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Examiners' Report
June 2011

GCE Chemistry 6CH04 01

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June 2011

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Introduction

The paper was accessible to all candidates, with section C providing the most challenge. Only a small number of candidates did not complete the paper. The standard of answers on kinetics and thermodynamics was good, but answers on organic chemistry, including nmr spectroscopy, and acids and bases had more errors. A very large proportion of candidates seem unsure about the choice of an appropriate number of significant figures in numerical answers. There were no questions asking for a specific number of significant figures, and as long as there were at least two significant figures this was not penalised. However candidates at this level should realise that giving a full calculator read-out for a pH is inappropriate. Many rounding errors were seen. Candidates often gave the first two figures in their calculations even if the third figure indicated that they should have rounded up. This also produced errors in the final answers of calculations with more than one stage and marks were lost.

Question 15 (a) (i)

Many candidates knew that the reaction was nucleophilic addition, but a significant number described it as "nucleophilic addition, SN1", indicating a lack of understanding of the letter S in the abbreviation.

(a) (i) Name the type and mechanism of the reaction in **step 2**. (2)

Type: Nucleophilic addition Mechanism: Nucleophilic substitution

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Examiner Comments

Credit cannot be given if there are two alternative answers which contradict, in this case addition and substitution. The nucleophilic mark was given.

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Examiner Tip

If you are not sure of an answer, don't give two alternatives which cannot both be possible.

Question 15 (a) (ii)

The most popular choice of answer was hydrogen cyanide plus potassium cyanide. Use of hydrogen cyanide with an alkali or potassium cyanide with a strong acid were also allowed, but in a question asking for "the substances" which need to be added, it was not enough to simply write CN^- or H^+. Some answers gave long lists of suggestions, and these could not be accepted.

(ii) Which **two** substances need to be added to ethanal to carry out the reaction in **step 2**?

(2)

HCN , acid.

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Examiner Comments

When using hydrogen cyanide, a source of cyanide ions is also needed. This could be potassium cyanide. Alternatively sodium hydroxide could be added, which would react with the hydrogen cyanide to produce cyanide ions. This answer scored 1 mark for the HCN.

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Examiner Tip

If a question asks for substances which are needed, the names or formulae of the substances must be given, not just a general term like "acid". Acids can be strong or weak so all acids might not be suitable. In this case the name or formula of a strong base was needed.

(ii) Which **two** substances need to be added to ethanal to carry out the reaction in **step 2**?

(2)

HCN and CN^- (The CN^- can be produced by reacting HCN with NaOH).

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Examiner Comments

This answer shows the source of the cyanide ions and scores 2 marks.

(ii) Which **two** substances need to be added to ethanal to carry out the reaction in **step 2**?

(2)

acidyied KCN and H^+ aqueous

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Examiner Comments

Adding a strong acid to potassium cyanide would liberate HCN. However, the question asked for the substances needed, so this scored 1 as a suitable acid was not named.

Question 15 (a) (iii)

The mechanism for addition of cyanide to an aldehyde was generally well known. Common errors were to forget the charge on the cyanide ion, or to draw a curly arrow coming from a H^+ ion. Since the last mark was allowed either for reaction with H^+ or with HCN, there was no penalty for candidates who used HCN and forgot to show that CN^- was also produced. However, this error suggests that candidates are not checking that equations are balanced which is disappointing.

(iii) Give the mechanism for the reaction in **step 2**, using curly arrows to show movements of electron pairs.

(3)

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Examiner Comments

This answer showed the intermediate correctly and included a correct curly arrow from the negatively charged oxygen to the hydrogen ion. However, the first mark for attack by the cyanide ion was not scored. The hydrogen atoms on the ends of the bonds should be shown.

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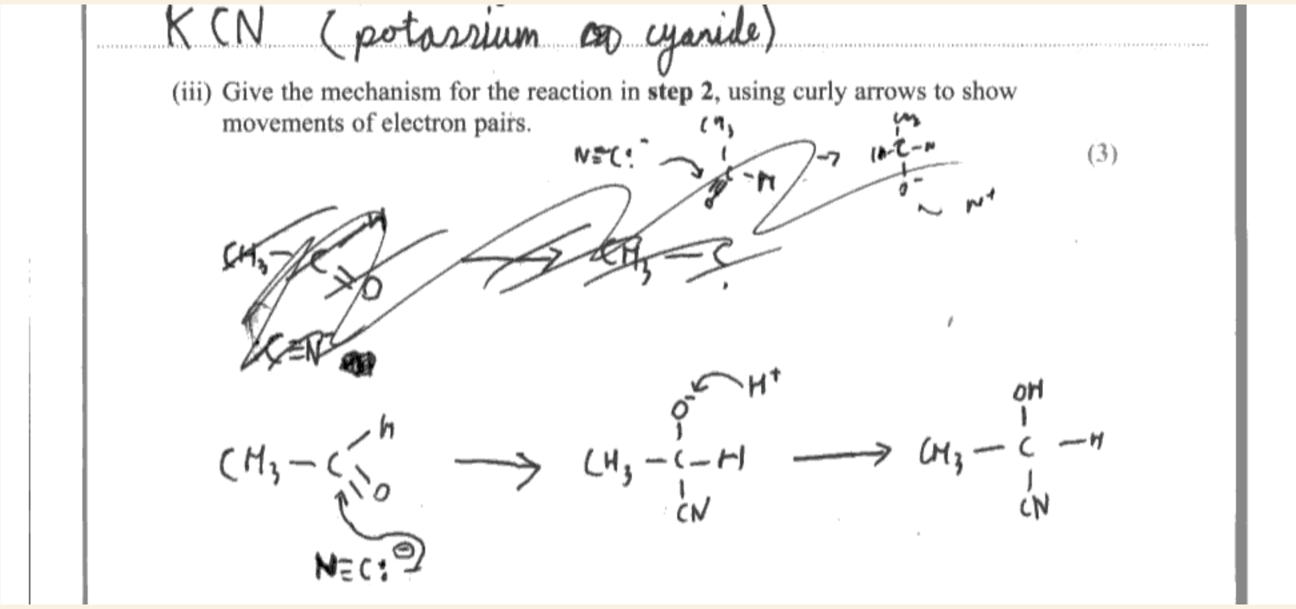
Examiner Tip

The first stage in this mechanism is attack by a cyanide ion. Another error is that the curly arrow leading to the oxygen in the C=O bond comes from the carbon, not the bond. Curly arrows show movement of electron pairs and their position is very important. The hydrogen atoms on the ends of bonds should be shown.



KCN (potassium cyanide)

(iii) Give the mechanism for the reaction in **step 2**, using curly arrows to show movements of electron pairs.

(3)

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Examiner Comments

This scored 1 mark for a correct intermediate, but lost the first and third marks in the mark scheme.

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Examiner Tip

A hydrogen ion has no electrons. Since curly arrows show movement of electron pairs there can never be an arrow coming from a hydrogen ion.

Question 15 (a) (iv)

There was considerable confusion between addition to a planar site in an aldehyde, and attack by OH^- on a planar intermediate in hydrolysis of tertiary halogenoalkanes. There were many answers saying that the intermediate, which in this case was $CH_3CH(CN)O^-$ and not a carbocation, could be attacked from either side.

However, the second mark was gained more often for recognition that a racemic mixture forms. Some answers stated that two enantiomers form without making it clear that they form in equal proportions.

his answer is confusing, as cyanide ions are nucleophiles. The final product is not a carbocation and unless 50% of each enantiomer forms, the rotation of the plane of polarised light will not be cancelled.

*(iv) The product of **step 2** is not optically active even though it has a chiral carbon atom in its formula. Explain, by reference to the mechanism, the reason for the lack of optical activity.

(2)

The electrophile can attack from either above or below the molecule so 2 carbocations can be formed which rotate the plane of polaried light in opposite directions so they cancel out and overall, no optical activity formed

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Examiner Comments

A carbocation intermediate may be produced during hydrolysis of halogenoalkanes, but this is not the reaction occurring here.

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Examiner Tip

The optical activity of enantiomers is only cancelled out if there are equal amounts of each enantiomer, which is not stated in this answer.

*(iv) The product of **step 2** is not optically active even though it has a chiral carbon atom in its formula. Explain, by reference to the mechanism, the reason for the lack of optical activity.

(2)

The cyanide ions can attack, the electron defficent area of the carbon atom in Ethanal, on different sides of the carbonyl group. (C=O). This results in equal amounts of both enantiomers, giving a racemic mixture, as optical activity is cancelled out, by the two enantiomers.

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Examiner Comments

This scored both marks.

Question 15 (b)

Many candidates clearly knew that this was a hydrolysis reaction, and gave answers such as water plus sulfuric acid, which gained the marks. As in 15(a)(ii) some candidates optimistically gave long lists of reactants and these were not given any credit.

(b) What reactant, or combination of reactants, is needed to carry out **step 3**?

(1)

Water in acidic condition.

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Examiner Comments

This did not score the mark as a suitable acid was not given.

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Examiner Tip

A strong acid is needed here, so just saying that an acid is needed is not enough.

Question 15 (c) (i-iii)

Naming the lactic acid caused quite a lot of difficulty, perhaps because the three carbon atoms were not shown in a straight line. However, this representation made deducing the structure of the polymer slightly easier and many showed a polyester, though common mistakes were to include too many or too few oxygen atoms at the ends, or to miss out some hydrogen atoms. Answers to 15(a)(iii) had to be based on the chemistry of the molecule and vague comments such as "enzymes can break it down" were not allowed.

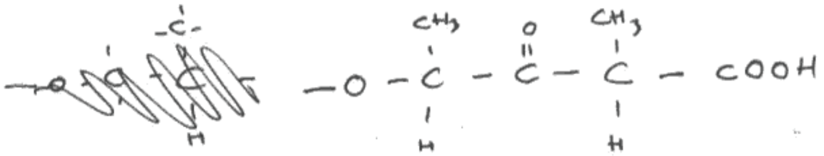
(c) (i) What is the systematic name of lactic acid?

(1)

~~1, hydroxy~~ 1-hydroxy, 1-methyl propanoic acid.

(ii) Lactic acid molecules can combine to form a biodegradable polymer, poly(lactic acid) or PLA. Draw a section of the polymer with **two** units of the polymer chain and showing all bonds.

(1)



(iii) Suggest why PLA is biodegradable.

(1)

PLA is biodegradable as the bond can be hydrolysed, and be broken down.

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Examiner Tip

This sort of error in naming the acid was common.

If a section of a polymer is required, the bonds at the ends of the section which can join on to other units should be shown.

The bond which can be hydrolysed is the ester link. There are other bonds in the molecule which, if broken,would not break it into monomers.

Question 15 (c) (iv)

There was a wide variety of acceptable answers here, including comments about ethene coming from a non-renewable source, the likely energy requirements of producing ethene, and the costs of chemicals and losses in yield in a multi-step synthesis.

However, there were many vague comments about milk being natural, or the process from ethene being cheaper, without any justification, and these did not gain a mark. There was a widely held view that because milk comes from cows there are no costs in producing it. The way the answers were expressed was often careless, for example saying that crude oil is burnt to produce ethene; the process is cracking and this requires considerable energy which is the point of the question.

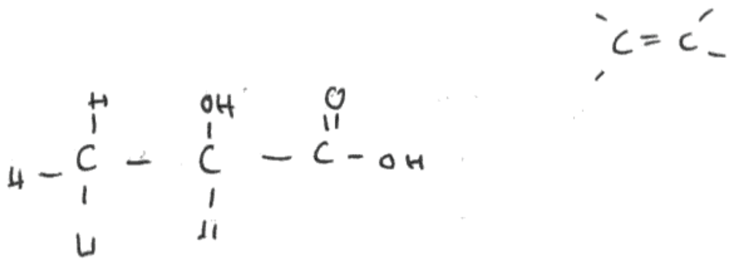
(iv) Lactic acid can be prepared from ethene as shown in the scheme. Lactic acid also forms when milk turns sour.

Suggest **one** reason why it would be advantageous to make lactic acid from milk rather than from ethene.

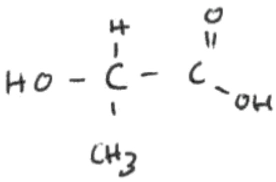
(1)

It is more environmentally frendily as ethene is ~~make~~ produced from oil, which is non-rewable where as milk is produced from cattel and is renewable source and it wold be cheaper to produce

(Total for Question 15 = 14 marks)



2 hydroxypropanic acid



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Examiner Comments

This scored the mark for saying that ethene comes from a non-renewable resource, but candidates should be aware that just saying that something is environmentally friendly is never likely to gain a mark.

(iv) Lactic acid can be prepared from ethene as shown in the scheme. Lactic acid also forms when milk turns sour.

Suggest **one** reason why it would be advantageous to make lactic acid from milk rather than from ethene.

(1)

Because to obtain ethene is a lot harder and more time consuming (extracting from crude oil) than it is to obtain milk.

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Examiner Comments

This did not score as there is nothing about sustainability or requirement of energy or other resources.

Question 16 (a)

This was a high scoring question. Candidates knew how to analyse the data given and answers were often well expressed, including references to the experiments being considered and the fact that the concentration of one reactant was staying constant while the other one changed. A few candidates forgot to include the rate constant in the rate equation and errors in the units of the rate constant were relatively common.

(i) State, with reasons, the order of reaction with respect to oxygen and the order of reaction with respect to nitrogen(II) oxide, NO.

(2)

The order of reaction with respect to oxygen is 1st order, as the change in concentration and rate are both proportional to each other. The order of reaction with respect to nitrogen (II) oxide is 2nd order, as the initial concentration has doubled and the rate has increased by a factor of 4.

(ii) Write the rate equation for the reaction.

(1)

$rate = k [O_2]^1 [NO]^2$

(iii) Calculate the value of the rate constant. Include units in your answer.

(2)

$5.10 \times 10^{-4} = k [0.005][0.0125]^2$

$\frac{5.10 \times 10^{-4}}{[0.005][0.0125]^2} = k$

units = $\frac{mol\,dm^{-3}\,s^{-1}}{mol\,dm^{-3} \times mol\,dm^{-3} \times mol\,dm^{-3}}$

units = $mol^{-2}\,dm^{6}$

k = ~~653~~ 652.8 $mol^{-2}\,dm^{6}\,s^{-1}$

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Examiner Comments

This is an example of a good answer which scores full marks.

Question 16 (b)

Writing the overall equation for the reaction was a simple task and only a few candidates failed to cancel the NO_3 which appeared on both sides. Most candidates deduced the rate equation correctly and realised that only species in the rate determining step appear in the rate equation.

(i) Write the equation for the overall reaction which takes place.

(1)

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

(ii) The overall reaction is second order. Suggest a rate equation for this reaction, justifying your answer.

(2)

Rate = $k[NO_2(g)]^2$

Although CO(g) is involved in the overall equation, it is not involved in the slowest step which is the rate determining step, therefore it is not involved in the rate equation - only $NO_2(g)$ is, which must therefore be 2nd order.

(Total for Question 16 = 8 marks)

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Examiner Comments

This is an example of a good answer.

(i) Write the equation for the overall reaction which takes place.

(1)

$2NO_2 + NO_3 + 2CO \rightarrow 2NO + 2CO_2$

(ii) The overall reaction is second order. Suggest a rate equation for this reaction, justifying your answer.

(2)

Rate = $[NO_2]^2$

This is the slow step which is the rate determining step ~~which~~ and therefore NO_2 alone will be in the rate equation.

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Examiner Comments

The overall equation is incorrect and the rate constant is missing from the rate equation. A mark was given for the idea that $NO_2$2 alone is in the rate equation as it is in the slow step.

Question 17 (a)

The calculation of the entropy change of the system caused some difficulty. Candidates who were familiar with the Data booklet would know that data on elements is given separately from data on compounds, but others tried to calculate a value for ammonia. Despite the information that data is given for half a mole of molecules, many candidates did not apply a factor of 2 when using the data for hydrogen. The correct answer was a negative value. However, candidates who got a positive value could score the marks in (a)(ii) as long as they explained that this was unexpected.

17 Ammonia is manufactured using the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(a) (i) Calculate $\Delta S^{\ominus}_{system}$ for this reaction at 298 K. Give your answer in J mol^{-1} K^{-1} and include a sign. You will need to refer to your data booklet.

[Note that the standard molar entropy values for gaseous diatomic elements are given for half a mole of molecules, and not per mole of molecules eg entropy for 1 mol of N_2 is 2 × 95.8 J mol^{-1} K^{-1}.]

(2)

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

$= 2(192.3) - [(191.6) + ((3 \times 2)(65.3))]$

$= 384.6 - 583.4$

$= -198.8$ kJ mol

$= -198800$ J/mol

(ii) Using ideas about disorder, explain whether the sign of your answer to (a)(i) is as expected.

(2)

Negative sign, ∴ reaction is becoming more ordered, hence as going from 4 moles of gas to 2, sign is expected as negative due to entropy decrease.

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Examiner Comments

This candidate has found the correct data and used the correct multiples, but has confused joules and kilojoules in the calculation so scores 1 mark in (i)

The second part is correct.

17 Ammonia is manufactured using the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(a) (i) Calculate $\Delta S^{\ominus}_{system}$ for this reaction at 298 K. Give your answer in J mol^{-1} K^{-1} and include a sign. You will need to refer to your data booklet.

[Note that the standard molar entropy values for gaseous diatomic elements are given for half a mole of molecules, and not per mole of molecules eg entropy for 1 mol of N_2 is 2 × 95.8 J mol^{-1} K^{-1}.]

(2)

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

$= ((3 \times 65.3) + (95.8)) - (2 \times 192.3)$

$= (291.7) - (384.6)$

$= -92.9$

(ii) Using ideas about disorder, explain whether the sign of your answer to (a)(i) is as expected.

(2)

Sign is a expected as two reactants are in gaseous form, highest entropy, and they react to form one gaseous product, so there is therefore a decreasing the disorder, so negative ΔS_{system}.

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Examiner Comments

This candidate has subtracted values for the entropy of products from the entropy of reactants and has missed the multiple on the value for nitrogen, even though it was given in the question, so scores no marks in (i).

The explanation in (ii) did not refer to the decrease in number of molecules as the reaction goes forward. Saying that there is one gaseous product, when it is of different complexity to the reactants, was not enough.

17 Ammonia is manufactured using the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(a) (i) Calculate $\Delta S^{\ominus}_{system}$ for this reaction at 298 K. Give your answer in J mol^{-1} K^{-1} and include a sign. You will need to refer to your data booklet.

[Note that the standard molar entropy values for gaseous diatomic elements are given for half a mole of molecules, and not per mole of molecules eg entropy for 1 mol of N_2 is 2 × 95.8 J mol^{-1} K^{-1}.]

(2)

ΔS system = ΔS products – ΔS reactants.

H = 65.3 x2
130.6
391.8
N = 191.6.

192.3x2

383.4

583.4 – 384.6 = + 198.8 J mol^{-1} K^{-1}

(ii) Using ideas about disorder, explain whether the sign of your answer to (a)(i) is as expected.

(2)

The sign is unexpected. An increase in disorder brings an increase in entropy. However in this reaction 4 moles of gas has decreased to two moles of gas, meaning less disorder and a decrease in entropy.

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Examiner Comments

Though the sign in (i) is wrong the candidate scores full marks in (ii) as the answer says that the sign is unexpected.

Question 17 (b)

Most candidates knew how to calculate the entropy change of the surroundings from the enthalpy change, but errors occurred by using a temperature of 298K instead of 700K, and confusing the sign and units. In (ii) some candidates added a value stated to be in

kJ mol^{-1} K^{-1} to the total entropy change in J mol^{-1} K^{-1} . The negative value of the total entropy change shows that the reaction is in equilibrium and favours the reactants, but it was often interpreted as indicating that no ammonia would be produced.

(b) At 700 K, the enthalpy change for this reaction, $\Delta H = -110.2$ kJ mol^{-1}.

(i) Calculate the entropy change of the surroundings, $\Delta S_{surroundings}$, at 700 K. Include a sign and units in your answer.

(2)

$\Delta S_{surroundings} = \frac{110.2 \text{ kJ mol}^{-1}}{700 \text{ K}} = +157.4 \text{ J mol}^{-1} \text{K}^{-1}$

(ii) Calculate ΔS_{system} for this reaction at 700 K. At this temperature the total entropy change, $\Delta S_{total} = -78.7$ J K^{-1} mol^{-1}. Include a sign and units in your answer.

(1)

$-78.7 \text{ J K}^{-1} = \Delta S_{system} + 157.4 \text{ J mol}^{-1} \text{K}^{-1}$

$\Delta S_{system} = 78.7 \text{ J mol}^{-1} \text{K}^{-1}$

(iii) What does the value of ΔS_{total}, which is -78.7 J K^{-1} mol^{-1} at 700 K, indicate about the relative proportions of nitrogen, hydrogen and ammonia at equilibrium?

(1)

the proportions are 1:1:0, because the reaction does not start. The negative ΔS_{total} makes the reaction unfeasible at 700K

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Examiner Comments

There is a calculation error in (ii).
The equilibrium position has to be considered when predicting the ratios present at equilibrium.

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Examiner Tip

The calculation in (i) is correct, but the entropy change of the system is not going to change to a positive value at this temperature.
The negative value of the toal entropy change is not low enough to mean that there is no ammonia at equilibrium.

(i) Calculate the entropy change of the surroundings, $\Delta S_{surroundings}$, at 700 K. Include a sign and units in your answer.

(2)

ΔS surroundings $= \frac{-\Delta H}{T}$

$= \frac{-(-110.2)}{700}$

$= +0.157$

(ii) Calculate ΔS_{system} for this reaction at 700 K. At this temperature the total entropy change, $\Delta S_{total} = -78.7$ J K^{-1} mol^{-1}. Include a sign and units in your answer.

(1)

ΔS total $= \Delta S$system $+ \Delta S$surrounding

$= -78.7$

ΔSsystem $= \Delta S$ total $\div \Delta S$ surroundings.

$= -501.3$ J mol^{-1} K^{-1}

(iii) What does the value of ΔS_{total}, which is -78.7 J K^{-1} mol^{-1} at 700 K, indicate about the relative proportions of nitrogen, hydrogen and ammonia at equilibrium?

(1)

That the yield of ammonia is very low and nitrogen and hydrogen is left over. The process is not feasible with a negative ΔStotal.

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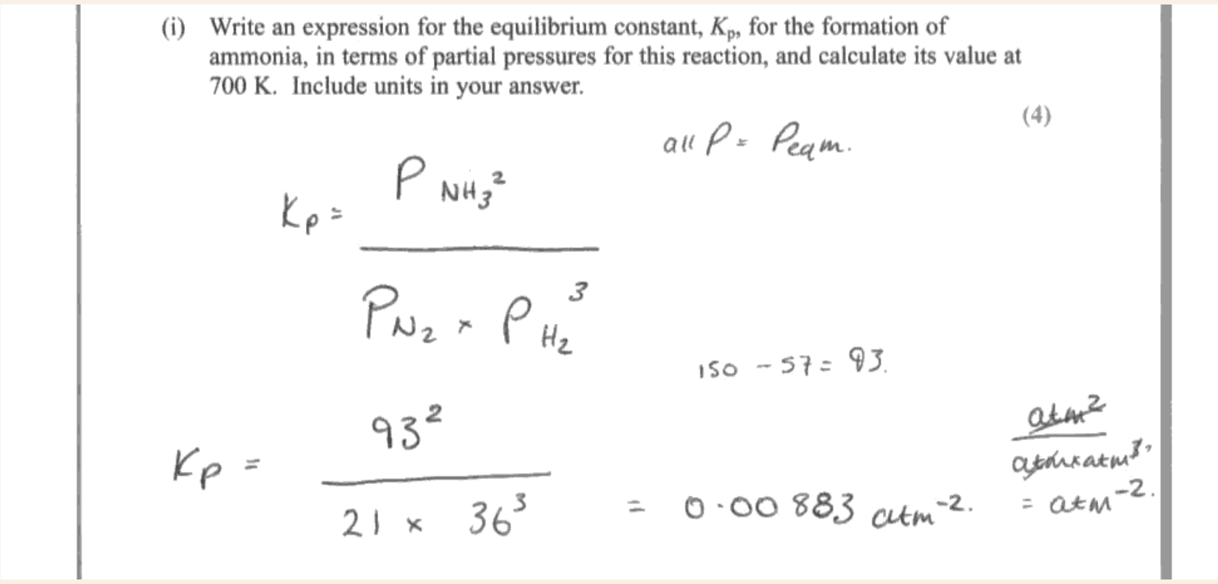
Examiner Comments

Both marks would have been given in (i) if units had been included, and this might have helped the candidate to do (ii) correctly.

In (iii) the candidate is aware that there will be much more nitrogen and hydrogen than ammonia at equilibrium.

Question 17 (c) (i)

Many candidates thought that they had to calculate mole fractions in order to find the partial pressure of hydrogen. They found the mole fractions of nitrogen and ammonia, then the mole fraction of hydrogen and then the partial pressure. All the extra calculations involved inevitably led to errors. Another common error was to use the partial pressure of nitrogen as the value for ammonia when substituting into the expression for K_p. Some candidates answered the question by using the relationship $\Delta S_{total} = R\ln K$ and this alternative was accepted.



(i) Write an expression for the equilibrium constant, K_p, for the formation of ammonia, in terms of partial pressures for this reaction, and calculate its value at 700 K. Include units in your answer.

(4)

all P = Peqm.

$$K_p = \frac{P_{NH_3}^2}{P_{N_2} \times P_{H_2}^3}$$

150 − 57 = 93.

$$K_p = \frac{93^2}{21 \times 36^3} = 0.00883 \text{ atm}^{-2}.$$

$\frac{atm^2}{atm \times atm^3}$ = atm^{-2}.

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Examiner Comments

This is an example of a candidate producing a number without saying what it is and then using it incorrectly. The partial pressure of hydrogen is 93 atm, but this is not stated and this value has then been used as the partial pressure of ammonia. The expression for the equilibrium constant and the units are correct for two marks.

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Examiner Tip

When you do a calculation, state what the number you have calculated refers to. If you just give a number it could be the value at an intermediate stage or it could be your final answer.

Question 17 (c) (ii)

Many answers stated that the yield of ammonia would increase at higher pressure without giving an explanation in terms of the change in the number of moles as the reaction proceeded. Some candidates answered that since the equilibrium constant does not change, the partial pressures of ammonia must increase more than the partial pressures of nitrogen and hydrogen. This is only true because there are more molecules on the bottom of the equilibrium constant expression than on the top. However, many candidates who attempted an answer based on the expression for K_p

did not seem to know the difference between a numerator and a denominator or what exactly a quotient is in fractions. This led to candidates losing the mark due to poor mathematical vocabulary.

(ii) In the manufacture of ammonia, pressures of between 100 and 250 atm are used. State and explain **one** advantage, in terms of the yield of ammonia, of using a pressure above 100 atm.

(1)

Using a pressure above 100 atm increases the yield of ammonia as the equilibrium moves to the side with fewest moles to oppose the increase in pressure ie to the side of ammonia.

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Examiner Comments

This is an example of an answer which scored the mark.

Question 17 (c) (iii)

Some answers to this question were impressively logical and succinct. Other answers showed that though candidates can manipulate numbers in straightforward calculations of entropy changes, they do not really understand the significance of the values and the signs. Answers could be completely contradictory for the effect of a change in $\Delta S_{surroundings}$ on ΔS_{total}, and the effect of a change in ΔS_{total} on the equilibrium constant. These answers usually reverted to Le Chatelier's principle when considering the effect of a temperature rise on the yield of ammonia. Le Chatelier's principle allows predictions to be made, but does not provide explanations and one aim of teaching about entropy is to provide the explanation.

*(iii) In the manufacture of ammonia, a temperature of about 700 K is used.

For this exothermic reaction how does $\Delta S_{surroundings}$ change as temperature increases?

Explain how this change affects the value of ΔS_{total} and the equilibrium constant as temperature increases.

Hence explain the disadvantage of using a temperature higher than 700 K.

(4)

As the temperature increases $\Delta S_{surroundings}$ decreases. This means a higher temperature causes a decrease in ΔS_{total}, and ~~so therefore~~ an increase in the equilibrium constant.
This means that use of a higher temperature shifts the equilibrium to the left, which therefore gives a reduced yield of ammonia. This means if the temperature is increased above 700K the yield of ammonia will drop.

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Examiner Comments

The comments on entropy change are correct but this candidate does not understand the link between the magnitude of the total entropy change and equilubrium constant or between the magnitude of the equilibrium constant and the yield of product.

*(iii) In the manufacture of ammonia, a temperature of about 700 K is used.

For this exothermic reaction how does $\Delta S_{surroundings}$ change as temperature increases?

Explain how this change affects the value of ΔS_{total} and the equilibrium constant as temperature increases.

Hence explain the disadvantage of using a temperature higher than 700 K.

(4)

As the temperature increase $\Delta S_{surroundings}$ will remain positive but will decrease.

This will cause ΔS_{total} to become more negative. The equilibrium constant will ~~increase~~. decrease

The disadvantage of using a temperature higher that 700K is that ~~it~~ ~~becomes less~~ the yield of ammonia will decrease as the increase in temperature causes the position of equilibrium to move to the left in the endothermic direction.

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Examiner Comments

This is clear and correct.

Question 17 (c) (iv)

Many candidates said that a temperature rise allowed more successful collisions, but interpreted this as meaning that more ammonia would be made. It is true that more ammonia would be made per second, but this is a rate increase, not a yield increase. Some candidates said that the rates of both forward and reverse reactions would be increased. This means that equilibrium would be reached faster and was allowed. Other answers said that it was an advantage if the rate of the reverse reaction increased and this was not allowed as the aim of the process is to produce ammonia.

(iv) Suggest **one** advantage of using a temperature higher than 700 K.

(1)

Each molecule has more kinetic energy, so more of them have sufficient energy and geometry when they collide to cause a reaction – EA is achieved by a higher proportion.

(Total for Question 17 = 18 marks)

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Examiner Comments

It is not clear that the higher proportion of molecules with the activation energy leads to a higher rate.

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Examiner Tip

Raising temperature always makes a reaction go faster. If the reaction goes to equilibrium, then equilibrium will be reached faster but the yield may not be as good.

Question 18 (a)

This was left blank in some scripts, suggesting that candidates had not read the question carefully enough. A few candidates looked at the patterns in the numbers and gave the incorrect answer of 1.8×10^{-6}.

Question 18 (b)

Only a few candidates gave the approximation for K_a in (i) instead of the full expression and there were many correct answers for the pH, though as stated in the introduction, some answers were rounded incorrectly.

(b) (i) Write the expression for K_a for methanoic acid, HCOOH.

(1)

$$K_a = \frac{[H_3O^+][A^-]}{[HCOOH]}$$

(ii) Calculate the pH of a solution of methanoic acid with concentration 0.50 mol dm^{-3} at 298 K.

(3)

At Equ $[H_3O^+][A^-] = [H^+]^2$

$$\therefore \quad 1.6 \times 10^{-4} = \frac{[H^+]^2}{0.5}$$

$[H^+] = 8.94\ldots \times 10^{-3}$

pH = 2.05 (2dp)

(iii) State **one** of the assumptions you have made when calculating the pH in (ii).

(1)

That the contribution of H^+ is solely from the acid, ∴ contribution by water is negligible.

ResultsPlus

Examiner Comments

This is an example of a good answer. The reason given in (iii) shows more understanding than simply saying that the concentrations of hydrogen ions and methanoate ions are equal.

(b) (i) Write the expression for K_a for methanoic acid, HCOOH.

(1)

$$Ka = \frac{[H^+]^2}{[HCOOH]}$$

(ii) Calculate the pH of a solution of methanoic acid with concentration 0.50 mol dm^{-3} at 298 K.

(3)

$$[H^+] = \sqrt{Ka \times [HCOOH]}$$

$$= \sqrt{1.6 \times 10^{-4} \times 0.5}$$

$$= 8.94 \times 10^{-3}$$

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

$$= -\log[8.94 \times 10^{-3}]$$

$$= 2.05 \text{ mol}$$

(iii) State **one** of the assumptions you have made when calculating the pH in (ii).

(1)

The methanoic acid fully dissociated.

ResultsPlus

Examiner Comments

The expression in (b)(i) is an approximation and not the full expression for the constant. The calculation in (ii) is correct, even though the assumption given in (iii) is incorrect and not the one which has been used.

Question 18 (c)

Many errors were made here. In (i) it was common to see the acids given as HCOOH and CH_3COOH. Sometimes equations were written for the acid/base conversions without stating which species were acids.

In (ii) the most common answer was $CH_3COOH_2^+$, presumably because this appeared in (i), and IO^-. Only a minority of candidates used the data in (a) and deduced that the weaker acid, HIO, would accept a proton.

(c) The following equilibrium occurs in a mixture of pure methanoic and ethanoic acids.

$$HCOOH + CH_3COOH \rightleftharpoons HCOO^- + CH_3COOH_2^+$$

(i) Give the formulae of the two Brønsted-Lowry acids in this equilibrium. (1)

$HCOOH \rightarrow HCOO^- + H^+$

$CH_3COOH + H^+ \rightarrow CH_3COOH_2^+$

ResultsPlus
Examiner Comments

The answer to (i) does not actually state which species are acids.

ResultsPlus
Examiner Tip

Make sure that you read the question and give the information required to answer it.

(c) The following equilibrium occurs in a mixture of pure methanoic and ethanoic acids.

$$HCOOH + CH_3COOH \rightleftharpoons HCOO^- + CH_3COOH_2^+$$

(i) Give the formulae of the two Brønsted-Lowry acids in this equilibrium. (1)

HCOOH $CH_3COOH_2^+$

(ii) Write an equation showing the products of the equilibrium which is set up when iodic(I) acid is mixed with ethanoic acid. (1)

$HIO + CH_3COOH \rightleftharpoons$ IO^- + $CH_3COOH_2^+$

ResultsPlus

Examiner Comments

After identifying the correct acids in (i) it was common to see $CH_3COOH_2^+$ again in (ii).

ResultsPlus

Examiner Tip

Here you have to decide which acid is stronger and therefore the proton donor. The pKa values are in the Data booklet and in (a).

Question 18 (d)

The impression given in this question was that candidates did not know what was meant by a ratio. The first mark was for calculating the hydrogen ion concentration and this was usually correct though it is not good practice simply to put an unlabelled number in the middle of the space without saying what it is. However, using the K_a expression directly to find the ratio or taking logs first, was beyond many candidates. Either the ratio of methanoate to methanoic acid or acid to methanoate was acceptable but to gain marks it had to be clear which was being given.

(d) A shampoo is buffered by the addition of a mixture of methanoic acid and sodium methanoate.

The pH of this shampoo is 4.9. Calculate the hydrogen ion concentration in the shampoo, and hence the ratio of methanoate ions to methanoic acid.

(2)

$Ka = \frac{[H^+][A^-]}{[HA]}$ $10^{-4.9} = 1.26 \times 10^{-5}$ mol dm^{-3}

H^+ concentration.

$HA \rightleftharpoons H^+ + A^-$

1 : 1.26×10^{-5} : 0.99

1 : 1 ratio

ResultsPlus

Examiner Comments

In (b) many candidates showed that they knew that in a weak acid the hydrogen ion concentration equals the concentration of base, in this case methanoate. However, a buffer is a mixture of a weak acid and its salt, so the hydrogen ion concentration does not equal the concentration of the conjugate base.

ResultsPlus

Examiner Tip

When you do calculations on buffers, you cannot use the approximation for Ka which you use when calculating the pH of a weak acid. This is because a buffer is not just a weak acid. A salt is also present.

(d) A shampoo is buffered by the addition of a mixture of methanoic acid and sodium methanoate.

The pH of this shampoo is 4.9. Calculate the hydrogen ion concentration in the shampoo, and hence the ratio of methanoate ions to methanoic acid. (2)

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

$[H^+] = 10^{-pH}$

$= 10^{-4.9}$

$[H^+] = 1.26 \times 10^{-5}\ mol dm^{-3}$

$\therefore$ HCOOH : $HCOO^-$

13 : 1

$Ka = \frac{[HCOO^-][H^+]}{[HCOOH]}$

$Ka \times [HCOOH] = [HCOO^-][H^+]$

ratio = HCOOH : $HCOO^-$

1.6×10^{-4} : 1.26×10^{-5}

13 : 1

(Total for Question 18 = 10 marks)

TOTAL FOR SECTION B = 50 MARKS

ResultsPlus

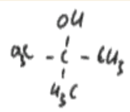
Examiner Comments

This candidate has made an error at the final stage and stated that this is the ratio of acid: salt, not the reverse.

Question 19 (a)

There were many incorrect names for the alcohol, though the catalyst was often correct.

(a) **Name** the alcohol and catalyst which would be used to make **X**. (2)



Alcohol 1,1- dimethyl- ethanol

Catalyst dilute sulphuric acid

ResultsPlus

Examiner Comments

This was a common error in the alcohol name.

ResultsPlus

Examiner Tip

To help work out a name, find a space where you can draw out the structure of the compound. Then count the number of carbon atoms in the longest chain and base the name on this.

Question 19 (b)

The practical knowledge of candidates on procedures in organic synthesis was very poor. Even though the ester was collected by distillation, the majority of candidates assumed it was a solid and suggested washing it in a Buchner funnel. The purpose of washing it in sodium carbonate was often said to be to remove impurities. This is much too vague. Few candidates knew suitable drying agents.

Requirements of the diagram were, a suitable flask with heat source and with a thermometer in the still head and the thermometer bulb opposite the opening to a downward sloping condenser. There were many examples of open flasks where all the organic material would have escaped, and also of completely sealed and therefore potentially explosive apparatus. When a thermometer was present the bulb was often in the liquid being heated or above or below the level of the condenser. Condensers were shown in a horizontal position as well as sloping upwards or downwards. Reflux apparatus was sometimes shown, sometimes completely sealed.

(b) After refluxing, the resulting mixture is distilled to give an impure product containing **X**. The impure product is washed several times with sodium carbonate solution and then dried.

(i) Name the piece of equipment in which the impure product would be washed. (1)

a vaccum condenser

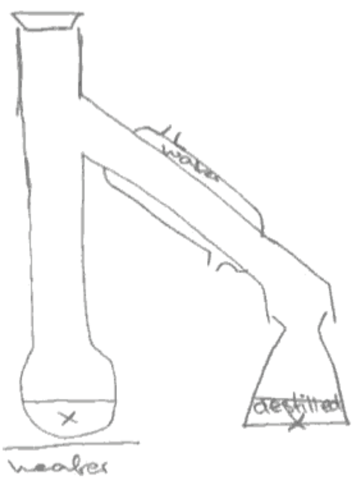
(ii) What is the purpose of washing the impure product with sodium carbonate solution? (1)

to prevent further reaction

(iii) Name a suitable drying agent. (1)

dry ether

(iv) The impure product is then redistilled and **X**, which has a boiling temperature of 97°C, is collected. Draw a labelled diagram of the apparatus you would use. (3)



ResultsPlus

Examiner Comments

There were many answers like this for sections (i) - (iii). There is no thermometer in the apparatus and very little of the distillate would end up in the collecting flask.

(b) After refluxing, the resulting mixture is distilled to give an impure product containing **X**. The impure product is washed several times with sodium carbonate solution and then dried.

(i) Name the piece of equipment in which the impure product would be washed.

(1)

a buckminster funnel

(ii) What is the purpose of washing the impure product with sodium carbonate solution?

(1)

to dicsolve some of the impurities and remove them.

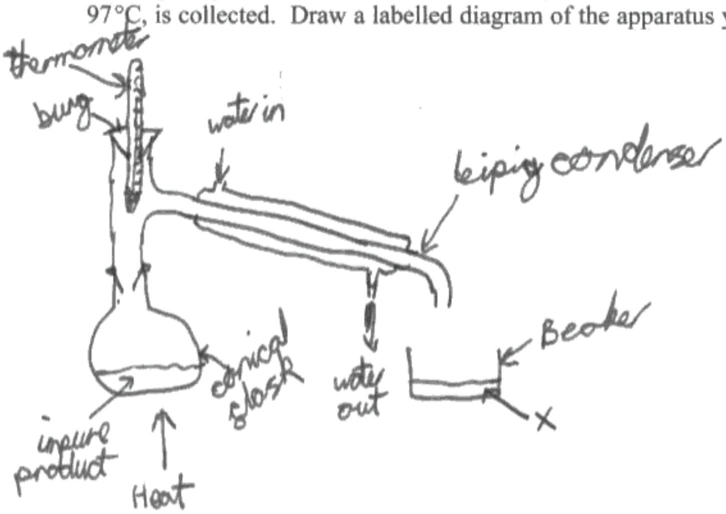
(iii) Name a suitable drying agent.

(1)

NaOH

(iv) The impure product is then redistilled and **X**, which has a boiling temperature of 97 °C, is collected. Draw a labelled diagram of the apparatus you would use.

(3)



ResultsPlus

Examiner Comments

Parts (i) -(iii) suggest little practical knowledge, but the diagram is correct in principle.

Question 19 (c)

The requirements of this question were specified clearly. There were two peaks and the first mark was for explaining that these were caused by two hydrogen environments, but not by two environments of methyl groups which was often given as the answer. One peak was three times the height of the other, showing that there were three times as many hydrogen atoms in one environment than the other. The easiest way to explain which atoms produced the peaks was to draw the formula of the molecule and mark the atoms on this. Candidates who used the data booklet often did not understand that reference to the H-C-C=O or H-C-C peak is to the hydrogen atoms in these groups, and thought that the C=O or some other bond was causing the signal. There was confusion in the language where singlets were concerned. Some candidates said that since all the hydrogen atoms in the $(CH_3)_3$- group were in the same environment they would produce a singlet.

Explain how **spectrum 1** is consistent with the structure of **X**. You should refer to the number and height of the peaks, the atoms which produce them and their splitting patterns.

(4)

- The number of Hydrogen environments in an NMR spectrum is hown by the number of peaks → in this case there are two as there are two Hydrogen environments: the Hydrogen in the methyl group on the ethanoate, and the three methyl group on the alkyl (these three methyl group have the same environment because they are bonded to the same Carbon atom
- Splitting is dictated by how many Hydrogens are on the adjacent atom (the n+1 rule is used → number of Hydrogen atoms +1) and in this case both Hydrogen environments are adjacent to a Carbon with no Hydrogens bonded to it so each peak is a singlet
- The height of the first peak is much higher as there are far more Hydrogens in that environment and so more spin, it should be three times as high
- The second peak has a higher shift value because it is closer to the electronegative Oxygen atoms

ResultsPlus

Examiner Comments

This is a good answer. The only missing point is that one peak is three times the height of the other because, there are three times as many hydrogen atoms in it.

ResultsPlus

Examiner Tip

In a question like this, work through each requirement in order, possibly ticking them off as you work through.

Explain how **spectrum 1** is consistent with the structure of **X**. You should refer to the number and height of the peaks, the atoms which produce them and their splitting patterns.

(4)

1·3 δ/ppm shows a H–C–C group, which is present on ~~the~~ X. 2·1 δ/ppm shows a H–C–C=O, which is also seen of X, as it is a Ester. However the signal strength of the Ester functional group is low, and the alkane functional group has a high signal. They do however prove that X is an ester and it contains a ~~ethane group~~ ethanoate group.

ResultsPlus

Examiner Comments

This answer does not refer to hydrogen environments and gives the impression that the Data booklet has been used without much thought being given to the structure of the ester.

Explain how **spectrum 1** is consistent with the structure of **X**. You should refer to the number and height of the peaks, the atoms which produce them and their splitting patterns.

(4)

There are only 2 peaks which is consistent as X only has 2 ~~p~~ different protonic environments and the n+1 rule states that the number of peaks on the spectrum relates to the number of hydrogens on the carbon next door plus 1. In this case the carbon next door to the carbons with hydrogens does not have any hydrogens in both instances so 0+1 = 1 which is the number of peaks which are observed. The height of the peak closest to 0 can be explained by the fact there are 9 hydrogens within the same environment of being next to ~~the~~ a carbon with no hydrogens so the signal strength is greater.

ResultsPlus

Examiner Comments

This candidate seems confused about the total number of peaks and the fact that each peak is a singlet.

ResultsPlus

Examiner Tip

When discussing an nmr spectrum, draw a displayed formula of the molecule so that you can see the hydrogen environments clearly. Each hydrogen environment produces a peak on the spectrum. Each peak may be split into doublets, triplets etc depending on whether there are adjacent hydrogen atoms.

Question 19 (d)

Though many candidates drew the structure of the ester correctly, a significant proportion thought that the C=O or some other part of the molecule caused the singlet peak.

Question 19 (e)

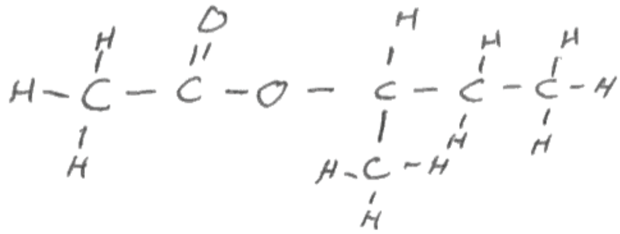
Many candidates assumed the isomer was another ester without studying the data carefully. The broad peak in the infrared would not be due to an alkyl group as this peak is a narrow one. Despite the molecular formula, some candidates stated that it was an alkane, misunderstanding the wording in the Data booklet which refers to C-H stretch in an alkane at 2962-2853 cm^{-1} , which is quite a narrow range. Many structures were drawn which were impossible in bonding terms, but structures where bonding was correct included molecules containing –OH and C=C groups. Credit was given for drawing a structure containing a chiral carbon if the molecule was theoretically possible. Marks could also be gained for recognising that the molecule was not an aldehyde or a ketone as long as these structures were not drawn. There was also a mark for linking the structure with the increased boiling point by showing a molecule which could take part in hydrogen bonding.

In the final section there was confusion about different types of spectroscopy. Some candidates said that different isomers would have different fragmentation patterns, thinking of mass spectra and other answers said that there would be different numbers of hydrogen environments or different splitting patterns, thinking of nmr.

*(i) Draw the structure of **one** of the isomers which is optically active, explaining how you use **all** the information in the question.

(5)

alkone no ~~aldehyde~~ aldehyde



the peak at ~~th~~ 2960 cm⁻¹ is caused by the molecule being saturated, (no C=C). It has a chiral carbon, (the first one to the right of the C=O (C-O). It doesn't have an aldehyde group and therefore won't react with 2,4 DNP. It has a higher boiling temperature because it has a greater surface area and therefore more Idids.

(ii) Could the compound you have drawn in (e)(i) be distinguished by infrared spectroscopy from its other isomers with the properties listed above? Explain your answer.

(1)

no, because they will all have the same functional groups.

(Total for Question 19 = 20 marks)

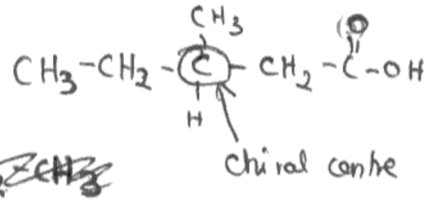
TOTAL FOR SECTION C = 20 MARKS

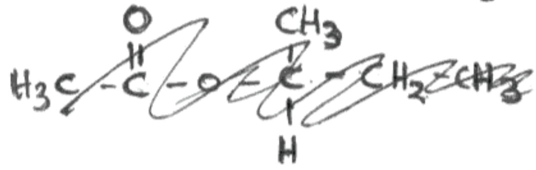
ResultsPlus

Examiner Comments

The infra red data was not interpreted correctly, and the negative test result with 2,4 dinitrophenylhydrazine also eliminates a ketone. The surface are of the ester is not significantly greater than for isomer X as it is still branched, so the mark about boiling temperature was not given. The abbreviation for instantaneous dipole/ induced dipole attraction, used at the end of the answer to (i) is not standard and should not be used without explanation.

*(i) Draw the structure of **one** of the isomers which is optically active, explaining how you use **all** the information in the question.





The data that there is broad peak at ~~296~~ 2960cm⁻¹ in IR spectra shows the presence C-O as the range for C-O is ~~2853 to 2962~~ 2500 - 3300. The absence of an aldehyde or ketone is is shown by the isomer not reacting with 24-DNP. The higher boiling point shows that the compound is ~~more~~ less branched than X' as less branched compounds are less volatile. ~~and that~~ Dimerisation is possible due to COOH increasing the Boiling point

(ii) Could the compound you have drawn in (e)(i) be distinguished by infrared spectroscopy from its other isomers with the properties listed above? Explain your answer.

(1)

Yes as there are 6 types of Hydrogen atoms and each will split in unique patterns, helping us determine the compound. The test results will also assist in confirming the compound.

ResultsPlus

Examiner Comments

The molecule is identified as an acid though the use of infrared data is not fully correct. The branching in the molecule is less important than the ability to form hydrogen bonds or dimers. The mark for the results of the 2,4-dinitrophenylhydrazine test is correct.

The answer to (ii) is based on nmr, not infrared.

Paper Summary

Questions such as 17(c)(iii) and 19(c) asked for several pieces of information in the answer. The questions outlined what was needed, but candidates often did not do what was required. Reading the question carefully is vital. There was often poor understanding of the way information is given in the Data booklet. It will help if candidates spend sometime to understand how to use the Data booklet.

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