

Examiners' Report
June 2013

GCE Chemistry 6CH04 01

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June 2013

Publications Code UA035565

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Introduction

The paper proved accessible to most candidates and appeared to provide reasonable opportunities for well-prepared candidates to demonstrate their knowledge and understanding. The mean score in the multiple choice section was above 75%. This was significantly higher than sections B or C. Almost all candidates gave the correct response (in order of decreasing difficulty) to the following multiple choice questions: 13, 11, 1a, 15 and 16. The multiple choice questions that proved the most challenging were: 2, 4b, and 7. Candidates displayed a sound knowledge of the topics examined and, for the most part, tackled the numerical questions with confidence. Only the better candidates were able to apply their knowledge in unfamiliar contexts and few demonstrated a secure understanding of the experimental aspects of the subject. There were quite a number of examples of errors which clearly arose from a failure to read the question fully or with sufficient care.

Question 17 (a) (b) (c)

Candidates scored extremely well on this group of entropy calculations, displaying a good understanding of the formulae involved. The most common errors were in the retrieval of data and the failure, despite very clear guidance in the stem of the question, to double the data booklet value for the standard molar entropy of hydrogen. Quite a number of candidates omitted the positive sign from the value calculated in 17b and/or neglected to correct their calculated value to three significant figures.

SECTION B

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

17 The equation for the combustion of hydrogen is



(a) Use the standard molar entropies on page 2 and page 25 of the data booklet to calculate the standard entropy change of the system ($\Delta S_{\text{system}}^{\ominus}$) for this reaction.

Note that the standard molar entropies of the elements are given **per atom** so that the standard molar entropy of oxygen, $S^{\ominus}[\frac{1}{2}\text{O}_2(\text{g})] = +102.5 \text{ J mol}^{-1} \text{ K}^{-1}$.

$$S^{\ominus}[\text{H}_2] = 2 \times 65.3 \quad S^{\ominus}[\text{H}_2\text{O}] = 69.9. \quad (3)$$

$$\Delta S_{\text{system}}^{\ominus} = \sum S_{\text{products}} - \sum S_{\text{reactants}}.$$

$$\Delta S_{\text{system}}^{\ominus} = 69.9 - (130.6 + 102.5)$$

$$\Delta S_{\text{system}}^{\ominus} = \underline{\underline{-163.2 \text{ J mol}^{-1} \text{ K}^{-1}}}$$

(b) The standard enthalpy change for the combustion of hydrogen is $\underline{\underline{-285.8 \text{ kJ mol}^{-1}}}$. Use this value to calculate the entropy change of the surroundings for the combustion of hydrogen at 298 K. Give your answer to 3 significant figures and include a sign and units.

$$\Delta S_{\text{surr}} = \frac{-\Delta H}{T} = \frac{-(-285.8 \times 1000)}{298} \quad (3)$$

$$\Delta S_{\text{surroundings}} = \underline{\underline{+959.0 \text{ J mol}^{-1} \text{ K}^{-1}}}$$

(c) Use your answers to (a) and (b) to calculate the total entropy change ($\Delta S_{\text{total}}^{\ominus}$) for the combustion of 1 mol of hydrogen. Include a sign and units in your answer.

(2)

$$\Delta S_{\text{total}}^{\ominus} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

$$\Delta S_{\text{total}}^{\ominus} = -163.2 + 959.0$$

$$\Delta S_{\text{total}}^{\ominus} = + \underline{\underline{795.8}} \text{ J mol}^{-1} \text{ K}^{-1}$$



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Examiner Comments

The calculations have been completed successfully but in (b) it is apparent that the idea of significant figures is not understood.



ResultsPlus

Examiner Tip

One way of tackling significant figures is to write the number in scientific notation standard form when the number of significant figures must equal the number of digits in the coefficient (the number in front 10 to the power).

SECTION B

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

17 The equation for the combustion of hydrogen is



(a) Use the standard molar entropies on page 2 and page 25 of the data booklet to calculate the standard entropy change of the system ($\Delta S_{\text{system}}^\ominus$) for this reaction.

Note that the standard molar entropies of the elements are given **per atom** so that the standard molar entropy of oxygen, $S^\ominus[\frac{1}{2}\text{O}_2(\text{g})] = +102.5 \text{ J mol}^{-1} \text{ K}^{-1}$.

(3)

$$\begin{aligned} \Delta S_{\text{system}}^\ominus &= \sum S_{\text{products}}^\ominus - \sum S_{\text{reactants}}^\ominus \\ &= (109.6) - [(65.3 \times 2) + 102.5] \\ &= -123.5 \text{ J/mol/K} \\ &= -124 \text{ J/mol/K} \end{aligned}$$

(b) The standard enthalpy change for the combustion of hydrogen is $-285.8 \text{ kJ mol}^{-1}$. Use this value to calculate the entropy change of the surroundings for the combustion of hydrogen at 298 K. Give your answer to 3 significant figures and include a sign and units.

(3)

$$\begin{aligned} \Delta H_{\text{surrounding}}^\ominus &= -\frac{\Delta H}{T} = \frac{-(-285.8 \times 1000)}{298} \\ &= +959 \text{ J/mol/K} \end{aligned}$$

(c) Use your answers to (a) and (b) to calculate the total entropy change ($\Delta S_{\text{total}}^{\ominus}$) for the combustion of 1 mol of hydrogen. Include a sign and units in your answer.

(2)

$$\Delta S_{\text{total}}^{\ominus} = \Delta S_{\text{system}}^{\ominus} + \Delta S_{\text{surrounding}}^{\ominus}$$

$$\Delta S_{\text{total}}^{\ominus} = -123.5 + 959$$

$$\Delta S_{\text{total}}^{\ominus} = 835.6 \text{ J/mol/K}$$

$$\Delta S_{\text{total}}^{\ominus} = 836 \text{ J/mol/K}$$



ResultsPlus

Examiner Comments

In this example an incorrect value has been obtained from the Data booklet (a very common error) but the subsequent calculations are correct and gain full credit.



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Examiner Tip

Do note that, while the form J/mol/K is acceptable, $\text{Jmol}^{-1}\text{K}^{-1}$ should be preferred.

Question 17 (d)

The distinction between kinetic and thermodynamic stability was very poorly understood as was the link between kinetic stability and activation energy, and that between thermodynamic stability and ΔS_{total} . Many candidates discussed the kinetic and thermodynamic stability of the individual elements leading to statements like 'oxygen is an inert gas'.

* (d) By considering both the thermodynamic stability and the kinetic inertness of a mixture of hydrogen and oxygen, explain why hydrogen does not react with oxygen unless ignited.

ie its thermodynamically stable (2)

The reaction is not thermodynamically feasible because the reaction is decreasing in order (going from two gases to a liquid), and this is shown by the negative sign of the ΔS system. However the ΔS_{total} is positive because the ΔS° surroundings is large. This means that the reaction is kinetically feasible.

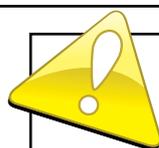
(Total for Question 17 = 10 marks)

enough positive value



ResultsPlus Examiner Comments

There are some typical errors in this response. The candidate states that the reaction is 'feasible i.e. stable' which immediately makes the first mark inaccessible. The discussion associates the thermodynamic feasibility with ΔS_{system} and the kinetic stability with ΔS_{total} .



ResultsPlus Examiner Tip

These are key ideas in Chemistry and well worth taking the time to understand properly.

* (d) By considering both the thermodynamic stability and the kinetic inertness of a mixture of hydrogen and oxygen, explain why hydrogen does not react with oxygen unless ignited.

(2)

Even though $\Delta S^{\ominus}_{\text{total}}$ for the reaction is positive, which indicates the reaction is feasible, due to the reactants being more stable than the products the reaction will not take place at ~~at~~ standard conditions of 25°C and 1 atm, as the ~~reactants~~ ^{reactants} will be kinetically inert at standard conditions it needs ignition before the particles have a high enough kinetic energy to react.



ResultsPlus

Examiner Comments

This candidate is working along the right lines but there is too much repetition of the question material at the expense of explanation of the meaning of these terms.

* (d) By considering both the thermodynamic stability and the kinetic inertness of a mixture of hydrogen and oxygen, explain why hydrogen does not react with oxygen unless ignited.

(2)

Despite a mixture of hydrogen and oxygen being ~~not~~ having a low thermodynamic stability (shown by the large positive value for $\Delta S^{\ominus}_{\text{total}}$), hydrogen and oxygen will not react ~~before~~ unless ~~heated~~ ignited as they have a high level of kinetic inertness due to the high activation energy that needs to be overcome. Ignition ~~for~~ provides energy to overcome this high activation energy.

(Total for Question 17 = 10 marks)



ResultsPlus

Examiner Comments

An excellent answer covering all the important points.

*d) By considering both the thermodynamic stability and the kinetic inertness of a mixture of hydrogen and oxygen, explain why hydrogen does not react with oxygen unless ignited.

(2)

This reaction can occur spontaneously, because the $\Delta S^{\circ}_{\text{total}}$ is positive, showing the reaction is thermodynamically favourable (feasible). However, the reaction does not take place at room temperature because hydrogen and oxygen are kinetically inert. The activation energy is too ~~to~~ high for hydrogen and oxygen to react unless ignited.

(Total for Question 17 = 10 marks)



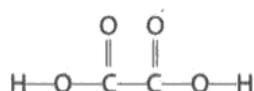
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Examiner Comments

Again this shows excellent use of the key vocabulary required in this question.

Question 18 (a)

Fully correct equations for the ionization of the hydrogenethanedioate ion, complete with states, were by no means uncommon but errors abounded. The most common involved incorrect charges, particularly on the ethanedioate ion and the omission of states but there were quite a number of candidates who gave the equation for the ionization of ethanedioic acid and a significant minority showed the hydroxide ion as the ionization product of the acid. Somewhat surprisingly, the expression for the acid dissociation constant was much more likely to be correct and was clearly written quite independently of the chemical equation. Similarly the calculation of the pH was extremely well done, even when both the previous two parts were incorrect. Near misses in this calculation often involved difficulties in converting pK_a values into K_a .

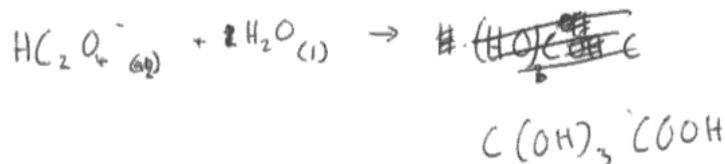
- 18 Ethanedioic acid, $H_2C_2O_4$, is a dicarboxylic acid which occurs in many plants, for example in rhubarb leaves, and is used as a rust remover and strong descaler. The structure of ethanedioic acid is shown below.



Ethanedioic acid is a much stronger acid than carboxylic acids such as ethanoic acid, having a pK_a of 1.38. The hydrogenethanedioate ion, $HC_2O_4^-$, is a weaker acid than ethanedioic acid, having a pK_a of 4.28, although slightly stronger than ethanoic acid.

- (a) (i) Write an equation for the reaction of the hydrogenethanedioate ion with water to form an acidic solution. Include state symbols in your equation.

(2)



- (ii) Write the expression for the acid dissociation constant, K_a , of the weak acid, $HC_2O_4^-$.

(1)

$$K_a = \frac{[C_2O_4^{2-}][H^+]}{[HC_2O_4^-]}$$

(iii) A solution containing hydrogenethanedioate ions behaves as a typical weak acid. Use your answer to (a)(ii) and the pK_a of the hydrogenethanedioate ion to calculate the pH of a $0.050 \text{ mol dm}^{-3}$ solution of sodium hydrogenethanedioate, NaHC_2O_4 .

$$K_a = 10^{-\overset{4.78}{\cancel{4.28}}} \quad (3)$$

$$= \cancel{0.0417} \quad 0.000052481$$

$$\frac{0.000052481}{\cancel{0.0417}} = \frac{[\text{H}^+]^2}{[0.05]} \quad [\text{H}^+]^2 = \frac{0.000002624}{\cancel{0.002084}}$$

$$[\text{H}^+] = \frac{1.6199}{\cancel{0.0457}}$$

$$\text{pH} = -\log [\text{H}^+]$$

$$= \cancel{+34} \quad 2.791$$



ResultsPlus

Examiner Comments

This type of answer was not unusual with the candidate completely unable to write the chemical equation for the ionization but thereafter scoring full marks.



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Examiner Tip

Aim to understand the principles underlying chemical ideas as it is expected at A2 that principles will be applied in unfamiliar situations.

Question 18 (b) (i)

Many of the difficulties associated with this question were due to the need to apply well-known ideas in an unfamiliar context. Thus, candidates used arguments involving generic acid formulae such as HA, stated that $[\text{HC}_2\text{O}_4^-] = [\text{H}^+]$ or referred, carelessly, to the ionization of sodium hydrogenethanedioate. There were quite a number of examples of candidates giving the same approximation twice but using a different form of words. Again it was evident that many candidates had applied these approximations correctly in their earlier calculation without fully understanding them.

Question 18 (b) (ii)

The answers to this question again emphasised the limited understanding of the approximations used in pH calculations and only the best candidates were able to provide cogent explanations. Instead of considering how the approximations might break down, candidates were reduced to guesswork which was usually based on the diprotic character of ethanedioic acid. Many suggested that ethanedioic acid was fully dissociated.

(ii) Explain why the calculation of the pH of a solution of sodium hydrogenethanedioate gives a more accurate value than a similar calculation for ethanedioic acid.

(2)

Ethanedioic acid can dissociate twice due to the ~~two~~ ^{sodium} carboxylic acid groups, whereas hydrogenethanedioate can only dissociate once, ~~losing~~ ^{losing one} proton, as there is only one proton to lose/donate. Also dissociates fully to hydrogenethanedioate ion because Na^+ is immediately made it weaker.



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Examiner Comments

An answer that typically focuses on the properties of ethanedioic acid, including the incorrect idea that it is fully dissociated, rather than analysing why the approximations used in calculating the pH of a weak acid might be inadequate in this case.

*(ii) Explain why the calculation of the pH of a solution of sodium hydrogenethanedioate gives a more accurate value than a similar calculation for ethanedioic acid.

(2)

Ethanedioic acid is a stronger acid so the initial concentration will differ more to the equilibrium concentration due to more dissociation resulting in an inaccurate value ~~with~~ if assuming $[H_2C_2O_4]_{initial} = [H_2C_2O_4]_{equilibrium}$.



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Examiner Comments

This response makes it all look very straightforward.

*(ii) Explain why the calculation of the pH of a solution of sodium hydrogenethanedioate gives a more accurate value than a similar calculation for ethanedioic acid.

(2)

Ethanedioic acid is a much stronger acid & dissociates ~~much~~ ~~in~~ much greater than ~~only partially~~ ~~unlike~~ $NaHC_2O_4$ which is a weak acid & dissociates partially. Hence use of $NaHC_2O_4$ is better as weak acids have an acid ionisation constant (K_a) which can be used to calculate pH unlike the ethanedioic acid which behaves similarly to a strong acid.



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Examiner Comments

In this response, the idea of ethanedioic acid being a stronger acid is noted but the significance of this in the calculation has not been understood.

Question 18 (c)

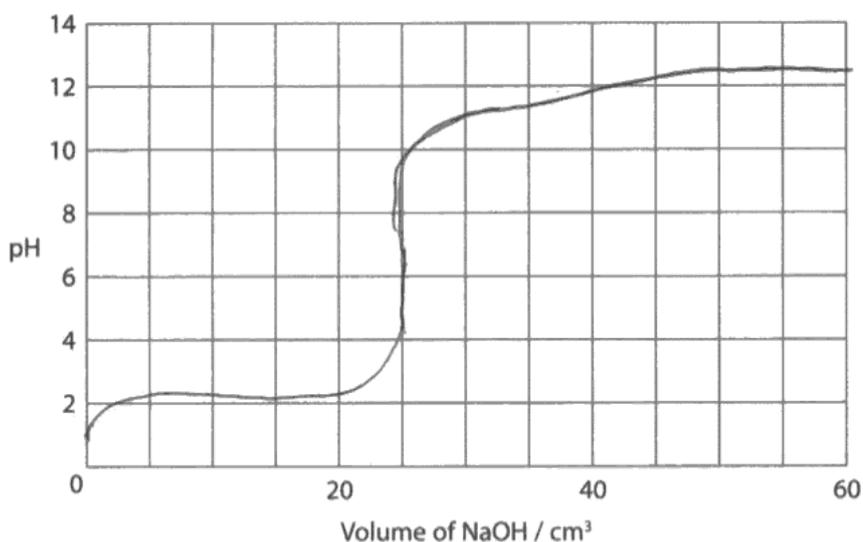
The quality of the pH curves was generally quite poor with far too many candidates taking the 'sketch' instruction to mean that little precision was required. The first mark, for the starting pH, was the most frequently scored but otherwise candidates took little account of the likely range of the final pH or the length or position of the vertical section.

The explanation for the characteristics of the titration of ethanedioic acid eluded all but the very best candidates and it was curious that the diprotic character of ethanedioic acid was rarely mentioned here. Although the mark for the indicator data was very frequently scored, a good number of candidates gave the range for methyl orange rather than methyl yellow.

(c) 25 cm^3 of a $0.050 \text{ mol dm}^{-3}$ solution of sodium hydrogenethanedioate was titrated with a sodium hydroxide solution of the same concentration.

(i) On the axis below, sketch the curve for this titration.

(3)



- *(ii) When 25 cm³ of a 0.050 mol dm⁻³ solution of **ethanedioic acid** is titrated with sodium hydroxide solution of the same concentration using phenolphthalein as the indicator, the end point is 50 cm³.

When methyl yellow indicator is used, the colour changes at around 25 cm³.

Using the information given at the start of the question and quoting data from page 19 of your data booklet, suggest why these volumes are different.

(2)

because methyl yellow has a lower pH range from 2.9 - 4.0 so colour change take place before neutralisation occurs

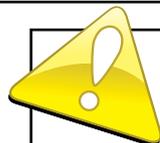
phenol phthaline has a higher pH range of 8.2 - 10 so changes colour in more alkali conditions



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Examiner Comments

A typically careless titration curve which starts at too low a pH, dips before the vertical section which also starts at too low a pH. The answer to (c)(ii) gained the data retrieval mark but there is no real attempt to explain the features of the ethanedioic acid titration.



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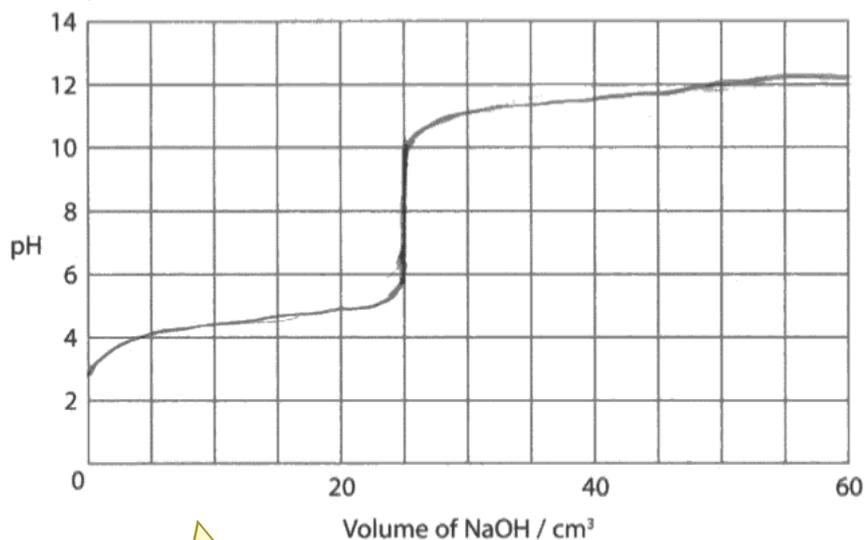
Examiner Tip

A pH curve will continue to rise throughout the range of a titration, only beginning to level off well after the end-point.

(c) 25 cm³ of a 0.050 mol dm⁻³ solution of sodium hydrogenethanedioate was titrated with a sodium hydroxide solution of the same concentration.

(i) On the axis below, sketch the curve for this titration.

(3)



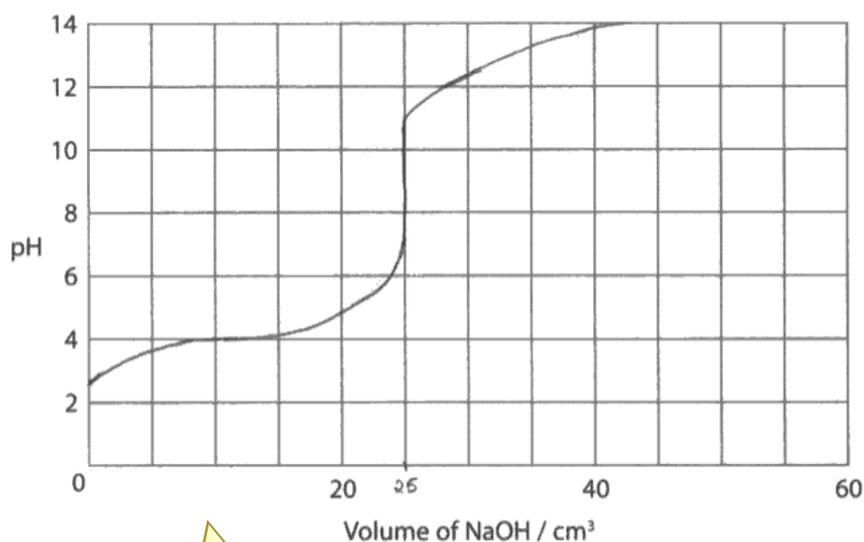
ResultsPlus
Examiner Comments

An excellent titration curve, not exact but meets all the essential criteria and 'looks' right.

(c) 25 cm³ of a 0.050 mol dm⁻³ solution of sodium hydrogenethanedioate was titrated with a sodium hydroxide solution of the same concentration.

(i) On the axis below, sketch the curve for this titration.

(3)



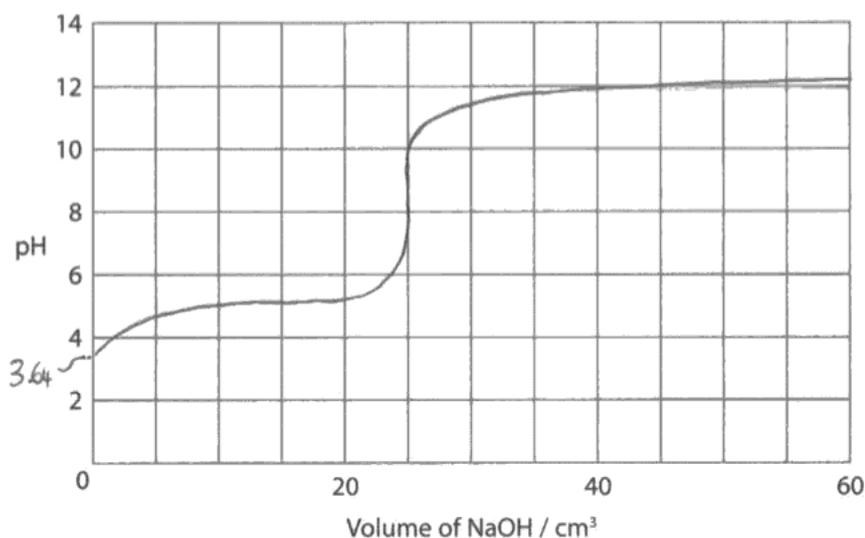
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Examiner Comments

This example typified the curves which showed excellent characteristics but took the final pH far above the value for 1 M NaOH.

(c) 25 cm³ of a 0.050 mol dm⁻³ solution of sodium hydrogenethanedioate was titrated with a sodium hydroxide solution of the same concentration.

(i) On the axis below, sketch the curve for this titration.

(3)



*(ii) When 25 cm³ of a 0.050 mol dm⁻³ solution of **ethanedioic acid** is titrated with sodium hydroxide solution of the same concentration using phenolphthalein as the indicator, the end point is 50 cm³.

When methyl yellow indicator is used, the colour changes at around 25 cm³.

Using the information given at the start of the question and quoting data from page 19 of your data booklet, suggest why these volumes are different.

(2)

Ethanedioic acid is a strong acid with a pK_a of 1.38 and a similarly low pH. The first endpoint, where all of the ethanedioic acid is converted to the hydrogenethanedioate ion occurs at 25 cm³, and changes the pH from below 2.9 to near 4.0 (this is the range of methyl - yellow, so this indicator will change colour here). After 25 cm³ more NaOH is added, the second endpoint occurs at 50 cm³, at around the pH range in the original graph, which is why phenolphthalein (whose range is 8.2-10) picks it up.

(Total for Question 18 = 15 marks)



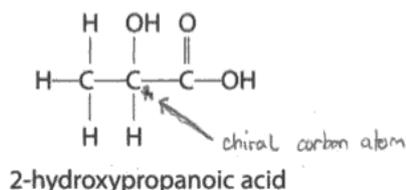
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Examiner Comments

The pH curve lost a mark because the vertical section was slightly short. The explanation in (c)(ii) is not perfect but the candidate does appreciate the key point that the ethanedioic acid is being neutralized in two stages.

Question 19 (a) (i)

The meaning of the term 'chiral' is not widely understood and it was usually taken to be synonymous with an atom being bonded to four different groups with candidates often repeating their answer in search of the third mark. The labelling of the asymmetric carbon was omitted with surprising frequency although candidates could still gain this mark by a description. Weaker candidates used some key terms very imprecisely in their description of the asymmetric carbon: different 'atoms' or even 'molecules' rather than 'groups' and 'surrounded by' rather than 'bonded to'.

- 19 2-hydroxypropanoic acid, lactic acid, is a chiral molecule which is found in muscles and in sour milk. The 2-hydroxypropanoic acid formed in muscles is optically active but that in sour milk is not.



- (a) (i) Explain the term **chiral**, stating the feature of 2-hydroxypropanoic acid that makes it chiral. Label this feature on the formula above.

(3)

The term chiral means that the molecule is optically active and that when polarised light is shone through it, the polarised light will rotate. In order for a molecule to be chiral it must have a carbon atom with four different groups attached to it, so two enantiomers are formed with the groups arranged differently on each of the carbon atoms in the separate enantiomers. The middle carbon has four different groups attached to it so its the chiral atom.



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Examiner Comments

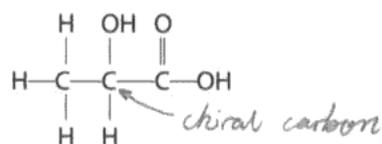
Here the candidate attempts to define chirality in terms of the effect of the molecule on plane polarized light.



ResultsPlus
Examiner Tip

Note the amount of repetition in this answer. Aim for brevity and do not repeat yourself.

- 19 2-hydroxypropanoic acid, lactic acid, is a chiral molecule which is found in muscles and in sour milk. The 2-hydroxypropanoic acid formed in muscles is optically active but that in sour milk is not.



2-hydroxypropanoic acid

- (a) (i) Explain the term **chiral**, stating the feature of 2-hydroxypropanoic acid that makes it chiral. Label this feature on the formula above.

(3)

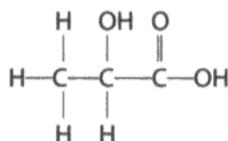
A chiral carbon has 4 different atoms or groups of atoms attached to it and is able to form non-super-imposable mirror images in 3D space.



ResultsPlus
Examiner Comments

This is an excellent answer, covering the key points in an impressively economical manner.

- 19 2-hydroxypropanoic acid, lactic acid, is a chiral molecule which is found in muscles and in sour milk. The 2-hydroxypropanoic acid formed in muscles is optically active but that in sour milk is not.



2-hydroxypropanoic acid

- (a) (i) Explain the term **chiral**, stating the feature of 2-hydroxypropanoic acid that makes it chiral. Label this feature on the formula above.

(3)

Chiral carbons have 4 different groups attached to a central carbon which can be optically active. 2-hydroxypropanoic acid has a H, CH₃, OH and COOH group on the central carbon, all different groups making it chiral.



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Examiner Comments

A surprising number of candidates described the chiral carbon, instead of labelling it.



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Examiner Tip

Read the question carefully and ensure that you have answered each part.

Question 19 (a) (ii)

There were many good answers to this question although some omitted the 2-hydroxypropanoic acid found in muscles. There were a number of attempts to describe the mechanisms of the reactions involved and a few candidates, presumably drawing on their knowledge of Biology, referred to lactic acid in muscles as though it was an entirely different compound.

Question 19 (b) (i)

These reagents were simply not well known. Few candidates appreciated the need to acidify the mixture in order to regenerate the acid.

Question 19 (b) (ii)

There were some clear, well set out, answers to this question but they were in the minority. Some candidates answered a different question to do with the formation of racemic mixtures and many offered a messy amalgamation of Sn1 and Sn2 mechanisms.

(ii) When an optically active isomer of 2-bromopropanoic acid is used in Stage 2, the resulting 2-hydroxypropanoic acid is also optically active. State and explain what this indicates about the mechanism of the first reaction in Stage 2.

(3)

This indicates that the mechanism of the first reaction is S_N2 because the Br⁻ nucleophile can only attack from one side of the 2-hydroxypropanoic acid so that it is not repelled by carboxylate group. This means only one optical isomer is produced.



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Examiner Comments

This answer covers the key points in a pleasingly precise way.

Question 19 (c) (i)

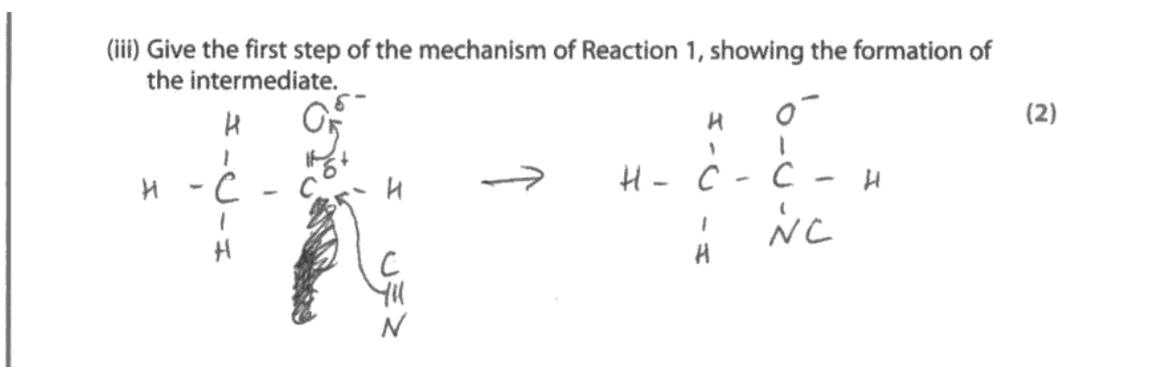
Nucleophilic addition was well known but some did suggest nucleophilic substitution and even 'nucleophilic addition, Sn2'.

Question 19 (c) (ii)

Most candidates were able to correctly identify the nucleophile. The common error was the omission of the charge.

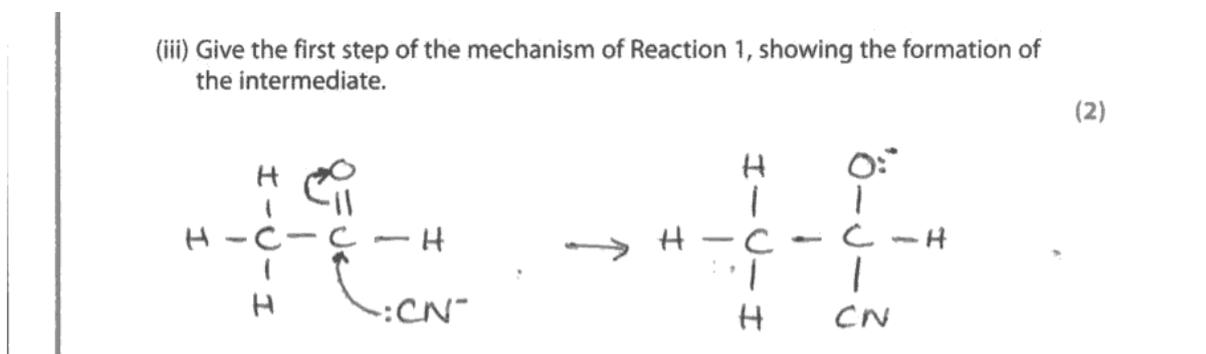
Question 19 (c) (iii)

Candidates seemed well-prepared for this mechanism although the placing of curly arrows still lacks precision, the most frequent error being the carbonyl curly arrow originating from the carbon rather than the double bond. There was some carelessness with charges; the charge was often omitted from the cyanide ion and a positive charge sometimes appeared in the intermediate.



ResultsPlus Examiner Comments

The curly arrow from the cyanide ion is coming from the triple bond rather than a lone pair on the carbon. This has not been penalized but the carbon-nitrogen bond in the intermediate has.

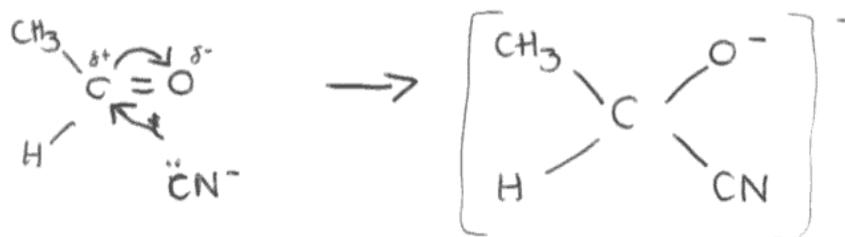


ResultsPlus Examiner Comments

Everything looks right here!

(iii) Give the first step of the mechanism of Reaction 1, showing the formation of the intermediate.

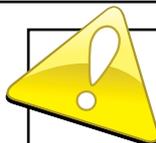
(2)



ResultsPlus

Examiner Comments

Note the careless use of the curly arrows: the top arrow originates from the carbon atom rather than the carbon-oxygen double bond and the bottom arrow is coming from nowhere in particular. To compound the problems the intermediate has two negative charges.



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Examiner Tip

Learning the precise use of curly arrows is key to handling mechanisms in organic chemistry. In any chemical equation, the total charge must always be the same on both sides of the equation.

Question 19 (c) (iv)

This question proved an effective discriminator, catching out the candidates relying purely on memory rather than applying their knowledge to the specific example. This led to references to a planar intermediate (rather than molecule or aldehyde group) in otherwise good answers and indiscriminate discussion of S_N1 mechanisms in less good responses.

*(iv) Explain, by referring to the mechanism in (c)(iii), why the 2-hydroxypropanoic acid formed from ethanal shows no optical activity.

(3)

The CN^- nucleophile can attack from either side as a carbocation intermediate is formed, ~~and~~ and so both ~~sides~~ ~~are~~ ~~all~~ optical isomers are produced, ^{in equal proportion} producing a racemic mixture and they cancel out each others effect on plane polarised light.



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Examiner Comments

This is a typical response in which the formation of a racemic mixture is correctly linked to the idea of attack from either side of a plane but incorrectly discussing a carbocation intermediate rather than the aldehyde group.

Question 19 (d) (i)

Most candidates were able to identify the OH group and suggest a possible wavenumber, the omission of one (usually the group) indicating a failure to read the question properly.

Question 19 (d) (ii)

While the mark for identifying the carbonyl group proved very accessible, far too many candidates simply went on to state that the compounds could not be distinguished because both had carbonyl groups and did not consider the infrared data at all.

*(ii) Identify the bond responsible for absorption peak Q in the spectrum. By considering the wavenumber of this peak, and the data on pages 5 and 6 of the data booklet, explain whether this peak **alone** can be used to distinguish between ethanal and 2-hydroxypropanoic acid.

(3)

this is the peak caused by the C=O group. This cannot be used to distinguish the two compounds as this group is present in both. The peaks would be very slightly different but not enough to distinguish the two.



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Examiner Comments

This type of answer was surprisingly common. The candidate has essentially ignored most of the question.

*(ii) Identify the bond responsible for absorption peak Q in the spectrum. By considering the wavenumber of this peak, and the data on pages 5 and 6 of the data booklet, explain whether this peak **alone** can be used to distinguish between ethanal and 2-hydroxypropanoic acid.

(3)

peak Q has a wavenumber of about ~~1700~~ ¹⁷⁰⁰ cm^{-1} and so is due to the bond $\text{C}=\text{O}$. as the wave number range of $\text{C}=\text{O}$ in aldehydes is $1740 - 1720$ and that of carboxylic acids is $1725 - 1700$; and the $\text{C}=\text{O}$ bond is present in both ethanal and 2-hydroxypropanoic acid, this peak would be present in the IR of both ethanal and 2-hydroxypropanoic acid, i.e. alone would not be enough to distinguish between the 2 compounds.



ResultsPlus Examiner Comments

Despite a lengthy response, the candidate fails to pin down the reason why the data cannot be used to distinguish the two compounds.



ResultsPlus Examiner Tip

Do make sure that your response actually answers the question.

*(ii) Identify the bond responsible for absorption peak Q in the spectrum. By considering the wavenumber of this peak, and the data on pages 5 and 6 of the data booklet, explain whether this peak **alone** can be used to distinguish between ethanal and 2-hydroxypropanoic acid.

(3)

$\text{C}=\text{O}$ group at $1725-1700\text{cm}^{-1}$, this peak alone cannot be used to distinguish between ethanal and 2-hydroxypropanoic acid because ~~the~~ ethanal has a $\text{C}=\text{O}$ group at $1740 - 1720\text{cm}^{-1}$ so ~~the~~ it will be difficult to tell them apart



ResultsPlus Examiner Comments

Marks have been lost here through a lack of precision. The $\text{C}=\text{O}$ range for carboxylic acids has not been linked explicitly with the functional group and the difficulty in distinguishing the groups has been associated with the nature of the group rather than the similarity of the IR wavenumbers.

Question 19 (e)

The chemical tests and their results were well known although some failed to take into account the fact that 2-hydroxypropanoic acid had two functional groups and suggested acidified potassium dichromate or the iodoform test. Common minor errors were failure to give an observation (e.g. 'gas' evolved rather than effervescence) or omitting the word 'precipitate'.

Question 20 (a) (i)

This was the item in Sections B & C of the paper that candidates seemed to find the most difficult. Not only did few understand the function of the thiosulfate in facilitating the measurement of the time required for a set amount of reaction, but many had no idea that it would react with iodine. The most frequent incorrect response involved thiosulfate oxidizing iodide ions but suggestions involving a titration or reaction with peroxodisulfate ions or catalysis were also common.

(i) Explain the purpose of the sodium thiosulfate solution.

(2)

The thiosulfate reacts with the liberated iodine producing a colour change from blue black to colourless which indicates that all the iodine has reacted. It also introduces a standard time delay which aids in timing the reaction.



ResultsPlus
Examiner Comments

The mark is for knowing that the thiosulfate reacts with iodine however, the attempt to explain how the reaction is being used is typically confused, although the notion of time delay has been recalled suggesting a familiarity with the experiment.

Question 20 (a) (ii) - (b) (iv)

This demanding section required precise use of language, an understanding of some of the more subtle aspects of experimental chemistry and sound mathematical skills.

The principles involved in deriving the rate equation (20(a)(ii)) seemed generally understood but the precision required was often lacking. There was confusion between rate and time, a failure to notice that the concentrations of both reagents changed between experiments 2 and 3 and often a failure to complete the process by writing the rate equation.

In 20(b)(i) despite the clear instruction, there were many answers which described a sampling method and few of the answers involving colorimetry gave the impression of any familiarity with the experimental procedure.

The most usual response in 20(b)(ii) was 'to ensure complete reaction' and even where the idea of keeping the concentration of peroxodisulfate ions constant was known, the idea of eliminating the effect of the *change* in concentration on the rate was simply too difficult.

20(b)(iii) was often well answered but once again imprecision cost marks unnecessarily. Common errors included suggesting a graph of iodide ion concentration against time, omitting to mention $t = 0$ and just stating 'measure the rate at $t = 0$ '.

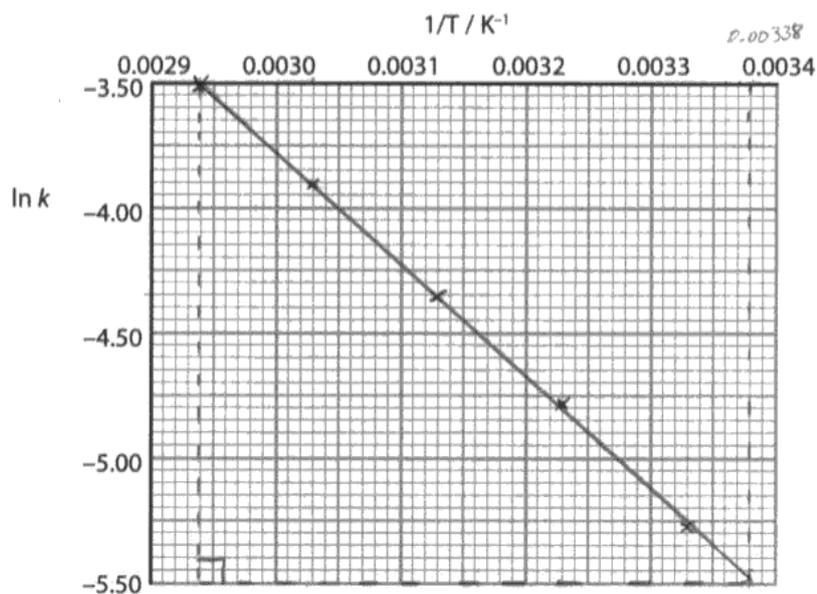
20(b)(iv) elicited some good responses and candidates seemed well-prepared for the derivation of units. Quite a number of calculations used quantities from the table instead of from the stem of 20b.

Question 20 (c)

This question required a range of skills and proved highly discriminating. Plotting the points proved demanding and weaker candidates often assumed that the line would pass through the 'origin' of the graph. Many candidates failed to complete the gradient calculation and the negative sign was often omitted; the latter error was often compounded by 'losing' the negative sign from the final step of the calculation. The units of E_a were often incorrect with J or $\text{J mol}^{-1}\text{K}^{-1}$ being frequent. Some candidate clearly had no idea how to use the gradient with the equation supplied and attempted an algebraic solution.

- (i) Use the data in the table to plot a graph of $\ln k$ (on the y axis) against $1/T$ (on the x axis) and draw a best fit line through the points.

(2)



- (ii) Determine the gradient of the best fit line in (c)(i) and use this value to calculate the activation energy, E_a , of the reaction, stating the units.

(4)

The rate constant of a reaction, k , is related to the temperature, T , by the expression

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

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

$$\Delta y = -5.50 - (-3.50) \\ = -2$$

$$\Delta x = 0.00338 - 0.00294 \\ = 0.00044$$

$$\text{gradient} = \frac{\Delta y}{\Delta x} = -4545.45$$

$$\frac{\ln k}{\left(\frac{1}{T}\right)} = -4545.45$$

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

$$\therefore E_a = - \left[\frac{\ln k - \text{constant}}{\left(\frac{1}{T}\right)} \right] R$$

ignoring the constant

$$E_a = -(-4545.45) \times 8.31$$

$$E_a = 37772.72 \text{ J} = \underline{\underline{37.8 \text{ kJ}}}$$

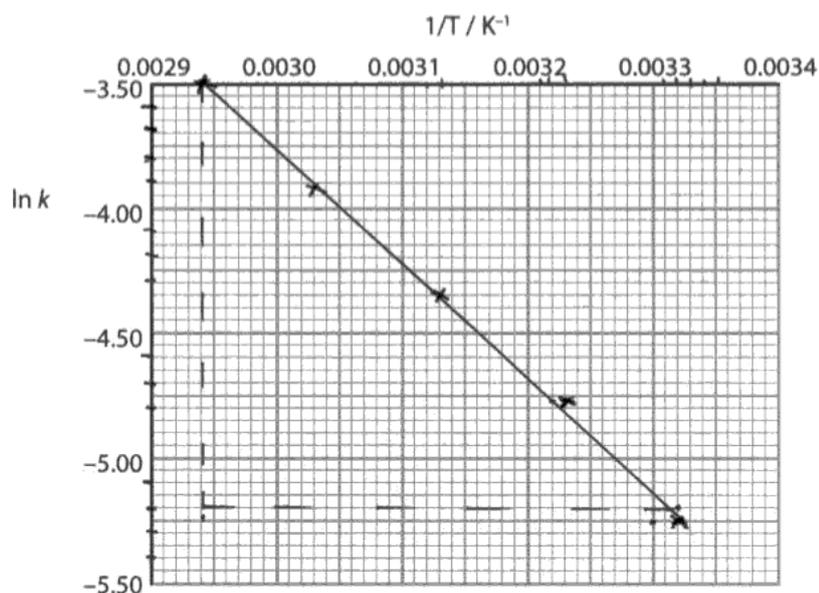


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Examiner Comments

The graph is accurately drawn, the gradient measured correctly and the calculation completed. Just the units are wrong.

- (i) Use the data in the table to plot a graph of $\ln k$ (on the y axis) against $1/T$ (on the x axis) and draw a best fit line through the points.

(2)



- (ii) Determine the gradient of the best fit line in (c)(i) and use this value to calculate the activation energy, E_a , of the reaction, stating the units.

(4)

The rate constant of a reaction, k , is related to the temperature, T , by the expression

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

$$\frac{E_a}{R} \approx \text{gradient}$$

$$E_a = \text{gradient} \times R$$

$$\text{gradient} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{-5.20 - (-3.50)}{0.00332 - 0.00294}$$

$$E_a = \text{gradient} \times R = -4473.7$$

$$\begin{aligned} E_a &= -4473.7 \times 8.31 \\ &= -37457 \text{ J mol}^{-1} \\ &= -37 \text{ kJ mol}^{-1} \end{aligned}$$

1.7



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Examiner Comments

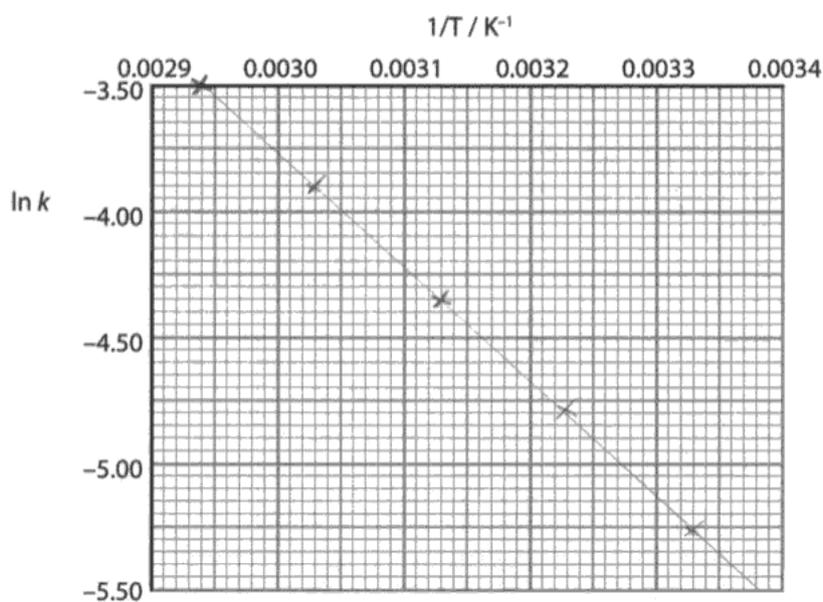
The negative E_a should have set alarm bells ringing! Otherwise a nice response.

- (c) Using the method outlined in (b), the rate constant for this reaction was determined at various temperatures. The data from these experiments are shown in the table below. Note that none of the temperatures corresponds to that used in (b) and that the rate constant is given in appropriate units.

Temperature T / K	Rate constant k	ln k	1/T / K ⁻¹
300	0.00513	-5.27	0.00333
310	0.00833	-4.79	0.00323
320	0.0128	-4.36	0.00313
330	0.0201	-3.91	0.00303
340	0.0301	-3.50	0.00294

- (i) Use the data in the table to plot a graph of ln k (on the y axis) against 1/T (on the x axis) and draw a best fit line through the points.

(2)



- (ii) Determine the gradient of the best fit line in (c)(i) and use this value to calculate the activation energy, E_a , of the reaction, stating the units.

(4)

The rate constant of a reaction, k , is related to the temperature, T , by the expression

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

$$\frac{0.00313 - 0.00294}{-4.36 - -3.50} = \frac{1.9 \times 10^{-4}}{-0.86} = -2.21 \times 10^{-4}$$
$$-\frac{E_a}{R} = -2.21 \times 10^{-4}$$
$$E_a = -\frac{(-2.21 \times 10^{-4})}{8.31} = 2.66 \times 10^{-5} \text{ J}$$
$$E_a = -(-2.21 \times 10^{-4} \times 8.31) = 1.84 \times 10^{-3} \text{ J}$$



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Examiner Comments

One would expect such a small value for E_a to prompt a check of the previous steps.



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Examiner Tip

An appreciation of the likely magnitude of quantities is a vital aspect of any scientific work. Try to develop a feel for what is a plausible answer.

Paper Summary

On the basis of their performance on this paper candidates are offered the following advice;

- Read the question carefully.
- Try to frame your answer to a question with an appreciation of the marks available.
- Make sure you can write accurate balanced equations, one of the basic skills of any advanced level candidate.
- Take care with units in calculations.
- Remember that this paper has a greater emphasis on applying knowledge and understanding in unfamiliar contexts than those at AS.

Grade Boundaries

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

<http://www.edexcel.com/iwantto/Pages/grade-boundaries.aspx>

Ofqual



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