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Examiners' Report
June 2018

IAL Chemistry 4 WCH04 01

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June 2018
Publications Code WCH04_01_1806_ER

Introduction

The WCH04 paper assesses entropy and equilibria to show how chemists predict quantitatively the direction of chemical change, how kinetics can quantitatively measure reaction rate and takes further the study of organic chemistry. This paper proved to both provide challenge to candidates and the opportunity to demonstrate their chemical knowledge and ability. This meant that it was an effective discriminator of candidate ability. There was little evidence of candidates running out of time to complete the paper as all questions were attempted to a satisfactory extent.

The mean on the multiple choice was quite high at 15, with questions 4d to 4f being the most challenging to candidates. The questions on the rest of the paper were from a wide range of topic areas, some in a familiar style while other more novel. Those candidates who had revised using past paper questions performed particularly well on the more familiar questions. The good candidates were able to also apply their knowledge and ability to the more novel questions and score highly.

There were numerous instances, as will be evident from the examples that follow, of candidates not addressing the requirements of the question and so not scoring as well as hoped. This was true in all types of question, from data analysis to calculations to descriptive accounts. Candidates desirous of achieving their maximum must apply themselves carefully to the task set and not to what might be perceived to be the case. In addition, chemistry employs a wide range of specialist terms that have particular meaning depending on the context and so attention to detail is required if an otherwise correct answer is not to be ruined by the use of an incorrect term. For example, ionically bonded compounds such as sodium chloride should not be referred to as molecules since this is a term used for covalently bonded molecules.

Question 11 (a)

The responses seen to this question revealed a lack of understanding of the difference between significant figures and decimal places because it was not unusual to see the answer 3.1 despite the question specifically requesting a value to two decimal places. Some candidates wrote "2sf" after their answer. Hence a clear reminder to candidates to read the question carefully and to make sure that the answer given matches the demands of the question.

11 This is a question about weak acids.

(a) Calculate the pH of a 0.0500 mol dm^{-3} solution of propanoic acid given that $K_a = 1.34 \times 10^{-5}$ mol dm^{-3} at 25 °C.

Give your answer to **two** decimal places.

$$CH_3CH_2COOH \rightleftharpoons CH_3CH_2COO^- + H^+$$

(2)

$Ka = \frac{CH_3}{\quad}$

$[H^+] = \sqrt{1.34 \times 10^{-5} \times 0.05}$

$\therefore$ pH = 3.1

ResultsPlus
Examiner Comments

This response scored one mark out of two because the answer is not to two decimal places.

ResultsPlus
Examiner Tip

Make sure that you know the difference between significant figures and decimal places.

Question 11 (b) (i) - (iv)

The parts in this question proved an effective test of a number of skills. The pH calculation was well done with the majority of candidates scoring the mark for part (i).

The sketch required in part (ii) proved much more discriminating as a vertical part of the curve extending to pH = 10-11 and a plateau between 12-12.6 were required.

In part (iii) some candidates gave an accuracy of 4.95 for the pH at half-equivalence point which is not actually achievable from the graph but in this instance was not penalised. It is worth reminding candidates that the value determined should be commensurate with the degree of accuracy of the measurement system. Most candidates who could determine the pK_a value from the graph were then able to determine the K_a value for both marks. Occasionally an answer was given to only 1SF or the answer given had incorrect units and these were penalised.

(b) A 0.0400 mol dm^{-3} solution of pentanoic acid with pH = 3.13 was used in a titration experiment at 25 °C.

A 25.0 cm^3 sample of the pentanoic acid solution was placed in a conical flask and the burette filled with a 0.0400 mol dm^{-3} solution of potassium hydroxide.

(i) Calculate the pH of the potassium hydroxide solution.

[K_w = 1.00 × 10^{-14} mol^2 dm^{-6}]

(1)

$[OH^-] = 0.04$ mol dm^{-3}

∴ pOH = −log (0.04)
= 1.40

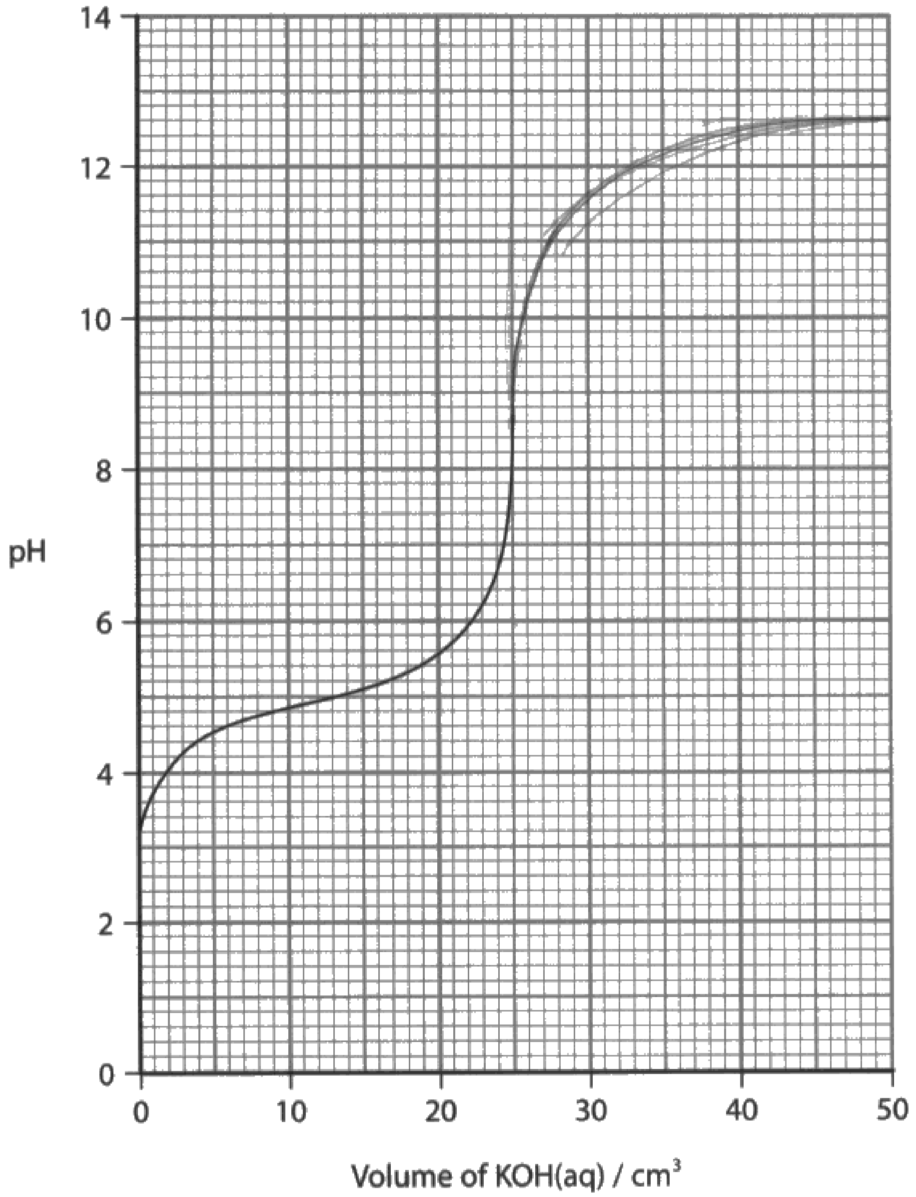
pH + pOH = pKw (pKw = −log (1×10^{-14}) = 14)

=> pH + 1.40 = 14

=> pH = 12.6 [Answer]

(ii) A total of 50 cm^3 of the potassium hydroxide solution was added. Complete the sketch to show how the pH changed as the potassium hydroxide solution was added.

(1)



(iii) From the sketch in part (b)(ii), read off the value of pK_a of pentanoic acid and hence calculate its K_a value at 25 °C.

Give your answer to **two** significant figures.

(2)

pKa = 8
⇒ −log Ka = 8
⇒ log Ka = −8
⇒ Ka = 1×10^{-8}
= 1.0×10^{-8} [Answer]

(iv) Some indicators are

Indicator	pH range
Bromophenol blue	2.8 – 4.6
Methyl red	4.2 – 6.3
Thymolphthalein	8.3 – 10.6
Alizarin yellow R	10.1 – 13.0

From these indicators, choose the best indicator for a titration of potassium hydroxide with pentanoic acid. Justify your choice.

(2)

Thymolphthalein because its pH range is closest to the pH of the ~~reaction~~ equilibrium mixture at equilibrium.

ResultsPlus
Examiner Comments

Part (i) scored one mark for the correct pH calculation. Significant figures were not penalised.

There was no credit given for the sketch in part (ii) because the vertical part of the sketch does not extend to a pH value between 10 and 11.

In part (iii) the pK_a value is determined from the pH at half-equivalence point. The vertical part of the curve which includes the equivalence point is at 25cm^3 and so the pH of the sketch at 12.3 cm^3 is required. This gives a value of 4.9 - 5.0. This response does not have a value in this range and so does not score. There was no transferred error from an incorrect value.

Part (iv) scored one mark for a correct choice of indicator but the justification is not suitable.

ResultsPlus
Examiner Tip

Drawing acid-base titration curves is a useful revision exercise.

Answers to 1SF are rarely acceptable and hence generally to be avoided.

Question 11 (c)

This question proved to be an effective discriminator as all possible scores from 0 to 4 were achieved by at least 15% of the candidates.

The initial number of moles of acid and salt was the 'easiest' mark and most frequently seen. The deduction to determine the equilibrium number of moles of acid was a very common omission. The pH of the buffer could be calculated using the Henderson-Hasselbach equation or not but either method was given full credit. Since the volumes cancel in the expression it was acceptable to use number of moles instead of concentration.

Transferred error was allowed throughout the calculation with the exception that for marking point 4 the pH of the acid buffer given had to be less than 7.

(c) To 25.0 cm^3 of a 0.0600 mol dm^{-3} solution of butanoic acid, 15.0 cm^3 of 0.0800 mol dm^{-3} potassium hydroxide solution was added to make a buffer solution.

Calculate the pH of this buffer solution.

[K_a = 1.50 × 10^{-5} mol dm^{-3} for butanoic acid at 25 °C]

(4)

n_1(butanoic acid) = VC = 0.025 × 0.06 = 1.5 × 10^{-3} mol

n_2(pottassium hydroxide) = VC = 0.015 × 0.08 = 1.2 × 10^{-3} mol

excess n_3(butanoic acid) = 1.5 × 10^{-3} mol − 1.2 × 10^{-3} mol = 0.3 × 10^{-3} mol

$$k_a = \frac{[H^+][CH_3CH_2CH_2COO^-]}{[CH_3CH_2CH_2COOH]}$$

$$C(CH_3CH_2CH_2COO^-) = \frac{n_2}{V} = \frac{1.2\times10^{-3}}{(0.025+0.015)} = 0.03\ mol\,dm^{-3}$$

$$C(CH_3CH_2CH_2COOH) = \frac{n_3}{V} = \frac{0.3\times10^{-3}}{(0.025+0.015)} = 7.5\times10^{-3}\ mol\,dm^{-3}$$

$$k_a = \frac{[H^+][CH_3CH_2CH_2COO^-]}{[CH_3CH_2CH_2COOH]}$$

$$[H^+] = \frac{k_a[CH_3CH_2CH_2COOH]}{[CH_3CH_2CH_2COO^-]} = 3.75\times10^{-6}\ mol\,dm^{-3}$$

$pH = -\log_{10}[H^+] = 5.43$ (3 s.f.)

ResultsPlus
Examiner Comments

This is an example of a response which lays out clearly the working of the calculation. The correct answer is determined and so full marks awarded.

ResultsPlus
Examiner Tip

Always clearly show your working so that if any mistakes are made then credit can be given for any transferred errors.

(c) To 25.0 cm^3 of a 0.0600 $mol\,dm^{-3}$ solution of butanoic acid, 15.0 cm^3 of 0.0800 $mol\,dm^{-3}$ potassium hydroxide solution was added to make a buffer solution.

Calculate the pH of this buffer solution.

[K_a = 1.50 × 10^{-5} $mol\,dm^{-3}$ for butanoic acid at 25 °C]

(4)

moles of butanoic acid = $\frac{25 \times 0.0600}{1000}$ = 1.5×10^{-3} mols.

moles of ~~KOH~~ salt = $\frac{15 \times 0.0800}{1000}$ = 1.2×10^{-3} mols

total volume = 25 + 15 = 40 cm^3

Concentration of acid = $\frac{1.5 \times 10^{-3} \times 1000}{40}$ = 0.0375 $mol\,dm^{-3}$

Concentration of ~~KOH~~ salt = $\frac{1.2 \times 10^{-3} \times 1000}{40}$ = 0.03 $mol\,dm^{-3}$

$K_a = \frac{[H^+][salt]}{[acid]}$ $1.50 \times 10^{-5} = \frac{[H^+][0.03]}{0.0375}$

$[H^+] = 1.875 \times 10^{-5}$

pH = 4.73

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Examiner Comments

A buffer pH of 4.7 was commonly seen and scored 3 marks. There is one error in the calculation; the omission of the calculation of the equilibrium number of moles of butanoic acid in the buffer. Transferred error was applied to the candidate's values and methodology of calculation.

ResultsPlus
Examiner Tip

In any calculation it advisable to make an attempt because credit can often be given for steps carried out correctly despite errors made at certain stages. A blank response will never gain any credit.

Question 11 (d)

A description of buffer activity continues to be a challenging task and results in a polarising outcome. Approximately 30% of candidates either scored full marks or zero. Hence candidate performance on this question was a good indicator of ability.

*(d) A buffer solution was made from ethanoic acid and sodium ethanoate.

Explain why there is no significant change in the pH of the buffer solution when a small quantity of sodium hydroxide is added.

(3)

Buffer solution resists change in pH.
The ammount of sodium hydroxide is negligible and reacts to form salts.

ResultsPlus
Examiner Comments

A definition of a buffer did not gain any credit, nor a vague answer as given here.

ResultsPlus
Examiner Tip

The workings of a buffer solution are challenging to grasp fully but well worth the effort.

*(d) A buffer solution was made from ethanoic acid and sodium ethanoate.

Explain why there is no significant change in the pH of the buffer solution when a small quantity of sodium hydroxide is added.

(3)

When a small amount of sodium hydroxide is added, the OH^- ions from sodium hydroxide that are added causes the equilibrium to shift ~~right; causing~~ Ethanoic acid ~~to~~ dissociate ~~more,~~ producing ~~more of~~ H^+ ions, ~~since OH^-~~ that react with OH^- ions. This reduces $[H^+]$, causing equilibrium to shift ~~to increase~~ to favour the ~~to~~ dissociation of ethanoic acid. This replaces the H^+ ions that reacted with OH^- ions from sodium hydroxide.

ResultsPlus
Examiner Comments

This response scores one mark for the description of the effect of the addition of the sodium hydroxide in terms of the reaction with ethanoic acid and the shift in the position of equilibrium. However, there is no mention of the large reservoir of both ethanoic acid and ethanoate ions, nor of the lack of significant change to their concentration ratio.

Question 12 (a) (i)

Skeletal formulae are another effective discriminator for higher ability candidates. Over 60% of candidates did not score any marks on this question. The errors ranged from drawing formulae with the wrong number of carbon atoms to not drawing ester isomers to drawing the esters given in the question.

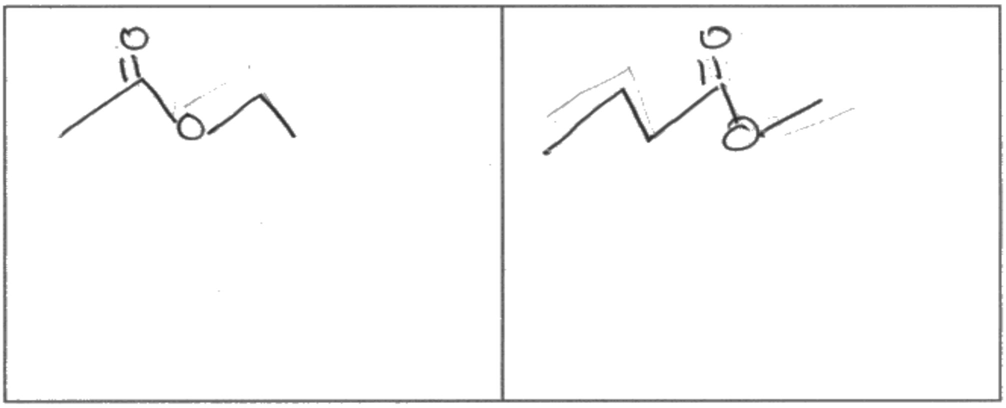
The mantra with the drawing of skeletal formulae is "Practise, Practise, Practise".

12 This is a question about esters.

(a) The esters ethyl ethanoate, $CH_3COOC_2H_5$, and methyl propanoate, $C_2H_5COOCH_3$, are structural isomers, with the molecular formula $C_4H_8O_2$.

(i) Draw the **skeletal** formulae for the two other ester isomers with this molecular formula.

(2)



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Examiner Comments

Neither of these skeletal formulae are correct. The one on the left is actually ethyl ethanoate which is given in the question. The formula on the right has five carbon atoms and so is not an isomer of the esters in the question.

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Examiner Tip

When drawing skeletal formulae, it can be useful to make a small dot at each apex so that the number of carbon atoms in the formula can be easily counted.

Question 12 (a) (ii)

A straight-forward question but roughly 25% of candidates did not score the mark. This is a significant number and suggests that more revision by these candidates would be beneficial.

(ii) Calculate the percentage by mass of carbon in these isomers.

(1)

$$\% \text{ mass} = \frac{12}{88} \times 100$$

$$= 14\%$$

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Examiner Comments

Correct method except that there are four carbon atoms in the isomers and not just one.

Question 12 (b)

A high-scoring question with over 70% being awarded both marks.

(b) Give the name of the reagent that could be used to react with propanoic acid to produce methyl propanoate, and complete the balanced equation. State symbols are not required.

(2)

Name of reagent H_2SO_4

C_2H_5COOH + Methanol ⇌ $C_2H_5COOCH_3$ + H_2O

ResultsPlus
Examiner Comments

Another example where the candidate has not read or understood the question. The 'name' of the reagent is clearly required but a formula has been written. Interestingly the formula given is of the catalyst for the reaction and is not of the reagent which may indicate a lack of understanding of the term 'reagent'.

ResultsPlus
Examiner Tip

The questions are very carefully worded and go through numerous checks to ensure that they are targeting certain requirements. Make sure that you pay close attention to these requirements and meet them.

Question 12 (c) (i)

This question proved an effective discriminator of ability at the middle-top end. A sizeable number of candidates wrote the ionic equation for the alkaline hydrolysis and consequently gave the name of one of the organic products as 'ethanoate' which was perfectly acceptable. Some candidates struggled and gave the equation for the acidic hydrolysis of an ester which did not score. There was no transferred error on the names of incorrect products.

(c) Ethyl ethanoate can be hydrolysed using alkali.

(i) Write the equation for the hydrolysis of ethyl ethanoate using sodium hydroxide and name the organic products.
State symbols are not required.

(2)

~~$C_2H_5COOC_2H_5$~~ $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COO^-Na^+ + C_2H_5OH$

Names of organic products ethanol .... Sodium ethanoate

ResultsPlus
Examiner Comments

It was expected that the names of the organic products would be written beneath their formula but as can be seen in this example, this was not always the case. In this instance it was not penalised.

Question 12 (c) (ii)

There is a reduction in the amount of 'scaffolding' or structure in A2 exam papers because it is felt that candidates at this level should be able to layout their responses in a lucid manner. The responses to this question revealed that this is still something that candidates need to work on. The question clearly asked for justification why NaOH can be viewed as a catalyst and why it isn't. Hence answers should have constructed in such a way to make it clear which argument was being justified but frequently this was not the case as can be seen in the example to follow.

This likely explains the overall poor performance on this relatively straight-forward question as less than 20% scored both marks and just under 50% scored zero.

(ii) One student says that the hydrolysis reaction is catalysed by the alkali.

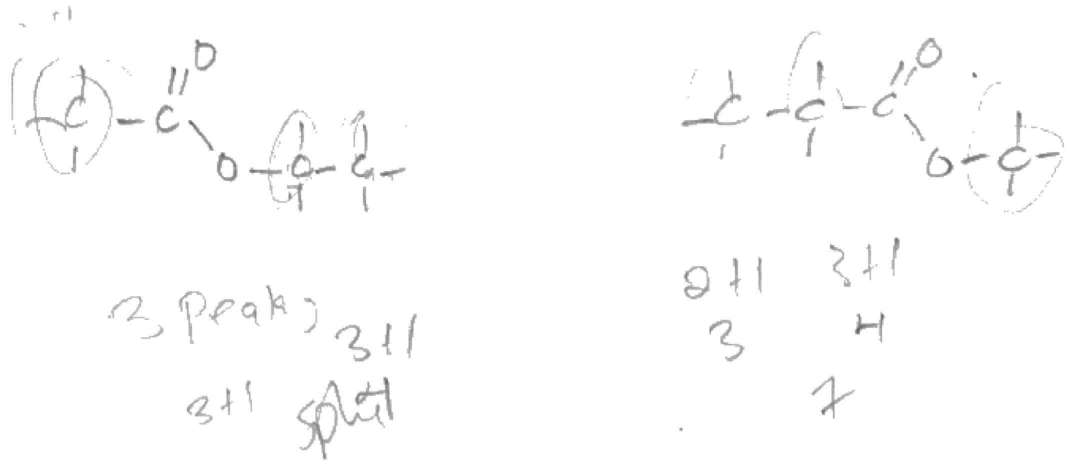
Another student says that the alkali is not a catalyst.

Suggest one piece of evidence in each case that supports the students' statements.

(2)

The reaction occurs and goes to completion when NaOH is added. ~~Showing it~~

A catalyst should be unused at the end of the reaction, NaOH is used up.



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Examiner Comments

This response is one example of many where the answer does not clearly address the question set. The first sentence does not state that this is the justification for the statement that NaOH is a catalyst. It can be inferred from the following sentence, but great care must be taken by examiners in inferring what a candidate might mean. The situation is somewhat alleviated by the fact that the opening sentence is an incorrect statement about a catalyst and so does not score anyway. It was not uncommon to see responses stating that catalysts ensure reactions go to completion, but this is not true. Catalysts speed up reaction rate but do not affect equilibrium.

The second sentence of this response is written in a rather cryptic way in that a correct statement is made about a catalyst being unused at the end but then stating that NaOH is used up. This presumably means that this is an argument for NaOH not being a catalyst. It would have been helpful to the examiner if the candidate had explicitly made this statement.

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Examiner Tip

Make sure that the answer given clearly matches the question asked.

Question 12 (d)

This was a challenging question to answer and to mark. The most common score was 0, followed by 3 marks but all marks within the 0-5 range were scored by an appreciable number of candidates.

A 'compare and contrast' style of question requires two things to be related to each other. It was not uncommon for some candidates to write about the NMR spectrum of one of the compounds in the question but then not to provide any contrast with the other compound. This meant that the only credit available was for the (n+1) rule explanation. Centres would do well to provide repeated practise sessions for their candidates with this type of question. Generally, those candidates who drew annotated diagrams scored higher marks because these helped the response to follow a logical pattern through the comparison.

Candidates often scored both marks for the similarities but marks for the differences were less often awarded.

*(d) Compare the **high** resolution proton nmr spectrum of ethyl ethanoate, $CH_3COOC_2H_5$, with that of methyl propanoate, $C_2H_5COOCH_3$. You should include

- **two** similarities and **two** differences
- information from the Data Booklet, quoting chemical shift ranges for all the peaks
- an explanation for **one** splitting pattern of your choice.

(5)

There are 3 proton environments in ethyl ethanoate. ~~They split~~ The splitting are ~~1:4:4:3~~ 4:4:3

In methyl propanoate there are also 3 ~~proton~~ proton environments. The splitting are 3:4:1

H–C–O ~~peak~~ is 4–3 ppm chemical shift

~~C–H – 6–5 ppm~~

~~CCO3~~ – H–C–C – 0.2 – 1.8 ppm

COO–H – 10ppm –12ppm.

According to (n+1) rule for ~~CH3COO~~ CH3 in ~~CH3~~ CH3COOC2H5. There are 3 hydrogen in the neo neighbouring carbon.

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Examiner Comments

This response scored one mark for the reference to both substances having three proton environments.

The splitting pattern of ethyl ethanoate is incorrect and the comment on the (n+1) does not explain what the splitting pattern is from having an adjacent carbon with three hydrogen atoms.

ResultsPlus
Examiner Tip

It is not sufficient to just state that there are three different environments; these must be identified as either 'proton' or 'hydrogen' environments.

*(d) Compare the **high** resolution proton nmr spectrum of ethyl ethanoate, $CH_3COOC_2H_5$, with that of methyl propanoate, $C_2H_5COOCH_3$. You should include

- **two** similarities and **two** differences
- information from the Data Booklet, quoting chemical shift ranges for all the peaks
- an explanation for **one** splitting pattern of your choice.

(5)

Both $CH_3COOC_2H_5$ and $C_2H_5COOCH_3$ will have 3 peaks as there are 3 proton environments. Both $CH_3COOC_2H_5$ and $C_2H_5COOCH_3$ will have a singlet, a triplet and a quartet. ~~Both will have H–C~~ Protons of CH_3 in $CH_3COOC_2H_5$ will give a singlet ~~as~~ at δ, ~~at~~ 1·8 – 3·0 ppm but protons of CH_3 in $C_2H_5COOCH_3$ will give a singlet at δ 3·0 – 4·1 ppm. The ~~triplet~~ quartet in $CH_3COOC_2H_5$ will be at δ 3·0 – 4·1 ppm but the quartet in ~~$CH_3COOC_2H_5$~~ $C_2H_5COOCH_3$ will be at δ 1·8 – 3·0 ppm. The triplet in both will be at δ 0·1 – 1·9 ppm. The protons of CH_3 in $CH_3COOC_2H_5$ give a singlet as there ~~are~~ is no protons or hydrogens attached to the adjacent carbon atom.

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Examiner Comments

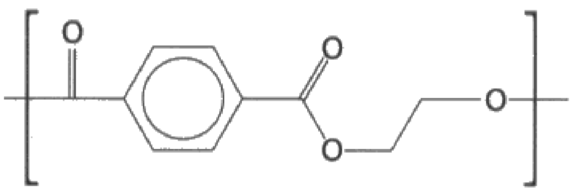
This response scored all 5 marks and is an example of one that was clearly laid-out.

Question 12 (e) (i)

Polymerisation and drawing of monomers remains a worthwhile topic of revision for candidates. Some candidates clearly knew this topic very well and were able to apply their understanding while other struggled. Likewise, the use of skeletal formulae is a beneficial area to practise.

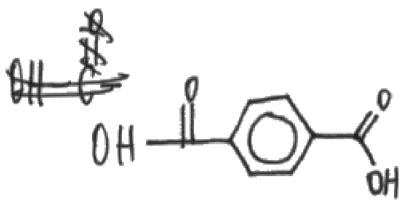
(e) Polyesters are condensation polymers.

(i) The polyester, polyethylene terephthalate, PET, has the following repeat unit.



PET is made from the condensation of two monomers. From the repeat unit shown, draw the structures of these monomers.

(2)

Monomer 1	Monomer 2
	

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Examiner Comments

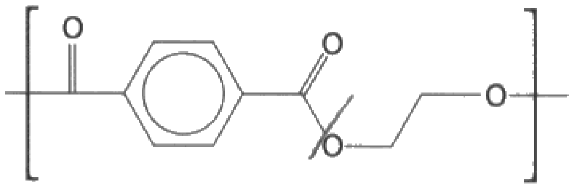
Note that the bond from the carbon clearly goes to the hydrogen of the OH group. This is often penalised when shown so obviously in a horizontal attachment. It was only penalised once and so this response scored one mark out of two.

ResultsPlus
Examiner Tip

Make sure that the point of bond attachment is to the correct atom.

(e) Polyesters are condensation polymers.

(i) The polyester, polyethylene terephthalate, PET, has the following repeat unit.



PET is made from the condensation of two monomers. From the repeat unit shown, draw the structures of these monomers.

(2)

Monomer 1	Monomer 2
	

ResultsPlus
Examiner Comments

The structure of the diol on the right is correct for one mark. The structure on the left has two aldehyde groups instead of two carboxylic acid groups and so did not score.

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Examiner Tip

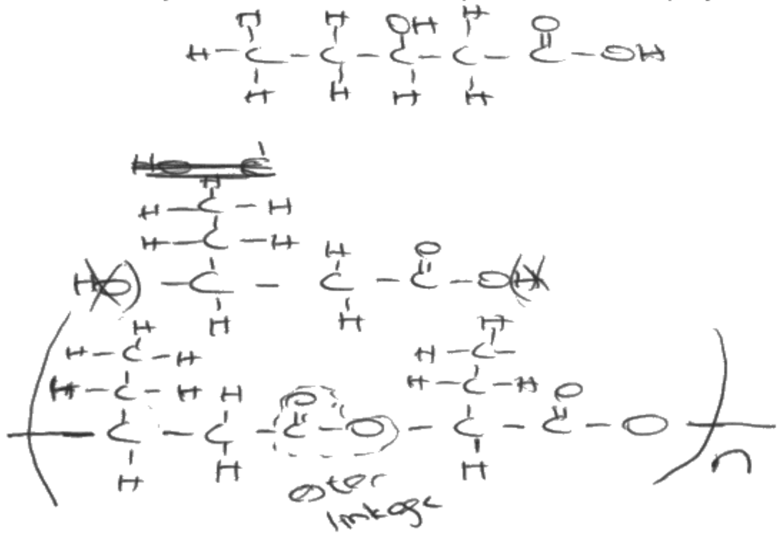
Condensation involves the loss of water and so the reverse must mean the addition of water or H_2O. Make sure that if a H is placed on one 'end' of a monomer then the other 'end' must have an OH added to make up the H_2O.

Question 12 (e) (ii)

This was the more challenging of the polymer questions and just under half of the candidates failed to score. It was disappointing to see the many errors in the 'main body' of the repeat unit. Nonetheless it enabled the more able to score and be differentiated from other candidates.

(ii) A biodegradable polymer can be made using 3-hydroxypentanoic acid as the only monomer. Draw two repeat units of this polymer.

(2)



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Examiner Comments

Use of space for working is fine and to be encouraged. This candidate has written out the monomer in order to deduce the repeat unit and done well. The placement of both oxygens at one end of the polyester was allowed although it is not technically correct as one oxygen comes from the 'alcohol' end and one oxygen from the 'carboxylic acid' end.

Unfortunately, one of the repeat units has a missing CH2 group and so the second mark was not awarded.

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Examiner Tip

Always double-check the drawing of formulae in order to eliminate 'simple' errors.

Question 13 (a)

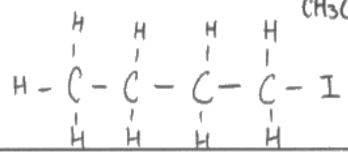
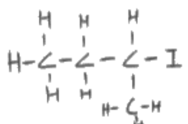
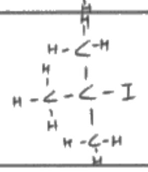
The requirement for structural formulae proved taxing for many candidates. About 40% scored both marks, roughly 40% scored one mark and 20% scored zero.

Hence the drawing of structural formula would seem to be a useful revision exercise for many candidates.

13 Kinetic data obtained from the hydrolysis of halogenoalkanes gives insight into the mechanisms of the reactions.

(a) Draw the **structural** formulae of a primary, a secondary and a tertiary iodoalkane, each with **four** carbon atoms and one iodine atom.

(2)

Classification	Example
Primary iodoalkane	 $CH_3CH_2CH_2CH_2I$
Secondary iodoalkane	 $CH_3CH_2CH(CH_3)I$
Tertiary iodoalkane	 $(CH_3)_3CI$

ResultsPlus
Examiner Comments

The displayed formulae given here would only have scored one mark out of two, but these were viewed as 'working' since there are structural formulae given alongside which score both marks.

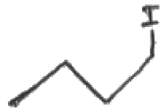
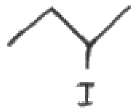
ResultsPlus
Examiner Tip

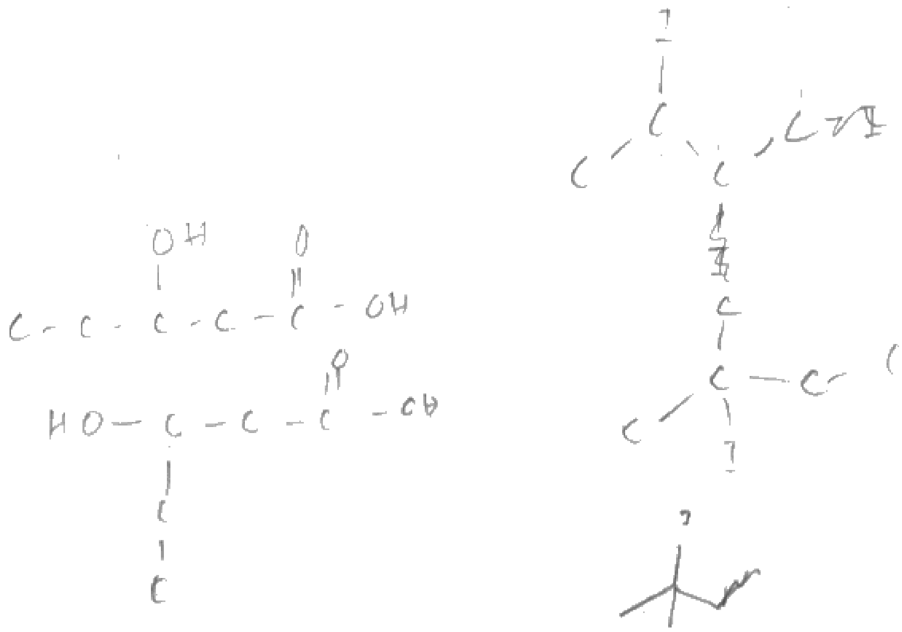
Make sure that the correct type of formulae given in the answer match that required in the question.

13 Kinetic data obtained from the hydrolysis of halogenoalkanes gives insight into the mechanisms of the reactions.

(a) Draw the **structural** formulae of a primary, a secondary and a tertiary iodoalkane, each with **four** carbon atoms and one iodine atom.

(2)

Classification	Example
Primary iodoalkane	
Secondary iodoalkane	
Tertiary iodoalkane	



ResultsPlus
Examiner Comments

Three correct skeletal formulae given but only one mark scored because the question requires structural formulae.

Question 13 (b) (i)

This familiar style of analytical question led to the majority of candidates scoring all four marks. However there remain a significant number of candidates who still forget to link their conclusions with the data/experiments given and so do not score full marks. Hence another useful reminder for centres to give to their candidates.

(b) The halogenoalkane, 1-bromopropane, was hydrolysed at 20 °C with aqueous sodium hydroxide. The results were:

Experiment number	$[C_3H_7Br]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	Rate of reaction / mol dm^{-3} s^{-1}
1	0.010	0.005	0.16
2	0.010	0.020	0.66
3	0.020	0.020	1.34

(i) Deduce the order with respect to 1-bromopropane and the order with respect to hydroxide ions in this reaction.
Fully justify your answers.

(4)

It is first order because when its concentration of C_3H_7Br double while the OH concentration stays constant the rate of the reaction also doubles. The order of C_3H_7Br is first order. The order with respect to OH is also first order because when ~~the OH concentration stays constant and the~~ the C_3H_7Br concentration stays constant and the OH concentration increases 4 times the rate also increases 4 times

ResultsPlus
Examiner Comments

This is an example of a response which did not score maximum marks because there was no justification linked to the table of data. The conclusions drawn were both correct, but the question does require the answer to be fully justified.

ResultsPlus
Examiner Tip

Scientific conclusions should always be based on evidence and thus when a full justification is required the data given must be referred to.

Question 13 (b) (ii)

A one-mark question can be difficult to answer sometimes because it can be a challenge to discern the depth of answer required. An indicator can be the number of lines provided. In this instance there needed to be some statement about the sodium/potassium ions being 'spectator ions' or that 'they do not take part in the reaction'. Only just over half of all candidates gave a suitable answer.

(ii) The replacement of sodium hydroxide with potassium hydroxide has no effect on the results obtained.
What does this indicate about the sodium and potassium ions in the steps of the reaction mechanism?

(1)

They have zero order and no effect on rate.

ResultsPlus
Examiner Comments

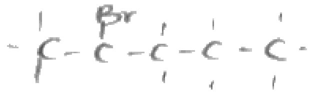
Unfortunately this type of response did not score because it does not go far enough in stating what it is about the sodium/potassium ions that means that they are 'zero order' or 'have no effect on rate'. The lack of effect on the rate is pretty much given in the question. Why do these ions have no effect on the rate?

Question 13 (c)

It was disappointing to see the large number of candidates that drew the wrong nucleophilic reaction mechanism in part (i). It was possible for these candidates to score 2 marks out of the 4 available for parts (i) and (ii). An alternative mark scheme was created to allow for these candidates to obtain credit in part (iii) as they followed through on their mechanism, so it was further frustrating to see a sizeable number of these candidates to make comments on a mechanism that they had not drawn. This confused response was further penalised.

Hence this question provided an opportunity for the more able candidates to demonstrate their true understanding of the subject matter and score highly.

(c) The halogenoalkane, 2-bromopentane, was hydrolysed at 20 °C with sodium hydroxide of similar concentration and the results gave the rate equation

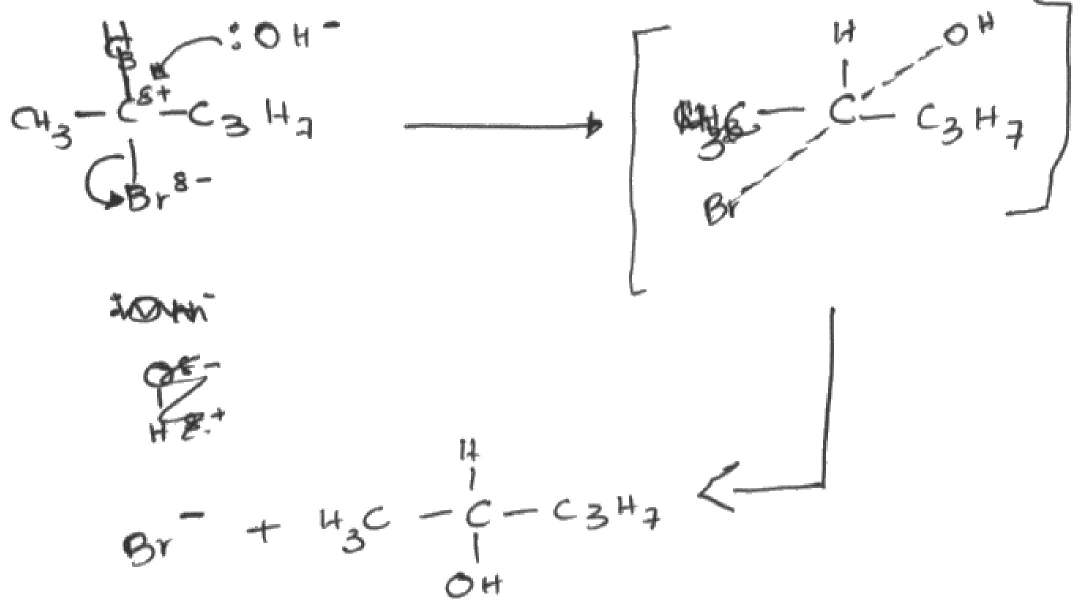


$$\text{rate} = k[CH_3CH_2CH_2CHBrCH_3]$$

(i) Write the mechanism for the hydrolysis of 2-bromopentane. Include curly arrows, and any relevant dipoles and lone pairs of electrons.

You may use R to represent the $CH_3CH_2CH_2$ group.

(3)



(ii) State how your mechanism is consistent with the rate equation.

(1)

~~the order with~~ this is a SN1 mechanism, therefore order with respect to 2-bromopentane is also 1.

(iii) A single optical isomer of 2-bromopentane is hydrolysed by this mechanism. Explain fully whether or not the product of this hydrolysis is optically active.

(3)

This is ~~optically~~ a racemic mixture, and the trigonal planar shape enables the OH⁻ to attack from either side. If plane polarized light would pass straight this mixture.

ResultsPlus
Examiner Comments

In part (i) an S_N2 mechanism is given instead of S_N1. However, two of the three marks were awarded for the curly arrow from the C-Br bond which has the correct dipole, and for the curly arrow from the lone pair of electrons on the hydroxide ion to the carbon atom with the delta positive charge.

No mark was possible in part (ii) because of the incorrect mechanism in part (i).

The comments made in part (iii) were suitable for a S_N1 mechanism but since the candidate has given a S_N2 mechanism only one mark was awarded for the racemic mixture reference.

ResultsPlus
Examiner Tip

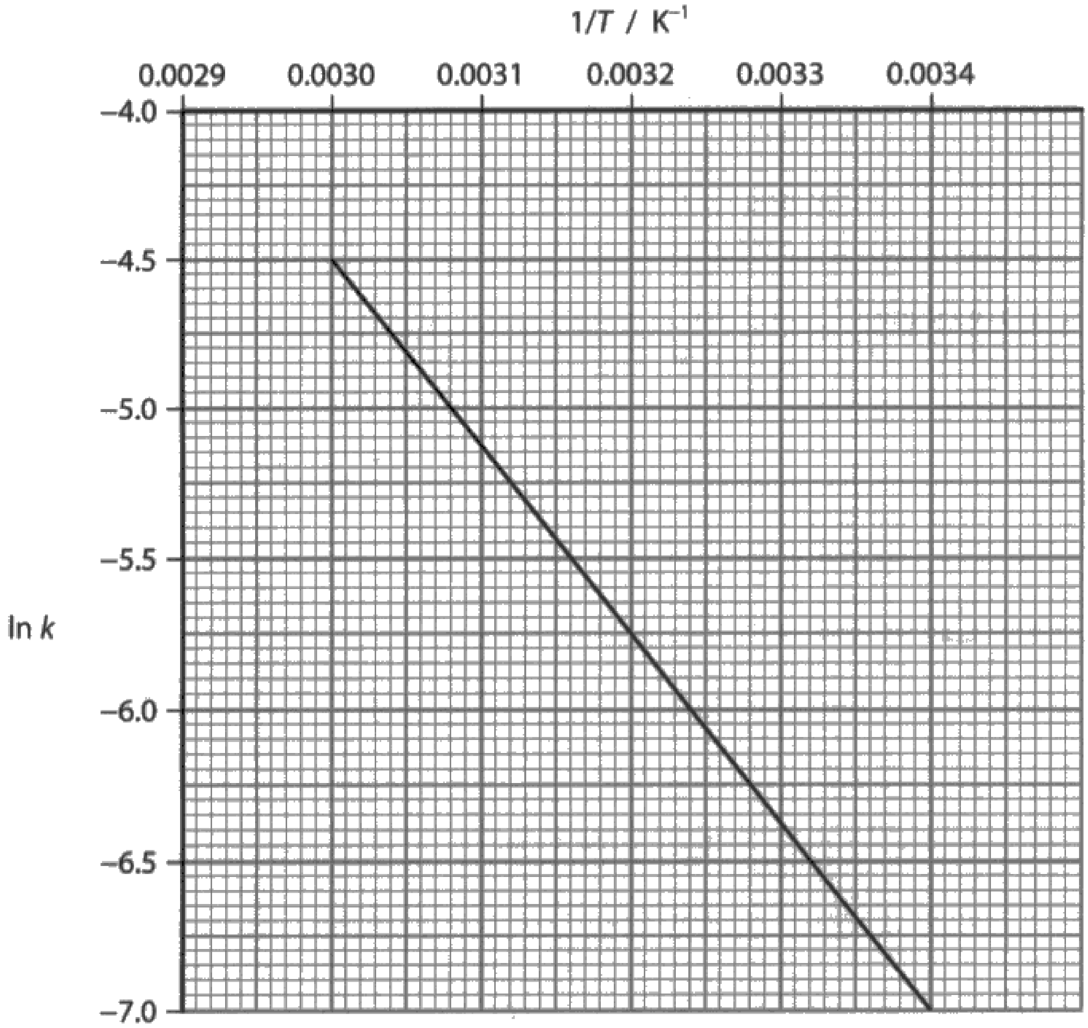
Transferred error can be awarded if the argument/reasoning is followed through.

Question 13 (d)

The wording of any question is important, and it certainly proved so in this instance. The question required "signs and units in your answers", i.e. plural or at least two answers needed signs and units. The question stated that candidates needed to determine the gradient of the line (answer one) and then to use this to calculate the activation energy (answer two).

This somewhat subtle demand of the question proved to be discriminating as generally only the more able candidates discerned the need for sign and units for both values or answers and scored full marks.

(d) The rate constant for the hydrolysis of a halogenoalkane with sodium hydroxide was measured at several different temperatures and the results plotted in the graph shown.



From the graph, determine the gradient of the line and hence calculate the activation energy for this reaction. Include signs and units in your answers.

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant} \qquad R = 8.31 \text{ J K}^{-1}\text{mol}^{-1}$$

(3)

gradient $= \frac{-4.5 - (-7.0)}{0.003 - 0.0034} = -6250$ K

Ea = −R × gradient

= −8.31 × −6250

= 51937.5 J mol⁻¹

ResultsPlus
Examiner Comments

The gradient value has both sign and unit so scores one mark. The activation energy is correctly calculated for a second mark, but it only has units and no sign. Thus there is no third mark awarded.

ResultsPlus
Examiner Tip

RTQ^2 = Read The Question Twice

Question 14 (a) (i)

It remains a source of frustration that many candidates do not adhere to the rubric or the demand of the question. The emboldening of the word 'two' should have emphasized to candidates that they should limit themselves to just two observations. However, a significant number of candidates took a "scatter gun" approach and likely wrote all of the possible observations imaginable. Any incorrect observations were penalised.

In the future all candidates should stick closely to the requirements of the question to maximise their potential.

14 Endothermic changes can be thermodynamically feasible.

(a) One example of an endothermic reaction is between the solids hydrated barium hydroxide and ammonium chloride. An equation for the reaction is

$$Ba(OH)_2.8H_2O(s) + 2NH_4Cl(s) \rightarrow BaCl_2(s) + 10H_2O(l) + 2NH_3(g)$$

(i) Suggest **two** experimental observations that you would expect to make when carrying out this reaction without additional chemical tests.

(2)

Effervesence (gas given off which is $NH_3(g)$ - this turns damp red litmus paper blue).

Liquid formed : $H_2O(l)$. ~~This~~

white precipitate formed: $BaCl_2$.

ResultsPlus
Examiner Comments

Despite the question only asking for two observations, the candidate of this response has given four. Two observations are correct, one is of an additional test and ignored, while one observation (precipitation) is incorrect. The two correct observations would have scored two marks but one of these is negated by the incorrect observation and so this response scored 1 mark.

ResultsPlus
Examiner Tip

Never give more answers/observations than are required in the question as this can results in marks gained being negated.

Question 14 (a) (ii)

This was a familiar question testing the candidates understanding of entropy and done reasonably well. However, a significant number of candidates appeared to miss the fact that the example tested in this question was of ionically bonded salts and not covalently bonded molecules. Hence the use of incorrect terms was penalised and served to differentiate between those candidates who truly appreciated what was being tested and those who didn't.

(ii) Predict the sign of the standard entropy change of the system ($\Delta S^{\ominus}_{system}$) for this reaction and give **two** reasons to justify your prediction.

(2)

$\Delta S^{\ominus}_{system}$ is positive because no. of molecules on product side is greater than no. of molecules on reactant side. Two solid reactants react to produce a solid, liquid and a gas product.

ResultsPlus
Examiner Comments

This response only scored one mark out of two because although there are more moles of products than reactants, these are not 'molecules'.

ResultsPlus
Examiner Tip

Make sure that any chemical terminology used does match the substance(s) referred to.

Question 14 (b)

The series of questions in part (b) were usually well-answered as they were in a similar format to such questions in previous years. However, the errors seen were also similar to those in previous years, namely errors in signs and units. It was fortunate for many candidates that transferred error was applied throughout the parts of this question.

(b) Another example of a reaction between two solids involves anhydrous barium hydroxide and ammonium nitrate. An equation for this reaction is

$$Ba(OH)_2(s) + 2NH_4NO_3(s) \rightarrow Ba(NO_3)_2(s) + 2H_2O(l) + 2NH_3(g)$$

(i) Use the standard molar entropies from your Data Booklet to calculate the standard entropy change of the system ($\Delta S^{\ominus}_{system}$) for this reaction at 298 K. Give a sign and units with your answer.

(3)

ΔSsystem = ΣS°products − ΣS°reactants
= (213.8 + 2(69.9) + 2(192.3)) − (99.7 + 2(151.1))
738.2 − 401.9
= 336.3 J mol⁻¹ K⁻¹

(ii) Use the standard enthalpy changes of formation given in Table 1 to calculate the standard enthalpy change of this reaction at 298 K. Include a sign and units in your answer.

(2)

Table 1

Compound	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$Ba(OH)_2(s)$	−944.7
$NH_4NO_3(s)$	−365.6
$Ba(NO_3)_2(s)$	−992.1
$H_2O(l)$	−285.8
$NH_3(g)$	−46.1

((−992.1) + (−285.8)(2) + (−46.1)(2)) − ((−365.6)(2) + (−944.7))
= −1655.9 − (− 1675.9)
= 20

(iii) Using your answer to (b)(ii), calculate the standard entropy change of the surroundings ($\Delta S^{\circ}_{surroundings}$) for this reaction at 298 K. Include a sign and units in your answer.

(2)

$\Delta S^{\circ}_{surrounding} = \frac{-\Delta H}{T} = \frac{-20 \times 10^3}{298} = -67.11 \ J\,mol^{-1}\,K^{-1}$

(iv) Using your answers to (b)(i) and (b)(iii), calculate the total entropy change (ΔS°_{total}). Include a sign and units in your answer.

(1)

$\Delta S_{total} = \Sigma \Delta S_{system} + \Delta S_{surroundings}$

$= 336.3 + (-67.11) = 269.19 \ J\,mol^{-1}\,K^{-1}$

ResultsPlus
Examiner Comments

The decision in this instance was to only penalise sign and units once in the question parts of (b). This candidate clearly benefits from this because in part (i) there is a missing sign and so one mark is lost but in part (ii) no mark was lost for the missing sign (and units). Likewise, the mark was also awarded in part (iv) despite the missing sign again.

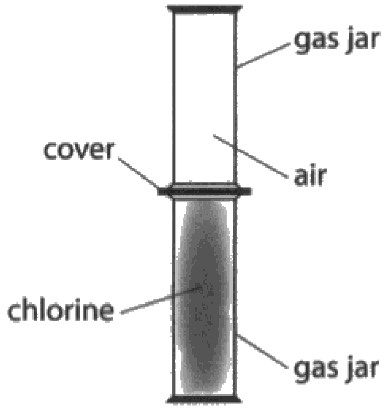
ResultsPlus
Examiner Tip

Missing signs and units will be penalised. The extent of this will depend on the situation and the exam series so the best advice is to always remember sign and units.

Question 14 (c) (i)

This question required a relatively simple demonstration of the principle of entropy and approximately half of all candidates wrote confidently and correctly to score both marks. However, a small but significant number of candidates demonstrated a rather alarming misunderstanding of the situation by referring to the chlorine gas reacting with the air or that chlorine molecules would gain energy from their mixing with air.

(c) The feasibility of chemical changes can be related to entropy in terms of the dispersal of molecules and of energy quanta between molecules.



(i) Describe what happens to the chlorine gas when the cover between the gas jars is removed. Explain the change in terms of entropy.

(2)

It spreads and diffuses with the air in the other jar. This is because The surrounding volume has increased and the particles start colliding with each other

ResultsPlus
Examiner Comments

This response addresses the first part of the question, namely a description of what happens to the chlorine gas for one mark. However, the question specifically asked for reference to the change in terms of entropy and this is lacking in this response. Hence only one mark out of two is scored.

ResultsPlus
Examiner Tip

Re-read your answer and the question to ensure that the answer addresses all aspects required by the question.

Question 14 (c) (ii)

This question tested an introductory aspect of entropy that is often covered in the very first lesson on entropy or in the first few pages of a textbook on entropy. It was perhaps surprising that only 60% of candidates could answer it correctly. It suggests that perhaps more emphasis is needed on the basic understanding of such topics.

(ii) Complete the table to show the five different ways that **four** energy quanta can be shared between two molecules, compared with just a single way for one molecule.

(1)

Molecule A	Molecule B
2	2
3	1
1	3

ResultsPlus
Examiner Comments

There was no real evidence of candidates running out of time in the exam, but the response seen here does raise a doubt in this regard. The candidate has correctly filled in the first empty row in the table but gains no credit because the mark available is for the whole table to be completed. Surely it wouldn't have taken a few seconds to have guessed some numbers for the remaining rows. It is possible that this candidate intended to go back to this question and complete the table but never got round to it. This is a habit that is easy to do but should be avoided.

ResultsPlus

Examiner Tip

Do not leave a question blank with the intention to come back later to fill it in because oftentimes the 'coming back' never happens. Always attempt the question and if you do come back then you can change or amend any answer.

Question 14 (d)

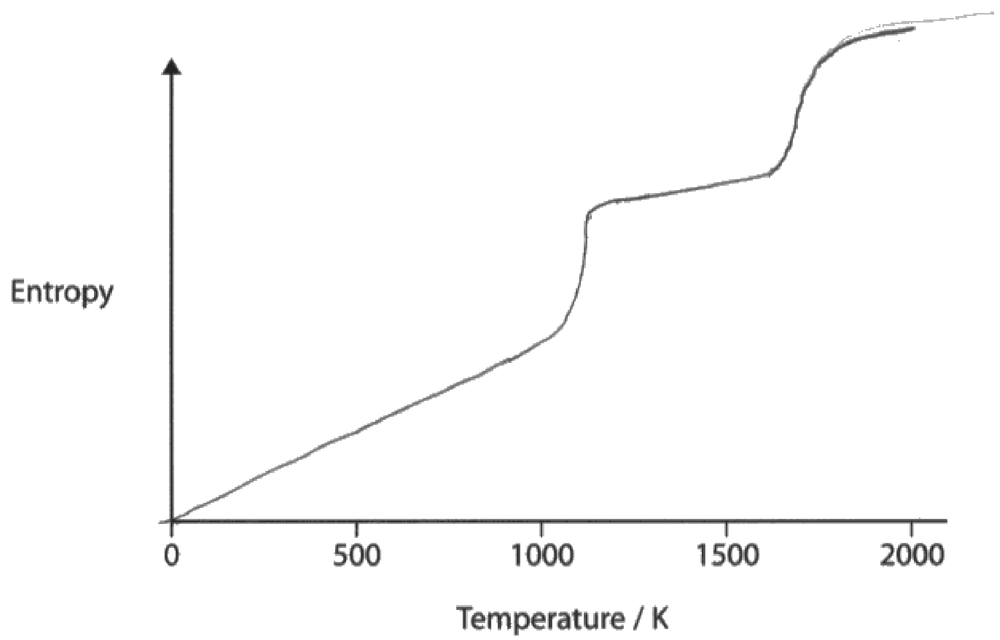
This proved to be a very challenging question which only the top 10% of candidates scored full marks on. As stated on previous questions candidates frequently let themselves down by not addressing all of the requirements of the question. Labels for the significant entropy changes were clearly asked for but commonly missing. The candidates with a poor understanding of entropy revealed themselves with a wide array of graphical shapes for the entropy sketch.

One particular error which is worth noting in the interests of greater understanding is the drawing of horizontal sections. If temperature is increased then the entropy of any substance will always increase and never remain the same. The vibration of the particles and thus their entropy will increase.

(d) Complete the sketch of entropy against temperature for sodium chloride to illustrate the entropy changes as temperature increases, and the sodium chloride changes state.

Use your Data Booklet to find any temperatures where significant entropy changes occur. Label these changes. The vertical axis does not have to be to scale.

(3)



ResultsPlus
Examiner Comments

This candidate has demonstrated a good level of understanding of the changes in entropy with increasing temperature by including two vertical sections and an overall gradual increase. However, one mark has been lost in this response because of a failure to meet one of the requirements of the question, namely to label the significant energy changes. The question referred the candidates to the Data Booklet and so the labels 'melting' and 'boiling' temperatures should have been accompanied by their respective values, 1074K and 1686K.

ResultsPlus
Examiner Tip

Again, the familiar tip is to consider the question on more than one occasion to ensure that the answer meets all of its requirements.

Question 14 (e)

This question was very poorly answered with about 75% of candidates scoring zero. It is impossible to discern if this is due to it being the last question in the exam paper or whether it was due to it being particularly difficult. The responses seen often referred to chemical impossibilities, for example sodium chloride reacting with water to give sodium hydroxide and hydrochloric acid. Other responses referred incorrectly to the dissolving of sodium chloride as being exothermic. These responses reflected a worryingly misunderstanding of chemistry and fundamental concepts. It was felt by examiners that this was more likely due to the pressure experienced in exams and if these candidates were questioned personally then these answers would quickly be corrected. If this is the case, then there is a real need by many candidates to try answering questions under 'exam pressure' in order to get used to working in these situations.

*(e) Explain why the entropy of the system increases when sodium chloride dissolves in water.

(2)

When sodium chloride dissolves the entropy increases as sodium chloride changes to ions dissociates number of molecule increase.

ResultsPlus
Examiner Comments

An example of a response where sodium chloride 'molecules' are referred to which was penalised. In addition, the lack of understanding is highlighted in the response by the statement that sodium chloride 'changes to ions' whereas sodium chloride is always ions in all of the states/forms it exists.

ResultsPlus
Examiner Tip

Make sure that the chemical terminology used is correct for the substance referred to.

Paper Summary

Based on their performance on this paper candidates are offered the following advice:

- RTQ^2 or 'Read The Question Twice' and make sure that the answer written matches the demands of the question
- RYA^2 or 'Read Your Answer Twice' to double-check that your answer does meet all of the requirements of the question
- Use specialist chemical terms carefully and in the correct context to ensure that they are appropriate to the topic area being discussed
- Review the basic understanding or tenets of key concepts such as entropy so that all answers given are in harmony with them
- In extended calculations make sure that the 'workings' are clearly shown so that if necessary credit can be given
- Practise writing different types of chemical formulae such as skeletal and structural repeatedly so that it becomes error-free

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