Examiners' Report
June 2016

IAL Chemistry WCH04 01

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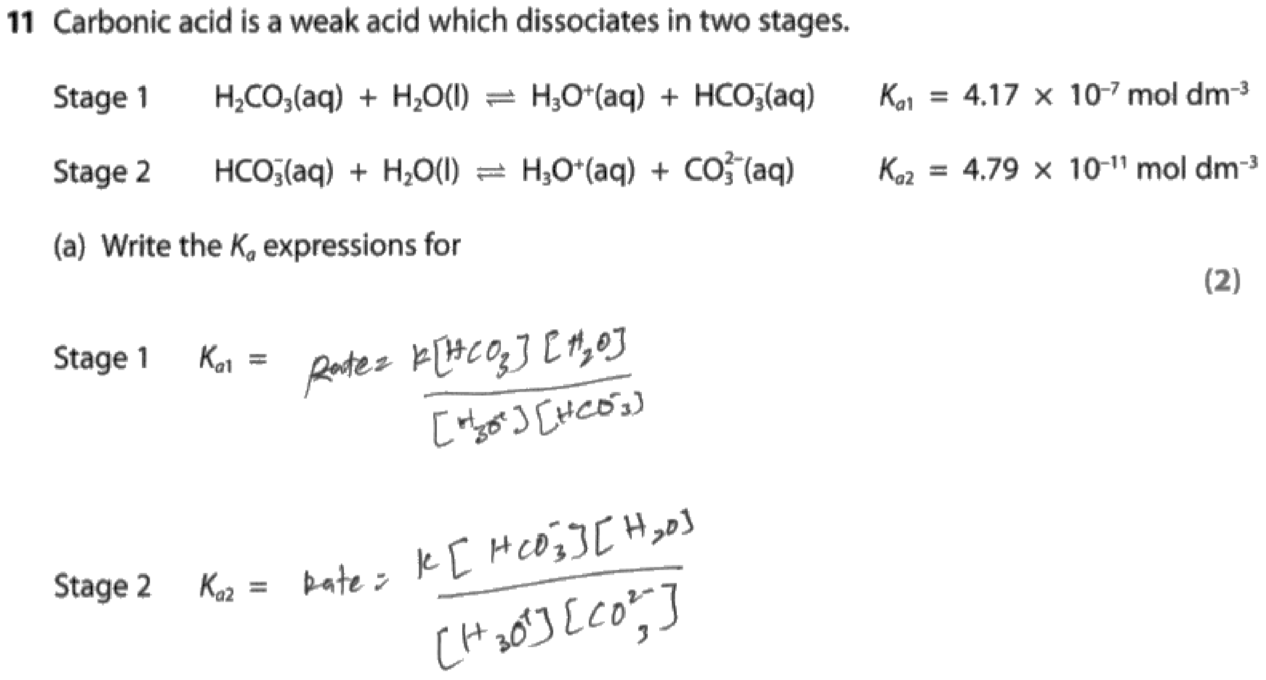
Introduction

This paper was evidently accessible to most candidates as seen from the wide range of marks awarded; it also provided opportunities for candidates to express their knowledge and understanding of topics from unit 4. There were no reports, nor any evidence seen of any candidates lacking the time to complete the paper. The mean of the multiple choice was just over 14/20 with Q6b and Q8b proving to be the most challenging. The ability to clearly explain key ideas and differences proved to be of great significance in determining how well a candidate performed on the paper. This was especially evident in such questions as Q12biv, Q12c, Q13d, Q14e and Q4f. In addition the sketches required for Q11c and Q14g were very discriminatory across the ability range.

Question 11 (a)

A high-scoring question with the majority of candidates scoring both marks; clearly this is a topic area/skill that candidates know well. It was very rare to see the omission of square brackets which was pleasing. Occasionally the charges on the species in the expression were incorrect which should not happen since the species are given in the exam paper immediately above the question space.



11 Carbonic acid is a weak acid which dissociates in two stages.

Stage 1 $H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$ $K_{a1} = 4.17 \times 10^{-7}$ mol dm^{-3}

Stage 2 $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$ $K_{a2} = 4.79 \times 10^{-11}$ mol dm^{-3}

(a) Write the K_a expressions for

(2)

Stage 1 K_{a1} = Rate= $\dfrac{k[HCO_3][H_2O]}{[H_3O^+][HCO_3^-)}$

Stage 2 K_{a2} = Rate= $\dfrac{k[HCO_3^-][H_2O]}{[H_3O^+][CO_3^{2-}]}$

ResultsPlus
Examiner Comments

A rather unusual example of an incorrect response but one that can be learnt from. The first error is that the denominator and numerator are the wrong way round; this was rather rare. The second error is the inclusion of water in the expressions.

The result of the two errors in a two-mark question is that zero marks were awarded.

ResultsPlus
Examiner Tip

All expressions of *K* in their various forms have 'products over reactants' and this phrase is a useful one to memorise.

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0·100 0 0 0

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(a) Write the K_a expressions for

(2)

Stage 1 $K_{a1} = \dfrac{[H_3O^+]}{[HCO_3^-]}$

Stage 2 $K_{a2} = \dfrac{[H_3O^+]}{[CO_3^{2-}]}$

ResultsPlus
Examiner Comments

In this response the concentration of one product is 'put over' the concentration of the other product and obviously does not score.

ResultsPlus
Examiner Tip

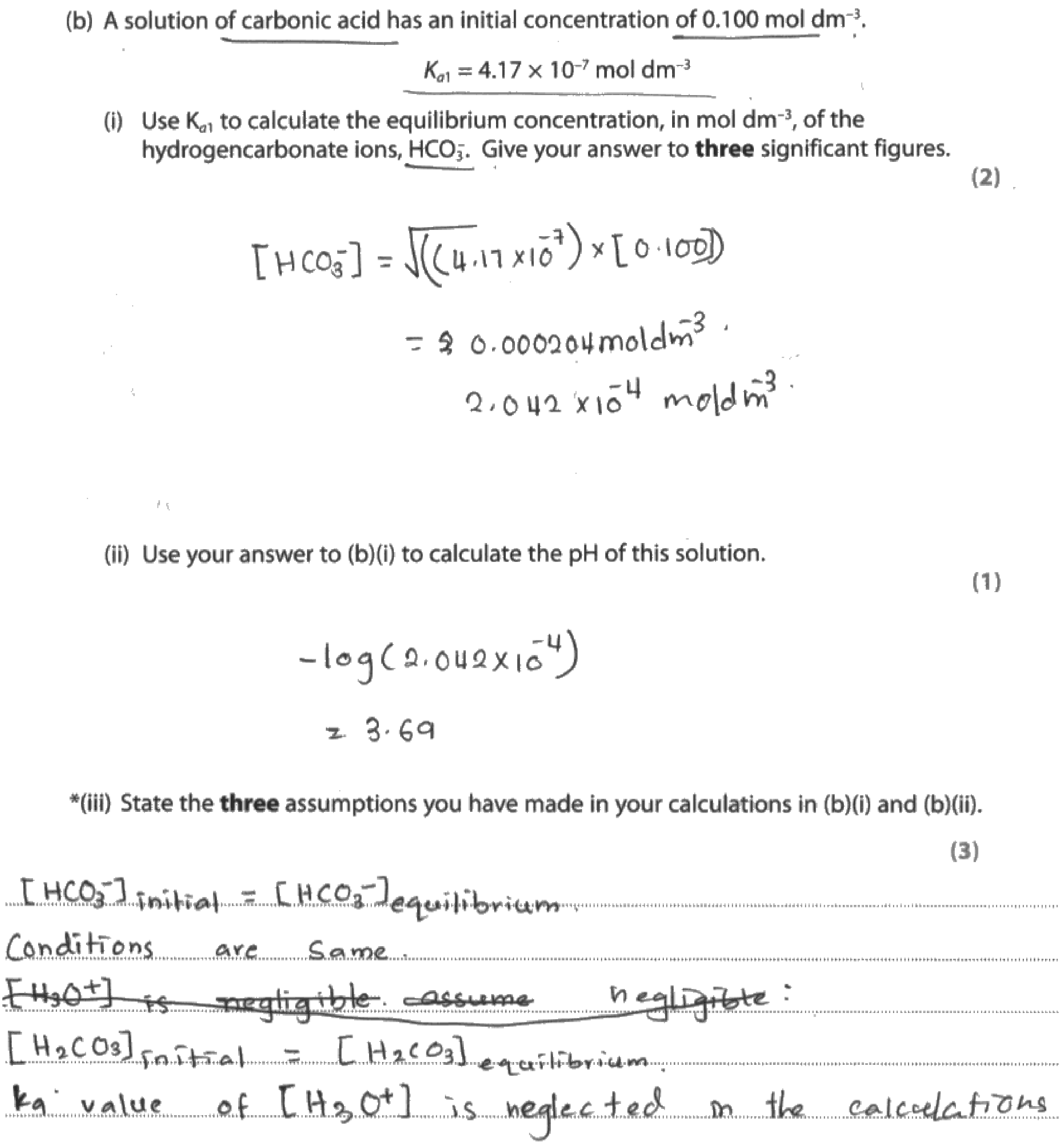
The expression for K_a is used for many calculations and so should be thoroughly learned.

Question 11 (b)

In part (i) the vast majority of candidates could use their Ka expressions to calculate the equilibrium concentration of the hydrogencarbonate ions. At times more than three significant figures were given which was penalised since this request was emboldened in the question.

The pH value calculated in part (ii) should obviously have been less than 7 but a significant minority of candidates apparently forgot that they were dealing with an acid and gave a pH above 7. No transferred error (TE) was allowed for this.

Many candidates scored two marks for two valid assumptions in part (iii). The mark scheme made provision for four possible alternative assumptions. One of the assumptions often missed was that the hydrogencarbonate ion itself does not significantly dissociate which was disappointing since the question had asked for the expression for the second K_a and it was only the very best answers that gave this assumption.



(b) A solution of carbonic acid has an initial concentration of 0.100 mol dm^{-3}.

$K_{a1} = 4.17 \times 10^{-7}$ mol dm^{-3}

(i) Use K_{a1} to calculate the equilibrium concentration, in mol dm^{-3}, of the hydrogencarbonate ions, HCO_3^-. Give your answer to **three** significant figures.

(2)

$[HCO_3^-] = \sqrt{((4.17 \times 10^{-7}) \times [0.100])}$

$= \cancel{2}\ 0.000204$ moldm^{-3}

2.042×10^{-4} moldm^{-3}

(ii) Use your answer to (b)(i) to calculate the pH of this solution.

(1)

$-\log(2.042 \times 10^{-4})$

$= 3.69$

*(iii) State the **three** assumptions you have made in your calculations in (b)(i) and (b)(ii).

(3)

$[HCO_3^-]$ initial = $[HCO_3^-]$ equilibrium

Conditions are same.

~~$[H_3O^+]$ is negligible. assume~~ negligible:

$[H_2CO_3]$ initial = $[H_2CO_3]$ equilibrium

ka value of $[H_3O^+]$ is neglected in the calculations

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Examiner Comments

In part (i) the calculation is all correct except that there seems to be confusion between three decimal places and three significant figures because the answer is given to the former but the question required the latter. Hence only one mark was awarded for this response in part (i).

The pH value determined in part (ii) is correct and scores the mark. Significant figures were not required here but it is worth appreciating the lack of precision that can be given to pH values.

There is only one valid assumption given in part (iii) for one mark.

Question 11 (c)

This was a very effective discriminating question with the full range of marks awarded, allowing candidates of all abilities to gain at least some credit. A number of points are worthy of note:

Four marks out of five were available for a monobasic curve so that candidates who were unable to grasp the concept of a dibasic carbonate were still able to score well.

Question instructions should be adhered to carefully as many candidates lost a relatively easy mark for not labelling their equivalence point despite being clearly told to do so.

It should have been clear from the beginning of this question that a carbonate is not a strong base and so in a titration there will not be a large vertical section. Examiners penalised only those vertical sections of eight pH units or more.

The equivalence point is midway in the vertical section and this should be understood even though some leeway was given in the mark scheme for this annotation.

The question gave the starting pH value, and the final pH value can be easily determined for a strong acid such as hydrochloric acid, thus the starting and end points for the curve should have been easily discernible.

Practise at drawing such titration curves is always advisable and well worth the investment in time and energy.

(c) Carbonic acid forms two types of salt: carbonates and hydrogencarbonates.

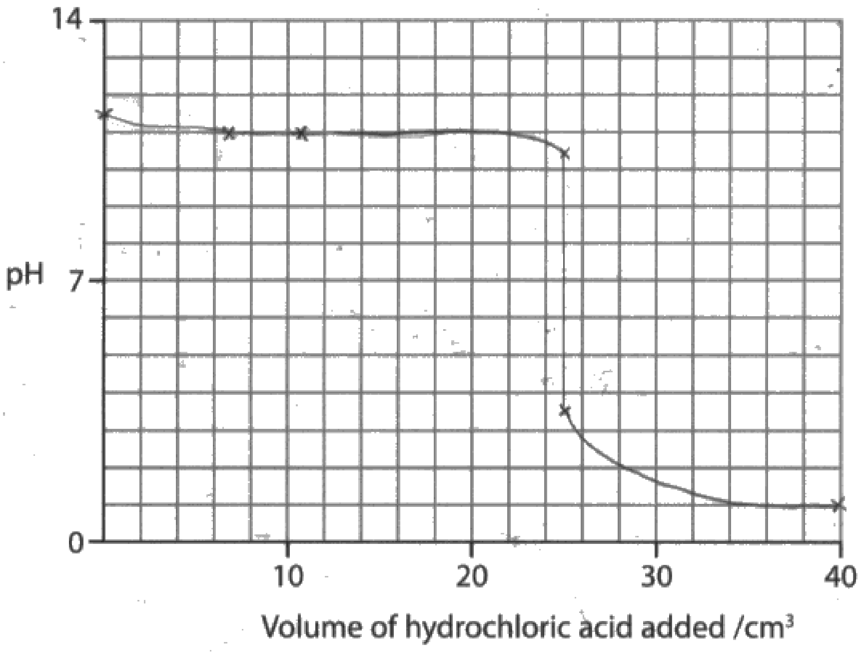
A solution of sodium carbonate is titrated with hydrochloric acid.

On the grid below, sketch the likely shape of the titration curve during this reaction given that:

- carbonates require **two** moles of H^+ ions per mole of carbonate for complete reaction
- 10 cm^3 of sodium carbonate with a concentration of 0.100 mol dm^{-3} is used
- the sodium carbonate solution has a pH of 11.3
- 40 cm^3 of hydrochloric acid with a concentration of 0.100 mol dm^{-3} is added
- $pK_{a1} = 6.4$ and $pK_{a2} = 10.3$

Clearly label any equivalence points in the sketch.

(5)



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Examiner Comments

This response scores 2 marks. The general shape is suitable plus the initial and the final pH values with plateau are correct.
The vertical section is not at either 10 or 20 cm^3 and there is no labelling of an equivalence point.

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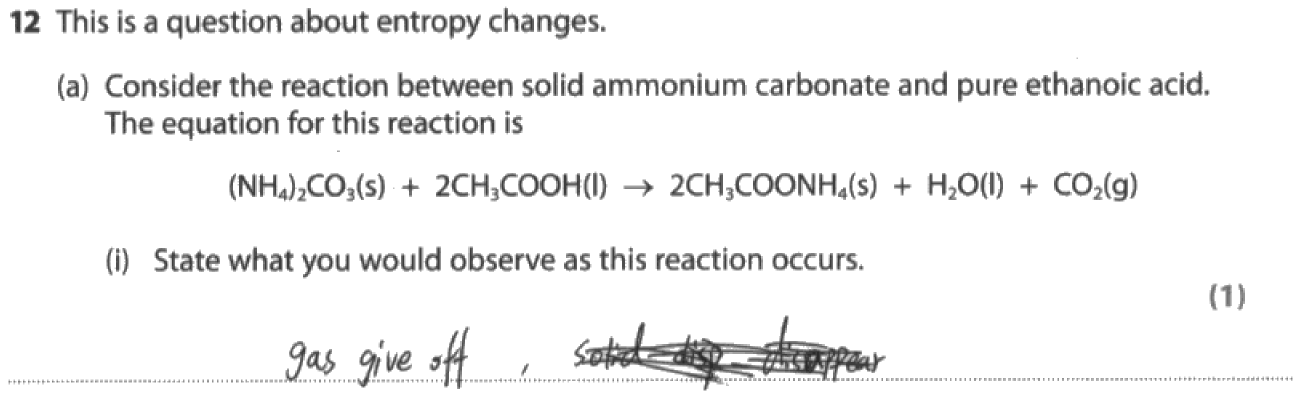
Examiner Tip

Check that all of the information provided in the question is used to construct the response.

Question 12 (a) (i)

Over 80% of the candidates were able to correctly state the observation from an acid plus carbonate reaction which was pleasing.



12 This is a question about entropy changes.

(a) Consider the reaction between solid ammonium carbonate and pure ethanoic acid. The equation for this reaction is

$$(NH_4)_2CO_3(s) + 2CH_3COOH(l) \rightarrow 2CH_3COONH_4(s) + H_2O(l) + CO_2(g)$$

(i) State what you would observe as this reaction occurs.

(1)

gas give off , ~~Solid disp disappear~~

ResultsPlus

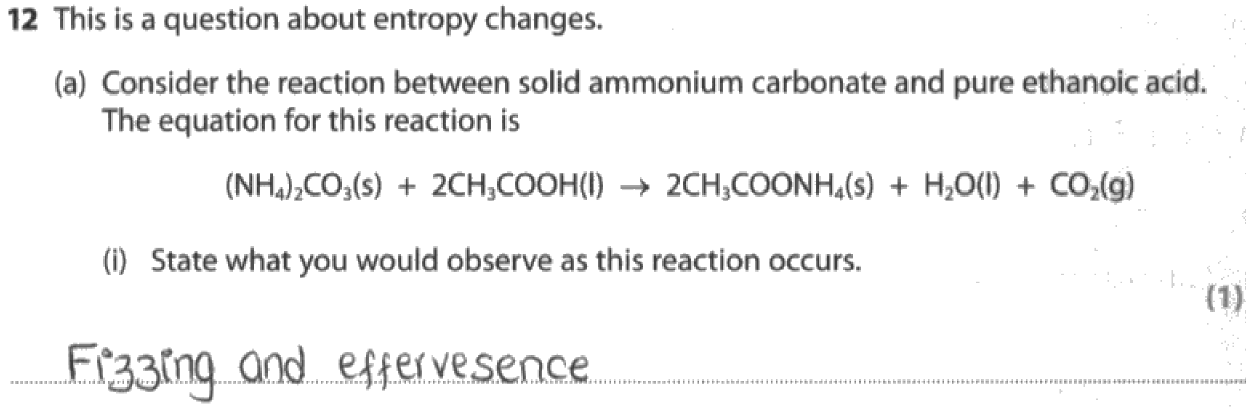
Examiner Comments

This is not an appropriate observation as it cannot be 'seen'.

ResultsPlus

Examiner Tip

It is worth learning observations of chemical tests thoroughly.



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(i) State what you would observe as this reaction occurs.

(1)

Fizzing and effervesence

ResultsPlus

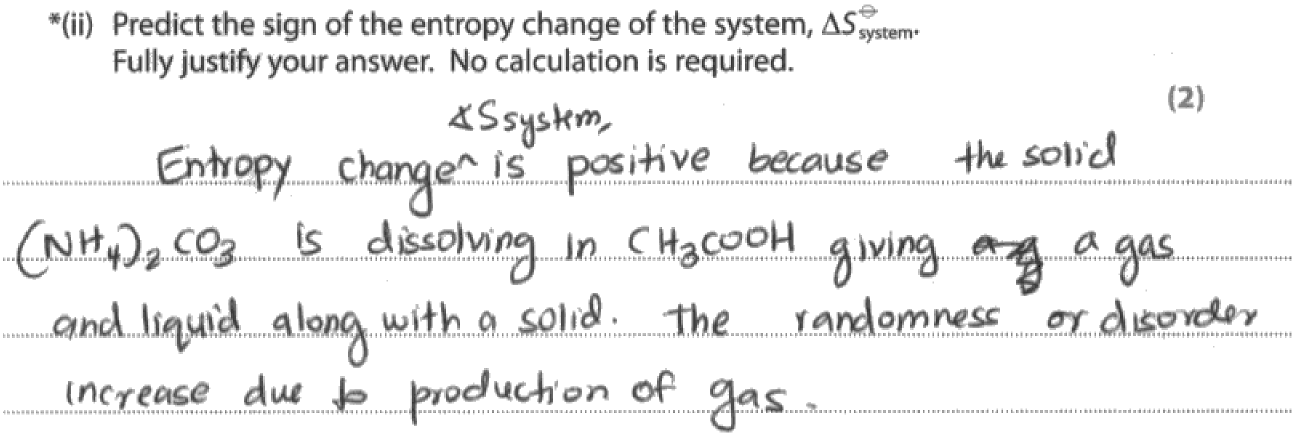
Examiner Comments

Fizzing and effervescence (and bubbling) are alternatives of the same observation. Nonetheless this response obviously scores the mark.

Question 12 (a) (ii)

This proved to be an effective discriminator and gave a good spread of marks. It was insufficient simply to state that the sign of the entropy change was positive as some justification was required. The question did ask for candidates to "fully justify your answer" and the allocation of two marks for this part should have alerted candidates to the need for more than a cursory answer. The tendency was for candidates to give one justification but the better candidates did 'go the extra mile' and by giving two justifications they were subsequently awarded two marks.

On rare occasions answers were given in terms of the increased ways of distributing energy or quanta and this was also awarded credit.



*(ii) Predict the sign of the entropy change of the system, $\Delta S^{\ominus}_{\text{system}}$. Fully justify your answer. No calculation is required.

(2)

Entropy change ΔS_{system} is positive because the solid $(NH_4)_2CO_3$ is dissolving in CH_3COOH giving ~~aq~~ a gas and liquid along with a solid. the randomness or disorder increase due to production of gas.

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Examiner Comments

This is an example of a response where the increase in randomness or disorder was only given a single reason, namely that of the formation of a gas. Hence this response only scores one mark.

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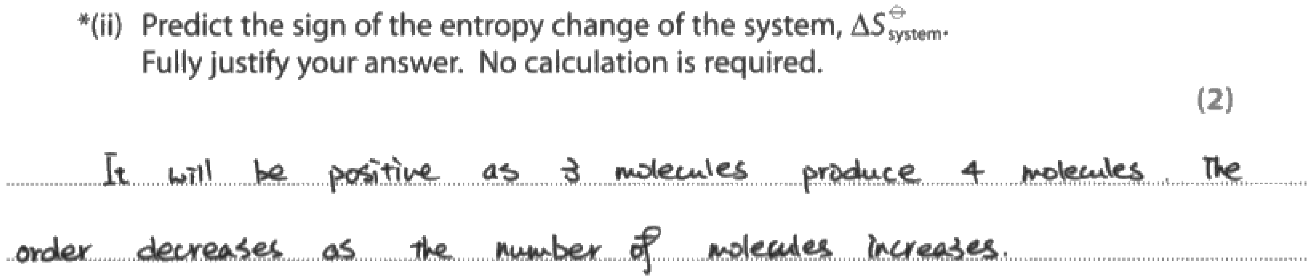
Examiner Tip

Note the wording of the question and the requirement to "fully justify" suggests a more in-depth answer.



*(ii) Predict the sign of the entropy change of the system, $\Delta S^{\ominus}_{\text{system}}$. Fully justify your answer. No calculation is required.

(2)

It will be positive as 3 molecules produce 4 molecules. The order decreases as the number of molecules increases.

ResultsPlus
Examiner Comments

This response also gives one reason for the decrease in order but this time the reason given is the increase in the number of molecules, which was allowed as an alternative for moles. This candidate has avoided the mistake that some candidates made of giving the number of different molecules which would not have scored.

ResultsPlus
Examiner Tip

The number of lines or the space provided for the answer does give some indication of the depth required for the answer.

Question 12 (b) (i)-(iii)

A wide range of scores were seen and thus this proved to be a useful discriminating question.

The usual errors in entropy calculations were seen, namely the omission of the positive sign and the use of incorrect units.

In part (i) the emboldening of "per atom" was ignored by some so that the molar entropy of fluorine was not doubled to give the value for the fluorine molecule, F_2. However the most common error was the use of data for monoclinic sulfur instead of rhombic as required from the question.

At times candidates forgot to convert the enthalpy change to joules per mole by multiplying by one thousand. The other error seen rarely but certainly to avoid was the omission of numerals in the units given, such that J mol^{-} K^{-} was seen instead of J mol^{-1} K^{-1}.

Examiners applied TE to answers in part (iii) so that any errors in the previous parts were not penalised twice.

(b) The rhombic allotrope of sulfur reacts with fluorine to produce sulfur hexafluoride:

$$S(s, \text{rhombic}) + 3F_2(g) \rightarrow SF_6(g) \qquad \Delta H_f^{\ominus} = -1209 \text{ kJ mol}^{-1}$$

(i) Use the standard molar entropies on pages 2, 3 and 29 of the Data Booklet to calculate the standard molar entropy change of the system ($\Delta S^{\ominus}_{\text{system}}$) for this reaction. Include a sign and units in your answer.

Note that the standard molar entropies of the elements are given **per atom** so that the standard molar entropy of fluorine, $S^{\ominus}[\frac{1}{2}F_2(g)] = +158.6 \text{ J mol}^{-1} \text{ K}^{-1}$.

(2)

$\Delta S^{\ominus}\text{system} = \Sigma S^{\ominus}\text{products} - \Sigma S^{\ominus}\text{Reactants}.$

$= SF_6 - 3F_2$

$= +291.7 - (+31.8 + 6 \times +158.6)$

$+291.7 - 983.4$

$= -691.7 \text{ J mol}^{-1} \text{K}^{-1}$

(ii) Use the value of the standard enthalpy change of formation ($\Delta H_f^{\ominus}$) given above to calculate the entropy change of surroundings ($\Delta S^{\ominus}_{\text{surroundings}}$) for this reaction at 298 K. Include a sign and units in your answer.

(2)

$\Delta S^{\ominus}\text{Surr} = -\frac{\Delta H}{T}$

$= -\frac{(-1209) \times 1000}{298}$

$= 4057 \text{ J mol}^{-1} \text{K}^{-1}$

(iii) Use your answers to (b)(i) and (b)(ii) to calculate the total entropy change ($\Delta S^{\ominus}_{\text{total}}$) for the formation of one mole of sulfur hexafluoride.
Include a sign and units in your answer.

(1)

$\Delta S^{\ominus}\text{total} = S^{\ominus}\text{system} + S^{\ominus}\text{Surrounding}.$

$= -691.7 + 4057$

$= 3365.3 \text{ J mol}^{-1} \text{K}^{-1}$

ResultsPlus
Examiner Comments

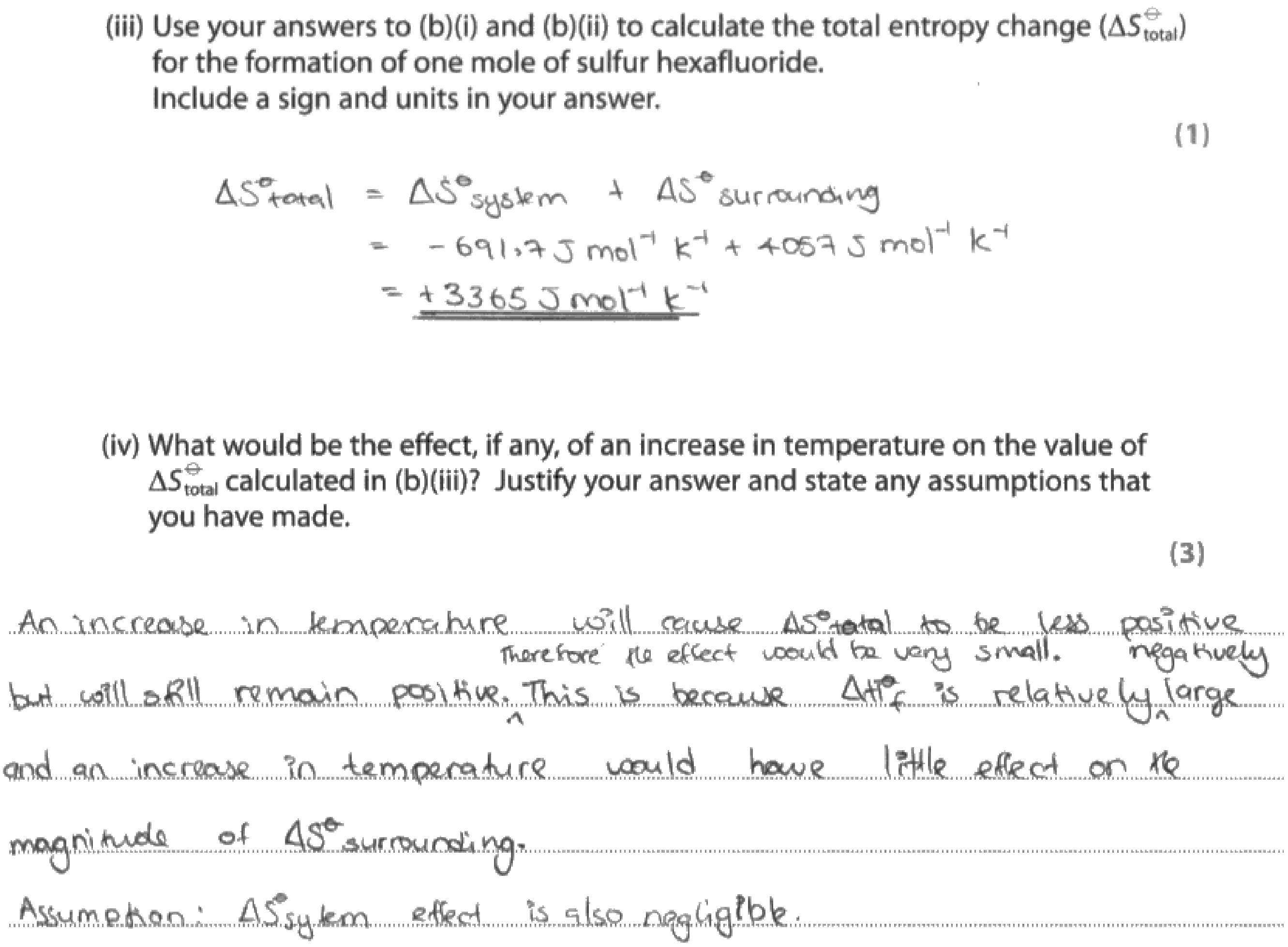
The lack of or use of incorrect units/sign was penalised once only. In this response the numerical answers are all correct but the answer for part (ii) is lacking the positive sign and so was only awarded one mark.

ResultsPlus
Examiner Tip

If the question states "include a sign and units in your answer" then do just that!

Question 12 (b) (iv)

Generally this question was answered well. It is a good reminder for candidates that all entropy changes should be commented on when answering questions of this type. One of the marking points was for the entropy change of the system remaining the same. It appeared that because there was no effective change some candidates did not comment on this. However if something does not have a change or remains the same then this can be a valid statement.



(iii) Use your answers to (b)(i) and (b)(ii) to calculate the total entropy change ($\Delta S^\ominus_{total}$) for the formation of one mole of sulfur hexafluoride.
Include a sign and units in your answer.

(1)

$\Delta S^\circ_{total} = \Delta S^\circ_{system} + \Delta S^\circ_{surrounding}$

$= -691.7\ J\ mol^{-1}\ K^{-1} + 4057\ J\ mol^{-1}\ K^{-1}$

$= \underline{+3365\ J\ mol^{-1}\ K^{-1}}$

(iv) What would be the effect, if any, of an increase in temperature on the value of $\Delta S^\ominus_{total}$ calculated in (b)(iii)? Justify your answer and state any assumptions that you have made.

(3)

An increase in temperature will cause ΔS°_{total} to be less positive but will still remain positive. Therefore the effect would be very small. This is because ΔH°_f is relatively negatively large and an increase in temperature would have little effect on the magnitude of $\Delta S^\circ_{surrounding}$.

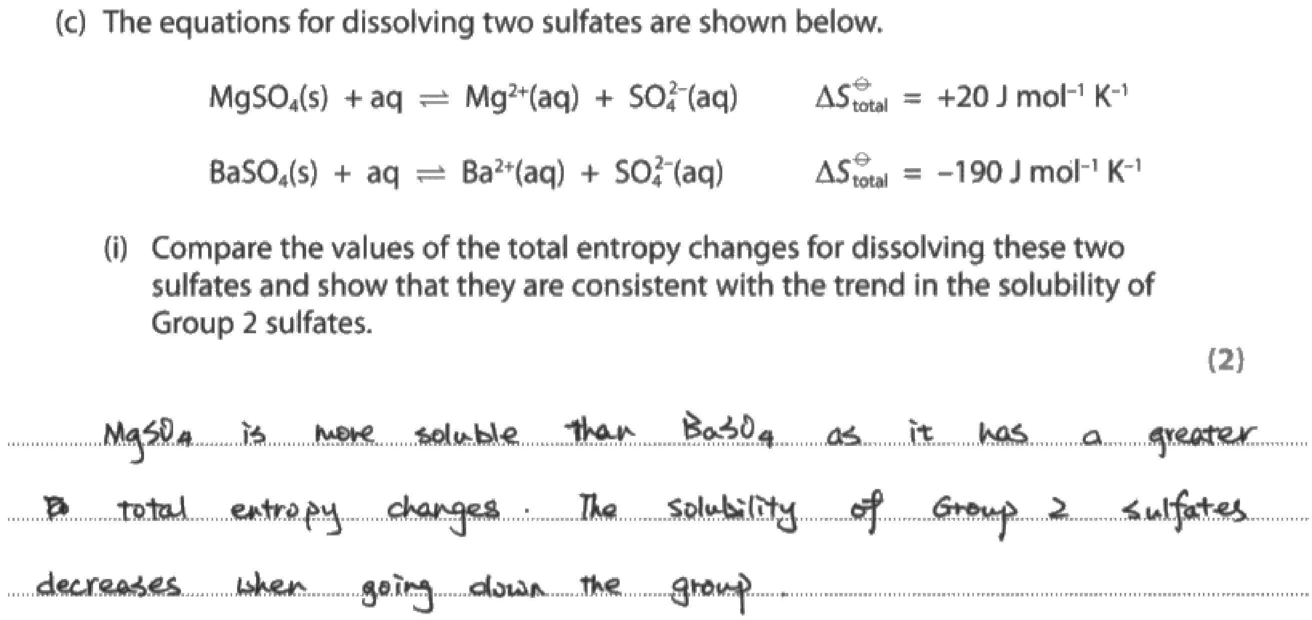
Assumption: ΔS°_{system} effect is also negligible.

ResultsPlus
Examiner Comments

There is an expression that "you can't have it both ways" which is illustrated in this response. Marking point one was awarded for the statement that the entropy of the surroundings becomes less positive and marking point two was awarded for a comment that the entropy of the system was unchanged. In this response the candidate states that there will be very little change in both the entropy of the surroundings and the entropy of the system. Obviously if this statement is taken to mean that there is effectively no change then marking point two can be awarded but if it is taken that there is a change then it's correct for marking point one. It can't be taken to mean one thing for one marking point and another for another marking point.

Question 12 (c) (i)

The answer required in this question needed a comment comparing a negative number and a positive one and care needs to be exercised when doing this because it is insufficient to simply state that the entropy just gets 'smaller' as described below. Occasionally candidates omitted any comment about the second part of the question, namely the trend of sulfate solubility down group 2. Thus this is another reminder to re-read the question in order to make sure that the answer given addresses all that is required.



(c) The equations for dissolving two sulfates are shown below.

$$MgSO_4(s) + aq \rightleftharpoons Mg^{2+}(aq) + SO_4^{2-}(aq) \qquad \Delta S^{\ominus}_{total} = +20\ J\ mol^{-1}\ K^{-1}$$

$$BaSO_4(s) + aq \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \qquad \Delta S^{\ominus}_{total} = -190\ J\ mol^{-1}\ K^{-1}$$

(i) Compare the values of the total entropy changes for dissolving these two sulfates and show that they are consistent with the trend in the solubility of Group 2 sulfates.

(2)

$MgSO_4$ is more soluble than $BaSO_4$ as it has a greater ~~B~~ total entropy changes. The solubility of Group 2 sulfates decreases when going down the group.

ResultsPlus
Examiner Comments

This is an example of a response which did not give the appropriate description when comparing the entropy values. It is important when commenting on negative numbers not just to refer to 'bigger' or 'smaller' as this can be ambiguous.

The trend is correctly stated and so this mark was awarded.

ResultsPlus
Examiner Tip

When referring to negative numbers it is good practice to comment on the magnitude of the value which is unambiguous or to state that the change is to become, for example, 'more negative' or 'less positive'.

(c) The equations for dissolving two sulfates are shown below.

$$MgSO_4(s) + aq \rightleftharpoons Mg^{2+}(aq) + SO_4^{2-}(aq) \qquad \Delta S^{\ominus}_{total} = +20\ J\ mol^{-1}\ K^{-1}$$

$$BaSO_4(s) + aq \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \qquad \Delta S^{\ominus}_{total} = -190\ J\ mol^{-1}\ K^{-1}$$

(i) Compare the values of the total entropy changes for dissolving these two sulfates and show that they are consistent with the trend in the solubility of Group 2 sulfates.

(2)

The total entropy change of MgSO4 ~~a~~ is ~~hegt higher~~ less negative than that of BaSO4 so that as the ~~de de~~ moving down of the elements along the Group 2, the solubility of elements are decreasing.

ResultsPlus
Examiner Comments

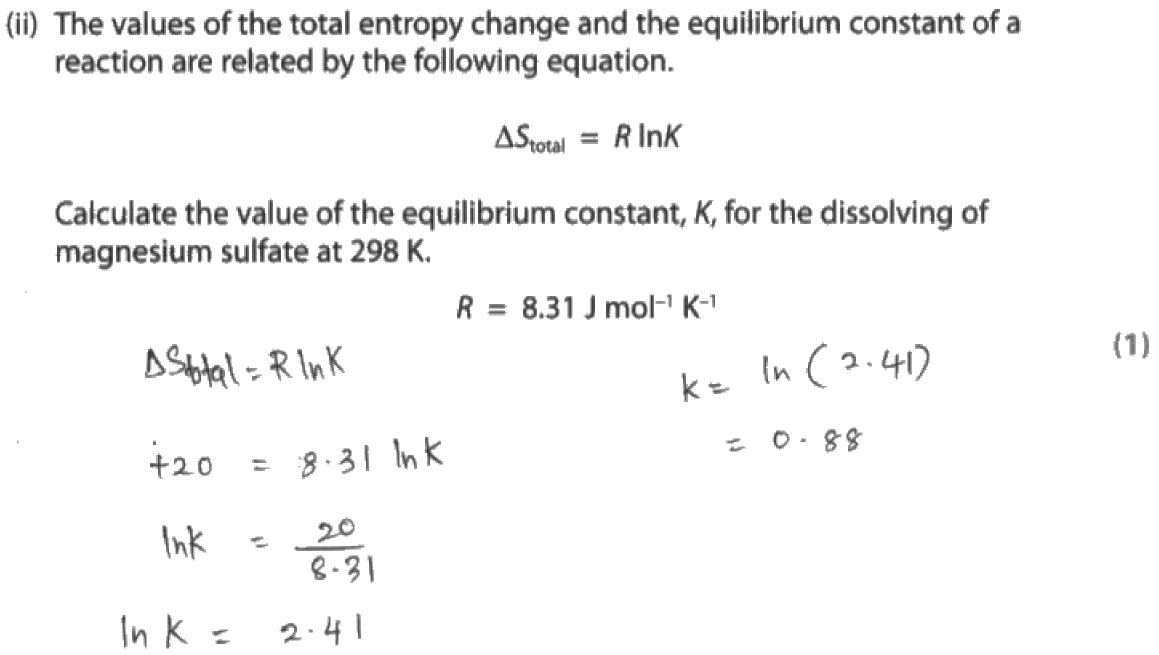
This response illustrates the need to use appropriate terminology at all times. In many ways the 'hard bit' has been done by using the correct comparison between the two entropy values but then the trend is stated with respect to the "elements" and not the sulfates. These are not equivalent and so the second mark is not awarded.

ResultsPlus
Examiner Tip

Avoid over-using abbreviations in case the meaning can be misunderstood.

Question 12 (c) (ii)

While the inverse of logarithms to the base 10 is not unusual, the inverse of a natural logarithm is somewhat novel to candidates nonetheless the better answers were characterised by successfully completing the task. On rare occasions, the process was carried out well but then a rounding error appeared and this was obviously disappointing.



(ii) The values of the total entropy change and the equilibrium constant of a reaction are related by the following equation.

$$\Delta S_{total} = R \ln K$$

Calculate the value of the equilibrium constant, *K*, for the dissolving of magnesium sulfate at 298 K.

R = 8.31 J mol^{-1} K^{-1}

(1)

$\Delta S_{total} = R \ln K$

$+20 = 8.31 \ln K$

$\ln K = \frac{20}{8.31}$

$\ln K = 2.41$

$k = \ln(2.41)$

$= 0.88$

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Examiner Comments

This response is an example where the final answer given is the correct one. The penultimate value of 11.09 is not actually correct because it should be 11.098 but benefit of the doubt is applied here in that the full answer may not have been written down. In any case the final answer of pH =11.1 is correct and is awarded the mark.

ResultsPlus

Examiner Tip

The final answer given is always the one marked so make sure that you are confident that this value is correct.

(ii) The values of the total entropy change and the equilibrium constant of a reaction are related by the following equation.

$$\Delta S_{\text{total}} = R \ln K$$

Calculate the value of the equilibrium constant, K, for the dissolving of magnesium sulfate at 298 K.

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

(1)

$$\frac{\Delta S_{tot}}{R} = \ln K \quad , \quad K = e^{\frac{\Delta S_{tot}}{R}}$$

$$K = e^{\left(\frac{20}{8.31}\right)} = 11.09 \approx 11.1 \,//$$

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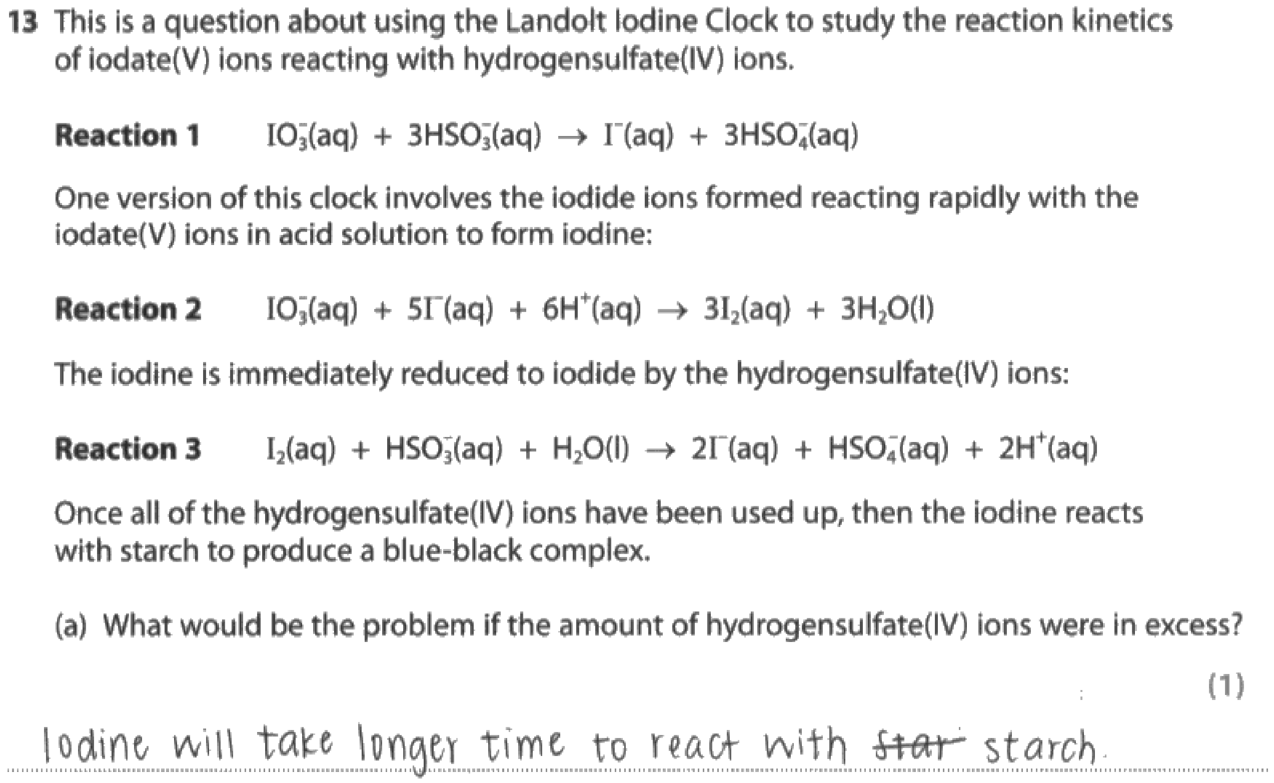
Examiner Comments

The first division step has been done correctly but not the inverse of the natural logarithm and so this response does not score.

Question 13 (a)

Practical work and the understanding of the steps to experimental procedures are always essential to chemistry and its assessment. From some of the answers given it appeared evident that some candidates were not familiar with the 'Iodine Clock' reaction but this is a fairly fundamental example in the study of reaction kinetics and centres are encouraged to carry out such investigations with their candidates. Those who had actually done a practical of this type were more likely to deduce that the issue of the question was that the blue-black complex would not form.



13 This is a question about using the Landolt Iodine Clock to study the reaction kinetics of iodate(V) ions reacting with hydrogensulfate(IV) ions.

Reaction 1 $IO_3^-(aq) + 3HSO_3^-(aq) \rightarrow I^-(aq) + 3HSO_4^-(aq)$

One version of this clock involves the iodide ions formed reacting rapidly with the iodate(V) ions in acid solution to form iodine:

Reaction 2 $IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + 3H_2O(l)$

The iodine is immediately reduced to iodide by the hydrogensulfate(IV) ions:

Reaction 3 $I_2(aq) + HSO_3^-(aq) + H_2O(l) \rightarrow 2I^-(aq) + HSO_4^-(aq) + 2H^+(aq)$

Once all of the hydrogensulfate(IV) ions have been used up, then the iodine reacts with starch to produce a blue-black complex.

(a) What would be the problem if the amount of hydrogensulfate(IV) ions were in excess?

(1)

Iodine will take longer time to react with ~~star~~ starch.

ResultsPlus

Examiner Comments

The iodine would not in fact take longer because if the hydrogensulfate(IV) ions were in excess there would never be iodine to form the complex.

Question 13 (b)

The weaker answers simply stated that Reaction 1 would be 'the rate determining step' but this was insufficient. Candidates needed to state that if this Reaction 1 was the slow step then the kinetics of the entire reaction could be studied. Some excellent responses recognised that if Reaction 1 was not slower than Reactions 2 and 3 then the iodine complex would form too soon.

(b) Why is it important that **Reaction 2** and **Reaction 3** are very much faster than **Reaction 1**?

(1)

To stop the end point ~~come~~ appearing too early.
(So the starch can't react with iodine ions.

ResultsPlus
Examiner Comments

This is an example of a vague response which does not address the main issue and so did not score.

ResultsPlus
Examiner Tip

When engaging in practical work or observing such activities make sure that the reasons for each step of the procedure are clearly understood.

Question 13 (c) (i)

The majority of candidates scored the mark for this question by referring to how temperature affects the rate of a chemical reaction. The most common poor response simply stated that reliability or validity was the issue and did not refer to rate at all.

(c) A series of experiments is carried out in which different volumes of the iodate(V) ions solution are used.

(i) Why is it important that the temperature is kept constant?

(1)

Temperature effects the rate of reaction and the value
of the Rate constant.

ResultsPlus
Examiner Comments

Both statements are correct and make the relevant point so the mark is awarded.

ResultsPlus
Examiner Tip

If two points are made then both must be correct otherwise the concern is that an incorrect one will negate the correct one. Hence make one point clearly and well for this type of reaction.

Question 13 (c) (ii)-(vii)

In part (ii) the graphs were fairly well-drawn with many scoring full marks. The common errors were:

- Omission of the value 1.11 to complete the table; which occasionally happened even though the point was plotted
- The lack of units on the axes
- Failure to extend the line through the origin

The majority of candidates chose a suitable piece of equipment with the appropriate precision in part (iii) but the use of a measuring cylinder and teat pipette were seen in poor answers.

The proportionality of volume to concentration in this practical was likewise understood by most candidates in part (iv).

Part (v) was also high-scoring with first order being commonly identified and a suitable reason being given. Interestingly the reason given was often that the line went through the origin by some candidates who didn't themselves do this. Nonetheless the mark was awarded to avoid penalising twice. On rare occasions the order was given as zero which scored no marks for this part but TE was allowed in part (vii).

The responses to part (vi) were generally not of such a high standard with many vague references to plotting graphs, but not explaining clearly how such could be used to confirm first order. Similarly, reference to constant half-life was frequently seen but no means given of how this would have been determined.

In part (vii) the subject of the rate equation was often given just 'hanging', i.e. without the preface "rate=". This did not score. In addition, a significant number of candidates that had correctly deduced the reaction order of the iodate(V) ions suddenly changed it to third order. These types of question frequently are part of a series of questions that naturally follow-on and so candidates should check that their answers match their earlier deductions. Practice at writing units for rate constants remains an area that candidates need to practice as these were often further sources of error.

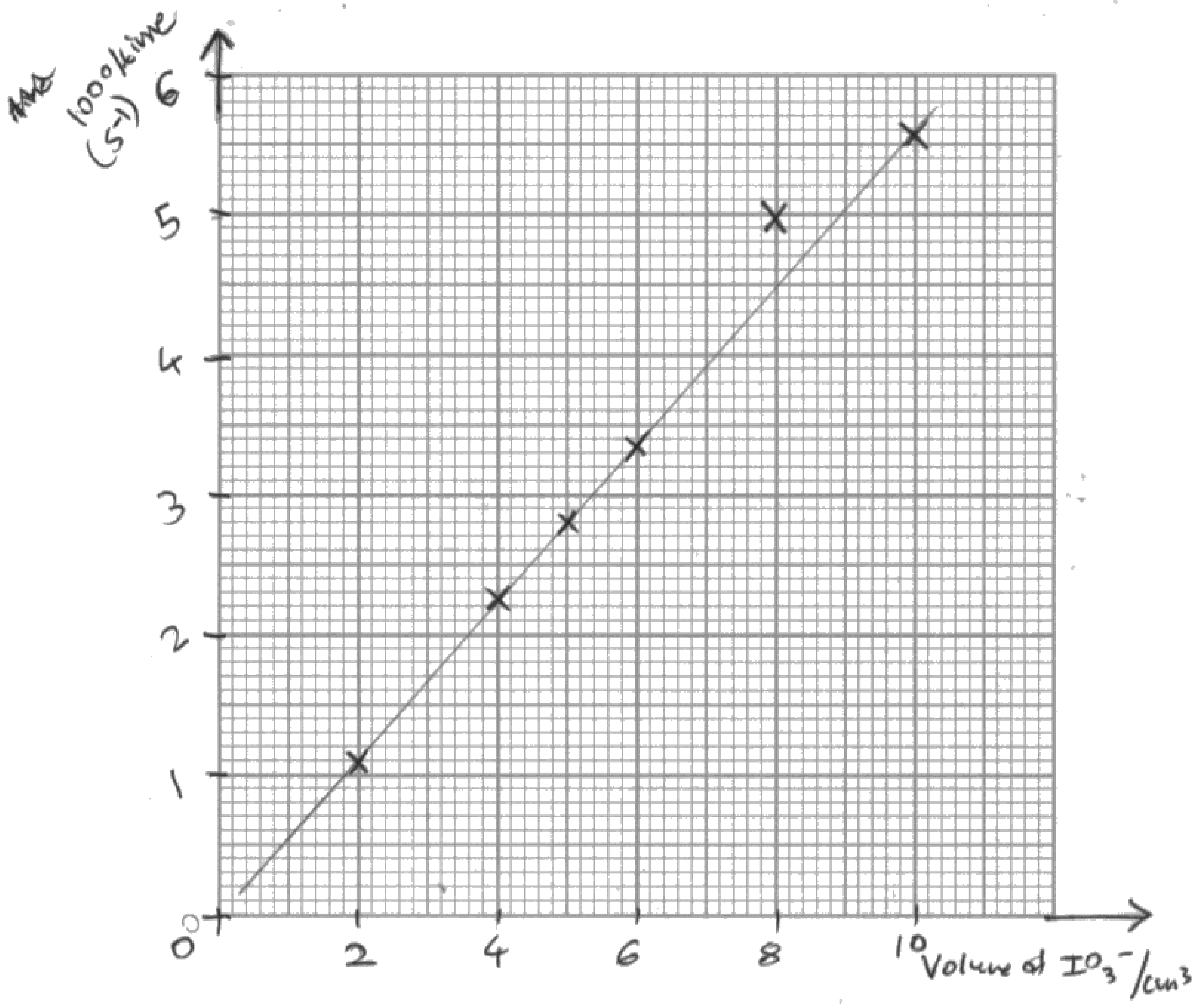
(ii) It is assumed that the initial rate of reaction is proportional to 1/time taken for the blue-black complex to form.

The following results are obtained.

Complete the table and use the results to plot a graph of 1000/time on the vertical axis, against the volume of iodate(V) ions on the horizontal axis.

(5)

Volume of IO_3^-(aq) / cm^3	10.0	8.0	6.0	5.0	4.0	2.0
Time taken, t / s	180	200	300	357	444	900
1000 t / s^{-1}	5.56	5.00	3.33	2.80	2.25	1.11



(iii) Suggest a suitable piece of apparatus for measuring the volume of the solution containing iodate(V) ions.

(1)

burette

(iv) If the total volume of the reaction mixture is kept constant, the volume of the iodate(V) ion solution may be used instead of the concentration to plot the graph.

Explain why this is possible

(1)

if total volume is constant; volume of IO_3^- solution is proportional to concentration of ~~$[IO_3^-]$~~ IO_3^-

(v) Deduce the order of the reaction with respect to iodate(V) ions.

Justify your answer.

(2)

1st order. rate is proportional (directly) to conc of IO_3^- ions. straight slanted line through origin. since $100/t \propto$ vol IO_3^-

(vi) **Reaction 1** is first order with respect to hydrogensulfate(IV) ions. Outline how you would show this.

(1)

double conc of Hydrogensulfite ions, gradient of this graph doubles

(vii) Write the rate equation for **Reaction 1**. State the units of the rate constant.

(2)

Rate equation: rate = $k[HSO_3^-][IO_3^-]$

Units of rate constant $dm^3\,mol^{-1}\,s^{-1}$

$\frac{mol\,dm^{-3}\,s^{-1}}{mol^2\,dm^{-6}}$

ResultsPlus

Examiner Comments

In part (ii) four marks were awarded for the graph. The line does not extend sufficiently to go through the origin even with the margin of error of one small square. There was a missing 'forward slash' from the table to show that one thousand was divided by the time to give the rate but this candidate has correctly inserted it. Since it was missing from the table its omission by a candidate was not penalised.

Parts (iii)-(v) were all correct and scored the relevant marks.

Part (vi) is incorrect since if the concentration doubles for a first order reactant the rate doubles but not the gradient.

The answers for part (vii) are correct for both marks.

Question 13 (d)

This question was an excellent discriminator and certainly gave marks across the whole range.

In part (i) only the better responses mentioned that both time and temperature measurements would need to be taken. If mention was made in this section of temperature in kelvin (K) then this was noted for M1 in part (ii).

The first bullet point in part (ii) stated that the candidates should include how the data is processed. This requires that the temperature measured is converted into K before the reciprocal is taken. This M1 mark was the most frequently omitted mark but if present then it was most likely to be the better quality answer.

The graph to be plotted was ln rate against 1/T and of course because rate is 1/t there was the potential for confusion between the two reciprocal values. Benefit of doubt was given when possible but at times it was clear that the candidate writing 1/T actually meant 1/t or 1/time and so this was penalised. This is obviously a concern and the difference between these two should be continually stressed to candidates.

One mark in part (ii) was for either stating that the line of the graph was a **straight** line or using a drawing. Candidates need to appreciate that the use of words such as 'slope' or even 'line of best fit' do not necessarily mean a straight line and so these were viewed as insufficient on their own.

There was one generous mark for any reference to measurement of the 'gradient' but the sixth mark was for an explanation of the rearrangement of the expression to show how the activation energy can be determined. It was not sufficient to simply state that the equation was to be rearranged. In addition there was a need to show that the gradient, which is a negative number, should be multiplied by a negative value of the gas constant. This was usually only seen in the better answers.

(d) The Landolt Iodine Clock can be used to determine the activation energy of **Reaction 1** using the equation:

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

(i) State the experimental measurements you would make to provide the numerical data for the calculation of the activation energy.

(1)

Keep the temperature constant.

(ii) Describe how you would use your experimental measurements to obtain a value for the activation energy.

$$\begin{array}{ccccccc} \ln \text{rate} & = & -\frac{Ea}{R} & \times & \frac{1}{T} & + & C \\ \downarrow & & \downarrow & & \downarrow & & \downarrow \\ y & = & m & & x & + & C \end{array}$$

You should include

- how the data are processed
- the graph you would plot and its expected shape
- how the activation energy of the reaction can be calculated from the graph produced.

(6)

Firstly we need to calculate the rate of the reaction for different concentrations of IO_3^- and record the values for ln (rate). Then ~~calculate~~ record the time for the blue black complex to form and calculate the value of $1/T$. Plot a graph of ln(rate) on the y-axis and $1/T$ on the x-axis. The graph should be a straight line with a negative gradient. Then calculate the value of the gradient and this value is equal to $(-Ea/R)$ We can then multiply the value of the gradient by the value of the gas constant to get the activation energy for the reaction.

ResultsPlus

Examiner Comments

This response is an example of where 1/T is clearly used in connection with time and so was not given credit.

Three marks were awarded in total, namely one mark for the use of ln rate on the vertical axis, one mark for the graph producing a straight line and then one mark for the reference to the gradient of the line.

ResultsPlus

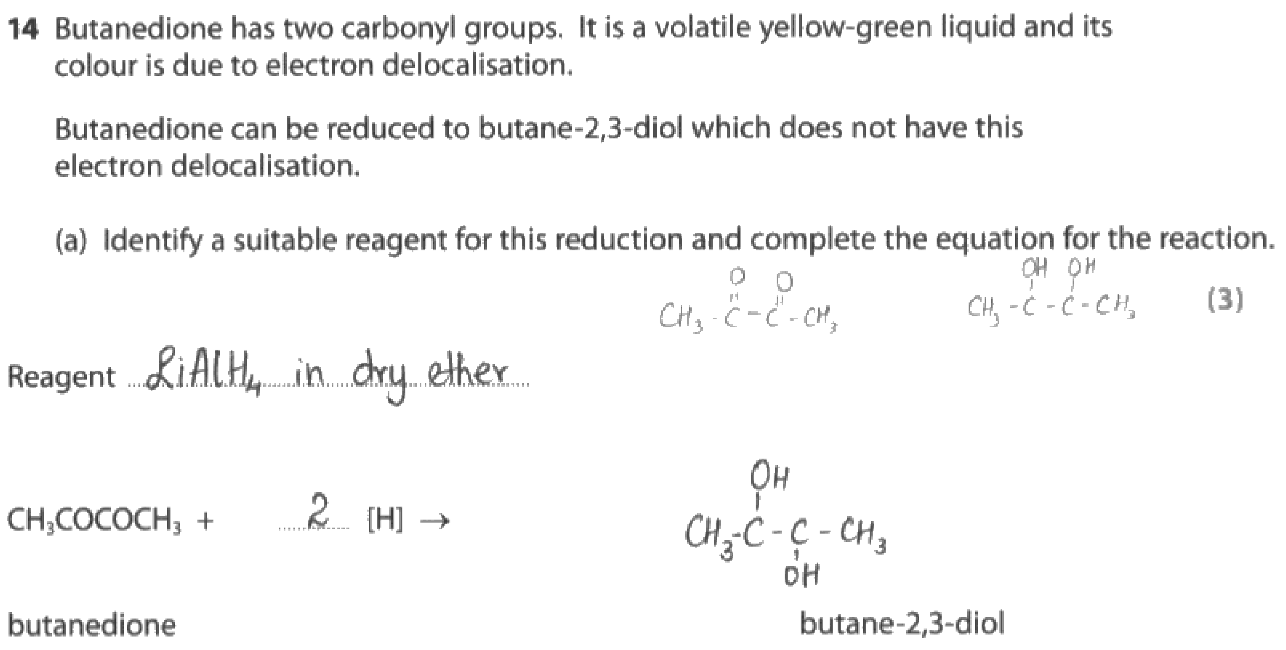
Examiner Tip

Learn and stick to the accepted meanings for abbreviations, for example T = temperature and t = time.

Question 14 (a)

The most common mark scored here was for the reducing agent which could be given by name or formula.

It was disappointing that many candidates could not correctly draw butane-2,3-diol when this could be asked on a unit 2 paper after only one year of A Level study.



14 Butanedione has two carbonyl groups. It is a volatile yellow-green liquid and its colour is due to electron delocalisation.

Butanedione can be reduced to butane-2,3-diol which does not have this electron delocalisation.

(a) Identify a suitable reagent for this reduction and complete the equation for the reaction.

$CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$ $CH_3-\overset{OH}{\overset{|}{C}}-\overset{OH}{\overset{|}{C}}-CH_3$ **(3)**

Reagent LiAlH$_4$ in dry ether

$CH_3COCOCH_3$ + 2 [H] → $CH_3-\overset{OH}{\overset{|}{C}}-\underset{OH}{\underset{|}{C}}-CH_3$

butanedione butane-2,3-diol

ResultsPlus

Examiner Comments

This is an example of a response where one error can lead to another.
A suitable reducing reagent is identified.
However the structure of butane-2,3-diol is drawn incorrectly with two trivalent carbon atoms. The result of this is that only the number '2' is placed before the symbol for the reducing reagent but there was no TE applied in this case.

Hence this response only scored one mark.

ResultsPlus

Examiner Tip

Carbon is in Group 4 of the periodic table and so should have four bonds. If this is mentally repeated then trivalent or pentavalent carbon atoms will be avoided.

Question 14 (b)

The very best answers described in full the colour change. It is worth noting that the answer of just "colour change" is insufficient because it could mean that colour is produced but in this instance the solution goes colourless.

(b) Suggest what you would see when this reaction occurs.

(1)

Colour of solution changes from yellow-green to colourless.

ResultsPlus

Examiner Comments

An excellent answer which scored the mark.

ResultsPlus

Examiner Tip

It is always good to give the 'before' colour and the 'after' colour when describing what would be seen in a reaction.

Question 14 (c)

Poor answers seen here to part (i) simply stated all of the types of intermolecular forces in a scattergun approach or stated that both molecules can form hydrogen bonds instead of just butane-2,3-diol.

In part (ii) the formation of hydrogen bonds **with water** was essential to score the mark.

(c) (i) A mixture of butanedione and butane-2,3-diol can be separated by distillation.

State which compound will have the higher boiling temperature. Justify your answer.

(1)

Butane-2,3-diol

~~Butanedione~~ will have a larger bioiling temperature as it can form 2 hydrogen bonds. which require alot of energy to be broken down. Also since it is large it forms more ~~hyd~~ london forces than butanedione.

(ii) Explain why both compounds are soluble in water.

(1)

Both compounds can form hydrogen bonds with water so therefore it is soluble.

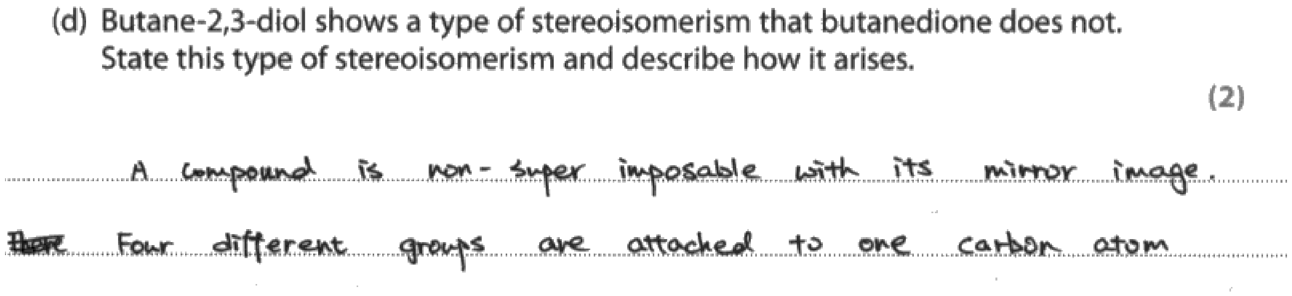
ResultsPlus

Examiner Comments

This response nicely illustrates how candidates correctly referred to the hydrogen bonding of butane-2,3-diol in part (i) and then the hydrogen bonding between both compounds and water in part (ii).

Question 14 (d)

Perhaps surprisingly only just over half of the candidates scored both marks. A third of candidates scored zero and a significant number of these referred to geometric isomerism that reveals a lack of understanding of isomerism. Optical isomerism is a different type of stereoisomerism to geometric isomerism and the chemical differences are profound so it is vital that candidates correctly understand the difference.



(d) Butane-2,3-diol shows a type of stereoisomerism that butanedione does not. State this type of stereoisomerism and describe how it arises.

(2)

A compound is non-super imposable with its mirror image.

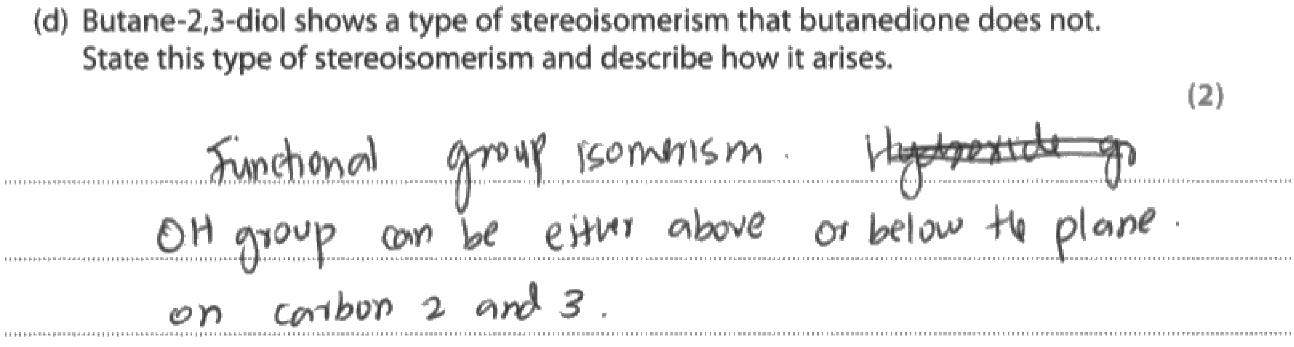
~~There~~ Four different groups are attached to one carbon atom

ResultsPlus
Examiner Comments

In this response the candidate has omitted to state the type of isomerism but does give an acceptable description. Thus only one mark was awarded.

ResultsPlus
Examiner Tip

Don't just gain the 'hard marks' but make sure that the 'easy ones' are gained as well.



(d) Butane-2,3-diol shows a type of stereoisomerism that butanedione does not. State this type of stereoisomerism and describe how it arises.

(2)

Functional group isomrism. ~~Hydroxide gp~~

OH group can be either above or below the plane.

on carbon 2 and 3.

ResultsPlus
Examiner Comments

Unfortunately this response reveals a misunderstanding about the nature of single bonds as these are freely able to move and rotate. Thus the position of the alcohol groups either 'up' or 'down' in the diagram is not important. Hence this response did not score.

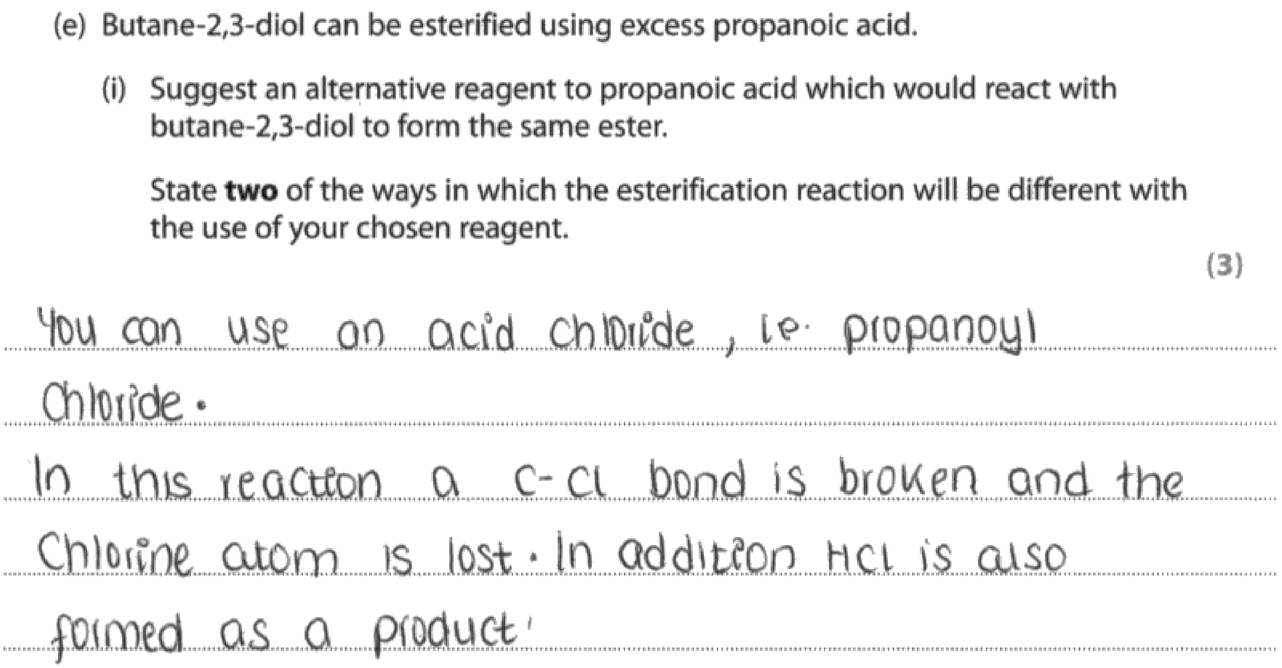
ResultsPlus
Examiner Tip

The effects of such things as steric hindrance can give a group a preference on a particular 'side' of the carbon chain but it is only bonds such as double bonds that are unable to rotate where their position is generally fixed with respect to carbon chain.

Question 14 (e) (i)

The full range of marks was seen on this question. A good answer was characterised by clear statements of the differences between the use of propanoic acid and the use of propanoyl chloride for esterification.

It should be noted that spellings which can be understood to be different substances will not gain credit. For example some candidates gave the esterifiying reagent as "propyl chloride" which is a halogenoalkane and would not work. This did not gain credit. Likewise the product from the use of an acyl chloride is not hydrochloric acid but hydrogen chloride.



(e) Butane-2,3-diol can be esterified using excess propanoic acid.

(i) Suggest an alternative reagent to propanoic acid which would react with butane-2,3-diol to form the same ester.

State **two** of the ways in which the esterification reaction will be different with the use of your chosen reagent.

(3)

You can use an acid chloride, ie. propanoyl Chloride.

In this reaction a C-Cl bond is broken and the Chlorine atom is lost. In addition HCl is also formed as a product.

ResultsPlus

Examiner Comments

The reagent mark is obviously awarded for a clear opening sentence.

The reference to the C-Cl bond being broken is not an appropriate difference and so was ignored. The reference to HCl being produced was acceptable but it should be noted that really for a difference to be given there should have been the comment that this was instead of H_2O, which is made if propanoic acid is used for esterification. However in this instance just the reference to HCl alone sufficed.

ResultsPlus

Examiner Tip

When stating any differences it is always best to state the two contrasts, i.e. what happens with one and what happens with the other.

(e) Butane-2,3-diol can be esterified using excess propanoic acid.

(i) Suggest an alternative reagent to propanoic acid which would react with butane-2,3-diol to form the same ester.

State **two** of the ways in which the esterification reaction will be different with the use of your chosen reagent.

(3)

Esterification is Slower with the reaction of butene-2,3-diol and Propanoic acid ~~hot~~ at room temperature. But if the ~~two~~ reagents where Acylchloride and buten-2,3-diol would react must faster to form an ester at room temperature.

- butene-2, 3-diol + Propanoic acid $\xrightarrow{\text{Slow}}$ ~~Propanoyl chloride~~ Ester
- butane-2, 3-diol + ~~Acyl~~ Propanoyl chloride $\xrightarrow{\text{faster}}$ Ester

ResultsPlus

Examiner Comments

This response was awarded two marks.

The reagent is initially simply termed an "acyl chloride" which would have been insufficient but towards the end of the response it is named for the mark.

There is actually only one difference given which is the whether the reaction was faster or slower since the use of heat amounts to the same point.

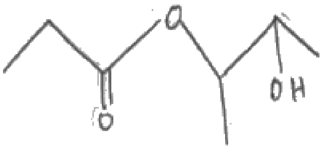
Question 14 (e) (ii)

Only a third of candidates could score both marks on this question, with just over half not gaining any credit. This is typical of questions involving skeletal formulae as these can be very challenging. Candidates who wrote out the formula in a displayed way as 'working' in order to determine the correct skeletal formula were by far the more successful.

The bond angles and bond lengths given were not penalised but at times it was possible that these actually hindered candidates and so candidates are also encouraged to take care with the way that their formulae are drawn.

(ii) Draw the **skeletal** formula of the ester produced from butane-2,3-diol and **excess** propanoic acid.

(2)



ResultsPlus
Examiner Comments

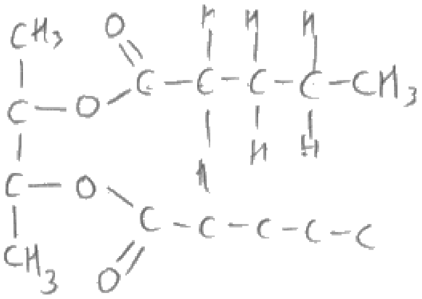
In this example the emboldening of the word "excess" seems to have been missed because there is only a single esterification. Hence only one mark was awarded.

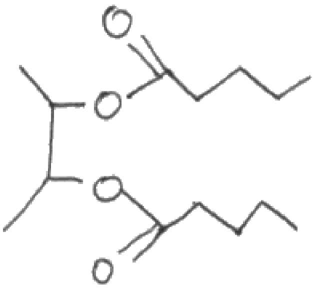
ResultsPlus
Examiner Tip

Questions only occasionally have emboldening to emphasize words and so when it is done then these words must be particularly crucial.

(ii) Draw the **skeletal** formula of the ester produced from butane-2,3-diol and **excess** propanoic acid.

(2)





ResultsPlus
Examiner Comments

This is a rather unusual example. On a quick, first glance the structure appears completely correct because it is a diester as required in the question. However on closer scrutiny it can be seen that the butane-2,3-diol has been esterified not with propanoic acid but butanoic acid. This extra carbon resulted in one mark being lost.

ResultsPlus
Examiner Tip

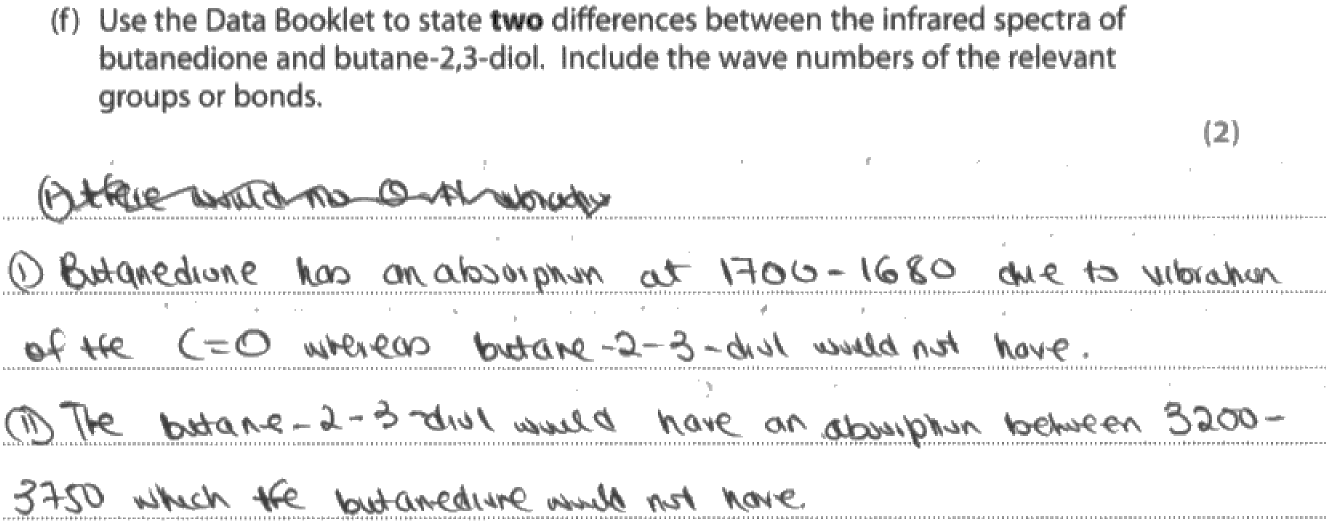
Mnemonics such as 'Most Elephants Prefer Bananas' or 'Monkeys Eat Peanut Butter' can be very helpful in remembering how many carbon atoms to give Meth-, Eth-, Prop- and But- compounds.

Question 14 (f)

Candidates of A Level standard need to be able to correctly use the Data Booklet and the good answers to this question were characterised by their clarity and by adhering to both the information required in the question and that given in the Data Booklet.

For example, it was not acceptable to give individual wavenumber values whether they are at the mid-point or not, because the peaks can be anywhere within the ranges quoted and not necessarily at some arbitrary point within that range.

In addition the question clearly asks for reference to the "relevant groups or bonds" and for these to be attributed to either butanedione or butane-2,3-diol. Hence if a response did not give all the detail required then often only one mark was awarded.



(f) Use the Data Booklet to state **two** differences between the infrared spectra of butanedione and butane-2,3-diol. Include the wave numbers of the relevant groups or bonds.

(2)

~~(1) there would no O-H [illegible]~~

① Butanedione has an absorption at 1700-1680 due to vibration of the C=O whereas butane-2-3-diol would not have.

(II) The butane-2-3-diol would have an absorption between 3200-3750 which the butanedione would not have.

ResultsPlus

Examiner Comments

This is an example of a response which only scores one mark because both of the relevant bonds are not stated for the respective peaks.

ResultsPlus

Examiner Tip

Re-read the answer given to ensure that all the information required is given.

Question 14 (g)

This was another very discriminating question based on the depth of description and explanation given by the candidates.

The first marking point on the mark scheme was for the statement that there are three different proton environments or three clear sets of peaks in the spectrum. Good answers were evident from the quality of language used in the way that the (n+1) rule was explained, which was the third marking point on the mark scheme.

The mark for the "ratio of the areas under each set of peaks" was often not awarded either because the candidate did not refer to it anywhere in their answer or gave the ratio as 3:2:1 without clearly identifying what the numbers referred to. The explanation could have been given in a paragraph or from a diagram and both were equally seen.

The splitting pattern and chemical shifts of the sets of peaks were usually evident from the NMR sketch. The drawings of triplet and quartet frequently 'left a lot to be desired' but this was not penalised. Occasionally the diagram contradicted the text which was disappointing and resulted in a loss of credit.

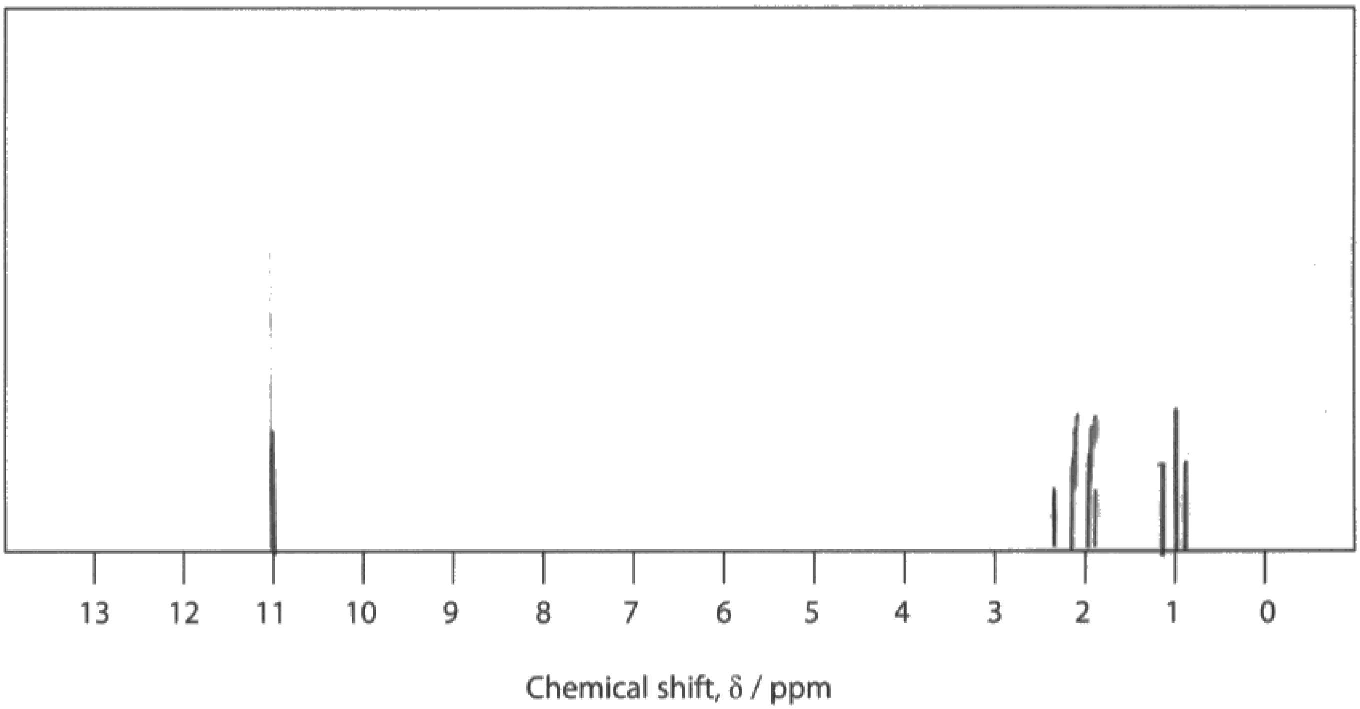
The splitting pattern of a triplet, quartet and singlet were usually correct but the description of the carboxylic acid proton being split into a triplet was seen.

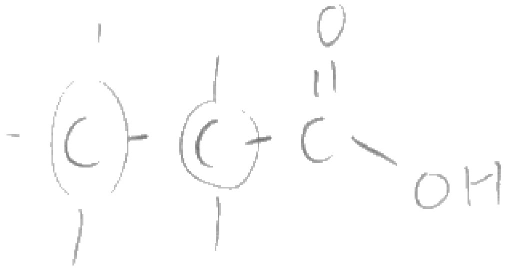
One of the most common errors was to give the quartet too low a chemical shift despite access to the Data Booklet.

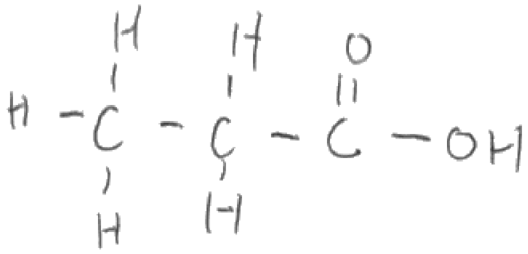
*(g) Use chemical shift data from the Data Booklet to sketch the **high** resolution proton nmr spectrum for propanoic acid. The peaks do not overlap.

Explain the number of peaks, their splitting pattern and the ratio of the areas under each set of peaks.

(5)







The C-C-H bond provides a peak at 1ppm and it splits to form 4 peaks as the neighbouring carbon atom has a chemical environment of 3 Hydrogens. The H-C-C-H peak at about 1.5ppm and splits to form 4 peaks as the neighbouring carbon atom has 3 H atoms. The singlet peak at 11ppm is due to COO-H which is labile and does not split.

ResultsPlus
Examiner Comments

This is an example of a response that scores four marks. It can quickly be noted that there is no reference to the "ratio of the areas under each set of peaks" and thus it is this mark that has not been awarded.

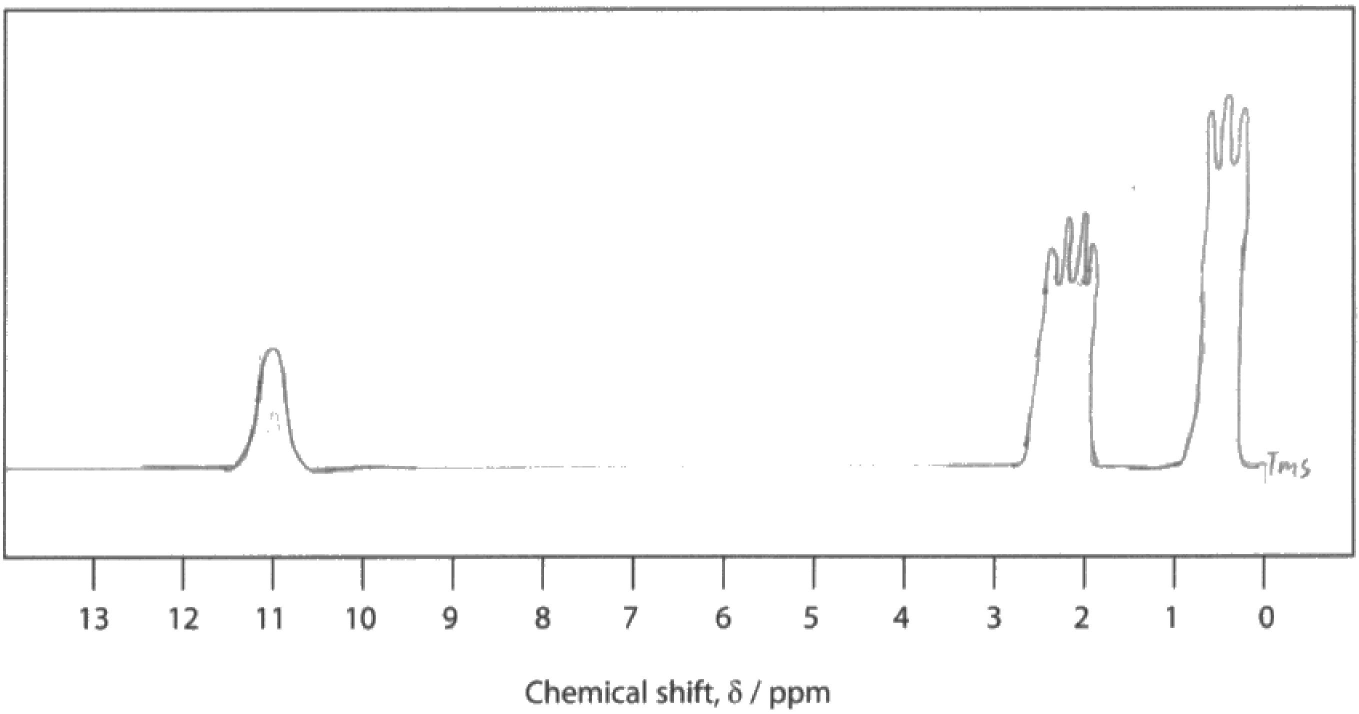
ResultsPlus
Examiner Tip

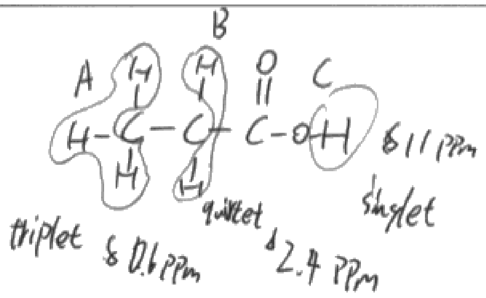
Always double or even triple-check an answer with the question instructions to make sure that all the necessary points have been addressed.

*(g) Use chemical shift data from the Data Booklet to sketch the **high** resolution proton nmr spectrum for propanoic acid. The peaks do not overlap.

Explain the number of peaks, their splitting pattern and the ratio of the areas under each set of peaks.

(5)





~~ba~~ by n+1 rule adjacent C has 1 hydrogen so the spl.

ResultsPlus
Examiner Comments

A number of the marks for this question can be gained from the sketch alone and this response scores 3 marks.

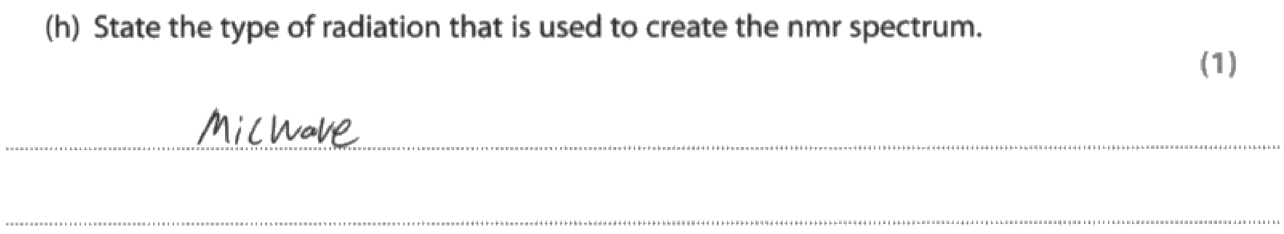
As in the previous example there is no reference to the 'area ratio' of the peaks. In addition, although the (n+1) rule is stated, the sentence is incorrect because from this candidate's own annotations there is no doublet, which would have been produced as stated by an adjacent carbon with a single hydrogen.

ResultsPlus
Examiner Tip

Make sure that a statement made does not contradict any previous comment.

Question 14 (h)

This was another good differentiating question and many candidates knew that radio waves are used to create an NMR spectrum.



(h) State the type of radiation that is used to create the nmr spectrum.

(1)

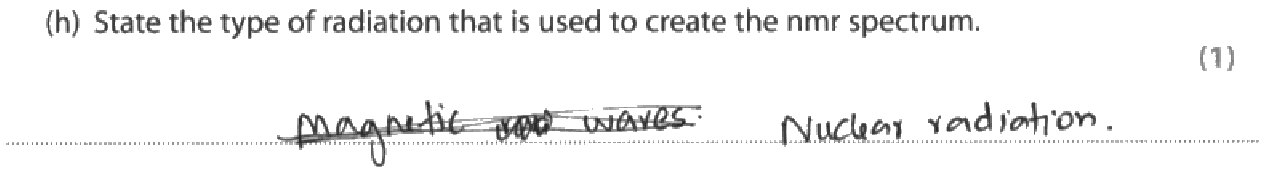
Micwave

ResultsPlus
Examiner Comments

The type of radiation is unfortunately spelt wrong but it is also the wrong choice of radiation and so does not score.

ResultsPlus
Examiner Tip

Spellings can be very important because the wrong thing may be inadvertently understood. Check spellings carefully.



(h) State the type of radiation that is used to create the nmr spectrum.

(1)

~~magnetic [illegible] waves.~~ Nuclear radiation.

ResultsPlus
Examiner Comments

If a visit to a university is not possible to see an NMR machine at work then a video such as on YouTube can be very beneficial in understanding how machines and suchlike work. If either of these had been the case then it is unlikely that this candidate would have suggested the answer shown as there are no special suits or danger signs around an NMR machine. The only concern is that the magnetic strip on a credit card can be 'wiped' by the large magnets in the machine.

ResultsPlus
Examiner Tip

Visits either in the virtual or the actual environment can really help to grasp how machines such as those involved in NMR spectroscopy work.

Paper Summary

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

- Lay out answers so that they match the demands of the question, such that if three assumptions or differences are required then organise the answer so that this is clearly expressed.
- Take careful note of all the information given and points made in the question introduction so that the answer composed fully addresses all the areas needed.
- When referring to the change of a negative number it is not sufficient just to state that it gets 'bigger' or 'smaller'. Either describe how its magnitude changes or that it becomes 'less negative' or 'more negative' as appropriate.
- Make sure that abbreviations or symbols used are not confused: for example a capital 'T' is used for temperature while a lower case 't' is used for time.
- infrared spectroscopy ranges should be quoted from the data booklet rather than giving the mid-point.
- Avoid giving multiple answers to questions that require a single one since correct responses can be negated by incorrect ones.
- Always double or even triple-check answers so that any 'simple' errors can be identified and corrected, and to make sure that the answer given does address the question asked.This response scores 2 marks. The general shape is suitable plus the initial and the final pH values with plateau are correct.
- The vertical section is not at either 10 or 20 cm^3 and there is no labelling of an equivalence point.

Grade Boundaries

Grade boundaries for this, and all other papers, can be found on the website on this link:

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