin so this response was not accepted.

Both marks awarded here.

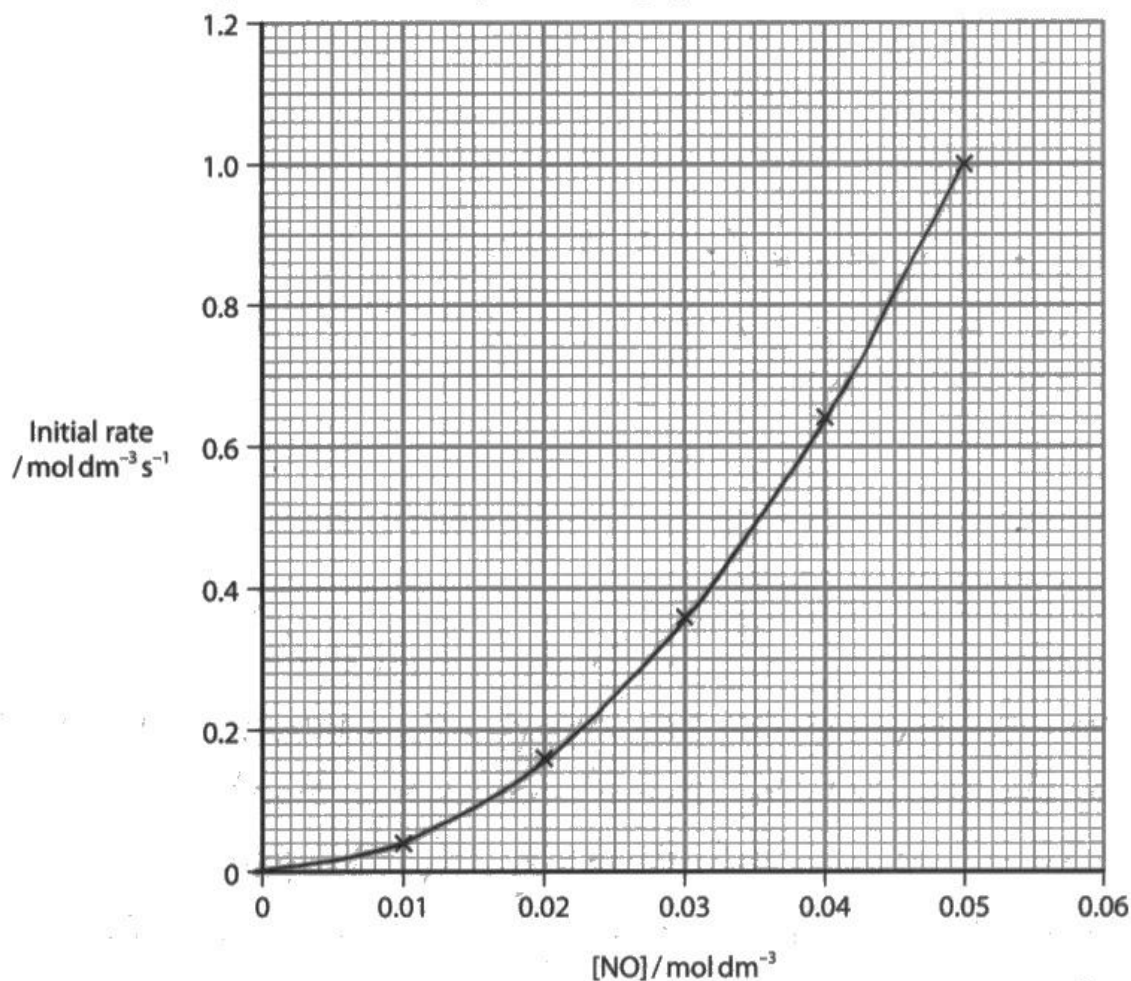
18 This question is about the reaction between nitrogen monoxide and oxygen.



(a) The results of a series of kinetics experiments are shown.

Experiment	Initial [NO] / mol dm ⁻³	Initial [O ₂] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
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3	0.030	0.050	0.360
4	0.040	0.050	0.640
5	0.050	0.050	1.000
6	0.020	0.025	0.080

The data for experiments 1–5 were plotted on a graph.



(i) Draw a best-fit line on the graph.

- (ii) State how the graph shows that the reaction is **not** first order with respect to nitrogen monoxide.

(1)

Graph is not a straight line so rate is not proportional to concentration of NO



ResultsPlus
Examiner Comments

This curve passes correctly through the points so scores the mark for Q18(a)(i). The answer for Q18(a)(ii) also gains the mark.

Question 18 (a)(iii-v)

Candidates were required to use the data to deduce the orders of reaction for the experiment. However, errors made at this stage could still gain credit if used correctly for the later parts and the values and units matched the orders stated. This allowed the mean mark to be 4 of the 5 marks available for this question.

- (iii) Deduce the orders of reaction with respect to NO and O₂, using the data from experiments 1–6.

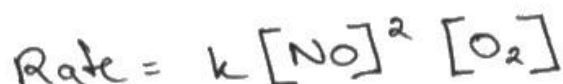
(2)

Order with respect to NO = 2

Order with respect to O₂ = 1

- (iv) Write the rate equation for the reaction, using your answer to (a)(iii).

(1)



- (v) Calculate the rate constant for this reaction using the data from experiment 1 and your rate equation. Include units in your answer.

(2)

$$0.04 = k (0.010)^2 (0.050)$$

mol dm⁻³

$$k = 8000 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$$



ResultsPlus
Examiner Comments

This is an example of a fully correct answer.

An example of a response where transferred error has been applied.

- (iii) Deduce the orders of reaction with respect to NO and O₂, using the data from experiments 1–6.

(2)

Order with respect to NO = first

Order with respect to O₂ = first

- (iv) Write the rate equation for the reaction, using your answer to (a)(iii).

(1)



- (v) Calculate the rate constant for this reaction using the data from experiment 1 and your rate equation. Include units in your answer.

(2)

$$\begin{aligned} 0.04 &= k (0.01 \times 0.05) \\ \therefore k &= \frac{0.04}{0.01 \times 0.05} \\ &= 80 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \end{aligned}$$

Handwritten units for the final answer: $\frac{\text{mol dm}^{-3} \text{ s}^{-1}}{\text{mol dm}^{-3} \text{ mol dm}^{-3}}$



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Examiner Comments

Though the candidate has the correct order for oxygen, their order for nitrogen oxide is incorrect. The candidate has then used these orders to produce a rate equation and gains the mark for Q18(a)(iv). In Q18(a)(v) the candidate has substituted in the values from experiment 1 and has a value for k that matches their orders for Q18(a)(iii) and rate equation given for Q18(a)(iv), along with appropriate units.



ResultsPlus
Examiner Tip

Feel free to use the answer spaces to work out your answers – this candidate has successfully worked out their units.

Another example of transferred error from incorrect orders.

- (iii) Deduce the orders of reaction with respect to NO and O₂, using the data from experiments 1–6.

(2)

Order with respect to NO = second order

Order with respect to O₂ = zero order

- (iv) Write the rate equation for the reaction, using your answer to (a)(iii).

(1)

$$\text{rate} = k[\text{NO}]^2$$

- (v) Calculate the rate constant for this reaction using the data from experiment 1 and your rate equation. Include units in your answer.

(2)

$$k = \frac{\text{rate}}{[\text{NO}]^2} = \frac{0.04}{(0.01)^2} = 400$$



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Examiner Comments

In this example the candidate has the correct order for nitrogen monoxide but not for oxygen. The rate equation matches these orders so the mark for Q18(a)(iv) is awarded. The numbers are substituted in correctly to calculate the value for k but no units are given so the second mark cannot be awarded.



ResultsPlus
Examiner Tip

Underline the important points in the question. This candidate has missed that the units are required.

Question 18 (b)

Two marks were available for this question but the mean mark awarded was less than one. Common errors were stating that the value is greater than 1, rather than commenting on the magnitude of the number and many candidates discussed the moving of the equilibrium to the right (some in relation to the moles of gas on either side) rather than the final position.

This is an example of a fully correct answer.

(b) The equilibrium constant, K_p , for the reaction at 298 K is $1.55 \times 10^6 \text{ atm}^{-1/2}$.

State what this value of the equilibrium constant indicates about the position of the equilibrium. Justify your answer.

$$K_p = \frac{p(\text{NO}) \times p(\text{O}_2)^{1/2}}{p(\text{NO}_2)} \quad (2)$$

Value of K_p is very large, so proportion of products is much greater than that of reactants as numerator of K_p expression is large. Hence position of equilibrium lies well to the right.



ResultsPlus
Examiner Comments

The candidate has used their understanding to comment on the size of the K_p value and explained what the number means mathematically (this was not necessary to gain M1, nor was the K_p expression above their answer).

M2 is awarded for the final sentence where the candidate comments the position "lies well to the right".



ResultsPlus
Examiner Tip

If you feel an expression will help you explain a concept then feel free to write it out, even if it is not asked for in your answer.

No credit for this response.

(b) The equilibrium constant, K_p , for the reaction at 298 K is $1.55 \times 10^6 \text{ atm}^{-\frac{1}{2}}$.

State what this value of the equilibrium constant indicates about the position of the equilibrium. Justify your answer.

(2)

The K_p value states that the reaction is in the product side as the K_p value is greater than 1.



ResultsPlus
Examiner Comments

Stating the K_p expression is bigger than 1 was not sufficient to gain M1.

The reaction being "in the product side" is not a suitable answer for M2, as a comment on the position of the equilibrium is required.



ResultsPlus
Examiner Tip

Include as much detail in your answers as possible – use the data.

A response that gains one of the two marks.

The K_p is much greater which shows more products are formed thereby the position of equilibrium is on the right.



ResultsPlus
Examiner Comments

This response lacks detail so is only awarded one mark. M2 is awarded for "the position of equilibrium is on the right" but " K_p is much greater" is insufficient for M1. There is no comparator for the K_p in this question, just a general statement on its side is required.

Question 19 (a)

This 6 mark extended response question was well answered with the full range of marks seen. It was linked to a prompt question and the average mark out of the 9 available was 3. Though Q19(a)(i) asked for skeletal formulae, credit was given for any correct structure with the number of C^{13} peaks. Many candidates drew displayed or mixed semi-structural formulae. Where candidates did not read the instructions to Q19(a)(i) carefully and drew branched isomers, or longer chain molecules, they usually struggled to gain marks in Q19(a)(ii) which may be the reason for the low average mark.

Candidates made good use of the spectrum, often labelling the peaks to assist in their answer. As the specification does not specifically give a name for a peak split into 5, all names that related to 5 were accepted along with multiplet. Candidates were most frequently awarded IP2 and IP3 with IP4 being given the least frequently. The symmetrical nature sometimes confused candidates when it came to peak areas, with 3:2:1 being a common answer.

This response highlights some common errors.

19 This question is about some bromoalkanes.

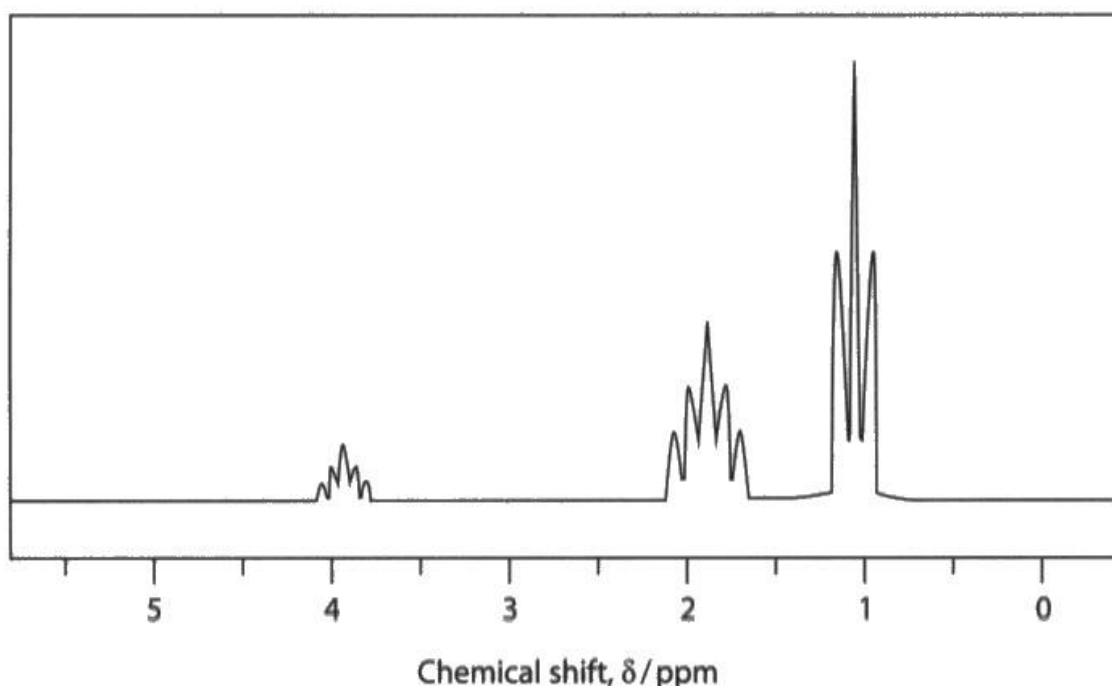
(a) There are three straight-chain structural isomers with the molecular formula $C_5H_{11}Br$.

(i) Complete the table for these three isomers.

(3)

Isomer	Skeletal formula	Number of peaks in ^{13}C NMR spectrum
1		2
2		3
3		3

*(ii) The high resolution proton NMR spectrum of one of these isomers is shown.



Deduce which isomer is present in the sample, explaining the splitting patterns and chemical shifts seen in the spectrum.

Include the name of the isomer and the relative peak areas.

Use your Data Booklet.

(6)

~~The~~ There are three peaks in total which means there are three different chemical environments of ~~proton~~ hydrogen. The peak at $\delta = 1.0$ ppm is for CH_3 group which is bonded to a CH_2 group so the peak splits into a triplet as the group which it is bonded to has two hydrogen atoms. The peak at $\delta = 1.8$ ppm is for CH_2 group as it is bonded to a methyl group so the peak splits into a quartet as the methyl group has three hydrogen atoms. The peak at $\delta = 3.9$ ppm is for CH_2Br group as it is bonded to a methyl group which has three hydrogen atoms so the peak splits into a quartet. This peak has a higher chemical shift value as it is bonded to electronegative bromine atom. So the full name of the isomer is 2-bromopentane.



In Q19(a)(i), the candidate has drawn displayed structures and all are correct. However, only the number of peaks ^{13}C for Isomer 2 is correct so the candidate scores 1 mark here (if the peak number was also incorrect for Isomer 2, they would still have scored 1 mark for 3 correct structures).

In Q19(a)(ii) the candidate has scored IP1 for the three hydrogen environments. IP3 is scored for the triplet splitting by 2 neighbouring but as the candidate goes on to describe the "quartet" being split by 3 hydrogen atoms IP4 cannot be awarded. IP2 is awarded for the identification of the CHBr group at a chemical shift of 3.9. There is no mention of peak areas so no IP5 and the isomer is incorrect so no IP6. 3 IPs scores 2 marks plus 1 reasoning mark = 3 marks for Q19(a)(ii).



Label spectra and graphs to help you structure your answers.

An example of a response that gained all 9 marks.

19 This question is about some bromoalkanes.

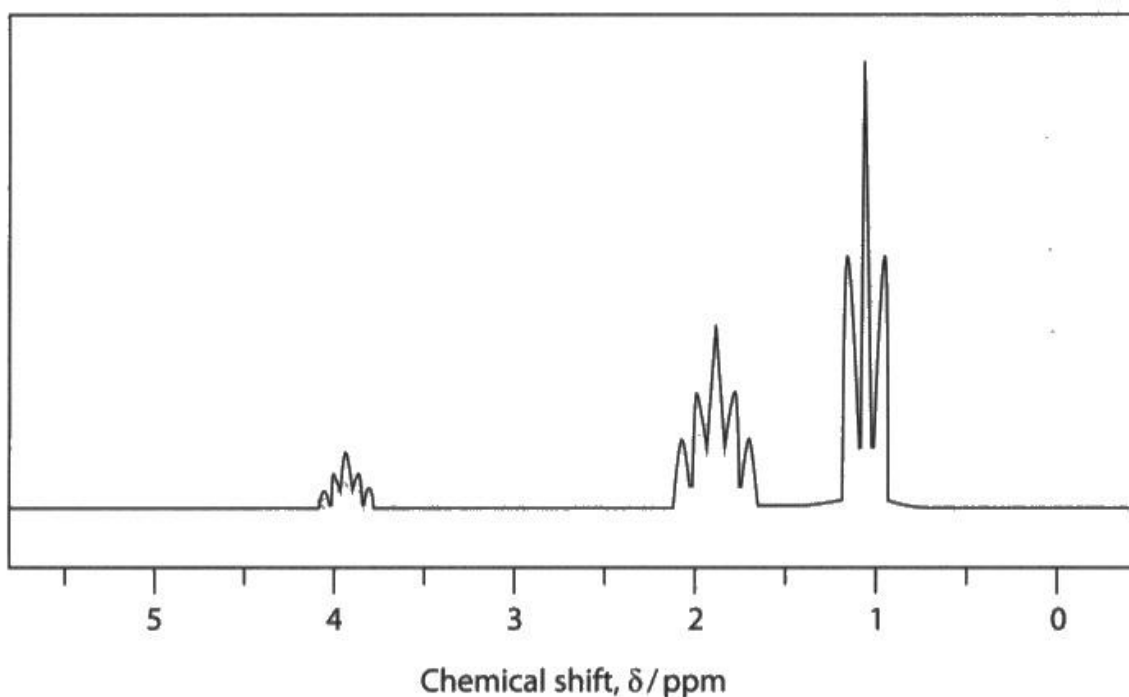
(a) There are three straight-chain structural isomers with the molecular formula $C_5H_{11}Br$.

(i) Complete the table for these three isomers.

(3)

Isomer	Skeletal formula	Number of peaks in ^{13}C NMR spectrum
1		5
2		5
3		3

*(ii) The high resolution proton NMR spectrum of one of these isomers is shown.



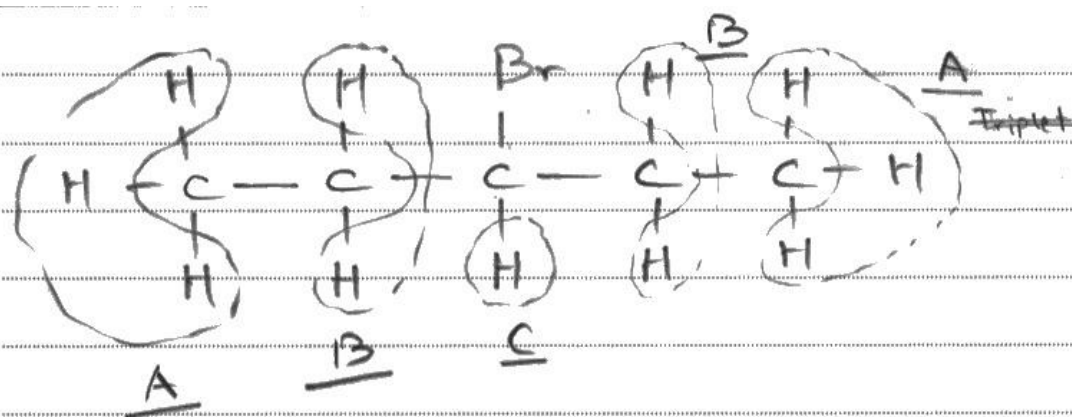
Deduce which isomer is present in the sample, explaining the splitting patterns and chemical shifts seen in the spectrum.

Include the name of the isomer and the relative peak areas.

Use your Data Booklet.

(6)

There are 3 set of peaks so there are 3 different hydrogen environments. Peak at 1 ppm is due to $\text{H}-\text{C}-\text{C}$. Peak is a triplet so there must be 2 H atoms on adjacent C atom according to $(n+1)$ rule. Peak at 1.8 ppm is due to $\text{H}-\text{C}-\text{C}$. Peak is a pentet so there must be 4 H atoms on adjacent C atom. Peak at 4.0 ppm is due to $\text{H}-\text{C}-\text{halogen}$, where halogen is Br. Peak is a pentet so there must be 4 atoms on adjacent C. Isomer is therefore 3-bromopentane.



There are a total of 6 H atoms in A, 4 in B and 1 in C. A is triplet, B is pentet and C is Pentet. ~~Re~~ Relative peak areas:

A : B : C
6 : 4 : 1



ResultsPlus
Examiner Comments

All 3 skeletal structures are correct, along with the number of carbon environments so all three marks are awarded.

IP1 is awarded for the first sentence. The candidate then explains the splitting pattern of the triplet using the $n+1$ rule for IP3. IP4 can be awarded for the correct chemical shift values for the peaks at 1ppm and 1.8ppm (along with the correct splitting patterns). IP3 is awarded for the identification of the H-C-halogen at 4.0 ppm. IP6 is awarded for the correct isomer name.

Over the page the candidate has drawn the displayed structure and highlighted the three hydrogen environments, this has also allowed them to calculate the peak areas for IP5.

6 IPs scores 4 marks plus 2 reasoning marks = 6 marks for Q19(a)(ii).



ResultsPlus
Examiner Tip

Drawing and labelling diagrams is a valid form of scientific communication in extended response questions.

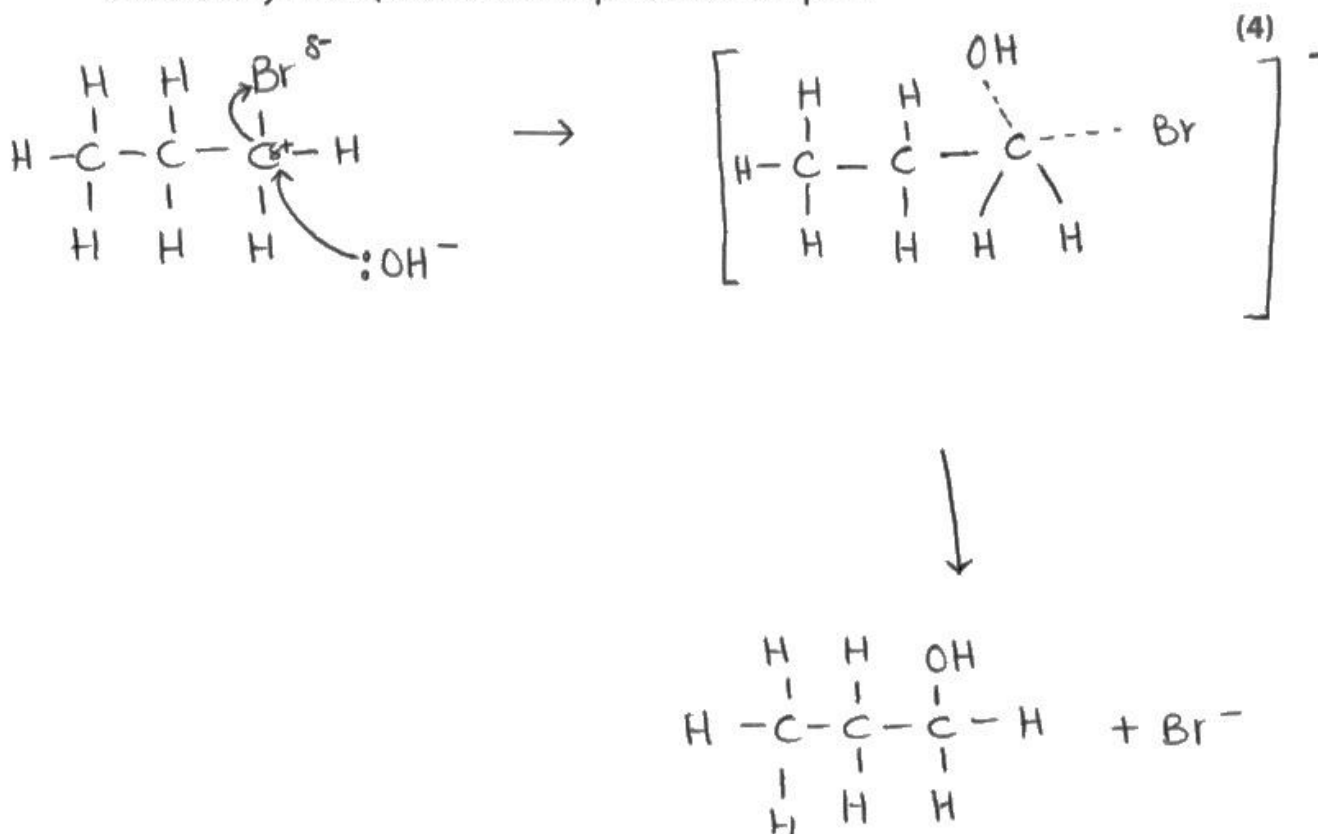
Question 19 (b)

The average mark for this mechanism was 2, with the transition state points being the least frequently awarded. Any one of the 7 points being omitted or incorrect led to three marks being scored and all possible errors and omissions were seen. Correct mechanisms using skeletal structures were accepted.

An example of a fully correct mechanism.

(b) Draw the S_N2 mechanism for the reaction of 1-bromopropane with hydroxide ions in aqueous solution.

Include curly arrows, and relevant dipoles and lone pairs.



ResultsPlus
Examiner Comments

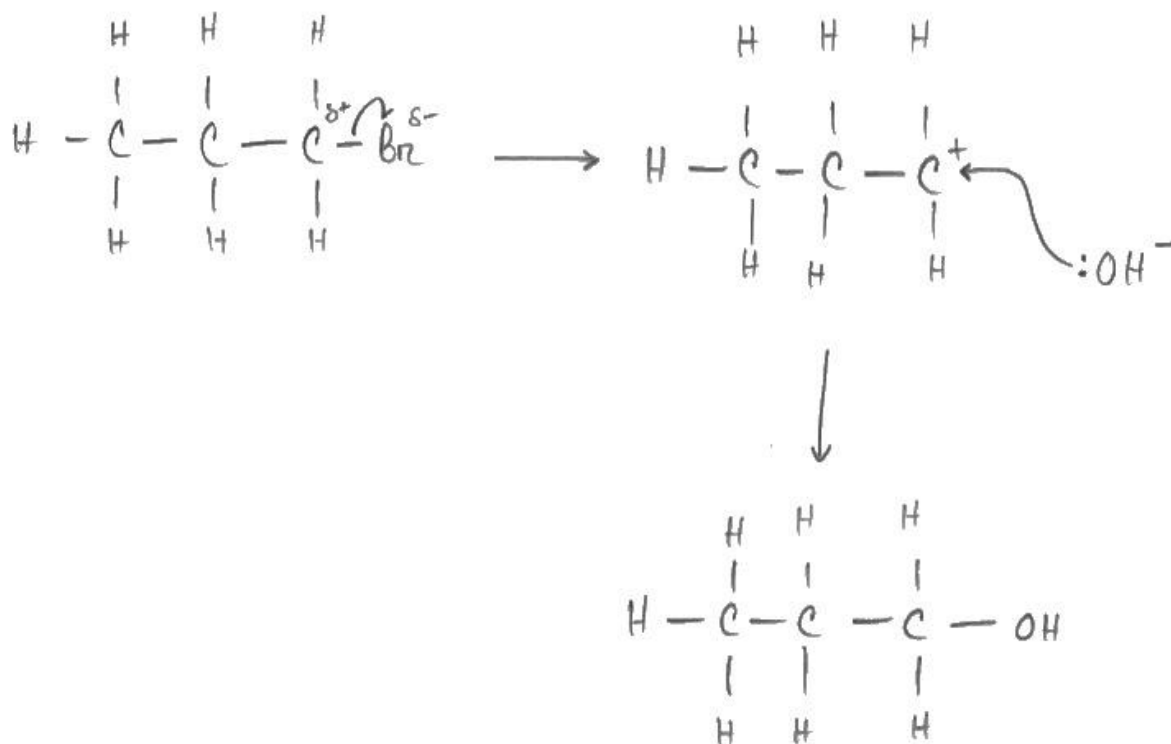
This candidate has gained all 7 points and scores 4 marks. The answer is very neat and the heads and ends of each arrow are precise.

This is an example of an S_N1 mechanism.

- (b) Draw the S_N2 mechanism for the reaction of 1-bromopropane with hydroxide ions in aqueous solution.

Include curly arrows, and relevant dipoles and lone pairs.

(4)



ResultsPlus
Examiner Comments

With the omission of the transition state the maximum that could be awarded for an S_N1 mechanism is 2 marks. This candidate has omitted the bromide ion so only scores 3 points but this is still 2 marks in total.



ResultsPlus
Examiner Tip

Read the questions carefully – the type of mechanism is clearly asked for here.

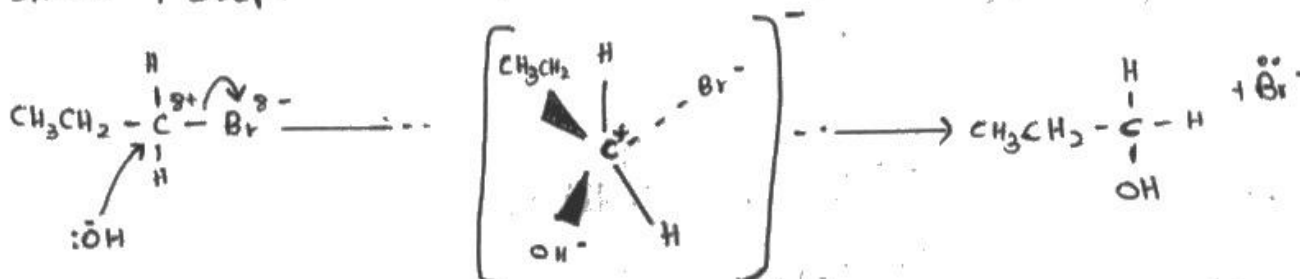
This response highlights some common errors.

(b) Draw the S_N2 mechanism for the reaction of 1-bromopropane with hydroxide ions in aqueous solution.

Include curly arrows, and relevant dipoles and lone pairs.

$S_N2 = 1 \text{ step.}$

(4)



ResultsPlus
Examiner Comments

This candidate has made two errors but scores 3 marks. Firstly, the arrow from the hydroxide ion does not start at the lone pair and then the transition state shows multiple charges inside the brackets as well as the overall charge on the outside of the brackets.



ResultsPlus
Examiner Tip

Ensure all curly arrows start at a lone pair or bond. Where square brackets are used around a complex ion, charges are not required inside the brackets.

Question 20

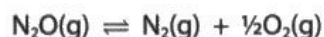
Of the 9 marks available for this question, the mean mark was 6 and the modal mark 7. Incorrect units were only penalised once for Q20(a)(i)-(iii) otherwise some candidates would have lost multiple marks here. A TE was also allowed from Q20(a)(i) and Q20a(ii) to Q20(a)(iii), and any values added together with correct units were accepted.

In Q20(b), some candidates omitted the negative sign for the gradient so lost M1. M2 was awarded as a TE but no TE from Q20(b) was allowed to Q20(c) so a negative value for activation energy was penalised here.

The final part proved the most problematic for candidates with many only commenting on the total entropy or even trying to compare the total entropy with the activation energy. An incorrect value for the total entropy was allowed as a transferred error from Q20(a)(iii). A comment on the (positive) value for total entropy scored M1 and multiple routes allowed M2 to be scored. Some candidates commented on the temperature in relation to the activation energy and were awarded the mark whether or not they said the temperature was high enough.

This is an example of a response scoring all 9 marks.

20 Nitrous oxide, N_2O , decomposes at high temperature to form nitrogen and oxygen.



(a) (i) Some standard molecular entropy data are shown.

Substance	Standard molecular entropy $S^\ominus$ $/\text{JK}^{-1}\text{mol}^{-1}$
nitrogen, N_2	192
oxygen, O_2	205
nitrous oxide, N_2O	220

Calculate the standard entropy change of the system for the decomposition shown.

Include a sign and units in your answer.

(2)

$$\begin{aligned}\Delta S_{\text{system}} &= S_{\text{product}} - S_{\text{reactant}} \\ &= 192 + (0.5 \times 205) - 220 \\ &= \underline{\underline{+74.5 \text{ JK}^{-1}\text{mol}^{-1}}}\end{aligned}$$

(ii) The standard enthalpy change of the forward reaction is -82 kJ mol^{-1} .

Calculate the entropy change of the surroundings at 2048 K.

Include a sign and units in your answer.

(2)

$$\begin{aligned}\Delta S_{\text{surrounding}} &= \frac{-\Delta H \times 1000}{T} \\ &= \frac{-(-82) \times 1000}{2048} \\ &= \underline{\underline{+40.04 \text{ JK}^{-1}\text{mol}^{-1}}}\end{aligned}$$

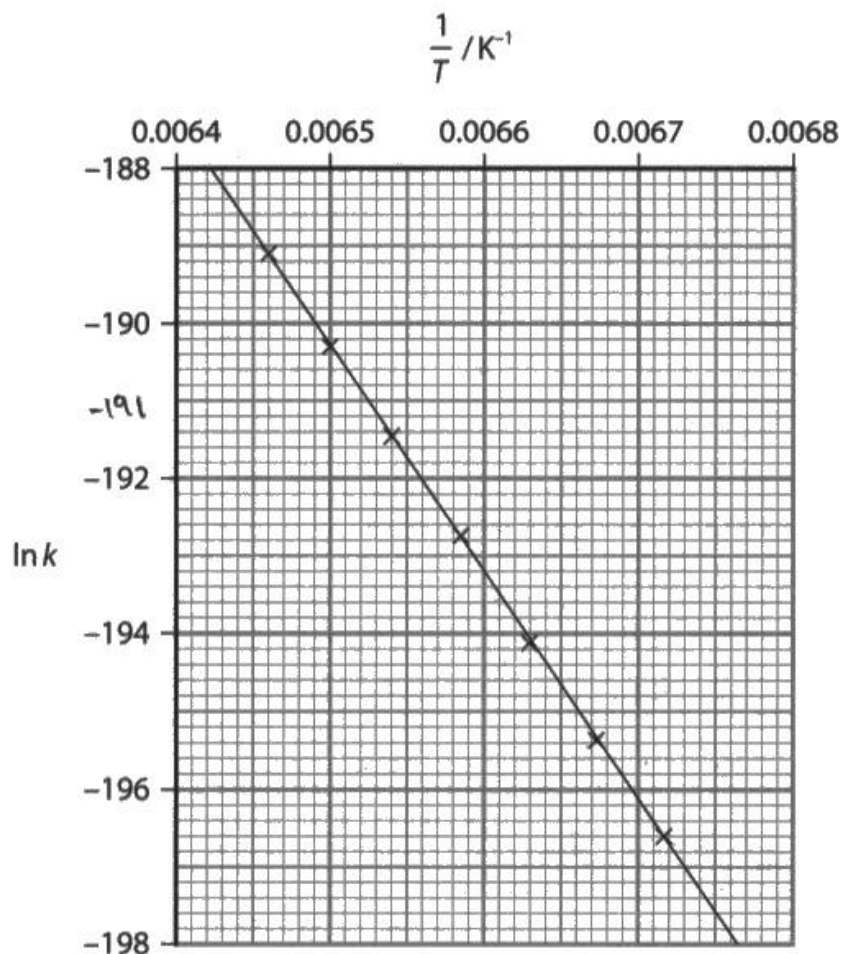
(iii) Calculate the total entropy change of the reaction at 2048 K.

Include a sign and units in your answer.

(1)

$$\begin{aligned}\Delta S_{\text{total}} &= \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} \\ &= 74.5 + 40.04 \\ &= \underline{\underline{114.5 \text{ JK}^{-1}\text{mol}^{-1}}}\end{aligned}$$

(b) Rate experiments on the decomposition of nitrous oxide produced the following graph.



Calculate the activation energy for the reaction in kJ mol^{-1} .
Include the value of the gradient.

$$\ln k = -\frac{E_a}{R} \frac{1}{T} + \text{constant}$$

$$R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$m = \frac{-E_a}{R} \quad m = \frac{y_2 - y_1}{x_2 - x_1} \quad \begin{matrix} (0.0067, -196) \\ (0.0065, -190.3) \end{matrix} \quad (2)$$

$$m = \frac{-196 + 190.3}{0.0067 - 0.0065} = -28500$$

$$-28500 = \frac{-E_a}{8.31}$$

$$\begin{aligned} -236835 \text{ J mol}^{-1} &= -E_a \\ + 236.84 \text{ kJ mol}^{-1} &= E_a \end{aligned}$$

(c) Explain whether or not this reaction occurs at 2048 K by considering the values calculated in (a) and (b).

(2)

Reaction is thermodynamically feasible as ΔS_{total} is a positive value and as E_a is a positive value, it will be reached since a high temperature is used so yes, the reaction does occur at 2048 K.

(Total for Question 20 = 9 marks)



ResultsPlus
Examiner Comments

The expression, answer and units are correct so 2 marks are scored for Q20(a)(i).

The answer for Q20(a)(ii) is fully correct as per the mark scheme.

The answers in Q20(a)(i) and Q20(a)(ii) have been added together for a correct answer to Q20(a)(iii).

In Q20(b) the gradient has been correctly worked out for M1 and this answer has been multiplied by a negative gas constant to calculate the positive activation energy with correct units.

The answer to Q20(c) scores M1 for "thermodynamically feasible as ΔS_{total} is a positive value" and M2 is awarded for a correct comment on the activation energy.



ResultsPlus
Examiner Tip

Always continue with your calculations using your previous answers even if you are not sure they are correct.

Question 21 (a)

Over half of candidates gained 2 marks for this question. It was acceptable for the name of the first organic product box to be blank along with a cross in the reaction box to score M1. A minority of candidates failed to realise that ketones cannot be further oxidised and identified a carboxylic acid as a product.

Candidates generally had more difficulty with M2 where some even suggested the ketone may form an acid with the reducing agent. There were occasional slips with the position numbers for the alcohol groups but the allowance of the absence of the "e" and even the "n" meant that some weaker candidates did score this mark. A number of candidates gave the correct numbers but failed to use the suffix – diol and 2,5-dihydroxyhexane was seen regularly. The name was required for this question and structural formulae did not score.

Where candidates failed to score any marks, it was often due to the lack of recognition of the reducing and oxidising agents and the answers were reversed.

21 Hexane-2,5-dione, $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COCH}_3$, is a toxic compound formed in the human body if hexane is consumed.

(a) Complete the table for hexane-2,5-dione.

Name the organic product formed if a reaction takes place.

(2)

Reagent and conditions	Reaction (✓ / ✗)	Name of organic product (if formed)
refluxed with excess acidified potassium dichromate(VI)	✗	No product
excess lithium tetrahydridoaluminate(III) in dry ether	✓	hexan-2,5-diol



ResultsPlus
Examiner Comments

An example of a fully correct answer.

Question 21 (b)

Nearly three quarters of the cohort gained the mark for this item. Most stated that there would be a yellow precipitate or yellow solid. Some included pale as a part of their answer. Quite a few candidates identified CH_3I in their answer though this was not required, or included mention of a smell which was the alternative answer.

Answers that were seen frequently but did not score included "yellow solution" and "turns yellow". A small minority of candidates mentioned the colour changes usually associated with iodine rather than iodoform eg "turns blue/black" or "purple colour" and a few gave observations for other reactions eg "fizzing and/or misty fumes".

(b) State the observation when hexane-2,5-dione reacts with iodine in the presence of alkali.

(1)

antiseptic smell is observed



ResultsPlus
Examiner Comments

An example of an infrequently seen, but correct answer.

Question 21 (c)(i)

Approximately 55% of the cohort scored this mark, with every type and mechanism seen from "electrophilic", "substitution", and even occasionally "hydrolysis" and "elimination". With only one mark available both parts needed to be correct to score and the addition of S_N1 or S_N2 to the correct name and type negated the mark.

An example of a response that did not score.

(c) Hexane-2,5-dione reacts with **excess** hydrogen cyanide, HCN, in the presence of potassium cyanide, KCN.

(i) Name the type and mechanism of this reaction.

(1)

Nucleophilic addition and S_N2



ResultsPlus
Examiner Comments

While the "nucleophilic addition" part of the answer is correct the addition of S_N2 means that the mark is not awarded. Phonetic and recognisable spellings are always allowed on IAL Chemistry papers but giving multiple answers always comes with a risk that if one of them is wrong the mark will not be awarded.



ResultsPlus
Examiner Tip

Only give one answer when one is asked for, "nucleophilic addition" is the type and mechanism of this reaction.

Question 21 (c)(ii)

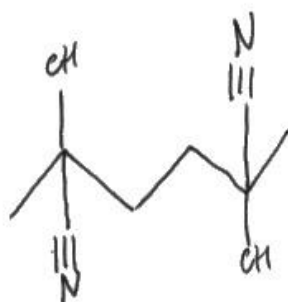
Fewer than 50% of candidates achieved this mark, though the type of structure was not specified so fully displayed, shortened structural, semi-structural and skeletal diagrams were accepted, along with combinations of these. Where displayed formulae were drawn it was expected that all the hydrogen atoms were shown but a minority of candidates omitted them.

Many candidates only showed the addition on one end of the molecule instead of both. Some candidates failed to show the alcohol group, instead replacing it with a hydrogen or more commonly just an unbonded oxygen.

Below are examples of responses that gained the mark.

(ii) Draw the structure of the product.

(1)



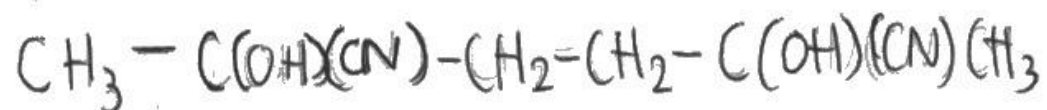
ResultsPlus
Examiner Comments

The O of each oxygen isn't complete but this response was given the benefit of the doubt. Ideally the triple bonds of the nitrile groups would also be joined up to the skeletal structure.



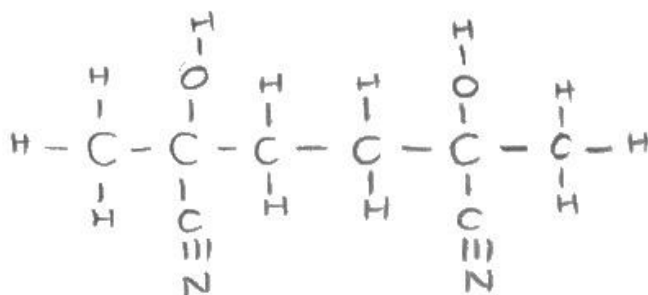
ResultsPlus
Examiner Tip

Practice drawing molecules from the specification using different formats.



ResultsPlus
Examiner Comments

This shortened-structural formula also scored the mark.



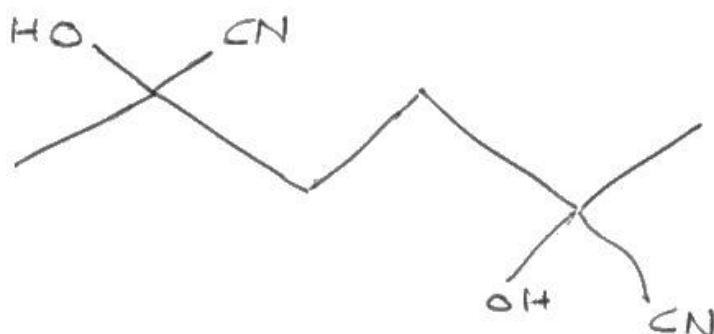
ResultsPlus
Examiner Comments

This candidate has drawn out a fully displayed structure.



ResultsPlus
Examiner Tip

Remember to include all hydrogens on fully displayed structures.



ResultsPlus
Examiner Comments

An unusual mixed formula that gains the mark.

Question 21 (d)(i)

Over 70% of candidates scored this mark with the most common correct answer being orange precipitate, though many combinations of yellow, orange and red were seen. Brown was not allowed and some candidates lost marks for giving an answer of a correctly coloured solution instead of solid/crystals etc.

Question 21 (d)(ii)

This question was poorly answered, with over 70% of the cohort not gaining either mark. Candidates needed to state that the precipitate would need to be recrystallised (M1) and then the melting point compared to known values (M2). Many candidates answers lacked precision for M1 and they stated that the sample would need to be purified without naming the method. For the second mark a large number of candidates said they would compare the **boiling** point to known values. A few candidates stated they would use infrared or NMR spectroscopy and while the interpretation of these spectra is on the specification, candidates are not expected to use these techniques in a school laboratory.

An example of a response scoring both marks.

(ii) Describe, in outline, how the product of this reaction may be used to confirm the identity of hexane-2,5-dione. Experimental details are not required.

(2)

- React the hexane-2,5-dione with 2,4-DNPH.
- Filter the precipitate and recrystallise the precipitate.
- The melting temperature of the precipitate formed is matched with that of the data booklet values to determine the identity of hexane-2,5-dione.



M1 is scored for "recrystallise the precipitate", the filtration step is not required but shows the candidate has a good understanding of this practical technique.

M2 is awarded for the third sentence.

(ii) Describe, in outline, how the product of this reaction may be used to confirm the identity of hexane-2,5-dione. Experimental details are not required.

(2)

This test shows that it is a carbonyl compound, ~~as~~ (An aldehyde or ketone) to confirm it, its melting temperature is measured and compared with data booklet as all have different melting points.



ResultsPlus
Examiner Comments

This example scores M2 but M1 is not attempted.



ResultsPlus
Examiner Tip

When two marks are available you need two pieces of information in your answer, do not repeat information already given in the question.

This response shows an incorrect response for both marking points.

- (ii) Describe, in outline, how the product of this reaction may be used to confirm the identity of hexane-2,5-dione. Experimental details are not required.

(2)

The organic product may be fractionally distilled and undergo infrared spectroscopy in order to identify the fingerprint region and allow us to confirm the identity of hexane-2,5-dione.



ResultsPlus
Examiner Comments

M1 is not awarded for fractional distillation.

Infrared spectroscopy is not a suitable laboratory technique for M2.



ResultsPlus
Examiner Tip

If the question includes the statement "experimental details are not required" then the technique is likely to be one that you have used on your course.

This is an example of an imprecise answer that fails to score.

- (ii) Describe, in outline, how the product of this reaction may be used to confirm the identity of hexane-2,5-dione. Experimental details are not required.

(2)

The product of this reaction can be filtered, purified and dried. Then the boiling point of this product can be used to test against data booklet to see if it matches with the product for hexane-2,5-dione as Brady's reagent products all have ~~unique~~ different boiling points.



ResultsPlus
Examiner Comments

The candidate has made an attempt at M1 but has not stated how the crystals will be purified.

They have then confused boiling point with melting temperature so M2 is not awarded.



ResultsPlus
Examiner Tip

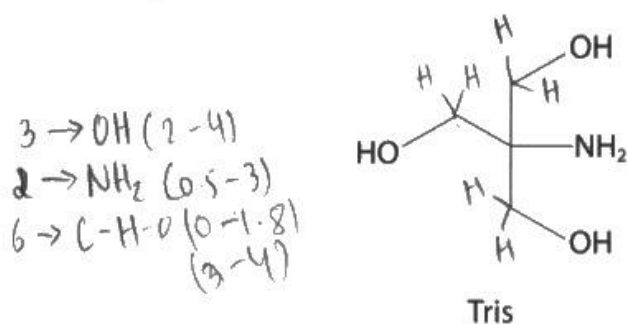
Ensure you revise the techniques on the specification

Question 22 (a)

This question was poorly answered with a mean score of 1 and over 30% of candidates failed to score a mark from the 3. The request to draw a low resolution H-NMR spectrum confused some candidates who still tried to draw split peaks. This made counting the number of peaks and estimating their area or height nearly impossible; so by attempting to draw a high resolution spectrum candidates limited their achievement to M3 alone. Both lines and "triangle" style peaks were accepted but spectra that showed more than 5 peaks did not score. An acceptable range for each peak was given and the area and location of the peaks were independent, with the stipulation that the tallest peak should not be on the right. M3 could be scored for any two peaks being in range. Some responses to this question were hard to mark where candidates had just drawn single lines for the peaks, particularly when one or more of their peaks was over a gridline.

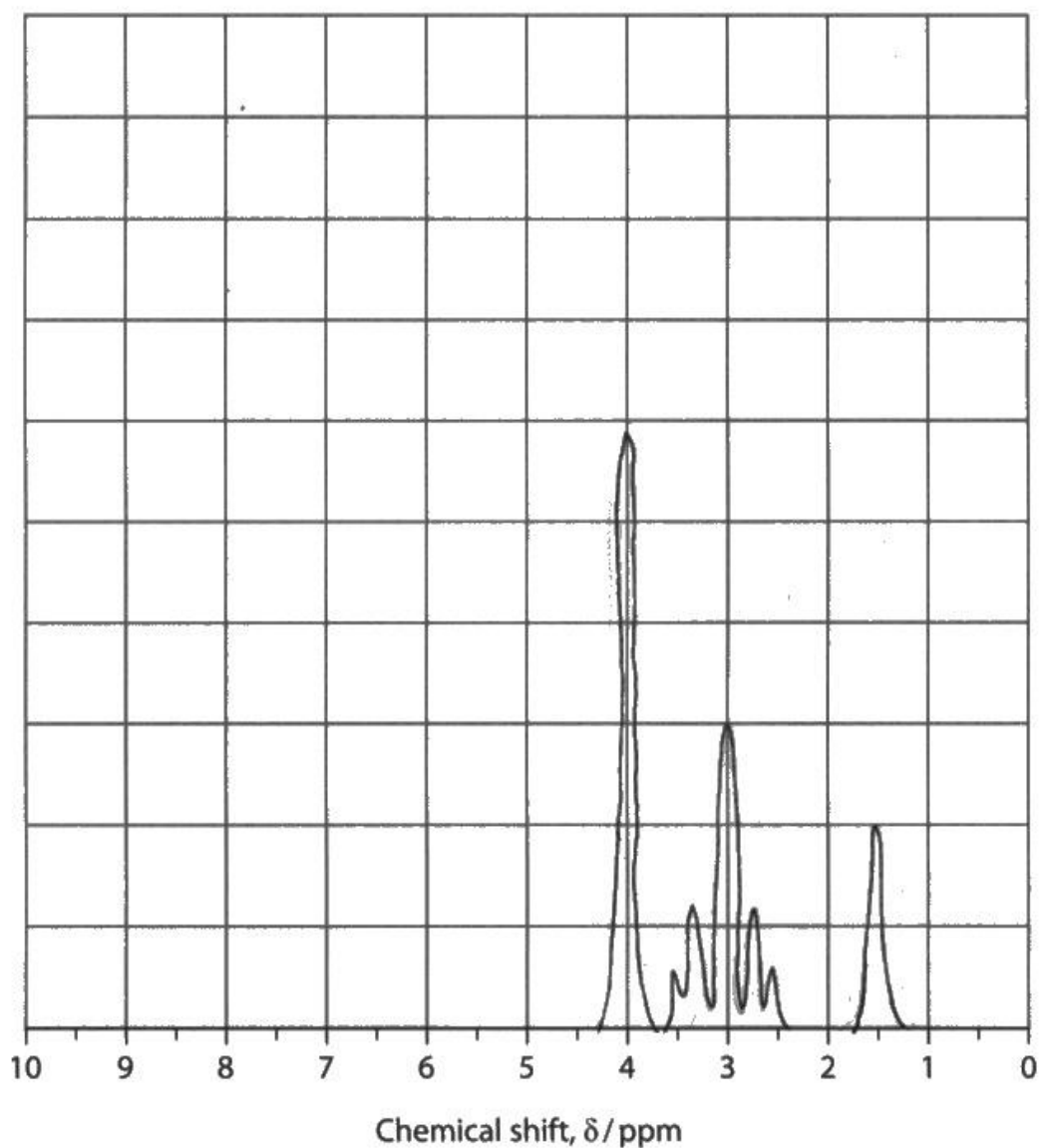
This response scored 1 mark.

22 The alkaline compound tris(hydroxymethyl)aminomethane, known as Tris, is used to make a buffer for biological research.



(a) Sketch the **low** resolution proton NMR spectrum of Tris ($\text{C}_4\text{H}_{11}\text{NO}_3$).
Use your Data Booklet.

(3)

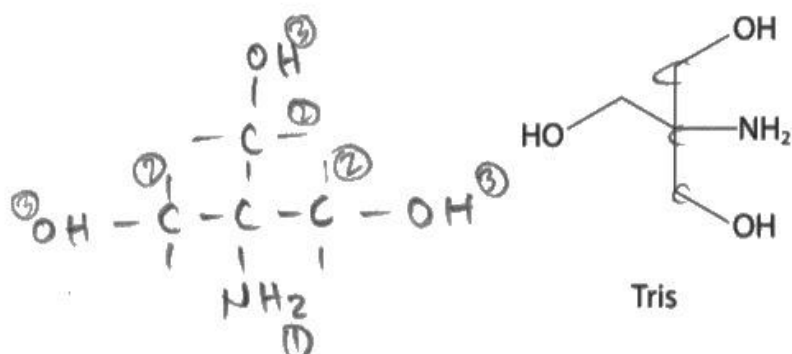




The splitting pattern of the middle peak means that M1 and M2 cannot be scored. M3 was awarded for 3 peaks in the correct locations.

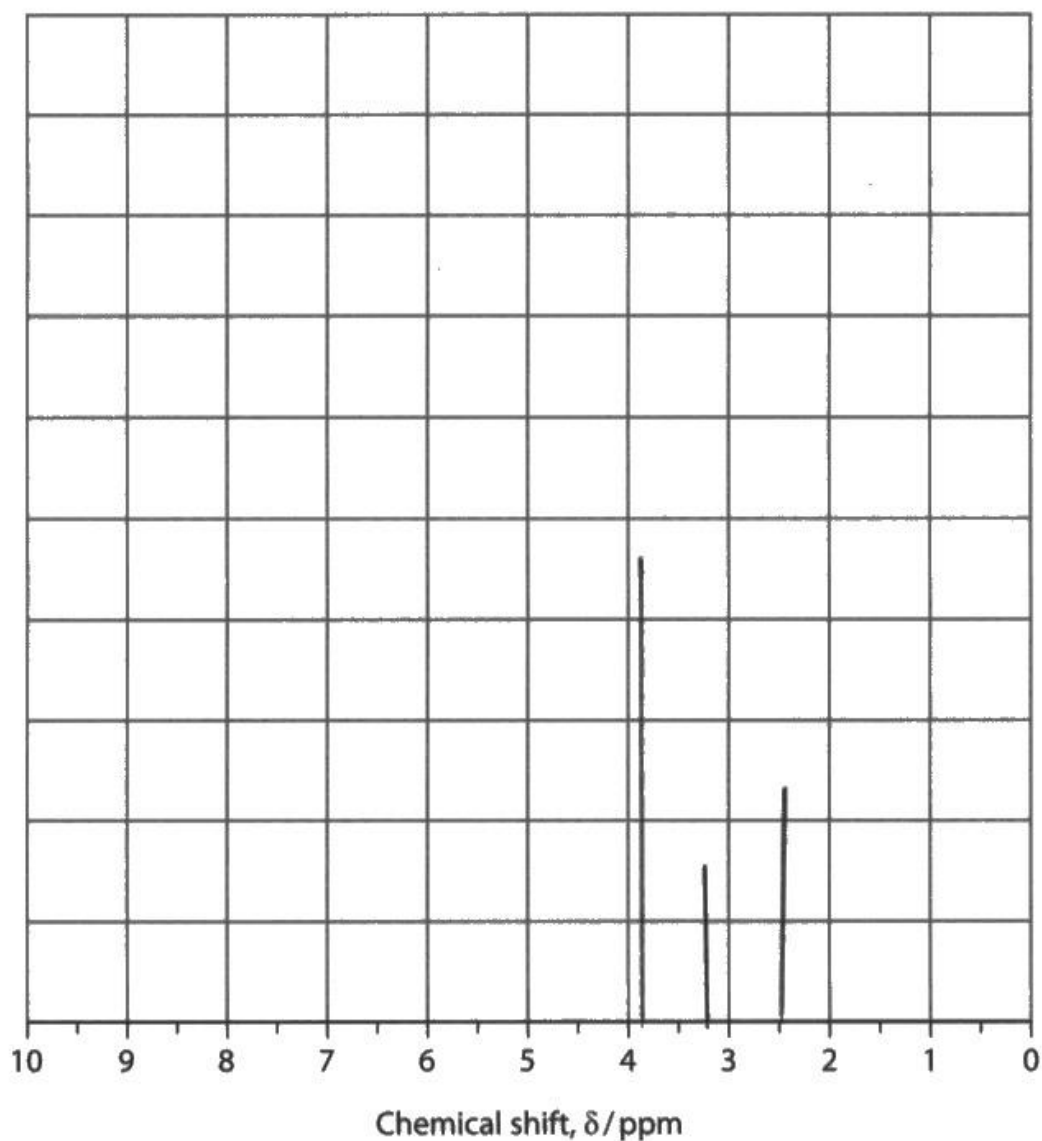
This response gains all 3 marks.

22 The alkaline compound tris(hydroxymethyl)aminomethane, known as Tris, is used to make a buffer for biological research.



(a) Sketch the **low** resolution proton NMR spectrum of Tris ($C_4H_{11}NO_3$).
Use your Data Booklet.

(3)

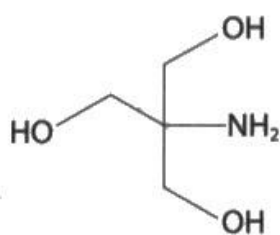




This response shows three clear, unsplit peaks so gains M1. The heights of the peaks are in the correct ratio and the tallest peak is not on the right so M2 is awarded (though the candidate hasn't used the lines on the grid as expected). The three peaks are within the ranges prescribed for M3.

This response scored 2 marks.

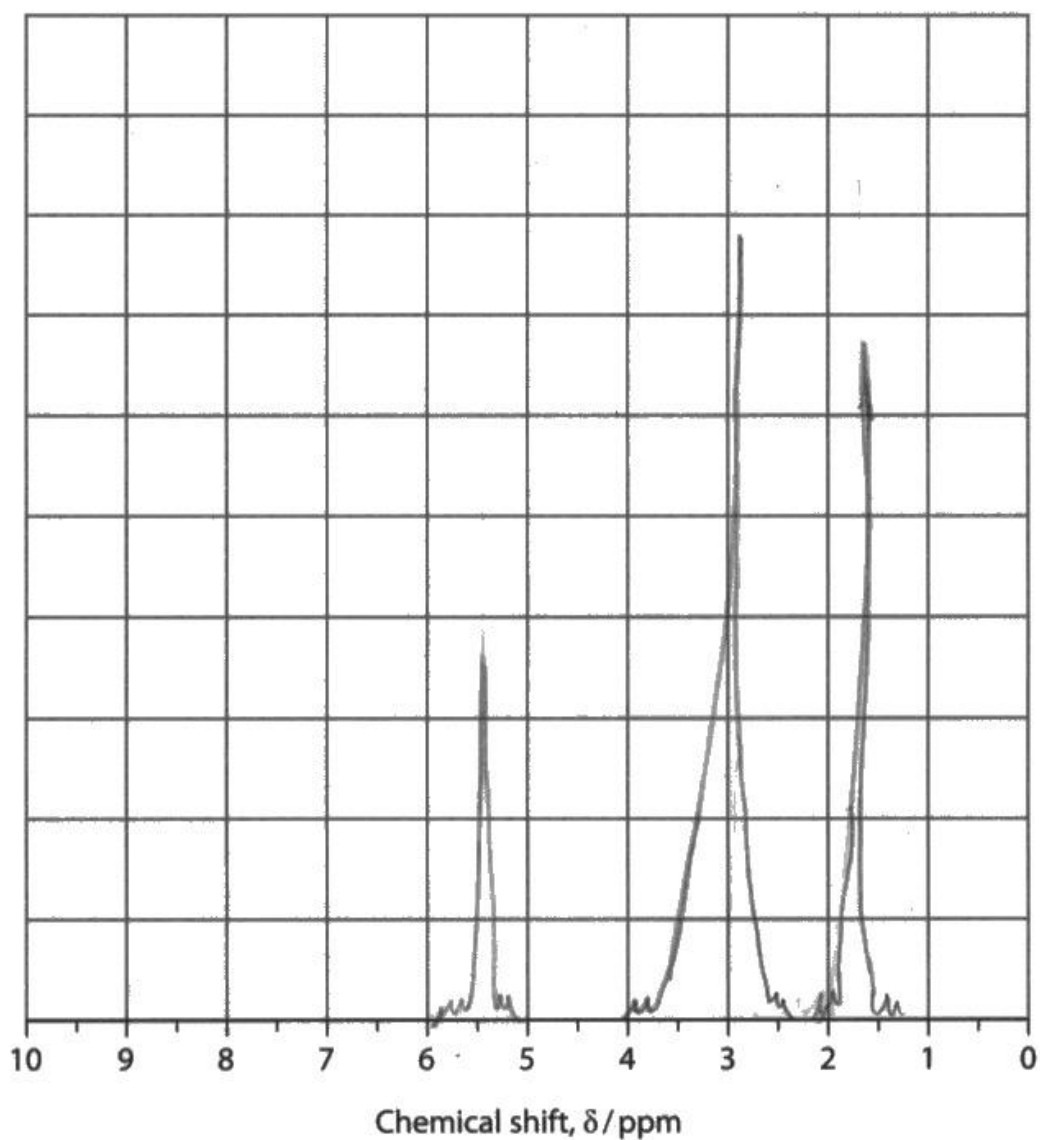
22 The alkaline compound tris(hydroxymethyl)aminomethane, known as Tris, is used to make a buffer for biological research.



Tris

(a) Sketch the **low** resolution proton NMR spectrum of Tris ($C_4H_{11}NO_3$).
Use your Data Booklet.

(3)





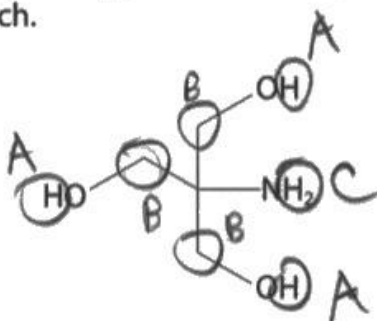
This response scored M1 and M3. The wiggles at the bases of the peaks were ignored. The three peaks (M1) do not have the correct height ratios to score M2 but two of the peaks are within the correct range to score M3.



Ensure you have a ruler in your exam to help you draw straight lines.

This is an example of a response that was hard to mark after scanning.

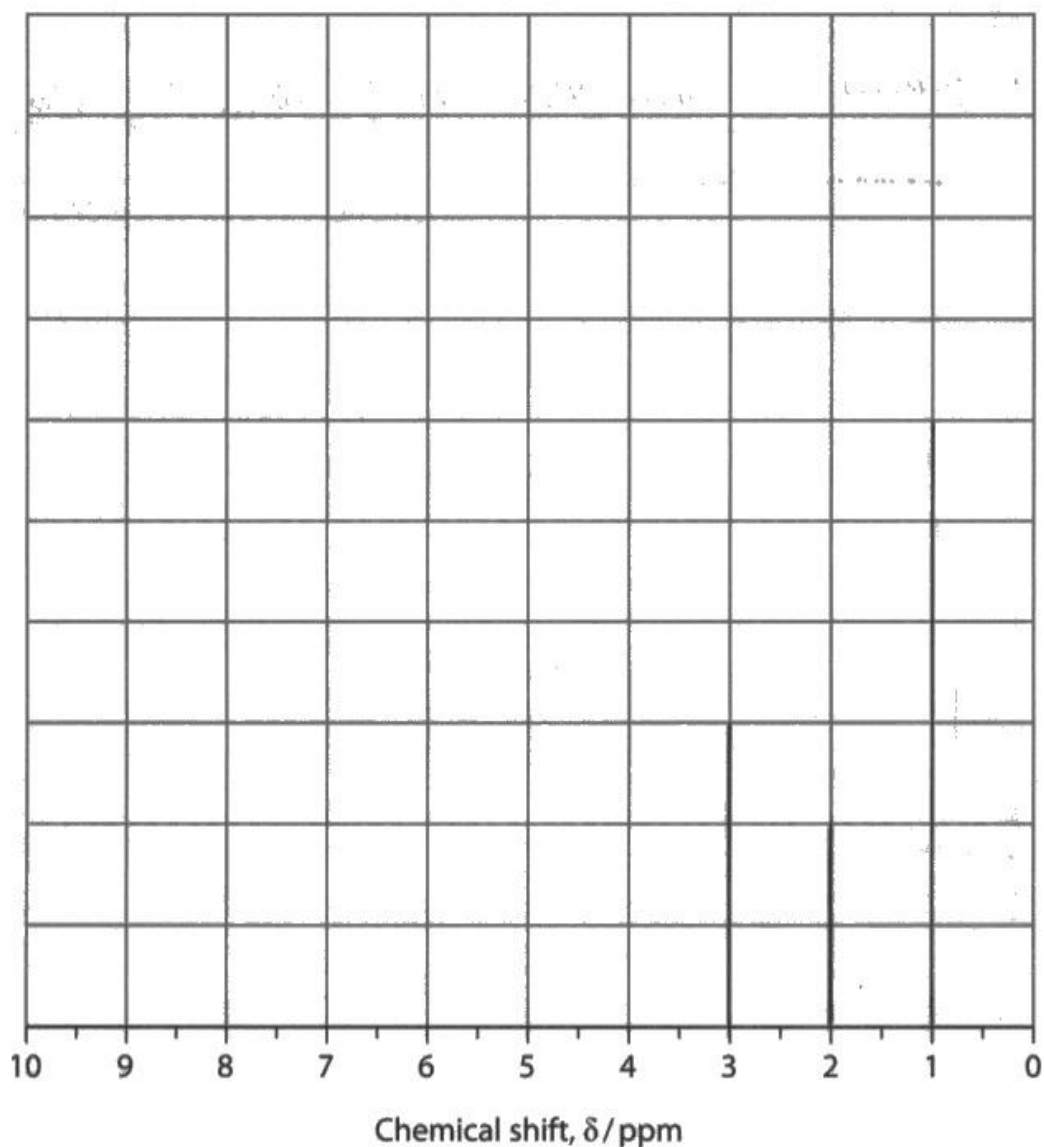
22 The alkaline compound tris(hydroxymethyl)aminomethane, known as Tris, is used to make a buffer for biological research.



Tris

- (a) Sketch the **low** resolution proton NMR spectrum of Tris ($C_4H_{11}NO_3$).
Use your Data Booklet.

(3)





On zooming in it can be seen that the candidate has drawn three peaks (at chemical shifts of δ 3, 2 and 1) and that these peaks are of heights 3:2:6. As the tallest peak is on the right hand side, M2 cannot be scored but the peaks are within the ranges for M3 to be awarded. Where candidates are drawing over printed lines it is important that they widen peaks sufficiently to ensure they can be clearly seen by examiners.



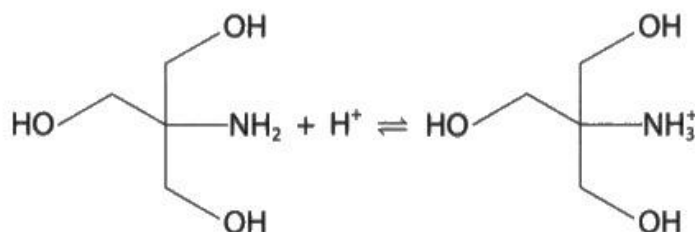
Ensure your answer can be seen when it is scanned in. HB or B pencil should be used as an alternative to black pen but your lines must be bold enough to stand out from the answer grid.

Question 22 (b)(i)

The mean mark for this question was one out of the three available. Almost a third of candidates did not gain a single mark here, despite the mark scheme and question being very similar to those set in previous series. Some confusion could have been around Tris being a basic buffer rather than the acid buffers candidates are used to.

An example of a fully correct answer.

(b) Tris is a Brønsted–Lowry base and its conjugate acid is formed as shown.



- (i) Explain how a mixture of Tris and its conjugate acid acts as a buffer solution when a small amount of acid is added.

There are large concentration of both $\text{HO-CH}_2\text{-C(OH)}_2\text{-NH}_2$ and $\text{HO-CH}_2\text{-C(OH)}_2\text{-NH}_3^+$ when small amount of acid is added it'll react with $\text{HO-CH}_2\text{-C(OH)}_2\text{-NH}_2$ to form $\text{HO-CH}_2\text{-C(OH)}_2\text{-NH}_3^+$, since ratio of 2 species changes little equilibrium constant hence pH changes little



ResultsPlus
Examiner Comments

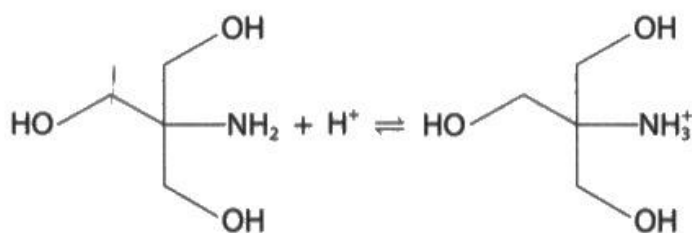
This candidate has chosen to draw the molecules rather than referring to them by name or molecular formula which is fine. The first sentence gains M2, the second M1 and the final phrase scores M3.



ResultsPlus
Examiner Tip

Using formulae instead of names is fine unless a name is specifically asked for.

(b) Tris is a Brønsted–Lowry base and its conjugate acid is formed as shown.



(i) Explain how a mixture of Tris and its conjugate acid acts as a buffer solution when a small amount of acid is added.

(3)

When a small amount of acid is added, the equilibrium shifts to the right producing more of the conjugate acid to restore the pH.

As there are large reserve supplies of both Tris and its conjugate acid their concentrations don't change much. This keeps the pH constant.



ResultsPlus
Examiner Comments

This candidate scores M1 for the equilibrium moving to the right. M2 is awarded for the fourth line "large reserve supplies of both Tris and its conjugate acid" but the candidate does not mention the ratio of the substances so M3 cannot be scored.

This is an example where the candidate has confused themselves about conjugate acids and bases.

When a small amount of acid is added, Tris molecules react with it to neutralise it. The Tris molecules and its conjugate base are present in large reservoir in excess. As a result there is a negligible change in the concentration of acid or conjugate base; thus $\frac{[\text{acid}]}{[\text{base}]} = \frac{[\text{HA}]}{[\text{A}^-]}$ stays approximately constant, and as $\text{pH} = \text{pK}_a - \log\left(\frac{[\text{HA}]}{[\text{A}^-]}\right)$, pH stays approximately constant as well.

$\text{BA}^- = \text{Tris}$

$\text{HA} = \text{conjugate acid}$



ResultsPlus
Examiner Comments

M1 is awarded for the first sentence. M2 is not scored as Tris molecules do not have a conjugate base. M3 is awarded for the ratio and pH comment and the candidate clarifies what they mean by the terms HA and A – under the answer lines.

Question 22 (b)(ii-iii)

Candidates found Q22(b)(ii) difficult, mainly because they had to write the K_a expression for the conjugate acid of Tris. There was plenty of confusion over charges on the relevant species and the mean was 3 marks from 6, with a quarter of candidates failing to score a mark. Where candidates did get the first part incorrect a TE was available to Q22(b)(iii). Candidates did not require their answer to Q22(b)(ii) to gain the first three marks of the calculation. Some candidates further complicated their response by subtracting the moles of Tris from the moles of acid as though alkali had been added to a buffer and then the new pH needed to be calculated.

This is an example of a fully correct answer.

(ii) Write the expression for the K_a of the conjugate acid of Tris ($C_4H_{12}NO_3^+$).

(1)

$$K_a = \frac{[H^+][C_4H_{11}NO_3]}{[C_4H_{12}NO_3^+]}$$

(iii) When hydrochloric acid is added to Tris, the acid salt is formed.

The acid salt is a solid, which has the formula $C_4H_{12}NO_3^+Cl^-$, and contains the conjugate acid of Tris.

When 100 g of the acid salt is mixed with 500 cm³ of 0.200 mol dm⁻³ Tris, an alkaline buffer is formed.

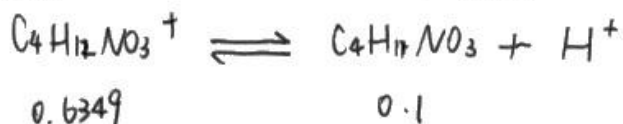
Calculate the pH of this buffer, assuming that there is no change in volume when the solid is added.

K_a for the conjugate acid of Tris is 8.413×10^{-9} mol dm⁻³.

(5)

$$n_{C_4H_{12}NO_3^+Cl^-} = \frac{100}{4 \times 12 + 12 \times 1 + 14 + 16 \times 3 + 35.5} = 0.6349 \text{ mol}$$

$$n_{\text{Tris}} = 0.2 \times 500 \times 10^{-3} = 0.1 \text{ mol}$$



$$0.6349$$

$$0.1$$

$$0.6349 - x$$

$$0.1 + x$$

$$x$$

Concentration: $1.2698 - 2x$

$$0.2 + 2x$$

$$2x$$

$$K_a = 8.413 \times 10^{-9} = \frac{(0.2 + 2x) 2x}{1.2698 - 2x}$$

$$2x = 5.3414 \times 10^{-8}$$

$$[H^+] = 2x = 5.3414 \times 10^{-8}$$

$$pH = -\log [H^+] = 7.27$$



The K_a expression is correct for Q22(b)(ii).

The candidate has achieved the correct answer for Q22(b)(iii), though there was no need for their complicated equilibrium expression.



Lay out your calculations neatly so that examiners can follow your logic.

This is an example of a response with a couple of errors.

(ii) Write the expression for the K_a of the conjugate acid of Tris ($C_4H_{12}NO_3^+$).

(1)

$$K_a = \frac{[H^+][C_4H_{12}NO_3^+]}{[C_4H_{11}NO_3]}$$

(iii) When hydrochloric acid is added to Tris, the acid salt is formed.

The acid salt is a solid, which has the formula $C_4H_{12}NO_3^+Cl^-$, and contains the conjugate acid of Tris.

When 100 g of the acid salt is mixed with 500 cm³ of 0.200 mol dm⁻³ Tris, an alkaline buffer is formed.

Calculate the pH of this buffer, assuming that there is no change in volume when the solid is added.

K_a for the conjugate acid of Tris is 8.413×10^{-9} mol dm⁻³.

(5)

$$n(\text{acid salt}) = \frac{100}{(12 \times 9) + 12 + 14 + (6 \times 3) + 35.5}$$

$$= \frac{100}{122} = 0.8197 \text{ mol}$$

$$n(\text{Tris}) = \frac{500}{1000} \times 0.2 = 0.1 \text{ mol}$$

$$K_a = 8.413 \times 10^{-9}$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$[A^-][H^+] = K_a [HA]$$

$$[H^+] = \frac{K_a [HA]}{[A^-]}$$

$$[H^+] = \frac{(8.413 \times 10^{-9})(0.1)}{(0.8197)}$$

$$[H^+] = 1.0264 \times 10^{-9}$$

$$pH = -\log(1.026 \times 10^{-9})$$

$$\therefore pH = 8.99$$



No credit in Q22(b)(ii) as the candidate has confused the Tris and the acid salt. This is given as a TE for M3 in Q22(b)(iii), as the Tris and its conjugate acid have been confused in both parts.

No M1 for Q22(b)(iii) as the M_r is incorrect. The number of moles calculated (M2 as TE) is then substituted into the K_a expression (as the volumes cancel out in the rearrangement this is fine). The rearrangement (M3 as TE from Q22(b)(ii), using numbers from M2 as a TE) gives the value for the hydrogen ion concentration (M4 as a TE) and the negative log of this value gives the pH (M5 as a TE).

This is an example of the transferred error from Q22(b)(ii) to Q22(b)(iii) using the Henderson-Hasselbalch (H-H) method.

(ii) Write the expression for the K_a of the conjugate acid of Tris ($C_4H_{12}NO_3^+$).

(1)

$$K_a = \frac{[C_4H_{12}NO_3^+]}{[C_4H_{11}NO_3][H^+]}$$

(iii) When hydrochloric acid is added to Tris, the acid salt is formed.

The acid salt is a solid, which has the formula $C_4H_{12}NO_3^+Cl^-$, and contains the conjugate acid of Tris.

When 100 g of the acid salt is mixed with 500 cm³ of 0.200 mol dm⁻³ Tris, an alkaline buffer is formed.

Calculate the pH of this buffer, assuming that there is no change in volume when the solid is added.

K_a for the conjugate acid of Tris is 8.413×10^{-9} mol dm⁻³.

(5)

~~$$\text{mol of salt} = \text{mol of Tris} = 0.1 \text{ mol}$$~~

~~$$\text{mol of salt} = 0.1 \text{ mol}$$~~

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{mol of salt} = \frac{100}{157.5} = 0.635 \text{ mol}$$

$$[\text{salt}] = \frac{0.635}{500/10^3} = 1.2698 \text{ mol dm}^{-3}$$

$$pH = -\log 8.413 \times 10^{-9} + \log \frac{1.2698}{0.2}$$

$$= 8.878 \text{ Any.}$$



No credit for Q22(b)(ii) as the expression is upside down. The candidate has confused the acid salt and Tris so this is not penalised in Q22(b)(iii).

In Q22(b)(iii), M1 is awarded for the M_r of the acid salt. M2 is awarded for the concentration of the "salt" (this is really the Tris). The candidate then substitutes into the (H-H) expression and calculates their answer. The answer 8.88 shows that the salt and Tris were incorrectly substituted into the equation and as this confusion has already been penalised in Q22(b)(ii) the candidate gains all 5 marks on this calculation.



Show all steps in your working for each calculation.

Question 22 (c)

This question was well attempted by many candidates. The average mark for this question was 2 but over 40% of the cohort achieved full marks. The mark that was least frequently awarded was M3, as many candidates neglected to square the $[H^+]$ on the top of the expression. M4 was available as a TE for answers that were less than one.

This is an example of a response that scored full marks.

(c) A solution of chloroethanoic acid is prepared for titration with Tris.

0.0150 g of chloroethanoic acid ($M_r = 94.5$) is dissolved in 1500 cm³ of distilled water. The resulting solution has a pH of 3.42.

Calculate the K_a of chloroethanoic acid.

(4)



$$n(\text{CH}_2\text{ClCOOH}) = \frac{0.015}{94.5} \Rightarrow c(\text{CH}_2\text{ClCOOH}) = \frac{n}{1500 \times 10^{-3}} = \frac{1}{9450} = 1.0582 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\therefore \text{pH} = 3.42 \Rightarrow [\text{H}^+] = 10^{-3.42}$$

$$\text{As } [\text{H}^+] = [\text{CH}_2\text{ClCOO}^-], \text{ then } K_a = \frac{[\text{H}^+]^2}{[\text{CH}_2\text{ClCOOH}]} = 1.366 \times 10^{-3} \text{ mol dm}^{-3}$$



ResultsPlus
Examiner Comments

M1 is awarded for the concentration of the acid.

M2 is awarded for the hydrogen ion concentration calculated from the pH.

M3 is for the K_a expression and M4 for the final answer.

This is a response that highlights some common errors.

(c) A solution of chloroethanoic acid is prepared for titration with Tris.

0.0150 g of chloroethanoic acid ($M_r = 94.5$) is dissolved in 1500 cm^3 of distilled water. The resulting solution has a pH of 3.42.

Calculate the K_a of chloroethanoic acid.

$$K_a = \frac{[\text{H}^+]^2}{[\text{Acid}]}$$
$$\therefore K_a = \frac{[10^{-3.42}]^2}{[2.385 \times 10^{-4}]}$$
$$\therefore K_a = 6.06 \times 10^{-4}$$

(4)

moles of chloroethanoic acid

$$= \frac{0.0150}{94.5}$$
$$= 1.59 \times 10^{-4}$$

conc. of acid

$$= 1.59 \times 10^{-4} \times 1500 \times 10^{-3}$$
$$= 2.385 \times 10^{-4}$$
$$\text{pH} = -\log[\text{H}^+]$$
$$3.42 = -\log[\text{H}^+]$$
$$[\text{H}^+] = 10^{-3.42}$$



ResultsPlus
Examiner Comments

M1 is not awarded as the moles are multiplied by the volume, instead of divided.

The $[\text{H}^+]$ concentration is not evaluated so M2 is not awarded, but M3 (as a TE) is given for the substitution into the expression and M4 (as a TE) is awarded for the final answer.



ResultsPlus
Examiner Tip

Show every step of your calculation in your answer, rather than just putting the numbers in your calculator.

Question 22 (d)(i)

Though there were two marks available here, 70% of candidates did not score a mark. The main reason for not gaining a mark was not referencing the graph or using the vertical portion instead of the part that is nearly horizontal. Where candidates had only referred to the volume of acid at the end of the buffer region one mark was available as a rescue mark. Some candidates chose to mark the buffer region on the graph, which was fine as long as they stated that they had done so in their written answer.

This is an example of a response that did not score.

(i) Explain how this graph shows Tris and its conjugate acid act as a buffer.

(2)

There is a buffer region at the very beginning of the curve where the pH decreases from 9. There is a vertical region in the range of pH 7-5.



ResultsPlus
Examiner Comments

This candidate only refers to the areas of the graph using pHs instead of volumes. No credit could be given for this answer.

This is an example of a response that scores both marks.

(i) Explain how this graph shows Tris and its conjugate acid act as a buffer.

(2)

Since When a volume of 2cm^3 to 16cm^3 of acid is added, the graph shows that the pH stays almost constant, therefore, by the addition of acid, the pH change is negligible. Hence, it acts as a buffer.



ResultsPlus
Examiner Comments

The candidate gives the range of volumes over which the buffer operates for M1 and says "the pH stays almost" for M2.



ResultsPlus
Examiner Tip

If you are asked to explain using a graph, ensure you quote values from it.

Another answer that scores both marks.

(i) Explain how this graph shows Tris and its conjugate acid act as a buffer.

(2)

From volume 4 cm^3 to 16 cm^3 , the gradient is almost zero, meaning there is no significant change in pH.

Therefore, this part shows the buffer action of Tris and its conjugate acid.



ResultsPlus
Examiner Comments

This candidate quotes a smaller range of volumes (M1) and uses gradient to identify the buffer range, then stating the meaning (M2). An excellent answer.

This is an example of the rescue mark being awarded.

(i) Explain how this graph shows Tris and its conjugate acid act as a buffer.

(2)

A large volume of acid is required to neutralise Tris. pH decreases very slightly up to 18 cm^3 of acid added.



ResultsPlus
Examiner Comments

The candidate gains 1 mark for this response, 18 cm^3 is outside the range allowed for M1 but "a large volume of acid" is acceptable for the rescue mark (large volume relative to the titration) only decreasing the pH slightly.

Question 22 (d)(ii)

Nearly 60% of candidates scored this mark. Incorrect answers were seen both above and below the allowed range, and many candidates gave values in the alkaline or acidic buffer regions.

Question 22 (d)(iii)

Just over half of candidates gained the mark for this question. Some went into far more detail than was required, we were expecting a brief explanation of why pH is important to living things. Where candidates failed to score, they did not link their comment to a biological context and just explained what a buffer is or does.

This is an example of a common response that did not gain the mark.

(iii) Suggest a reason why buffers are so important in biological systems.

(1)

To keep the pH constant



ResultsPlus
Examiner Comments

This answer is not linked to a biological context so cannot be awarded the mark.



ResultsPlus
Examiner Tip

Reread your responses to check you have answered the question.

This is an example of a response that goes into more detail than required.

(iii) Suggest a reason why buffers are so important in biological systems.

(1)

Enzymes only work at a certain pH, so buffers are necessary to maintain that pH, as enzymes can get denatured at too high or too low pH.



This candidate has obviously studied enzymes in Biology. Words like "denatured" were not expected or required as they are not on the specification. The first part of the first sentence was sufficient to score.

This is another example of a response that scored the mark.

(iii) Suggest a reason why buffers are so important in biological systems.

(1)

Buffers resist the pH change in the blood, so that cells can work properly.



This is the answer that is on the specification and was expected. No detail is required, just an example of a buffer in a biological context.

Paper Summary

Based on their performance on this paper, candidates should:

- Read the questions carefully, underlining or highlighting key words and using this to structure their answers.
- Practice writing K_a expressions for alkaline buffer molecules and conjugate salts.
- Always give units with their answers.
- Practise deducing the orders of reactions from rates data.
- Practise drawing S_N2 mechanisms, including transition states, for different reactions.
- Practice identifying buffer regions on titration graphs.
- Practise explaining splitting patterns for different organic molecules and be able to predict the products for molecules in different chemical reactions.