Examiners' Report
June 2016

GCE Chemistry 6CH04 01

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June 2016

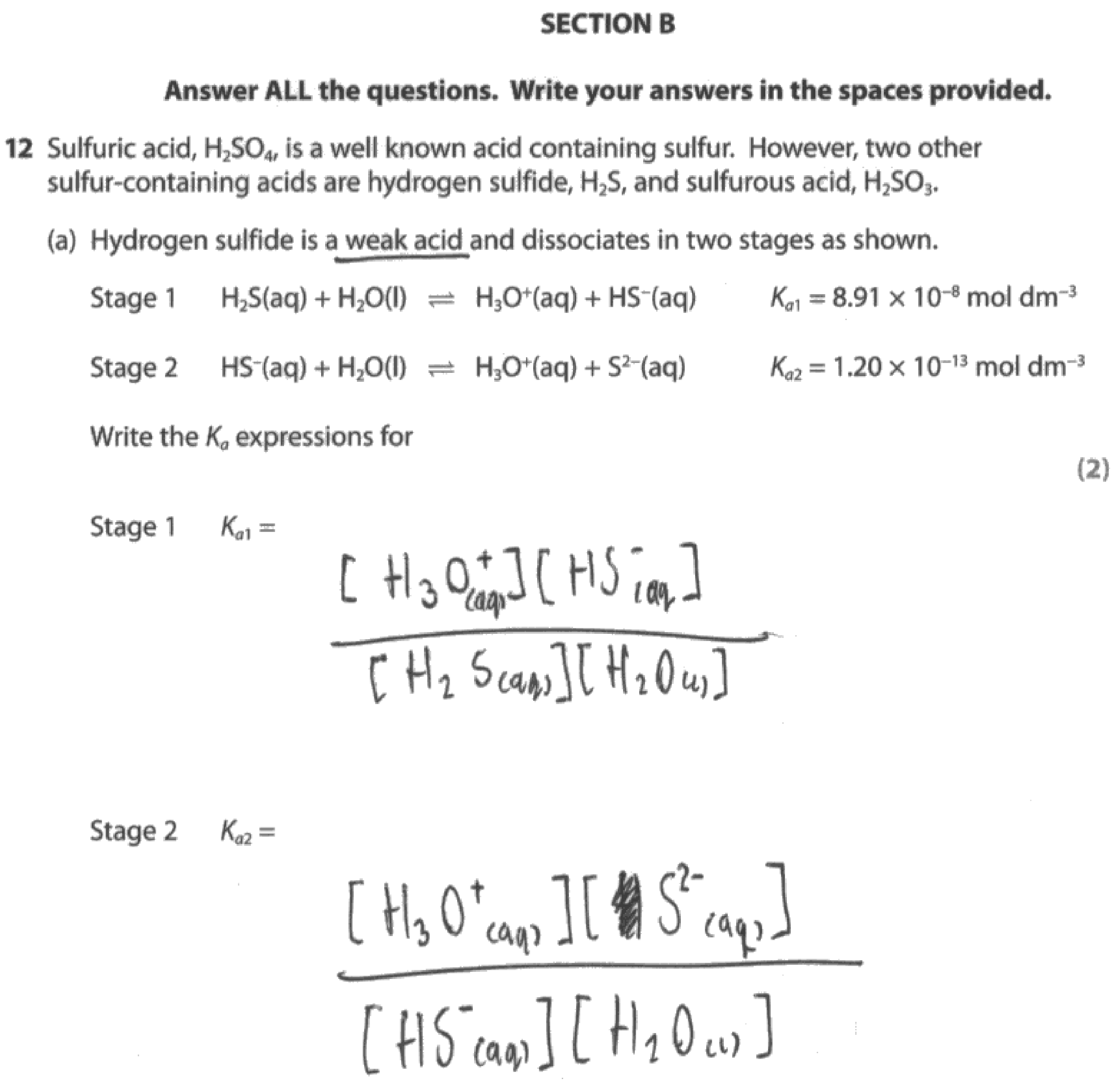
Publications Code 6CH04_01_1606_ER

Introduction

This paper was evidently accessible to most candidates as seen from the wide range of marks awarded and 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 high at just over 16/20 with Q5c and Q7b 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 Q13d, Q13eiii, Q14d, Q15c and Q15dii. In addition the sketches required for Q12c and Q15e were very discriminatory across the ability range.

Question 12 (a)

A high-scoring question with the majority of candidates scoring both marks, clearly showing that this was a topic area/skill that candidates know well. It was very rare to see the omission of square brackets which was pleasing.



SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

12 Sulfuric acid, H_2SO_4, is a well known acid containing sulfur. However, two other sulfur-containing acids are hydrogen sulfide, H_2S, and sulfurous acid, H_2SO_3.

(a) Hydrogen sulfide is a weak acid and dissociates in two stages as shown.

Stage 1 $H_2S(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq)$ $K_{a1} = 8.91 \times 10^{-8}$ mol dm^{-3}

Stage 2 $HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq)$ $K_{a2} = 1.20 \times 10^{-13}$ mol dm^{-3}

Write the K_a expressions for

(2)

Stage 1 $K_{a1} =$

$$\frac{[H_3O^+_{(aq)}][HS^-_{(aq)}]}{[H_2S_{(aq)}][H_2O_{(l)}]}$$

Stage 2 $K_{a2} =$

$$\frac{[H_3O^+_{(aq)}][S^{2-}_{(aq)}]}{[HS^-_{(aq)}][H_2O_{(l)}]}$$

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Examiner Comments

This is an example of an error that some candidates made, namely the inclusion of water in the expression for K_a. This was only penalised once.

ResultsPlus

Examiner Tip

Water should never be included in the expression for K_a.

SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

12 Sulfuric acid, H_2SO_4, is a well known acid containing sulfur. However, two other sulfur-containing acids are hydrogen sulfide, H_2S, and sulfurous acid, H_2SO_3.

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Write the K_a expressions for

(2)

Stage 1 $K_{a1} = \dfrac{[H_3O^+][HS^-]}{[H_2S]}$

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

ResultsPlus

Examiner Comments

State symbols were not required and either H^+ or the H_3O^+ ion were acceptable as seen here.

ResultsPlus

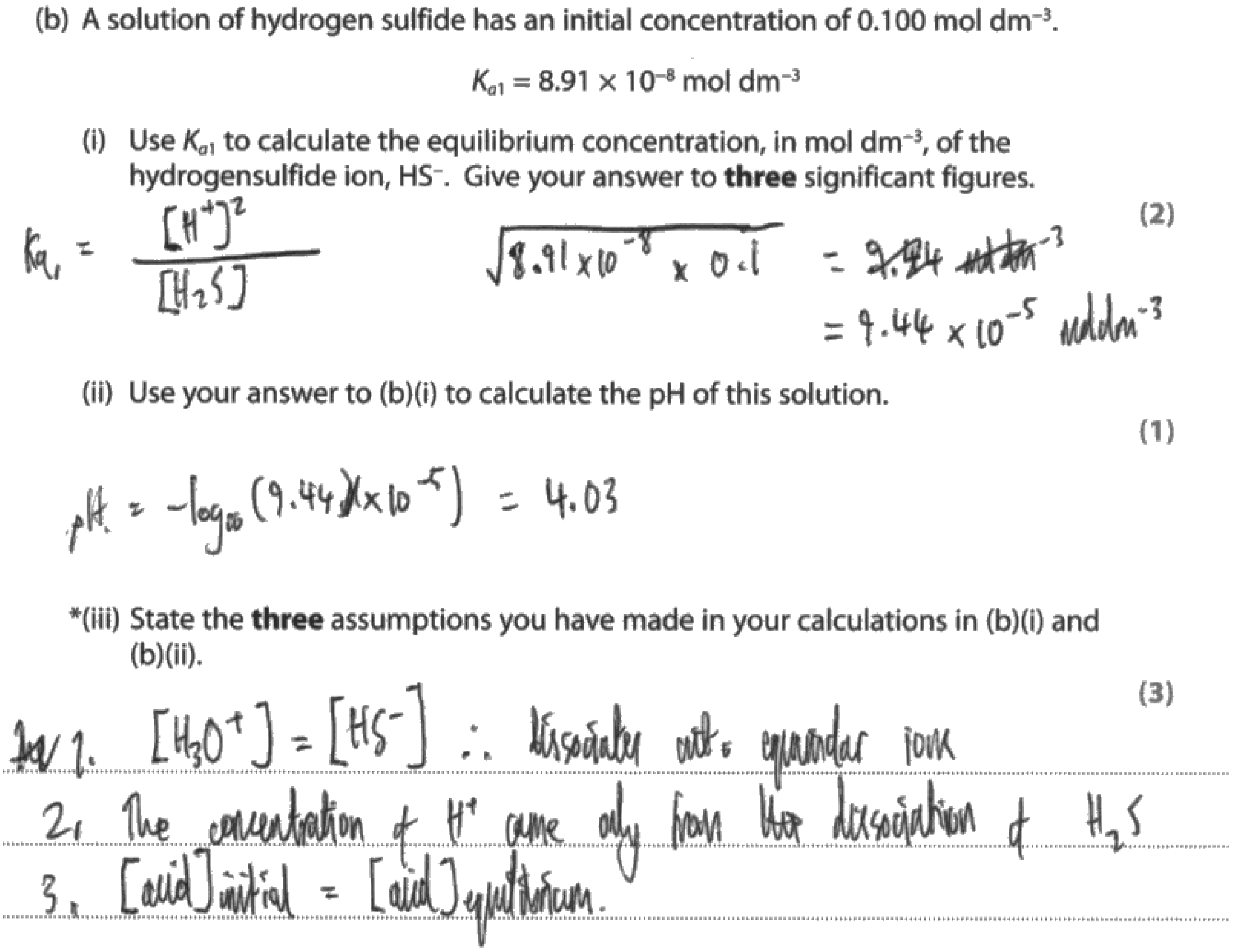
Examiner Tip

If state symbols are required then they will generally be asked for.

Question 12 (b) (iii)

Over half of the total candidates scored two marks for two valid assumptions. The mark scheme made provision for four possible alternative assumptions. One of the assumptions often missed was that the hydrogen sulfide ion itself does not significantly dissociate which was disappointing since the candidates had been asked to write the expression for the second K_a and only some candidates gave this assumption.

The clip also shows the candidates answers to b(i) and (ii) in case there were any creditworthy comments made above. In reality this did not prove to be necessary as there were no candidates reported as having made such comments in this area.



(b) A solution of hydrogen sulfide has an initial concentration of 0.100 mol dm⁻³.

$$K_{a1} = 8.91 \times 10^{-8} \text{ mol dm}^{-3}$$

(i) Use K_{a1} to calculate the equilibrium concentration, in mol dm⁻³, of the hydrogensulfide ion, HS^-. Give your answer to **three** significant figures. **(2)**

$Ka_1 = \frac{[H^+]^2}{[H_2S]}$ $\sqrt{8.91 \times 10^{-8} \times 0.1}$ = ~~9.44 moldm~~$^{-3}$

= 9.44×10^{-5} moldm^{-3}

(ii) Use your answer to (b)(i) to calculate the pH of this solution. **(1)**

pH = $-\log_{10}(9.44 \times 10^{-5})$ = 4.03

*(iii) State the **three** assumptions you have made in your calculations in (b)(i) and (b)(ii). **(3)**

1. $[H_3O^+] = [HS^-]$ ∴ dissociates into equimolar ions

2. The concentration of H^+ came only from the dissociation of H_2S

3. [acid] initial = [acid] equilibrium.

ResultsPlus

Examiner Comments

This response scores two marks. It is good to see the layout showing three clear points made. However the assumption that the concentration of hydrogen ions is equivalent to the concentration of hydrogen sulfide ions is the same as stating that the hydrogen ions only come from dissociation of the hydrogen sulfide. Hence in this response the assumptions given as 1 and 2 are essentially the same and score one mark. The assumption given as 3 is valid for another mark giving a total of two marks.

ResultsPlus

Examiner Tip

Care needs to be taken to ensure that what is perceived as two separate statements is not just one statement but made from a different perspective.

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

$$K_{a1} = 8.91 \times 10^{-8} \text{ mol dm}^{-3}$$

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

(2)

$$8.91 \times 10^{-8} = \frac{[HS^-]^2}{[H_2S]}$$

$$[HS^-] = \sqrt{8.91 \times 10^{-8} \times 0.1}$$

$$= 9.44 \times 10^{-5} \text{ moldm}^{-3}$$

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

(1)

$$-\log(9.44 \times 10^{-5}) = \underline{4.03}$$

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

(3)

The concentration of water is constant.

$[H^+]$ = $[HS^-]$ - there is no H^+ from the ionisation of water.

$[H_2S]_{\text{initial}} = [H_2S]_{\text{equilibrium}}$.

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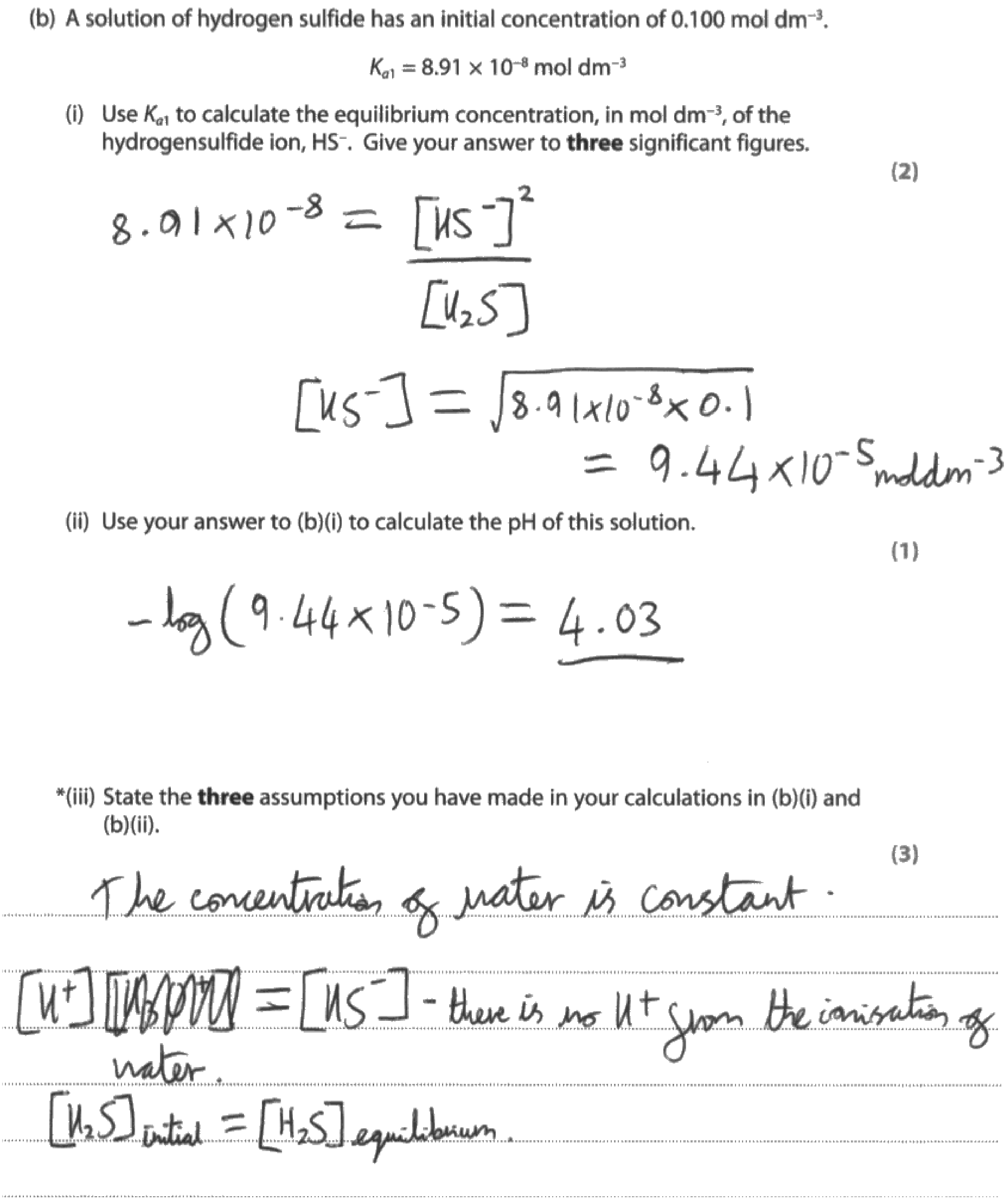
Examiner Comments

Comments that made reference to the concentration of water were ignored. The candidates had already noted this point in their expressions of K_a and so it was viewed as neutral. The other two assumptions given are correct for two marks.

Question 12 (b) (i)-(ii)

This was a straightforward question which has been similarly assessed on many previous occasions and three quarters of the candidates correctly calculated K_a and pH.

This clip begins with the candidates response to part (a) in case this had an influence on the answer given in parts (b)(i) and (ii). This was rarely the case.



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

(2)

$$8.91 \times 10^{-8} = \frac{[HS^-]^2}{[H_2S]}$$

$$[HS^-] = \sqrt{8.91 \times 10^{-8} \times 0.1}$$
$$= 9.44 \times 10^{-5} \text{ moldm}^{-3}$$

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

(1)

$$-\log(9.44 \times 10^{-5}) = \underline{4.03}$$

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

(3)

The concentration of water is constant.

$[H^+] = [HS^-]$ - there is no H^+ from the ionisation of water.

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

$$K_{a1} = 8.91 \times 10^{-8} \text{ mol dm}^{-3}$$

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

(2)

$$[HS^-] = \sqrt{[H_2S] \times Ka_1}$$

$$= \sqrt{0.1 \times 8.91 \times 10^{-8}}$$

$$= 9.44 \times 10^{-5} \text{ mol dm}^{-3}$$

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

(1)

$$ph = -\log(9.44 \times 10^{-5}) = 4.025...$$

$$= 4.0 \text{ (2.s.F)}.$$

ResultsPlus

Examiner Comments

In part (b)(i) the correct answer is given as requested to three significant figures and both marks were awarded.

In (ii) there was no such requirement for significant figures but when used they must be correct. In this example it is entirely appropriate given the somewhat nebulous nature of pH readings, to give the final value to one decimal place and the mark was awarded.

ResultsPlus

Examiner Tip

Make sure that if a question requires a specific number of significant figures then these will be given but if not then make sure that any rounding carried out is also correct.

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

$$K_{a1} = 8.91 \times 10^{-8} \text{ mol dm}^{-3}$$

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

(2)

$0.1 \times 8.91\times10^{-8} = 8.91\times10^{-9}$

~~$-\log(\sqrt{8.91\times10^{-9}}) = 4.025$~~

$8.91\times10^{-8} = [H_3O^+][HS^-]$

$\therefore [HS^-] =$ ~~9.45~~ 9.44×10^{-5}

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

(1)

$-\log(9.45\times10^{-5}) = 4.025$

$\therefore pH = 4.02$

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Examiner Comments

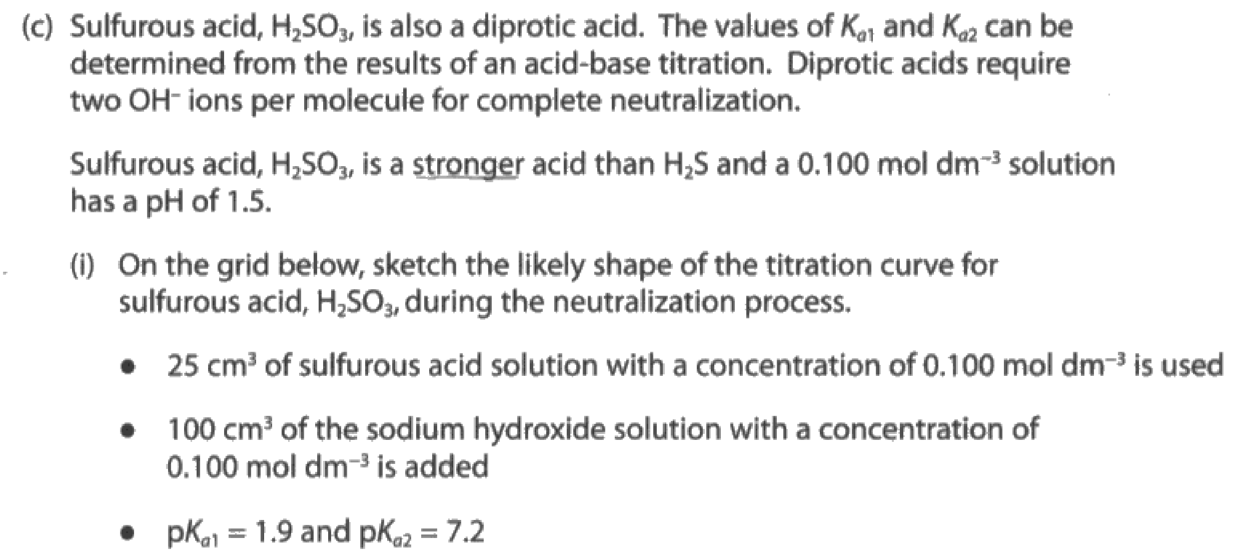
This is an example of an incorrect rounding in part (b)(ii) because 4.025.... if rounded correctly should be 4.03 and so this response did not score for this particular question.

Question 12 (c)

This was a very effective discriminating question with the full range of marks awarded and 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 in part (c)(i) for a monoprotic curve so that candidates who were unable to grasp the concept of a diprotic acid 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 was very clear from the beginning of this question that a relatively weak acid and not a strong acid was the subject of the question and so in a titration with a strong base there will not be a large vertical section. Examiners were given the generous guidance of penalising 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 base such as sodium hydroxide, 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) Sulfurous acid, H_2SO_3, is also a diprotic acid. The values of K_{a1} and K_{a2} can be determined from the results of an acid-base titration. Diprotic acids require two OH^- ions per molecule for complete neutralization.

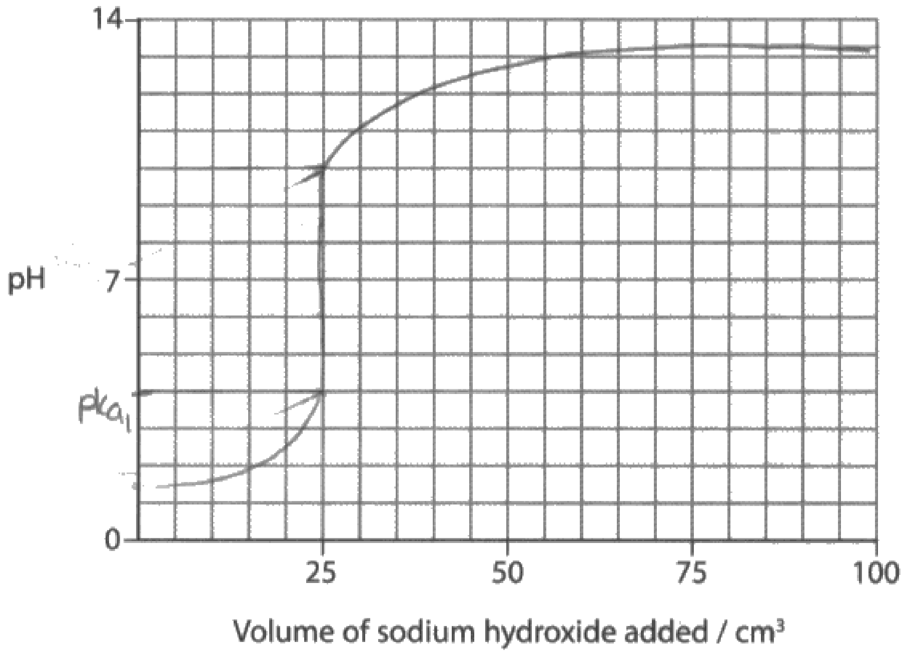
Sulfurous acid, H_2SO_3, is a stronger acid than H_2S and a 0.100 mol dm^{-3} solution has a pH of 1.5.

(i) On the grid below, sketch the likely shape of the titration curve for sulfurous acid, H_2SO_3, during the neutralization process.

- 25 cm^3 of sulfurous acid solution with a concentration of 0.100 mol dm^{-3} is used
- 100 cm^3 of the sodium hydroxide solution with a concentration of 0.100 mol dm^{-3} is added
- pK_{a1} = 1.9 and pK_{a2} = 7.2

Clearly label any equivalence points in the sketch.

(5)



(ii) Describe how you would use this graph to confirm the value of pK_{a1}.

(1)

Using the ~~vertical strip~~ Half the equivalence point.

Examiner Comments

This response scores 2 marks for (c)(i) and zero for (c)(ii).

There is no vertical section and 50 cm^3 and there is no labelling of any equivalence point. In addition the final plateau clearly goes above the pH = 13 horizontal line which was penalised.

This means that there was one mark awarded for the vertical section at 25 cm^3 and one mark for the general acid-base curve.

In part (ii) there is no mention of the pKa being the **pH** at half-equivalence point and this is the reason that this did not score.

Examiner Tip

The placement of any lines on a graph or sketch is very important. If a plateau needs to be drawn and there is concern over somewhat 'shakey' hands then the solution is to use a ruler.

(c) Sulfurous acid, H_2SO_3, is also a diprotic acid. The values of K_{a1} and K_{a2} can be determined from the results of an acid-base titration. Diprotic acids require two OH^- ions per molecule for complete neutralization.

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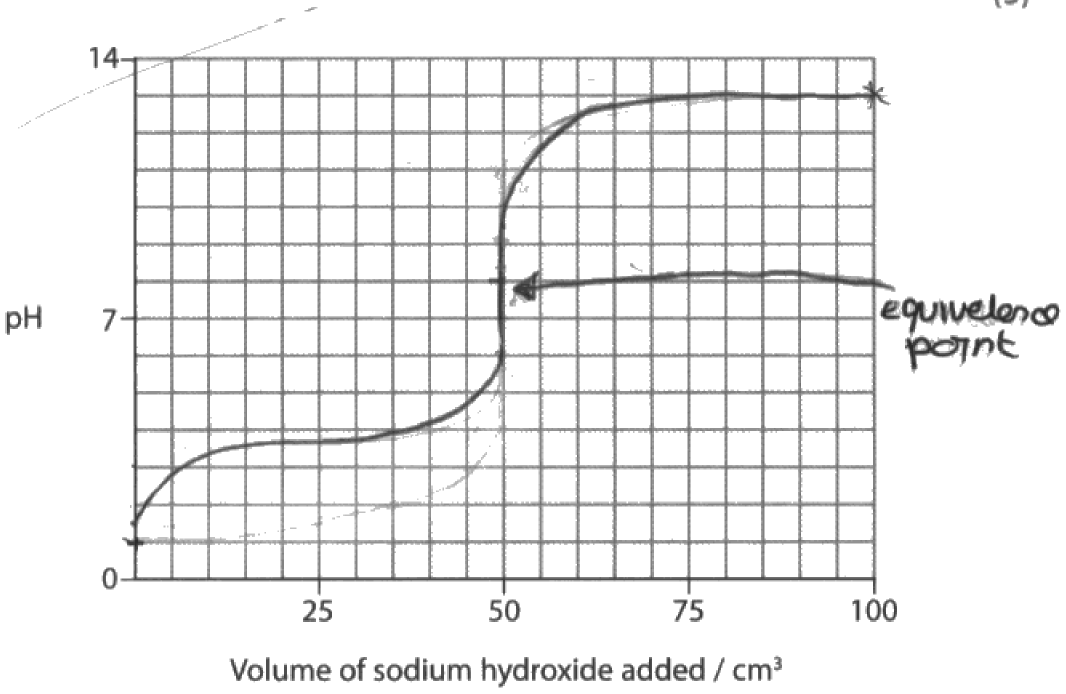

(ii) Describe how you would use this graph to confirm the value of pK_{a1}.

(1)

at half equivelence point, pKa = pH

(Total for Question 12 = 14 marks)

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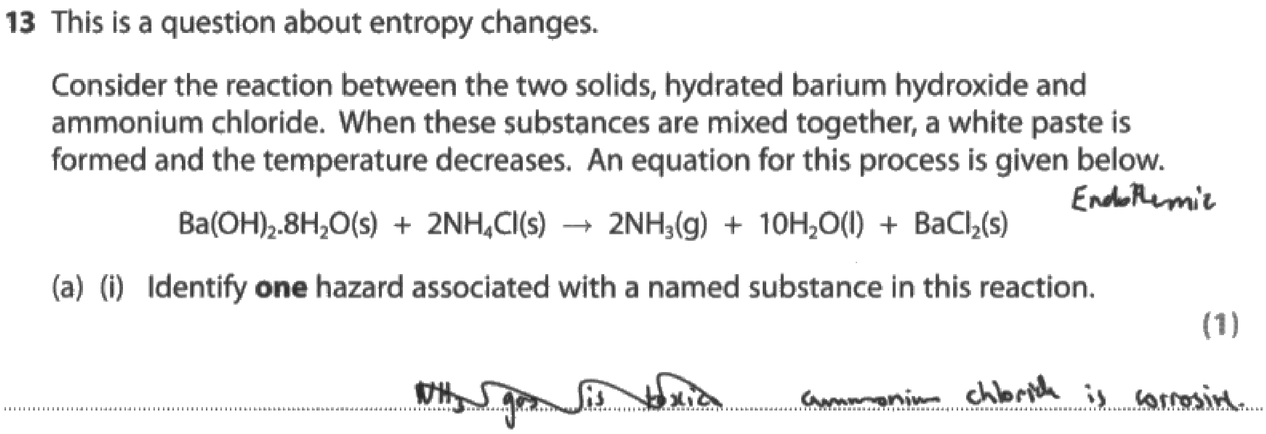
Examiner Comments

An example of a response where four out of five marks were scored for part (c)(i) for a monoprotic acid curve drawn corrrectly. In part (c)(ii) the mark was awarded for the reference to the pka value being the pH at the equivalence point.

Question 13 (a) (i)

The mark scheme allowed for a large number of different possibilities and so it proved a useful discriminator.

It was not usual to see comments referring to ammonium chloride being toxic but this is not true. It was anticipated that candidates would select substances that were well-known to them such as ammonia and barium chloride, and where these were kept to, then generally the mark was awarded.



13 This is a question about entropy changes.

Consider the reaction between the two solids, hydrated barium hydroxide and ammonium chloride. When these substances are mixed together, a white paste is formed and the temperature decreases. An equation for this process is given below.

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

(a) (i) Identify **one** hazard associated with a named substance in this reaction.

(1)

~~NH_3 gas is toxic~~ ammonium chloride is corrosive.

ResultsPlus

Examiner Comments

An example of a common erroneous comment about ammonium chloride that did not score.

ResultsPlus

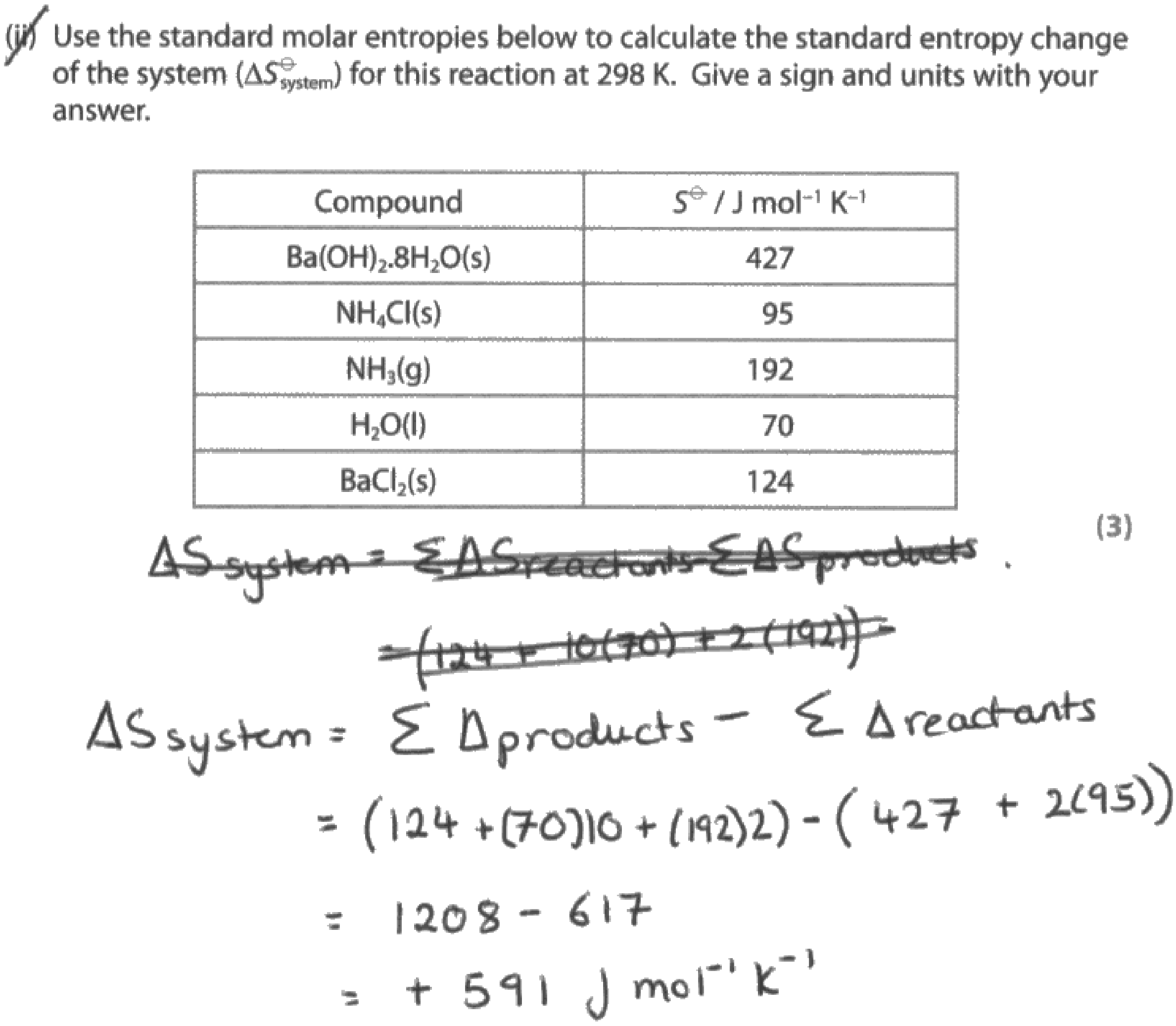
Examiner Tip

Keep to substances which are familiar and for which the hazards and its associated precautions are well-known.

Question 13 (a) (ii)-(c)

Entropy calculations are generally very well done and this one was no exception. It is clearly a topic area that is taught to a high standard and clearly understood by candidates. Over 80% of candidates were able to score seven or eight marks on this section.

The usual reminders apply, namely to take care with the consistent use of units and to give the correct number of reasons that the question asks for.



(ii) Use the standard molar entropies below 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.

Compound	$S^{\ominus}$ / J mol^{-1} K^{-1}
$Ba(OH)_2.8H_2O(s)$	427
$NH_4Cl(s)$	95
$NH_3(g)$	192
$H_2O(l)$	70
$BaCl_2(s)$	124

(3)

~~ΔS system = Σ ΔS reactants Σ ΔS products~~ .

~~= (124 + 10(70) + 2(192)) =~~

ΔS system = Σ Δ products − Σ Δ reactants

= (124 + (70)10 + (192)2) − (427 + 2(95))

= 1208 − 617

= + 591 J mol^{-1} K^{-1}

*(iii) Give **two** reasons why the sign of your answer to (a)(ii) is as you would expect.

(2)

ΔS system is positive because two solid reactants form a gas and a liquid product. Gases are more disordered than liquids. Also liquids are more disordered than solids. So ΔS system increase. Another reason is the reaction is endothermic as temperature decreases. So more energy is in the system, so ΔS system is positive.

(b) The standard enthalpy change for this reaction is $\Delta H_r^{\ominus} = +162 \text{ kJ mol}^{-1}$.

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

(2)

$$\Delta S_{\text{surroundings}} = -\frac{\Delta H}{T}$$

$$= -\frac{(162 \times 1000)}{298}$$

$$= -543.62 \text{ J mol}^{-1} \text{ K}^{-1}$$

(c) Use your answers to (a)(ii) and (b) to calculate the total entropy change ($\Delta S^{\ominus}_{\text{total}}$) for this reaction. Include a sign and units in your answer.

(1)

$$\Delta S \text{ total} = \Delta S \text{ system} + \Delta S \text{ surroundings}$$

$$\Delta S \text{ total} = 591 - 543.62$$

$$\Delta S \text{ total} = +47.38 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta S \text{ total} = +47.4 \text{ J mol}^{-1} \text{ K}^{-1} \text{ (3SF)}$$

ResultsPlus
Examiner Comments

Three marks were awarded for the correct answer with sign and units for part (a)(ii).
In part (a)(iii) the point about gases being made and so disorder increasing is made but there is no mention of the number of moles increasing and so only one mark was awarded for this part.

Parts (b) and (c) are carried out correctly for full marks.

ResultsPlus
Examiner Tip

The marks allocated to each question part often reflect the number of points that have to be made. Alternatively, as is the case here, the question has the number of reasons required in bold and so make sure that the answer given does match this requirement.

(ii) Use the standard molar entropies below 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.

Compound	$S^{\ominus}$ / J mol^{-1} K^{-1}
$Ba(OH)_2.8H_2O(s)$	427
$NH_4Cl(s)$	95
$NH_3(g)$	192
$H_2O(l)$	70
$BaCl_2(s)$	124

(3)

$\Delta S_{system} = S_{products} - S_{reactants}$

$= 1208 - 617$

$\Delta S_{system} = +591 \text{ J mol}^{-1} \text{K}^{-1}$

*(iii) Give **two** reasons why the sign of your answer to (a)(ii) is as you would expect.

(2)

endothermic ~~exothermic~~ reaction so temperature decreases. High disorder NH_3 Also there's 3moles to 13moles, more moles in forward reaction

(b) The standard enthalpy change for this reaction is $\Delta H_r^\ominus = +162 \text{ kJ mol}^{-1}$.

Use this value to calculate the standard entropy change of the surroundings ($\Delta S^\ominus_{\text{surroundings}}$) for this reaction at 298 K. Include a sign and units in your answer.

(2)

$$-\frac{\Delta H}{T} \qquad \frac{-162}{298} =$$ ~~-0.54 KJmol^-1~~

-0.54 KJmol^{-1}

(c) Use your answers to (a)(ii) and (b) to calculate the total entropy change ($\Delta S^\ominus_{\text{total}}$) for this reaction. Include a sign and units in your answer.

(1)

$+591 + (-540) = +51$ ~~K~~Jmol^{-1}

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Examiner Comments

As in the previous example all three marks were awarded for part (a)(ii) and one mark for part (a)(iii). However in the latter part the number of increasing moles is given but this time there is no mention of gases being produced.

In part (b) it was acceptable to give an answer in kilojoules as here but the units should have included K^{-1} and so one mark was lost for this omission. TE was applied in part (c) and so the mark was given even though the units are again incorrect.

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Examiner Tip

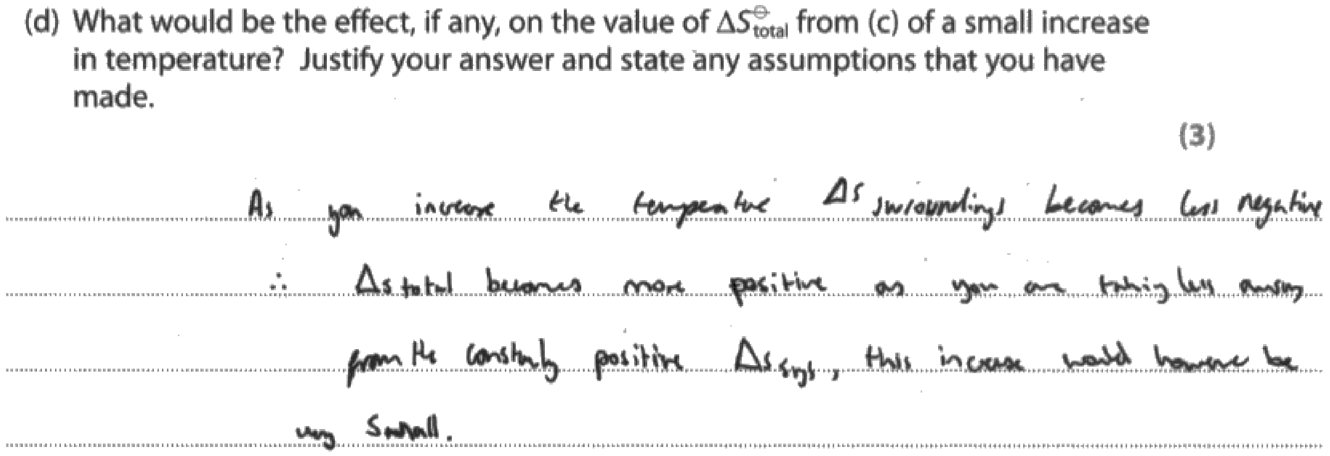
Every time a question states to "include a sign and units in your answer" make sure that this is done and double-checked for accuracy.

Question 13 (d)

The correct use of terminology clearly and effectively separated candidates of different abilities as the mean for a grade A candidate on this question was over one mark greater than a candidate at grade E.

When referring to negative numbers it is unclear what exactly is meant when a statement is made that the number is "smaller" or "decreases" because although -10 is less than -5 the number is 'larger'. Hence those candidates who answered in terms of 'less negative' or 'more positive' were credited but not those who just stated that the value of the netropy of surroundings got "bigger".

The assumption that the entropy of the system or the enthalpy change was unchanged was also more commonly seen in responses of better quality.



(d) What would be the effect, if any, on the value of $\Delta S^{\ominus}_{\text{total}}$ from (c) of a small increase in temperature? Justify your answer and state any assumptions that you have made.

(3)

As you increase the temperature ΔS surroundings becomes less negative

∴ ΔS total becomes more positive as you are taking less away

from the constantly positive ΔS_{sys}, this increase would however be

very small.

ResultsPlus

Examiner Comments

This response states that the entropy of the system change is very small but this is ambiguous and so did not score. There is the correct terminology used with respect to the entropy of the surroundings becoming less negative and subsequently that the total entropy increases, so two marks awarded.

ResultsPlus

Examiner Tip

When referring to negative numbers the best term that can be used is their 'magnitude' as this is unambiguous.

Avoid terms such as small or bigger unless substantiated.

(d) What would be the effect, if any, on the value of $\Delta S^{\ominus}_{total}$ from (c) of a small increase in temperature? Justify your answer and state any assumptions that you have made.

(3)

It would increase $\Delta S^{\ominus}_{total}$ and the ΔS_{surr} would decrease.
This would mean a smaller number would be taken
away from $\Delta S^{\ominus}_{system}$.
It ~~wd~~ would not be a large enough change however to make
this reaction happen spontaneously.
Assumptions: $\Delta H^{\ominus}_{r}$ will remain the same, even at higher
temperatures. and the molar entropies remain the same

ResultsPlus

Examiner Comments

This is an example of a response where the entropy of the surroundings is referred to as getting smaller but with negative numbers this can mean different things as previously stated and so this mark was not awarded. The rest of the response is valid and two marks awarded.

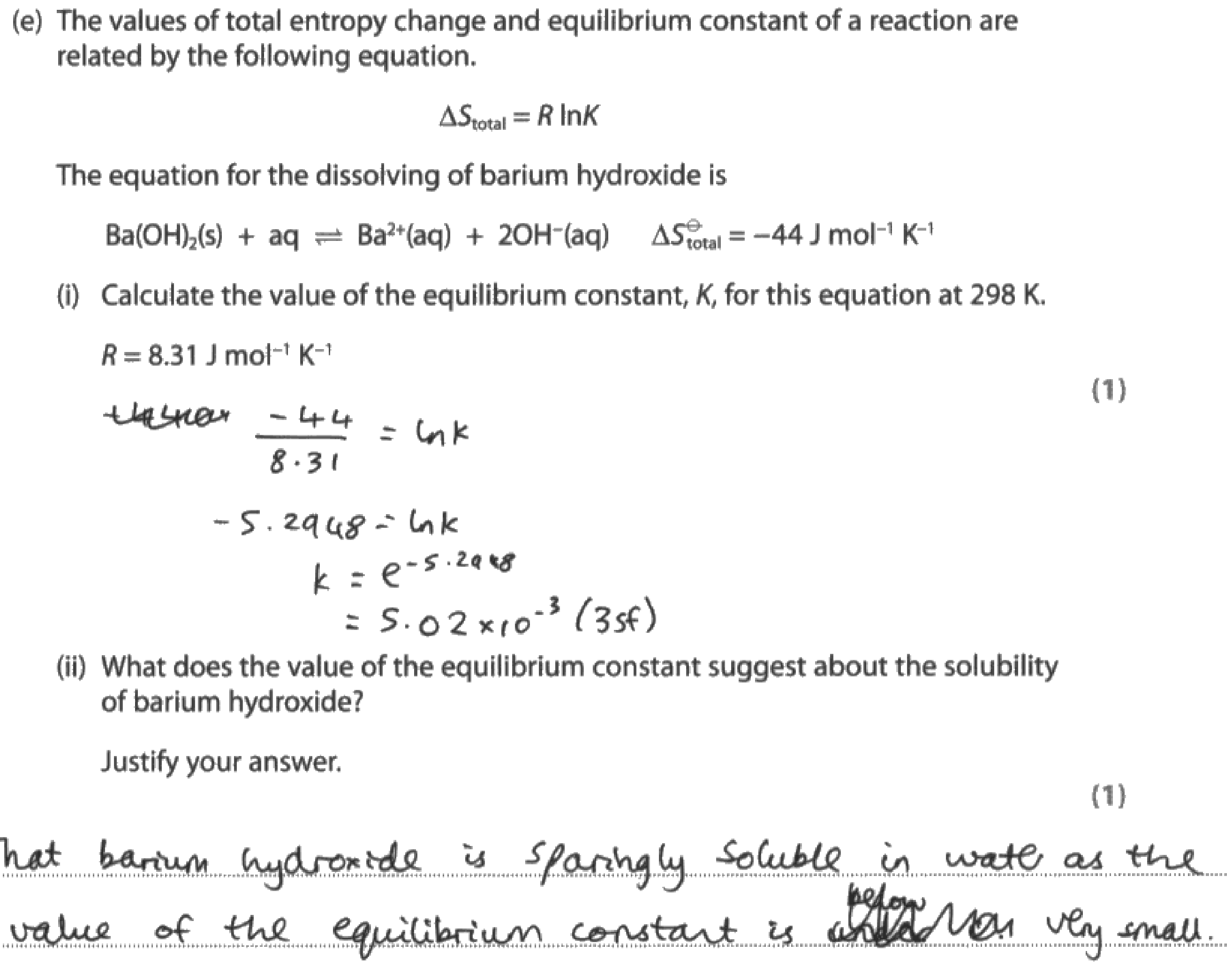
Question 13 (e)

The three questions of part (e) gave a good spread of marks and served to differentiate between candidates of different ability.

In part (i), while the inverse of logarithms to the base 10 is not unusual, the inverse of a natural logarithm is somewhat novel to candidates and so it tended to be only some candidates who could successfully complete the task. On rare occasions, the process was carried out well but then a rounding error appeared and this was obviously disappointing.

It is vital that candidates have some grasp of 'what the numbers mean' and credit was not given for candidates stating in part (ii) that the value of the equilibrium constant was "small".

The answer required in part (iii) again needed a comment about negative numbers and so the earlier points made about the care needed with expressions also applies here. Occasionally candidates omitted any comment about the second part of the question, namely the trend of hydroxide solubility down group 2. This is another reminder that candidates should re-read the question in order to make sure that the answer given addresses all that is required.



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

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

The equation for the dissolving of barium hydroxide is

$$\text{Ba(OH)}_2\text{(s)} + \text{aq} \rightleftharpoons \text{Ba}^{2+}\text{(aq)} + 2\text{OH}^-\text{(aq)} \qquad \Delta S^{\ominus}_{\text{total}} = -44 \text{ J mol}^{-1} \text{ K}^{-1}$$

(i) Calculate the value of the equilibrium constant, K, for this equation at 298 K.

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

(1)

$$\frac{-44}{8 \cdot 31} = \ln k$$

$$-5.2948 = \ln k$$

$$k = e^{-5.2948}$$

$$= 5.02 \times 10^{-3} \text{ (3sf)}$$

(ii) What does the value of the equilibrium constant suggest about the solubility of barium hydroxide?

Justify your answer.

(1)

That barium hydroxide is sparingly soluble in wate as the a value of the equilibrium constant is ~~under~~ below very small.

(iii) For the dissolving of calcium hydroxide, the value of the total entropy change is –106 J mol^{-1} K^{-1}

Compare the values of the total entropy changes for these two hydroxides and show that they are consistent with the trend in the solubility of Group 2 hydroxides.

(2)

The total entropy change for ~~fo~~ calcium hydroxide is lowe than that of barium hydroxide, so is less soluble in wate than barium hydroxide. This is consistent with the trend, as Group 2 hydroxides ~~get~~ ~~are~~ get more soluble down the group and barium hydroxide is further down the group than calcium and is more soluble than calcium hydroxide.

(Total for Question 13 = 16 marks)

ResultsPlus

Examiner Comments

In this example the candidate has correctly calculated the equilibrium constant in part (i).

However in part (ii)candidates needed to demonstrate an understanding of 'what the numbers mean'. It was insufficient to simply state that the value was "very small" because depending on your point of reference this can be different things. For example 100 can be viewed as very small compared to the Avogadro constant but alternatively viewed as very large compared to the K_a calculated earlier in this exam paper. Only a few candidates gave the position of equilibrium as the point of reference and stating that the reactants predominate.

In part (iii) the issue arises again when referring to negative number that it is insufficient to simply state that the value is just 'smaller' and so on, although in this response the trend in hydroxide solubility is given correctly for one mark.

ResultsPlus

Examiner Tip

Always have an understanding of 'what the numbers mean' in the context given and do not use ambiguous terms such as big or small unless a clear point of reference of comparison is given.

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

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

The equation for the dissolving of barium hydroxide is

$$Ba(OH)_2(s) + aq \rightleftharpoons Ba^{2+}(aq) + 2OH^-(aq) \qquad \Delta S^{\ominus}_{total} = -44 \text{ J mol}^{-1} \text{ K}^{-1}$$

(i) Calculate the value of the equilibrium constant, K, for this equation at 298 K.

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

(1)

$\ln K = \frac{-44}{8.31}$

-44 ~~[illegible]~~ = 8.31 x ln K

lnK ≈ $\frac{4.7}{8.31}$

K = ~~[illegible]~~ 5.02 x 10^{-3} $mol^2\ dm^{-6}$

(ii) What does the value of the equilibrium constant suggest about the solubility of barium hydroxide?

Justify your answer.

(1)

It is ~~not~~ only slightly soluble ~~[illegible]~~ as the K value is very small so the reactant $Ba(OH)_2(s)$ predominates.

(iii) For the dissolving of calcium hydroxide, the value of the total entropy change is $-106 \text{ J mol}^{-1} \text{ K}^{-1}$

Compare the values of the total entropy changes for these two hydroxides and show that they are consistent with the trend in the solubility of Group 2 hydroxides.

(2)

The total entropy change of calcium hydroxide is lower (more negative) than barium hydroxide so it is even less soluble. This is consistent with the Group 2 trends as hydroxides increase in solubility as you go down group 2 and barium is below calcium in group 2.

(Total for Question 13 = 16 marks)

ResultsPlus

Examiner Comments

In part (i) any units given were ignored on this occasion and so the correct figures given scored the mark.

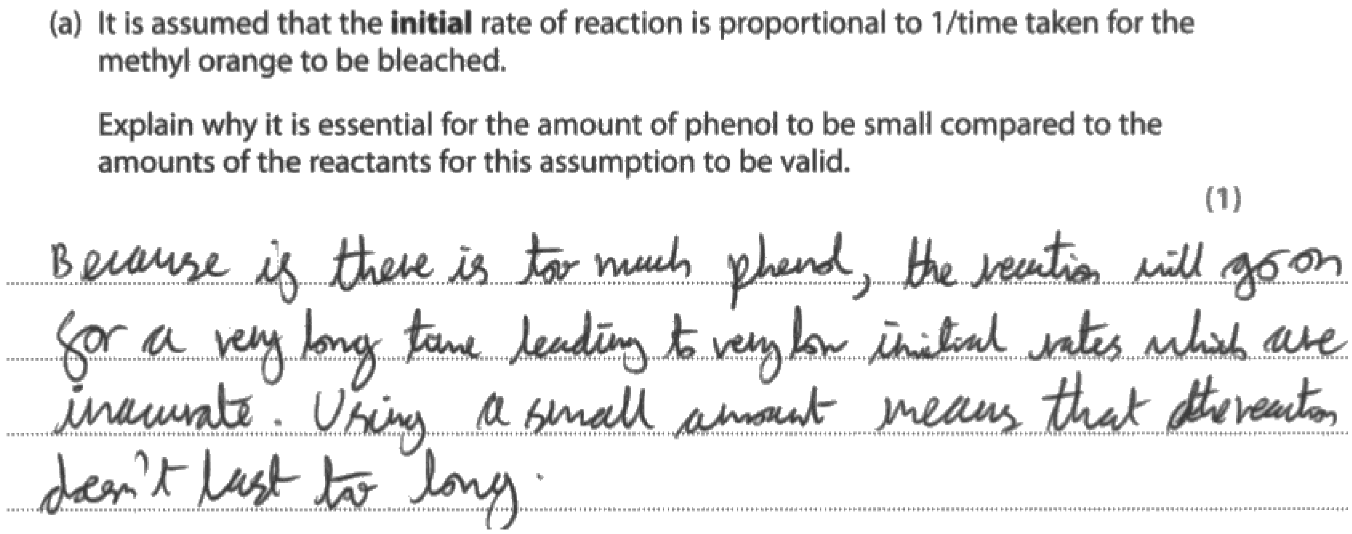
This candidate in part (ii) does justify the meaning of "very small" by referring to the predominance of the reactant barium hydroxide, which gains the mark.

In addition the clarification of the lowering of the entropy change for calcium hydroxide is given in brackets and so with the correct trend for hydroxide solubility, both marks were awarded for part (iii).

Question 14 (a)

This proved to be the most challenging question on the paper and had the lowest mean score with only approximately 20% of candidates gaining the mark. It was not uncommon to see answers from candidates that seemed to have some idea of the point being tested but their ability to clearly express themselves was lacking. The crucial issue is that the amount of phenol must be small so that it is all used up during the initial rate period before the rate of the reaction changes.

There were a large number of responses seemingly applying the 'scatter gun approach' and mentioning a number of effects with the vain hope that one of them might be right. This serves as a useful reminder to candidates that when a practical activity is carried out that they fully understand the purpose of each step in the procedure.



(a) It is assumed that the **initial** rate of reaction is proportional to 1/time taken for the methyl orange to be bleached.

Explain why it is essential for the amount of phenol to be small compared to the amounts of the reactants for this assumption to be valid.

(1)

Because if there is too much phenol, the reaction will go on for a very long time leading to very low initial rates which are inaccurate. Using a small amount means that the reaction doesn't last too long.

ResultsPlus
Examiner Comments

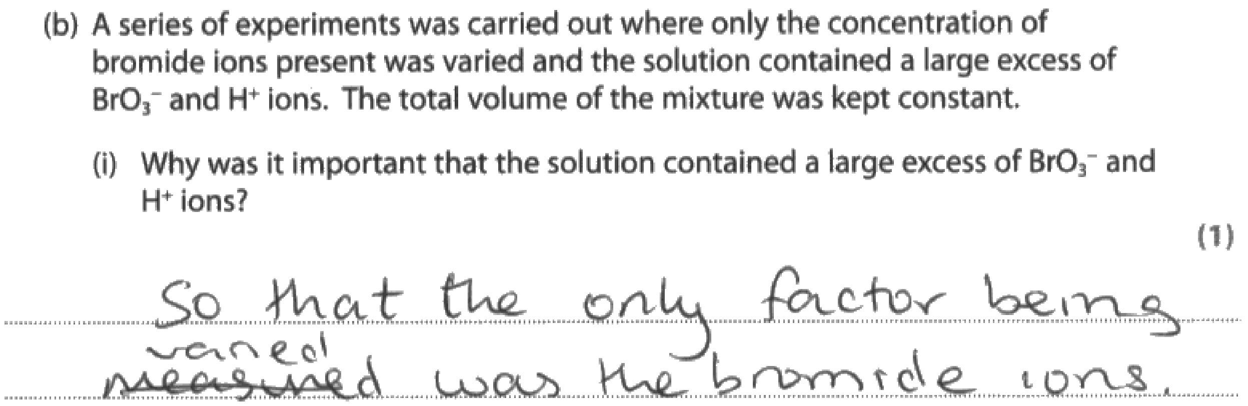
This is an example of a response that did gain the mark. However the last sentence is questionable because after the initial rate period the reaction does still proceed. Hence candidates need to be careful not to negate previously made correct comments.

ResultsPlus
Examiner Tip

The maxim 'less is more' often applies to answers given, as incorrect statements can negate correct ones. Hence care is needed to succintly answer the question and then move on to the next question.

Question 14 (b) (i)

The need for clarity of language and expression throughout the paper was also evident on this question. There was a clear need to refer to the 'concentration' of the species referred to in the candidates' answers if the mark was to be awarded. This should be well-appreciated by candidates since the subsequent rate equation question required the use of square brackets to represent concentration and there were no scripts reported that did not include these. It was acceptable to either refer to the bromate(V) and hydrogen ions as concentrations that would not change or to refer to the bromide ion concentration as the only one that should change.



(b) A series of experiments was carried out where only the concentration of bromide ions present was varied and the solution contained a large excess of BrO_3^- and H^+ ions. The total volume of the mixture was kept constant.

(i) Why was it important that the solution contained a large excess of BrO_3^- and H^+ ions?

(1)

So that the only factor being ~~measured~~ varied was the bromide ions.

ResultsPlus

Examiner Comments

An example of the frequently seen type of response which did not refer to the **concentration** of the species and so did not score.

ResultsPlus

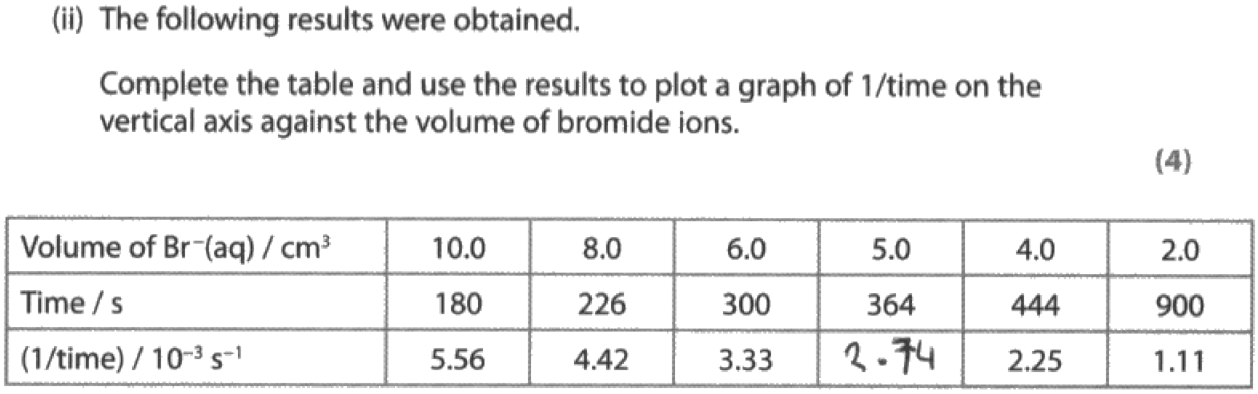
Examiner Tip

The rate equation includes the concentration of species and so when investigating the rate of a chemical reaction it is the concentration of the species that must be referred to.

Question 14 (b) (ii)-(iv)

In part (ii) the graphs were fairly well-drawn with many scoring full marks. The common errors were Omission of the value 2.75 to complete the table, which occasionally happened even though the point was plotted The lack of units on the axes or the lack of x10^{-3} on the y-axis Not extending the line through the origin Part (iii) 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 actually did not 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 (iv).

In part (iv) the subject of the rate equation was often given just 'hanging', that is, without the preface "rate=". This did not score. In addition a significant number of candidates that had correctly deduced the reaction order of the bromide ions suddenly changed it. 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. Writing units for rate constants remains an area that candidates need to practise as these were often further sources of error.

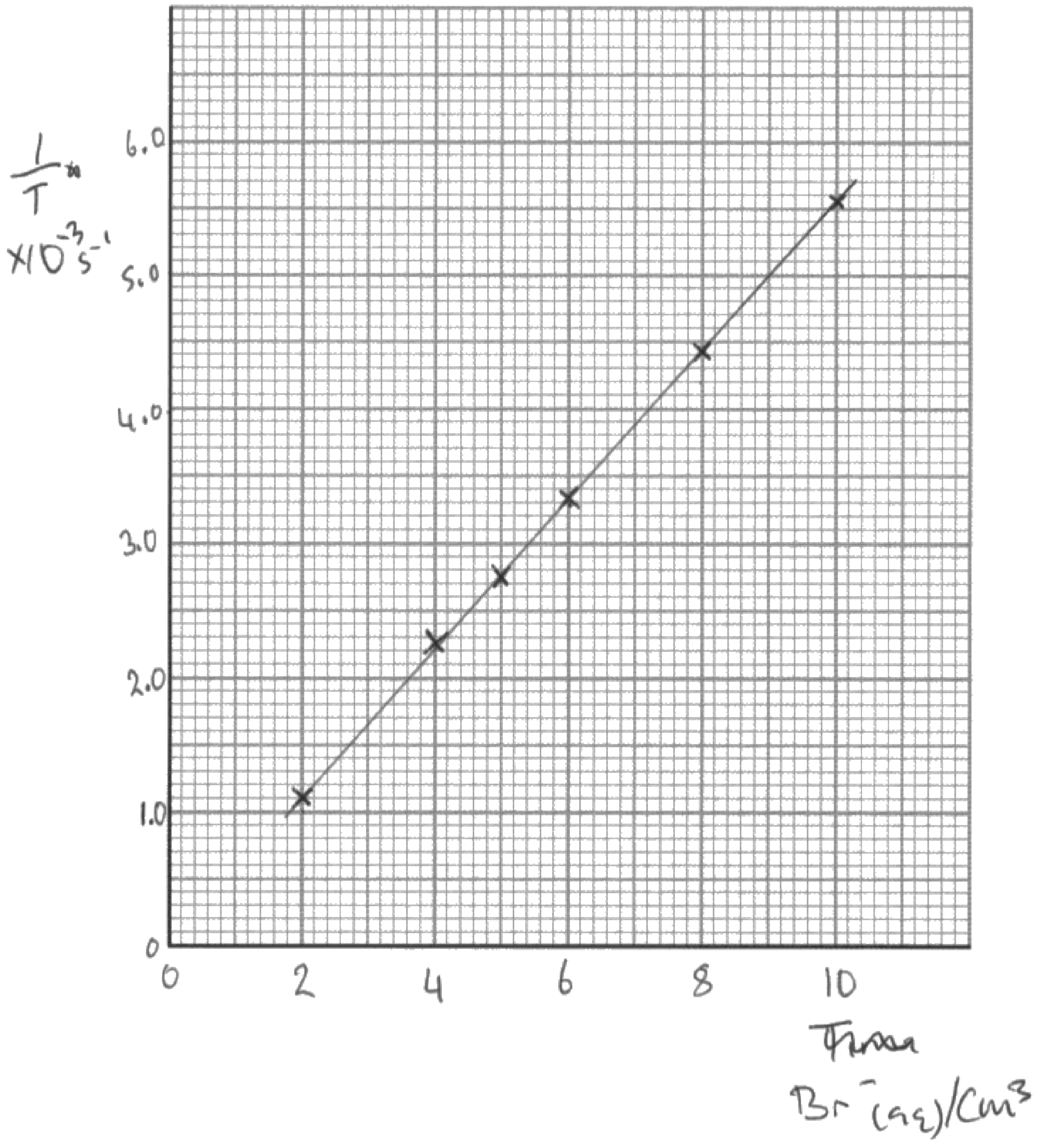


(ii) The following results were obtained.

Complete the table and use the results to plot a graph of 1/time on the vertical axis against the volume of bromide ions.

(4)

Volume of Br^-(aq) / cm^3	10.0	8.0	6.0	5.0	4.0	2.0
Time / s	180	226	300	364	444	900
(1/time) / 10^{-3} s^{-1}	5.56	4.42	3.33	2.74	2.25	1.11



(iii) Deduce the order of the reaction with respect to bromide ions.

Justify your answer.

rate ∝ $\frac{1}{T}$ rate = k $\frac{1}{T}$

(2)

~~1st order~~ ~~2nd~~ order 1st order

2nd

$\frac{1}{T} \times 10^{-3}\ s^{-1}$ is constant as the volume of Br^- ions ~~is~~ decreasing.

(iv) The reaction is first order with respect to bromate(V) ions and second order with respect to hydrogen ions. Write the overall rate equation for the 'bromine clock' reaction and deduce the units of the rate constant.

(2)

Rate equation:

$r = k[BrO_3^-][H_2]^2[Br^-]^{\cancel{\ }}$

$mol\,dm^{-3}s^{-1} = k(mol\,dm^{-3})^4$

$\frac{s^{-1}}{mol^3 dm^{-9}}$

Units of rate constant $mol^{-3}dm^{\cancel{\ }9}s^{-1}$

ResultsPlus

Examiner Comments

Part (ii) was awarded two marks because there were two key errors. Firstly the table has the incorrect value inserted and secondly, the line is not extended to zero.

Part(iii) scores one mark for the reaction order with respect to bromide ion concentration but the justification is incorrect.

Part (iii) has hydrogen molecules instead of hydrogen ions but the units given are appropriate; the units were allowed in any order although dm^9 mol^{-1} s^{-1} is preferred.

ResultsPlus

Examiner Tip

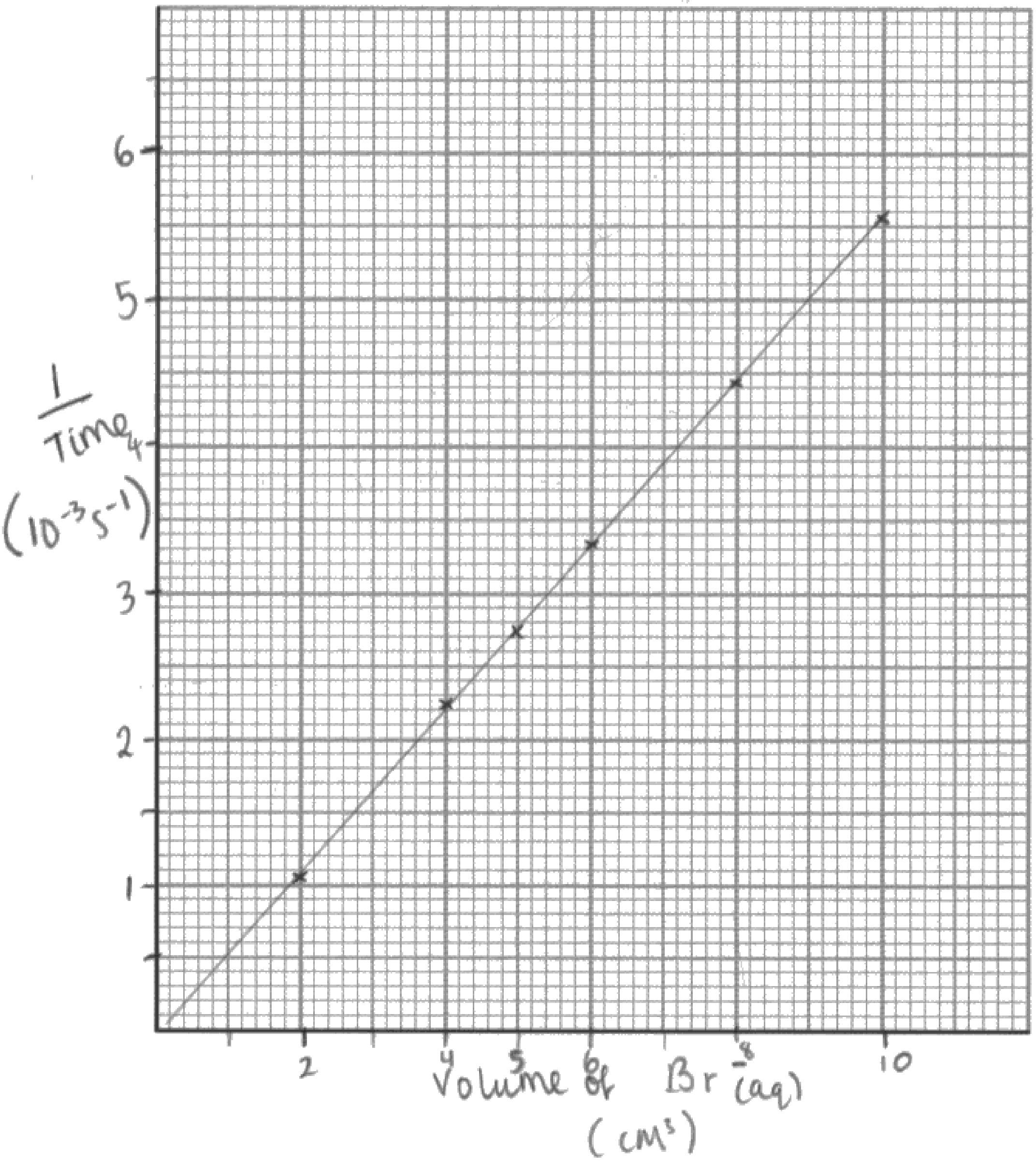
A simple and quick double-checking of the species in the question that are needed for the rate equation would have easily identified the error in part (iv) and so the practice of double-checking all work is very beneficial.

(ii) The following results were obtained.

Complete the table and use the results to plot a graph of 1/time on the vertical axis against the volume of bromide ions.

(4)

Volume of Br^-(aq) / cm^3	10.0	8.0	6.0	5.0	4.0	2.0
Time / s	180	226	300	364	444	900
(1/time) / 10^{-3} s^{-1}	5.56	4.42	3.33	2.75	2.25	1.11



(iii) Deduce the order of the reaction with respect to bromide ions.

Justify your answer.

(2)

first order because as the concentration of the ~~Br~~ bromide ions doubles, so does the rate which also doubles. The concentration is ∝ to the rate.

(iv) The reaction is first order with respect to bromate(V) ions and second order with respect to hydrogen ions. Write the overall rate equation for the 'bromine clock' reaction and deduce the units of the rate constant.

(2)

Rate equation: ~~RE~~ rate = $k[BrO_3^-][H^+]^2$ $(mol\,dm^{-3}\,s^{-1})^3$

Units of rate constant ~~moldm~~ $mol^3\,dm^{-9}\,s^{-3}$

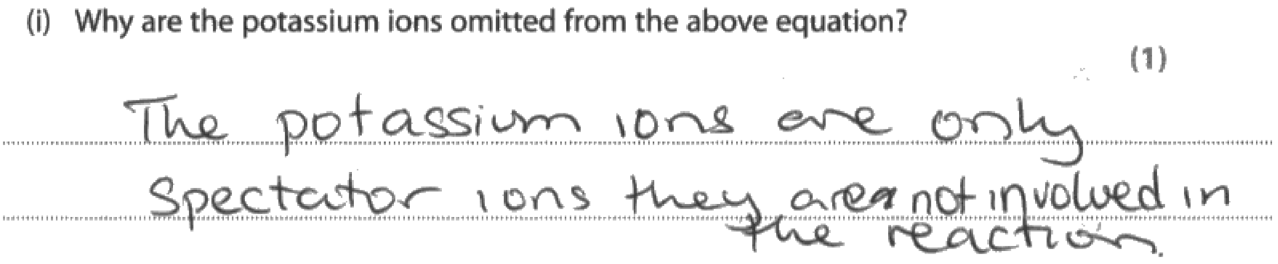
ResultsPlus
Examiner Comments

The response to part (ii) scores all four marks. It is noted that the line just extends slightly short of the origin but within the tolerance of one small square.

Part (iii) is correct for two marks but there is no credit given for part (iv) because the candidate has not included the bromide ions, which they have just deduced in part (iii), and the units do not match either their rate equation nor the true one.

Question 14 (c) (i)

It was pleasing to see that over 80% of candidates knew the term spectator ion or its meaning and so were able to gain the mark. Ionic equations are generally found to be very taxing for candidates but it would seem that at least the majority understand and can identify spectator ions.



(i) Why are the potassium ions omitted from the above equation?

(1)

The potassium ions are only Spectator ions they are not involved in the reaction.

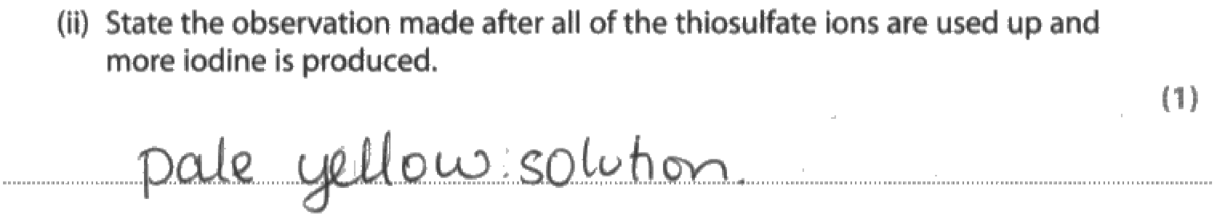
ResultsPlus

Examiner Comments

Either of these two statements would have been sufficient to have been awarded the mark.

Question 14 (c) (ii)

Again, a high-scoring question which demonstrates that the vast majority of candidates have a good grasp of the 'iodine clock' reaction and how starch is used as an indicator for reaction completion.



(ii) State the observation made after all of the thiosulfate ions are used up and more iodine is produced.

(1)

pale yellow solution.

ResultsPlus

Examiner Comments

This response is an example of where the situation has been misunderstood. While it is correct that iodine solution can be a pale yellow colour, the comment in the second bullet point has been missed namely that the "iodine produced preacts with the starch present".

ResultsPlus

Examiner Tip

Carefully read all of the information which precedes the question and those that follow it will use this information.

Question 14 (d)

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

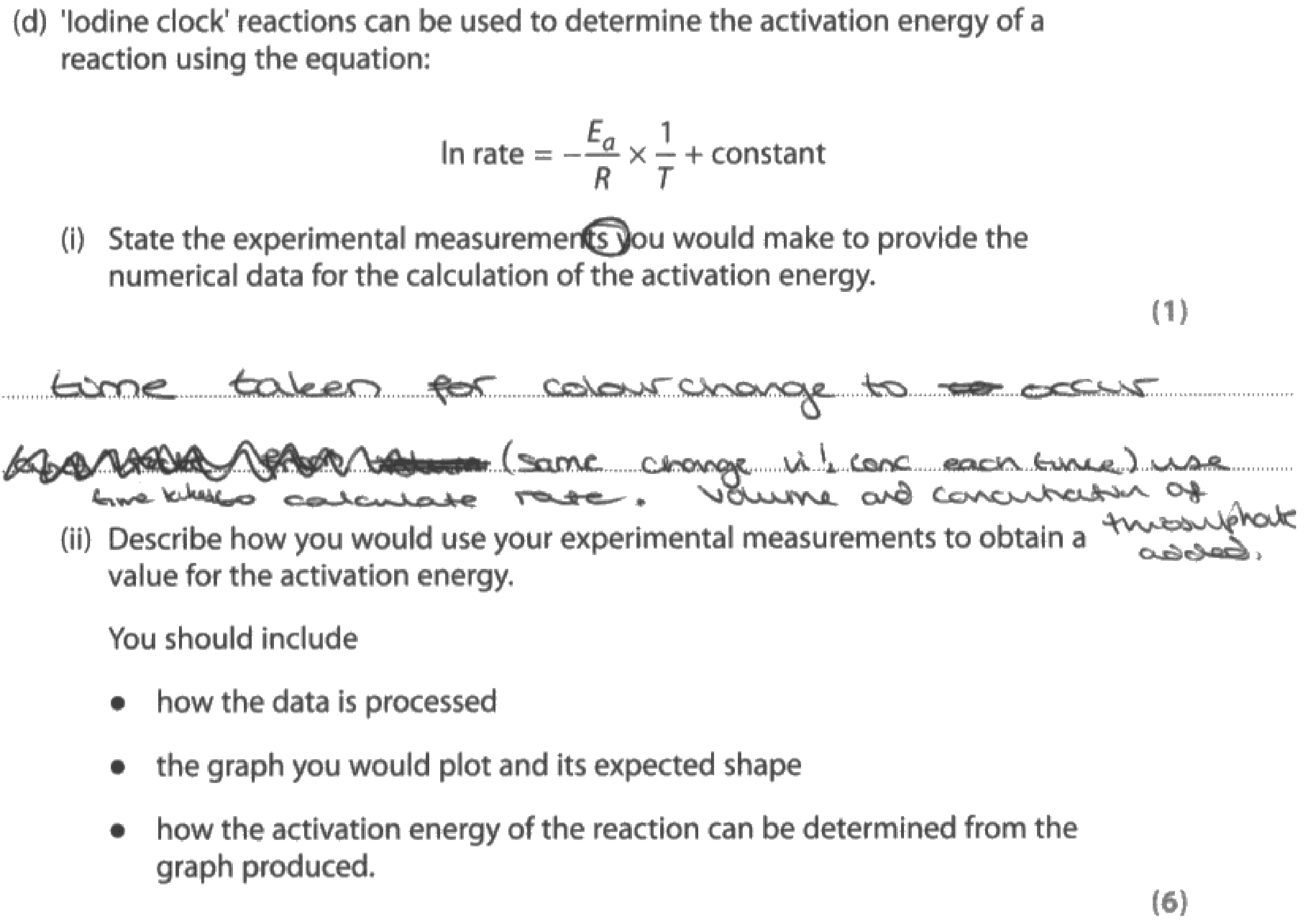
In part (i) responses of high quality stated that both time and temperature measurements would be needed to be taken. If mention was made in this section of temperature in kelvin (K) then this was noted for M1 in part (ii).

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 be taken. This M1 mark was the most frequently omitted mark but if present then it was most likely to be a high quality response.

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 via 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 mutliplied by a negative value of the gas constant. This served as a good discriminator and helped to identify high quality responses.



(d) 'Iodine clock' reactions can be used to determine the activation energy of a reaction 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)

time taken for colour change to ~~to~~ occur

[illegible] (same change in I_2 conc each time) use time taken to calculate rate. Volume and concentration of thiosulphate added.

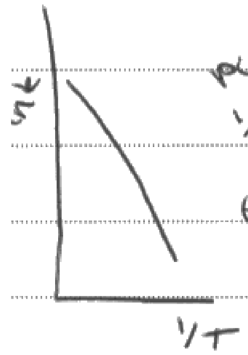
(ii) Describe how you would use your experimental measurements to obtain a value for the activation energy.

You should include

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

(6)

A known volume and concentration of thiosulphate ions are added when then react with a known ~~volume~~ amount of I_2. The time it takes for the blue black starch-iodine complex to form after all the thiosulphate ions have reacted is used to calculate initial rate. rate = 1/Time taken for colour change



plot graph of ~~rate~~ ln rate on vertical axis against Gives a negative linear correlation, 1/T on horizontal axis. The gradient is then calculated by change in y axis divided by change in x axis. This value is equal to $-\frac{Ea}{R}$. ~~[illegible]~~ multiply the gradient by −8.31 gives activation energy in kJ/mol.

(Total for Question 14 = 19 marks)

ResultsPlus

Examiner Comments

There is no mention of temperature being measured in part (i) and so no mark was awarded.

The first paragraph in part (ii) is concerned with rate and ln rate, with no mention of temperature. In this instance benefit of doubt was applied when 1/T is used as since there is no clear comment that this is time, it was taken as 1/Temperature and the mark awarded. On the sketch of the graph the y axis seems to have ln k rather than ln rate but this was allowed. This means that the only missing aspect of the answer is the absence of the correct temperature units.

ResultsPlus

Examiner Tip

Check that any comments made in a written section do match those given in a drawing or sketch.

(d) 'Iodine clock' reactions can be used to determine the activation energy of a reaction 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)

The time taken for the solution to turn black would be recorded, and the volumes of potassium iodide and hydrogen peroxide.

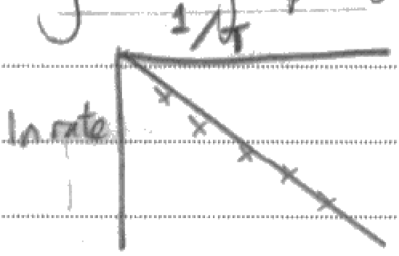
(ii) Describe how you would use your experimental measurements to obtain a value for the activation energy.

You should include

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

(6)

The reaction would be repeated using different concentrations of I^- (or H_2O_2). The time taken for the solution to turn black will be recorded. 1/time taken will give you 1/T which will be plotted on the x-axis of the graph. The natural log of these values will be used for the y-axis, forming a graph such as this:



It is expected that the line will be straight. The gradient of this line will be calculated $= \frac{\text{change in ln rate}}{\text{change in } 1/T}$.

From this $-\frac{Ea}{R}$ = gradient can be used to calculate thee activation energy.

(Total for Question 14 = 19 marks)

ResultsPlus

Examiner Comments

This is an example of a response where it is clear that the use of 1/T does not mean 1/Temperature but is clearly stated as 1/Time taken and so loses the mark for the x axis.

There is no reference to the temperature conversion units of kelvin, nor is the rearrangement to give activation energy explained. Hence this response scores 3 marks for part (ii) and nothing for part (i) since temperature is not mentioned.

ResultsPlus

Examiner Tip

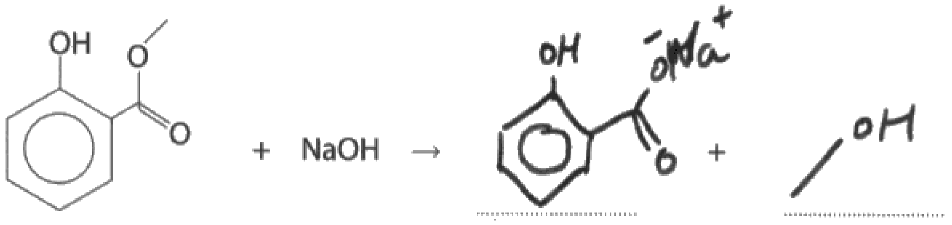
Make sure that the correct understanding of symbols is clear. Learn that the use of capital T is for temperature and the use of lower case t is for time.

Question 15 (a) (i)

A lot of work was required of candidates for only one mark. The skeletal drawing of the ester group in the methyl salicylate proved challenging to many because on hydrolysis the other product to the carboxylate salt was often given as water. If methanol was correctly given, then the drawing of the sodium carboxylate salt also proved challenging. The charges on the salt were not essential but if given then they must be correct.

(a) (i) Complete the equation for the alkaline hydrolysis of the ester group in methyl salicylate, using sodium hydroxide.

(1)

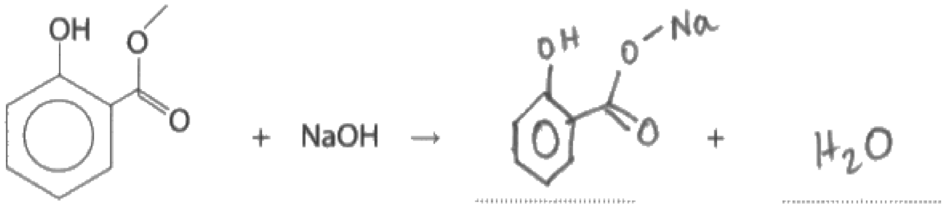


Examiner Comments

The formula of the sodium salt of methyl salicylate is correct and this candidate has given the skeletal formula for methanol which was acceptable. Hence the mark was awarded.

(a) (i) Complete the equation for the alkaline hydrolysis of the ester group in methyl salicylate, using sodium hydroxide.

(1)



Examiner Comments

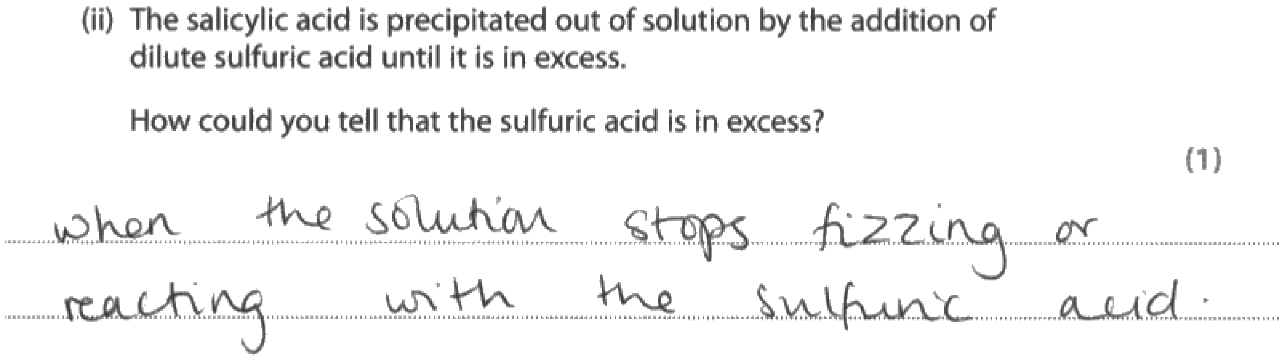
This is an example of a response that was penalised for the clear drawing of a covalent bond between the oxygen and the sodium. Of course the other product is also incorrect but the incorrect drawing of the organic product is worthy of note.

Examiner Tip

Single lines in formulae are always used to represent covalent bonds and care should be taken so that when used this is truly meant.

Question 15 (a) (ii)

Many candidates will have done a similar practical preparing aspirin and a similar precipitation step is required so they could draw on prior experience. Even those who had not done such practical work could work out the step required but a significant number of candidates simply referred to the solution as being acidic or that the pH would be below 7 without an explanation of how this would be determined. Use of a pH meter would have been a suitable suggestion. Similarly the reference to the use of an indicator was seen and this was acceptable as long as the appropriate colour change was given. In this instance the effect that this might have on the colour of the product was not a concern.



(ii) The salicylic acid is precipitated out of solution by the addition of dilute sulfuric acid until it is in excess.

How could you tell that the sulfuric acid is in excess?

(1)

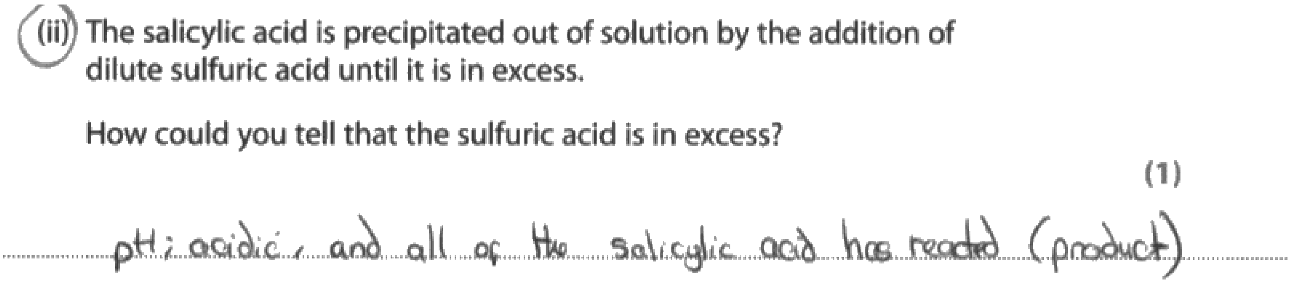
when the solution stops fizzing or reacting with the sulfuric acid.

ResultsPlus
Examiner Comments

This is an example of a response which incorrectly refers to the use of a carbonate and the observation of bubbles. While this is the test for an acid, it would not work for this situation of determining when the acid is in excess and did not score.

ResultsPlus
Examiner Tip

Practical tests for substances are very important and should be well-learnt. However their suitability or otherwise can depend on the context used and so this should be kept in mind.



(ii) The salicylic acid is precipitated out of solution by the addition of dilute sulfuric acid until it is in excess.

How could you tell that the sulfuric acid is in excess?

(1)

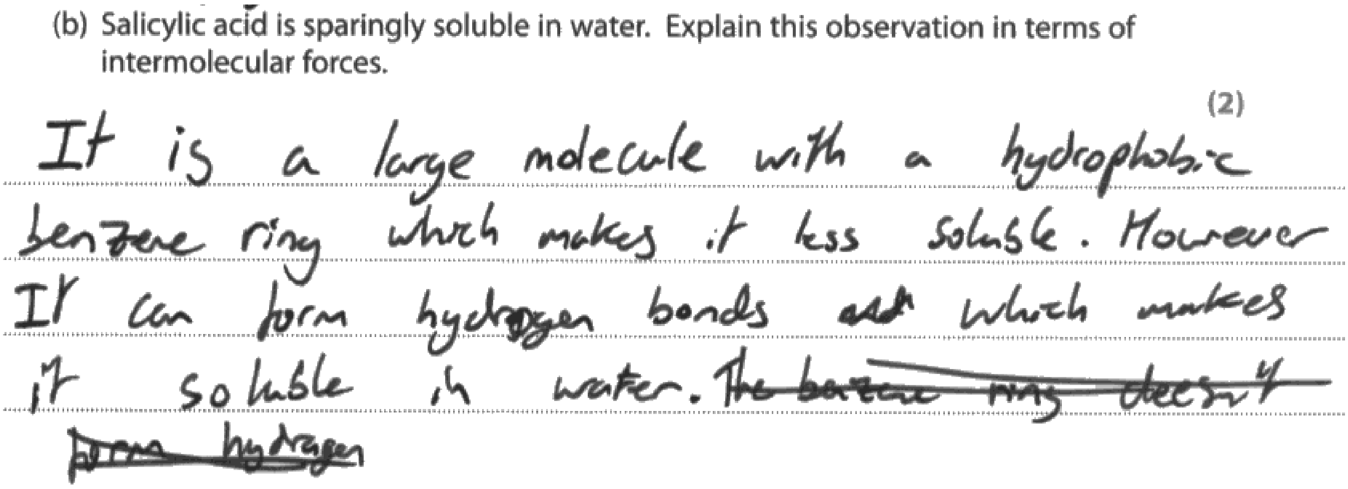
pH: acidic, and all of the salicylic acid has reacted (product)

ResultsPlus
Examiner Comments

Here is an example of a response which, while correct, does not answer the question. It is true that if the sulfuric acid is in excess then the pH will be acidic but the question requires an answer which states how someone could tell that. This is not given and so this response does not score.

Question 15 (b)

This question clearly states to explain the sparingly soluble nature of salicylic acid in terms of intermolecular forces. Most candidates correctly commented on the hydrogen bonding that can form between salicylic acid and water and so scored one mark. Only the top 10% of candidates commented on the London forces that exist between the rings of salicylic acid molecules and so hinder the solubility of salicylic acid in water. This is an area that candidates could benefit from greater consideration.



(b) Salicylic acid is sparingly soluble in water. Explain this observation in terms of intermolecular forces.

(2)

It is a large molecule with a hydrophobic benzene ring which makes it less soluble. However It can form hydrogen bonds ~~and~~ which makes it soluble in water. ~~The benzene ring doesn't form hydrogen~~

ResultsPlus

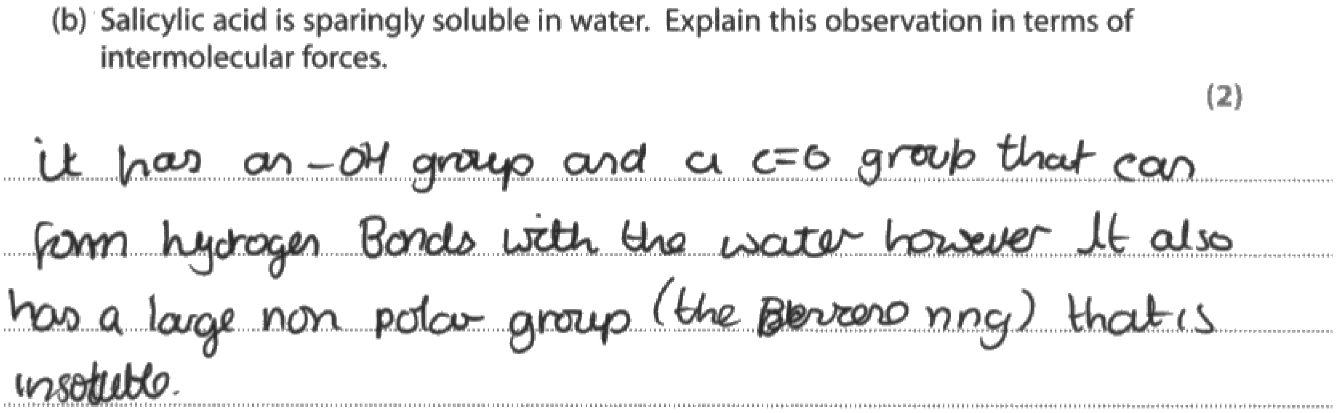
Examiner Comments

Although hydrogen bonds are referred to there is no explicit statement that these are between salicylic acid and water. Hence this mark was not awarded. The use of terms such as "hydrophobic" was ignored because the question clearly requires an explanation in terms of intermolecular forces.

ResultsPlus

Examiner Tip

Re-read the requirements of the question and then review the answer given to ensure that they match. If intermolecular forces are requested then either London forces, dipole-dipole forces or hydrogen bonding would be expected to be named and commented on.



(b) Salicylic acid is sparingly soluble in water. Explain this observation in terms of intermolecular forces.

(2)

it has an -OH group and a C=O group that can form hydrogen Bonds with the water however It also has a large non polar group (the Benzene ring) that is insoluble.

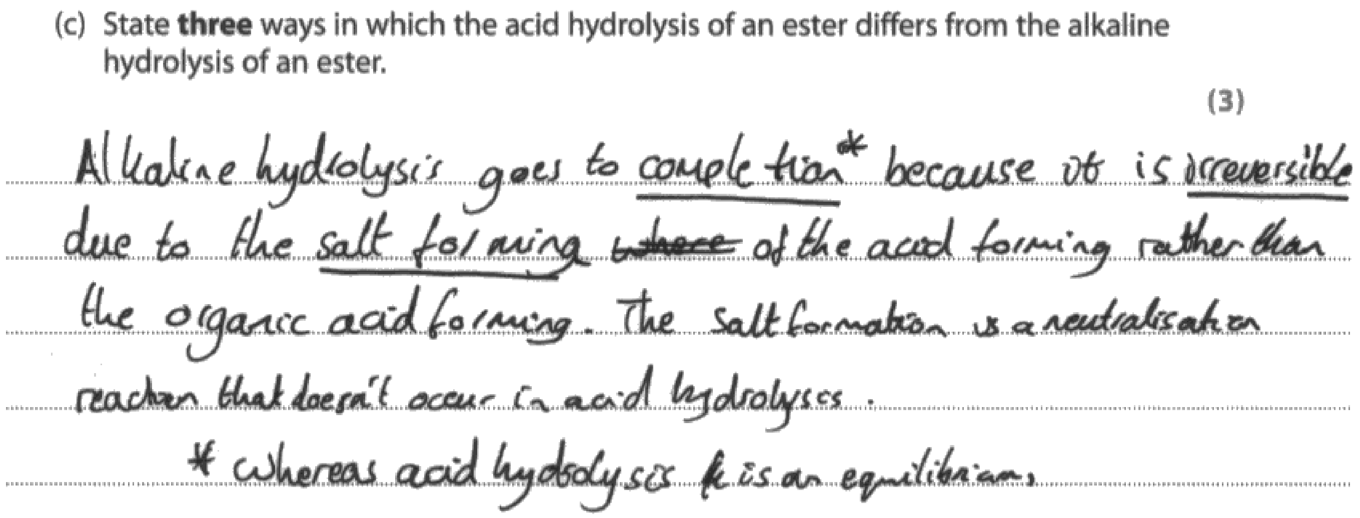
ResultsPlus

Examiner Comments

This is an example of a response that does make clear reference to hydrogen bonding between the salicylic acid and water which gains the mark. The statement that the benzene ring is non-polar is correct but does not go on to refer to the intermolecular forces that result from this and so the second mark is not awarded.

Question 15 (c)

This was a question which discriminated well between candidates. Some candidates were only able to give one difference in the hydrolysis reactions of acid and alkali or none at all, while others were able to give two or even three differences. The most common difference identified was the reversibility of acid hydrolysis compared to the irreversibility of alkaline hydrolysis. The difference in the products was the second most common difference identifiied by only a few candidates who were able to state that the acid is a catalyst whereas the alkali is a reagent.



(c) State **three** ways in which the acid hydrolysis of an ester differs from the alkaline hydrolysis of an ester.

(3)

Alkaline hydrolysis goes to completion* because it is irreversible due to the salt forming ~~where~~ of the acid forming rather than the organic acid forming. The salt formation is a neutralisation reaction that doesn't occur in acid hydrolysis.

* whereas acid hydrolysis ~~k~~ is an equilibrium,

Examiner Comments

The layout of the answer is not clearly done to show three differences between acid and alkaline hydrolysis. However there are two correct differences given, namely the irreversible reaction with alkali and the formation of the carboxylate salt with alkali.

Examiner Tip

Bullet points or a numbering system are appropriate methods of clearly laying out an answer when a number of different points of comparison are required.

(c) State **three** ways in which the acid hydrolysis of an ester differs from the alkaline hydrolysis of an ester.

(3)

- acid hydrolysis of an ester involves an acid
- HCl is a product also formed
- an acid ~~chroti~~ chloride is formed
- the product is in aqueous form

ResultsPlus
Examiner Comments

The layout is better in this response but unfortunately not the chemistry. The first bullet point cannot realistically be expected to be worthy of credit. The second bullet point gives the product of esterification using an acyl chloride which is needed in a subsequent question but does not score here. The third bullet point is also not relevant.

ResultsPlus
Examiner Tip

Avoid muddling answers to different questions.

Question 15 (d)

Over both parts of this question there was a good spread of marks and proved further opportunity for differentiation between candidates.

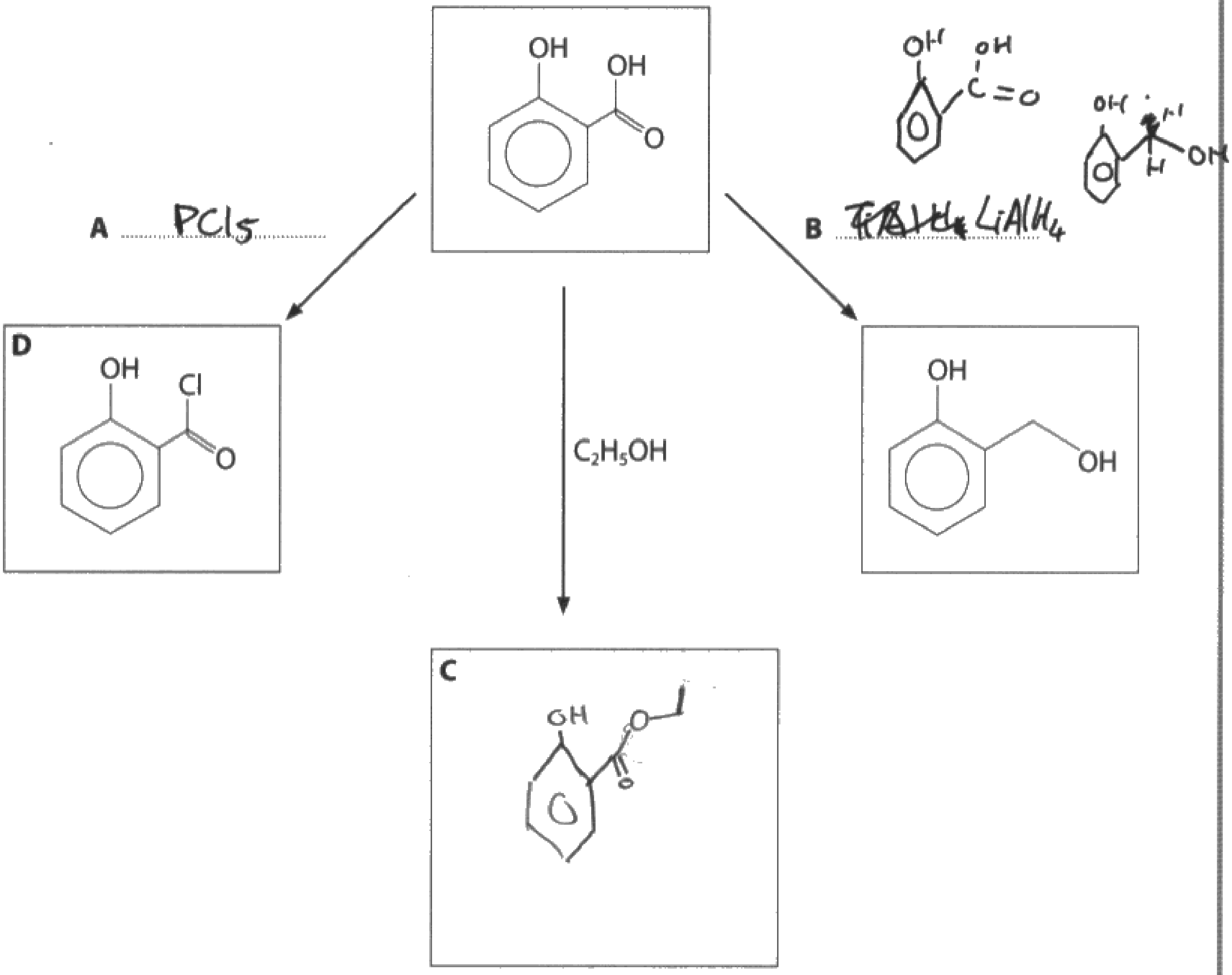
In part (i) the reducing agent was usually correct, closely followed by the structure of the ethyl ester. Candidates should know that PCl_5 and not HCl is used to convert a carboxylic acid group into an acyl chloride but this was frequently seen.

Part (ii) required two differences and so it was insufficient to make the statement that compound D would produce hydrogen chloride without also stating that salicylic acid would produce water. It was pleasing that the production of 'hydrochloric acid' rather than hydrogen chloride was very rarely seen. There were four differences allowed on the mark scheme so there was plenty of scope for candidates to gain both marks.

(d) Salicylic acid can undergo various reactions as outlined below.

(i) Give the **formula** of the reagents **A** and **B** and the **skeletal** formula of the product **C**.

(3)



(ii) Both compound **D** and salicylic acid react with ethanol. State **two** differences between these reactions.

(2)

The D produces toxic misty fumes.

~~D goes to completion without a catalyst~~.

D occurs without a catalyst or heating.

ResultsPlus
Examiner Comments

Part (i) is all correct in this response and scores three marks.

In part (ii) the identity of the steamy fumes is not given nor any comparison and so no credit given. The statement that "D occurs without a catalyst" implies that salicylic acid therefore does need a catalyst and so this was allowed as a comparison, thus one mark was awarded.

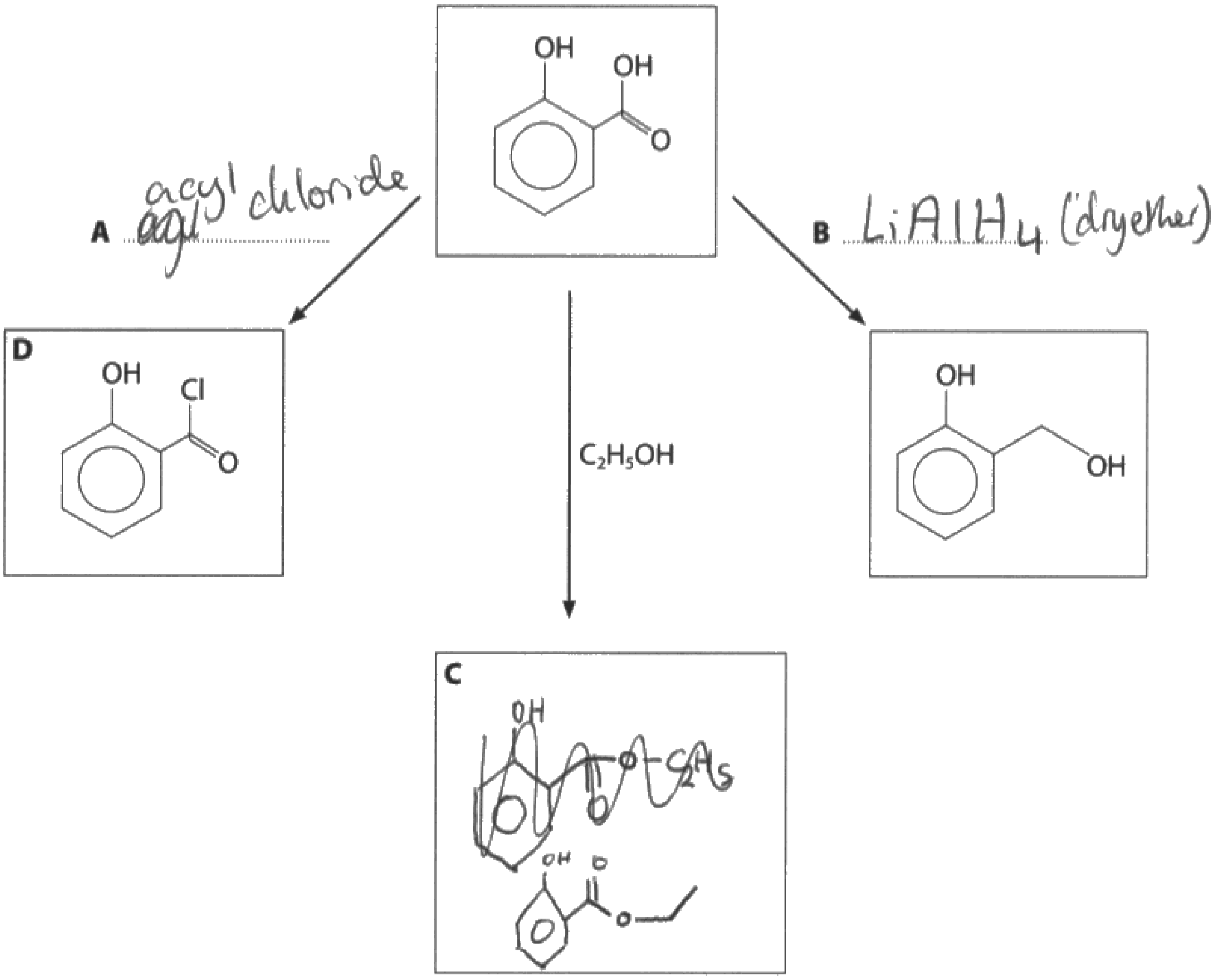
ResultsPlus
Examiner Tip

Clearly make a comparison when 'differences' are required.

(d) Salicylic acid can undergo various reactions as outlined below.

(i) Give the **formula** of the reagents **A** and **B** and the **skeletal** formula of the product **C**.

(3)



(ii) Both compound **D** and salicylic acid react with ethanol. State **two** differences between these reactions.

(2)

compound D will B produce HCl (g) as only on the products while salicylic acid will just form an ester molecule

ResultsPlus
Examiner Comments

This response scores two marks for part (i) as B and C are correct. The reference to the solvent for the reducing agent was not needed and the crossing out is clearly replaced.

In part (ii) this response is an example of where it is stated what compound D produces but not what salicylic acid produces. Both produce esters so that comment is not creditworthy. Hence no marks were given for this part of the question.

Question 15 (e)

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 an explicit statement that there are three different proton environments in ethanol. Some candidates often implied this but did not state it, with the resultant loss of this mark. The quality of language was also evident in the way that the (n+1) rule was explained which was the third marking point on the mark scheme.

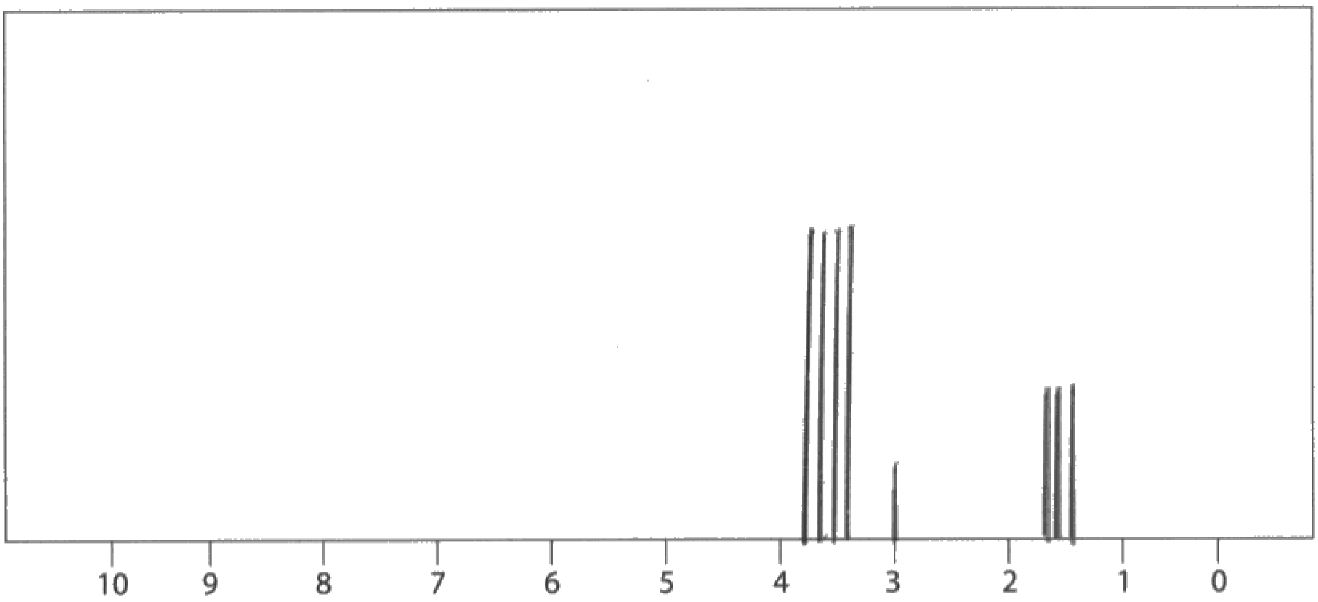
The mark for the "ratio of the areas under each set of peaks" was often not awarded either because the candidate did not refer to it anywhere in their answer or gave the ratio as 3:2:1 without clearly identifying what the numbers referred to. The explanation could have been given in a paragraph or from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

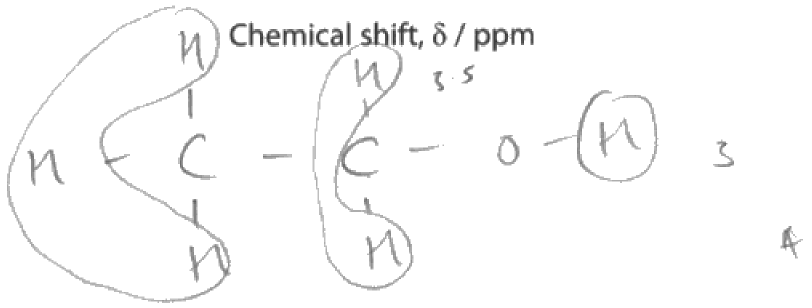
The splitting pattern and chemical shifts of the sets of peaks were usually evident from the NMR sketch. The drawings of triplet and quartet frequently 'left a lot to be desired' but this was not penalised. Occasionally the diagram contradicted the text which was disappointing and resulted in a loss of credit. The splitting pattern of a triplet, quartet and singlet were usually correct but the chemical shift of the quartet was frequently given too low a value so this mark was not awarded. Clearly further practice at reading the NMR charts is required.

*(e) Use chemical shift data from the Data Booklet to sketch the **high** resolution proton nmr spectrum for ethanol. 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)





There are 3 peaks as there are 3 different hydrogen environments and ethanol has a splitting pattern of 3, 1, 4.

The oxygen H in the OH group produces a singlet as it isn't adjacent to any carbons with a hydrogen. The oxygen hydrogens in the CH_2 group produce a quartet peak as it's adjacent to a CH_3 group. The hydrogens in the CH_3 group produce a triplet peak as it's adjacent to a CH_2 ~~grou~~ group. The areas under each peak are ~~3/4~~ 3:1:4 as there are 3 hydrogens in CH_3, 2 hydrogens in CH_2 and 1 in OH.

ResultsPlus

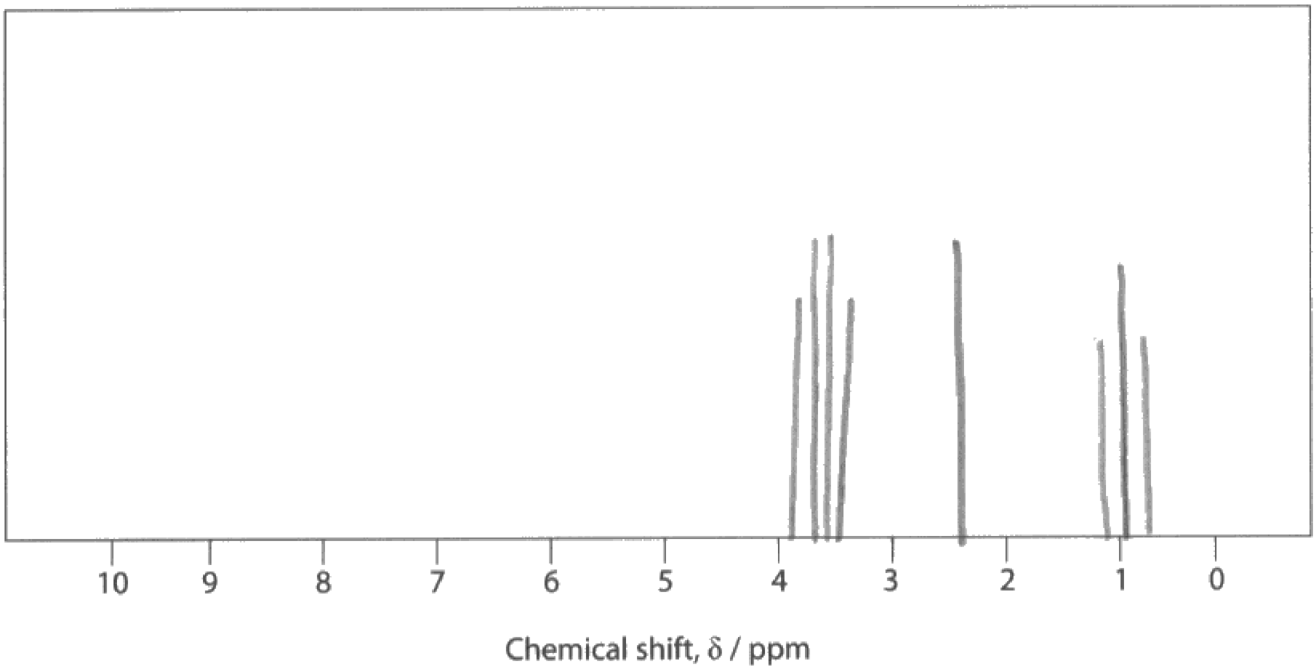
Examiner Comments

In this response at the end the area ratio is stated to be the same as the splitting pattern, namely 3:1:4 which is clearly incorrect. Otherwise the response correctly addresses the question in a suitable manner so was awarded four marks.

*(e) Use chemical shift data from the Data Booklet to sketch the **high** resolution proton nmr spectrum for ethanol. 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)



There are 3 peaks on the diagram as there are 3 proton environments. The first peak at 1 is caused by the CH_3 group. It is split into a triplet as there are 2 hydrogens on adjacent carbon. The second peak at around 2.4 is a singlet and is caused by the OH group, there are no adjacent carbons to the H. The peak at around 3.7 is caused by the C bonded to the OH group. It is a quartet as there are 3 hydrogens on adjacent carbon

ResultsPlus
Examiner Comments

This response was awarded three marks.

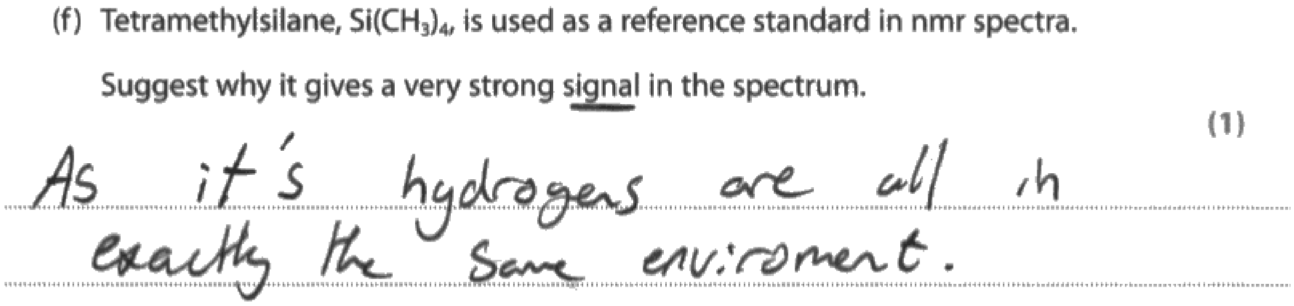
There is no mention or reference to the 'area ratios' of the peaks and so this mark is not awarded. Also, if the response is read carefully the candidate has written that the peak at chemical shift 3.7 is due to a "carbon" and not a hydrogen/proton and so a mark is lost.

ResultsPlus
Examiner Tip

An incorrect statement will negate a correct one.

Careful re-reading of all answers can eliminate or allow errors to be corrected.

There were two aspects to address in this question, namely why there is a single "signal" and why it is "very strong". It was insufficient to state that tetramethylsilane (TMS) had a single proton environment since many other molecules also have this, but would not give a strong signal. Similarly, vague or ambiguous terms such as TMS has "lots of" or "many" protons in an identical environment were not specific enough to score the mark. Sufficient detail and clarity of language were needed to achieve both aspects of the question.



(f) Tetramethylsilane, $Si(CH_3)_4$, is used as a reference standard in nmr spectra.

Suggest why it gives a very strong signal in the spectrum.

(1)

As it's hydrogens are all in exactly the same enviroment.

ResultsPlus
Examiner Comments

This is an example of a response which did not score because the specific number of hydrogen atoms in TMS was not stated.

ResultsPlus
Examiner Tip

If a question has two aspects then be sure to address both of them in your answer. Questions towards the end of a question typically increase in demand so make sure that the answer given does also.

(f) Tetramethylsilane, $Si(CH_3)_4$, is used as a reference standard in nmr spectra.

Suggest why it gives a very strong signal in the spectrum.

(1)

It has one proton enviroment, is non-toxic and is inert.

ResultsPlus

Examiner Comments

This response adds detail about why TMS is such a useful reference standard with respect to its non-toxicity but the aspect of the question about why the signal is 'very strong' has not been addressed. Hence the response does not score.

Question 15 (g)

The majority of candidates knew the type of radiation used to create an NMR spectrum which was pleasing. However a wide range of different radiation types were seen from the full electromagnetic spectrum.

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

(1)

microwave

UV

ResultsPlus

Examiner Comments

It would seem that this candidate is unsure which type of radiation is used in NMR spectroscopy and so has written two answers, neither of which is correct. However even if one of them had been correct, the incorrect response would have negated the correct one so this practice should always be avoided.

ResultsPlus

Examiner Tip

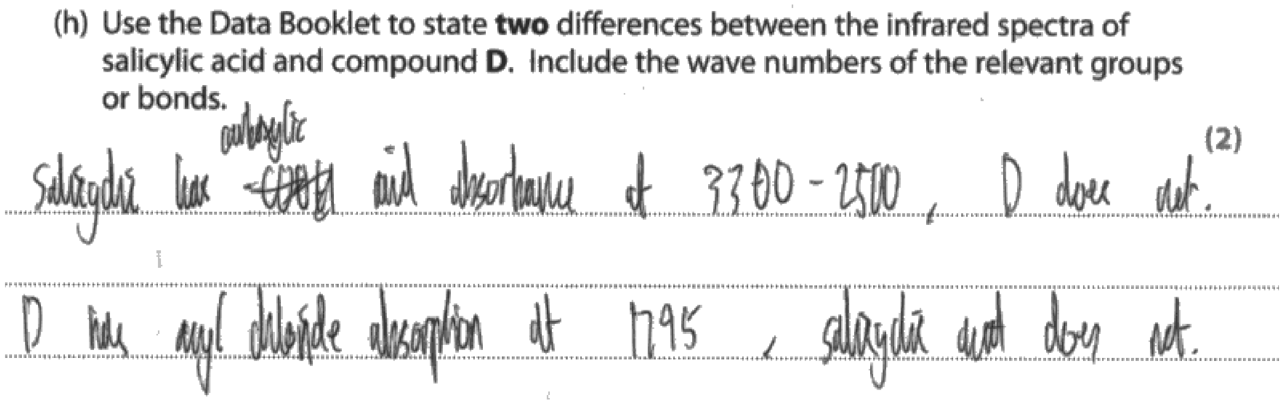
When one answer is required never give two answers.

Question 15 (h)

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 wave number 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 salicylic acid or compound D. Hence if a response did not give all the detail required then both marks were not awarded.



(h) Use the Data Booklet to state **two** differences between the infrared spectra of salicylic acid and compound **D**. Include the wave numbers of the relevant groups or bonds.

(2)

Salicylic has ~~COOH~~ carboxylic acid absorbance at 3300 - 2500, D does not.

D has acyl chloride absorption at 1795, salicylic acid does not.

Examiner Comments

This is an example of a response where the choice of infrared differences meant that either a brief answer was sufficient or a longer one.

The reference to the O-H peak/trough at 3300-2500 only needs a brief comment since a salicylic acid spectrum has one but is absent in a compound D spectrum. However both molecules will have a peak/trough in their spectra due to the C=O bond and so both wavenumber ranges, thus a longer answer is required to gain the mark. In this response both ranges are not given and so the second mark was not awarded.

(h) Use the Data Booklet to state **two** differences between the infrared spectra of salicylic acid and compound **D**. Include the wave numbers of the relevant groups or bonds.

(2)

Compound D will have a peak around 700 cm^{-1} due to a C–Cl bond, ~~Sali~~ salicyclic acid wont ~~have~~ have this. ~~&~~ Salicylic acid will have a peak around 1720 cm^{-1}, this is a C=O bond in carboxylic acids which D doesn't have.

(Total for Question 15 = 21 marks)

ResultsPlus

Examiner Comments

The candidate here has not given the wave number ranges for the relevant bonds in an infrared spectrum but has decided on a single numerical value. This was not acceptable because the peak or trough in the spectrum can be anywhere within that range and is not some 'middle figure'. Hence this response did not score.

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 whilst a lower case 't' is used for time.
- Data booklet infrared spectroscopy ranges should be quoted rather than the mid-point within such ranges.
- 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.

Grade Boundaries

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