Examiners' Report
January 2013

GCE Chemistry 6CH04 01

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Introduction

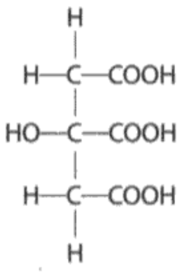
This paper tested a wide range of Unit 4 material and provided good opportunities for candidates to show their knowledge and understanding of the Chemistry covered by the Specification. Questions 18 and 19 provided the most challenge. The standard of answers to the questions on equilibrium and thermodynamics was often very good. However, the responses to the questions on organic chemistry, including nmr, and acid-base equilibria contained more errors. A very large proportion of candidates seemed unsure about the choice of a suitable number of significant figures in their numerical answers. There were no questions asking for a specific number of significant figures in the final answer, but as long as there were at least two significant figures a candidate's response was not penalised. However, candidates at this level should realise that giving a full calculator read-out for a pH value 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.

Question 15 (a)

Many candidates were able to identify that the citric acid molecule contains three carboxylic acid groups and so one mole of citric acid neutralizes three moles of sodium hydrogencarbonate.

15 Citric acid is found in lemon juice.

The structure and formula of citric acid are shown below.



$C_6H_8O_7$

(a) In the presence of a small amount of moisture, citric acid reacts with sodium hydrogencarbonate as shown in the equation below.

$$C_6H_8O_7(s) + 3NaHCO_3(s) \rightarrow Na_3C_6H_5O_7(s) + 3CO_2(g) + 3H_2O(l)$$

Use the structural formula of citric acid to explain why one mole of citric acid neutralizes three moles of sodium hydrogencarbonate.

(1)

Sodium hydrogencarbonate reacts with the "acidic element" of citric acid - the COOH group. As there are 3 of these groups present and 1 mole of sodium hydrogencarbonate reacts directly with <u>each one</u>, 3 moles of $NaHCO_3$ are required for the whole molecule.

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Examiner Comments

The presence of three COOH groups was acknowledged, so the mark was awarded.

Question 15 (b) (i)-(v)

The answers to (b)(i) to (b)(iv) showed good understanding by the vast majority of candidates.

The calculation in (b)(i) was usually correct. However, the most common errors were either selecting the standard entropy value for steam, rather than liquid water, from the data booklet or a failure to multiply the required standard entropy values by a factor of three. In (b)(ii), most candidates realised that a gas or liquid product is more disordered than a solid reactant.

In (b)(iii), very few candidates failed to convert the standard enthalpy change of the reaction in units of kJ mol^{-1} to J mol^{-1} before dividing by the temperature in K. This enabled the standard entropy change of the surroundings to be quoted in units of J $mol^{-1}K^{-1}$, to be consistent with the units used in the answer to (b)(i). Consequential marking allowed credit to be given for answers to (b)(iv) and (b)(v) that followed on from a candidate's answers to (b)(i) and (b)(iii).

(b) You will need to refer to the data booklet in the calculations which follow.

You should also use the values given below.

compound	$S^{\ominus}$ / J mol^{-1} K^{-1}
$Na_3C_6H_5O_7(s)$	200.5
$C_6H_8O_7(s)$	199.9

(i) Calculate the standard entropy change of the system, $\Delta S^{\ominus}_{system}$, for the following reaction at 298 K. Include a sign and units in your answer.

(2)

$$C_6H_8O_7(s) + 3NaHCO_3(s) \rightarrow Na_3C_6H_5O_7(s) + 3CO_2(g) + 3H_2O(l)$$

products − reactants

101.7 200.5 + 3× 213.6 640.8

$NaHCO_3$ CO_2

1051 − 505 = +54 J mol^{-1} K^{-1} 209.7

305.1 H_2O

*(ii) Explain how the sign of your answer to (b)(i) could be predicted from the equation for the reaction between citric acid and sodium hydrogencarbonate.

(2)

3 moles of CO_2 gas and 3 moles of liquid are produced, increase in disorder + ~~entropy~~ therefore positive entropy

(iii) Given that $\Delta H^{\ominus}_{298}$ for the reaction shown in (b)(i) is +70 kJ mol^{-1}, calculate the standard entropy change of the surroundings, $\Delta S^{\ominus}_{surroundings}$, for this reaction at 298 K. Include a sign and units in your answer.

(2)

70 ×1000 = 70000 / 298 = ~~234.9~~

−234.9 J mol⁻¹ K⁻¹

(iv) Calculate the total entropy change, $\Delta S^{\ominus}_{total}$, for this reaction at 298 K.

(1)

−234.9 + 54 = −180.9 J mol⁻¹ K⁻¹

(v) What does the sign of $\Delta S^{\ominus}_{total}$ suggest about this reaction at 298 K?

(1)

It is not thermodynamically feasible / spontaneous

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Examiner Comments

Part (b)(i) scores the first mark as the working correctly arrives at 1051 - 505. However, the subsequent arithmetic gets "+54", instead of "+546", so the second mark was not awarded.

In (b)(ii), the candidate mentions gas (and liquid) products to earn the first mark and an increase in disorder for the second mark.

In (b)(iii), the answer is correct to four significant figures with sign, answer and units all correct as required by the Mark Scheme.

In (b)(iv) and (v), full credit is awarded for both answers by the application of consequential marking.

(b) You will need to refer to the data booklet in the calculations which follow.

You should also use the values given below.

compound	$S^{\ominus}$ / J mol^{-1} K^{-1}
$Na_3C_6H_5O_7(s)$	200.5
$C_6H_8O_7(s)$	199.9

(i) Calculate the standard entropy change of the system, $\Delta S^{\ominus}_{system}$, for the following reaction at 298 K. Include a sign and units in your answer.

(2)

$$C_6H_8O_7(s) + 3NaHCO_3(s) \rightarrow Na_3C_6H_5O_7(s) + 3CO_2(g) + 3H_2O(l)$$

$S^{\ominus}[NaHCO_3] = 101.7$ $S^{\ominus}[CO_2] = 213.6$ $S^{\ominus}[H_2O] = 69.9$

$\Delta S^{\ominus}_{sys} = (3\times69.9 + 3\times213.6 + 200.5) - (3\times101.7 + 199.9)$

$= +546\ J mol^{-1} K^{-1}$

*(ii) Explain how the sign of your answer to (b)(i) could be predicted from the equation for the reaction between citric acid and sodium hydrogencarbonate.

(2)

More moles of products are produced from the reactants (4 moles of reactants makes 7 moles of products). Also both reactants are solid and one of the products is gaseous. Therefore the products have a higher entropy hence $\Delta S^{\ominus}_{sys}$ should be positive as calculated.

(iii) Given that $\Delta H^{\ominus}_{298}$ for the reaction shown in (b)(i) is +70 kJ mol^{-1}, calculate the standard entropy change of the surroundings, $\Delta S^{\ominus}_{surroundings}$, for this reaction at 298 K. Include a sign and units in your answer.

(2)

$\Delta S^{\ominus}_{sur} = -\frac{\Delta H}{T} = -\frac{70000}{298}$

$= -234.9\ J mol^{-1} K^{-1}$

(iv) Calculate the total entropy change, $\Delta S^{\ominus}_{total}$, for this reaction at 298 K.

(1)

$\Delta S^{\ominus}_{total} = 546 - 234.9$

$= +311.1 \text{ J mol}^{-1}\text{K}^{-1}$

(v) What does the sign of $\Delta S^{\ominus}_{total}$ suggest about this reaction at 298 K?

(1)

The sign is positive suggesting that the reaction is spontaneous at 298K.

ResultsPlus
Examiner Comments

In (b)(i), the sign and final answer are correct, so both marks were awarded.

For (b)(ii), the candidate states that one of the products is gaseous and also mentions that four moles (of reactants) form seven moles (of products), so both marks were awarded.

In (b)(iii), the working, sign, final answer and units are all correct so two marks were earned.

In (b)(iv), the answer is correct, stated to four significant figures.

In (b)(v), the available mark was awarded.

Question 16 (a) (i)-(ii)

In (a)(i), the K_w expression was usually given correctly. The most likely error to be made, however, was to include $[H_2O(l)]$ in the expression.

In (a)(ii), the pH of the sodium hydroxide was almost always calculated correctly. On occasions, a mark was lost for incorrect rounding of the final answer.

16 Methanoic acid, HCOOH, is present in ant stings.

A scientist analyzed 25.0 cm^3 of an aqueous solution of methanoic acid, solution **Z**, by titrating it with dilute sodium hydroxide, NaOH(aq).

- 20.0 cm^3 of sodium hydroxide was required to neutralize the methanoic acid
- The equation for the neutralization of methanoic acid is

$$HCOOH(aq) + NaOH(aq) \rightarrow HCOONa(aq) + H_2O(l)$$

(a) (i) Give the expression for K_w, the ionic product of water.

(1)

$k_w = [H^+][OH^-]$

(ii) The concentration of the sodium hydroxide, NaOH(aq), used in the titration was 0.00750 mol dm^{-3}.

Calculate the pH of the sodium hydroxide solution.

$[K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{dm}^{-6}]$

(2)

$pOH = -\log(0{\cdot}00750)$

$= 2{\cdot}12493...$

$pH = 14 - 2{\cdot}1249...$

$= 11{\cdot}875...$

$= 11{\cdot}9$ (3 s.f.)

ResultsPlus
Examiner Comments

In (a)(i) and (a)(ii), both answers are fully correct. State symbols were not required in (a)(i). In (a)(ii), the candidate uses the expression pK_w = pH + pOH to obtain the correct pH and this is, of course, a valid approach.

ResultsPlus
Examiner Tip

Remember not to include $[H_2O(l)]$ in the expression for K_w.

16 Methanoic acid, HCOOH, is present in ant stings.

A scientist analyzed 25.0 cm^3 of an aqueous solution of methanoic acid, solution **Z**, by titrating it with dilute sodium hydroxide, NaOH(aq).

- 20.0 cm^3 of sodium hydroxide was required to neutralize the methanoic acid
- The equation for the neutralization of methanoic acid is

$$HCOOH(aq) + NaOH(aq) \rightarrow HCOONa(aq) + H_2O(l)$$

(a) (i) Give the expression for K_w, the ionic product of water. **(1)**

$k_w = [H^+][OH^-]$

(ii) The concentration of the sodium hydroxide, NaOH(aq), used in the titration was 0.00750 mol dm^{-3}.

Calculate the pH of the sodium hydroxide solution.

$[K_w = 1.00 \times 10^{-14}$ $mol^2 dm^{-6}]$ **(2)**

$[H^+] = k_w / [OH^-]$

$= 1 \times 10^{-14} / 0.0075$

$= 1.33 \times 10^{-12}$

$pH = -\log(1.33 \times 10^{-12})$

$= 11.88$

ResultsPlus
Examiner Comments

Both parts (a)(i) and (a)(ii) are fully correct.
Note that in (a)(i), state symbols were not required.

ResultsPlus
Examiner Tip

In calculation questions, always show the steps in your working.

Question 16 (b)

In (b), most candidates were able to calculate the moles of methanoic acid reacting as they were the same as the moles of sodium hydroxide. This value then had to be divided by the volume of acid, in dm^3, to give the concentration in mol dm^{-3}. Occasionally, candidates used the volume of sodium hydroxide solution, instead of the volume of methanoic acid, in the second step.

(b) Use the equation for the reaction and the data from the titration to show that the concentration of the methanoic acid in solution **Z** was 6.00×10^{-3} mol dm^{-3}.

(2)

NaOH $m = cV$

$m = 0.0075 \times 20 \times 10^{-3}$

1:1 ratio

∴ HCOOH: $m = cV$

$0.0075 \times 20 \times 10^{-3} = c \times 25 \times 10^{-3}$

$c = 0.006$

$c = 6.00 \times 10^{-3}$ mol dm^{-3}

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Examiner Comments

The candidate has used a formula to solve a simple equation where the unknown, c, is the concentration of the methanoic acid in mol dm^{-3}. The value of c is correctly calculated.

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Examiner Tip

Set out mathematical expressions clearly, showing how the unknown value is calculated.

Question 16 (c) (i)

Both words in the term 'weak acid' were familiar to the majority of candidates.

(c) Methanoic acid is a weak acid.

(i) Explain the term **weak acid**.

(2)

Weak Does not fully dissociate in aqueous solution (is not fully ionised)

Acid Donates a proton to another species during reactions. A Brønsted-Lowry acid is a proton donor

ResultsPlus
Examiner Comments

This response scored the available marks, as both the words 'weak' and 'acid' were correctly explained.

ResultsPlus
Examiner Tip

Learn, and understand, all the key terms and definitions in the specification.

(c) Methanoic acid is a weak acid.

(i) Explain the term **weak acid**.

(2)

Weak Does not fully dissociate in water

Acid Is a proton donor, has pH < 7

ResultsPlus
Examiner Comments

This answer scores both marks. If the acid had only been defined as a substance "with a pH < 7", the mark for the definition of an 'acid' would not have been awarded.

ResultsPlus
Examiner Tip

Keep definitions, where appropriate, brief and to the point.

Question 16 (c) (ii)-(iii)

The K_a expression in (c)(ii) was almost universally known. However, the numerator in the expression was sometimes given incorrectly as $[H^+]^2$, instead of the product $[H^+][HCOO^-]$. In a buffer solution, for which the K_a expression still applies, the anion concentration $[HCOO^-]$ is considerably greater than that of $[H^+]$. The calculation in (c)(iii) was usually correct, with a very small number of answers taking into account the small degree of dissociation of the methanoic acid. Two assumptions used in the calculation were normally well known. The most frequent omission, however, was not stating that the $[\text{acid}]_{\text{initial}}$ is assumed to be equal to the $[\text{acid}]_{\text{equilibrium}}$. The assumption $[H^+] = [HCOO^-]$ at equilibrium was well known.

(ii) The equation for the dissociation of methanoic acid in aqueous solution is shown below.

$$HCOOH(aq) \rightleftharpoons HCOO^-(aq) + H^+(aq)$$

Write the expression for the acid dissociation constant, K_a, for methanoic acid.

(1)

$$K_a = \frac{[H^+_{(aq)}][HCOO^-_{(aq)}]}{[HCOOH_{(aq)}]}$$

*(iii) At 298 K, the acid in ant stings has a concentration of 6.00×10^{-3} mol dm^{-3} and a pH of 3.01.

Calculate the value of K_a for methanoic acid at 298 K.

State clearly any assumptions that you have made.

(4)

Calculation:

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]} = \frac{[H^+]^2}{[HCOOH]}$$

~~pH = pKa + log [HCOOH]/[HCOO⁻]~~

$$3.01 = -\log[H^+] \quad \therefore [H^+] = 10^{-3.01} = 9.7724 \times 10^{-4}$$

$$\therefore K_a = \frac{(9.7724 \times 10^{-4})^2}{6 \times 10^{-3}} = 1.59 \times 10^{-4} \text{ moldm}^{-3}$$

Assumption(s):

Assumed that $[H^+]_{eqb} = [HCOO^-]_{eqb}$

Assumed that $[HCOOH]_{eqb} = [HCOOH]_{initial}$ (or that the concentration of methanoic acid remains constant), and the equilibrium concentrations of $[H^+]$ and $[HCOO^-]$ are equal.

(Total for Question 16 = 12 marks)

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Examiner Comments

The calculation, and accompanying assumptions, were clearly set out and easy to follow.

ResultsPlus
Examiner Tip

Understand any assumptions made in a calculation rather than learning them by rote.

Question 17 (a)

In (a)(i), the K_c expression was almost always correctly given, although a few candidates were confused by the presence of water and omitted it from the numerator altogether. The calculation of the equilibrium moles in (a)(ii) proved problematic for some candidates, although consequential marking allowed the mark to be gained in (a)(iv). It was difficult to see how some of the values given were derived, especially where the moles of product(s) were given as zero at equilibrium. The candidates' *Quality of Written Communication* was tested in (a)(iii) where some candidates stated that "the moles of all the components cancelled" rather than 'the units of concentration cancelled out' in this particular K_c expression.

17 Ethanoic acid and ethanol react together to form the ester ethyl ethanoate, $CH_3COOC_2H_5$, and water.

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$$

(a) (i) Give the expression for K_c.

(1)

$$K_c = \frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]}$$

(ii) An equilibrium was reached when the amounts of substances shown in the table below were used.

Complete the table to show the amounts of each substance present at equilibrium.

(2)

Component	$CH_3COOH(l)$	$CH_3CH_2OH(l)$	$CH_3COOCH_2CH_3(l)$	$H_2O(l)$
Initial amount / mol	0.40	0.30	0.00	0.15
Equilibrium amount / mol	0.20	0·10	0·20	0.35

(iii) Explain why K_c for this reaction has no units.

(1)

Same no. of moles ~~of~~ on each side of equation so units cancel out.

(iv) Calculate the numerical value of K_c.

(1)

$$kc = \frac{[0.2][0.35]}{[0.2][0.1]}$$

$$Kc = 3.5$$

ResultsPlus

Examiner Comments

In (a)(i), the K_c expression is correct. The equilibrium moles are correct in (a)(ii), so both marks were awarded.

In (a)(iii), two correct reasons were given for the fact that K_c has no units; one reason would have sufficed.

In (a)(iv), the value of 3.5 scores the available mark.

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Examiner Tip

Use algebraic expressions to calculate equilibrium amounts of reactants and products. For example, (0.40 - x) is the equilibrium moles of ethanoic acid, CH_3COOH. Therefore, x = 0.20 mol. The amount of ethanol, CH_3CH_2OH at equilibrium (0.30 - x) = 0.10 mol. The moles of ester and water, therefore, are x (= 0.20 mol) and x + 0.15 (= 0.35 mol), respectively.

17 Ethanoic acid and ethanol react together to form the ester ethyl ethanoate, $CH_3COOC_2H_5$, and water.

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$$

(a) (i) Give the expression for K_c.

(1)

$$K_c = \frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]}$$

(ii) An equilibrium was reached when the amounts of substances shown in the table below were used.

Complete the table to show the amounts of each substance present at equilibrium.

change of 0.2

(2)

Component	$CH_3COOH(l)$	$CH_3CH_2OH(l)$	$CH_3COOCH_2CH_3(l)$	$H_2O(l)$
Initial amount / mol	0.40	0.30	0.00	0.15
Equilibrium amount / mol	0.20	0.10	0.20	0.35

(iii) Explain why K_c for this reaction has no units.

(1)

$\frac{mol^2 dm^{-6}}{mol^2 dm^{-6}}$ there are an equal number of units on the top / products and bottom / reactants. Therefore the units cancel

(iv) Calculate the numerical value of K_c.

(1)

$$K_c = \frac{0.2 \times 0.35}{0.1 \times 0.2}$$

$$= \frac{0.07}{0.02}$$

$$= 3.5$$

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Examiner Comments

In (a)(i), the mark is awarded for the correct K_c expression. State symbols are not required.

The moles are all correct in (a)(ii).

In (a)(iii), the idea of the units cancelling out is clearly expressed.

In (a)(iv), the numerical value of K_c is correct.

Question 17 (b)

This question was very well-answered with the vast majority of candidates aware that the presence of a catalyst increases the rate of a reaction, but has no effect on the position of equilibrium.

(b) The esterification reaction above was carried out in the presence of hydrochloric acid as the catalyst.

State the effect on the equilibrium position and the rate of attainment of equilibrium if the concentration of the acid catalyst were to be increased.

(2)

Catalyst would have no effect on the equilibruim position, however would increase the rate of attainment.

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Examiner Comments

This answer correctly addresses both the points required.

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Examiner Tip

Make sure that you understand the difference between the two questions "how fast?" (i.e. kinetics) and "how far?" (i.e. equilibrium).

Question 17 (c) (i)-(ii)

In (c)(i), the breaking of both the C-O and the O-H bonds was often noted. However, only the making of the C-O bond was acknowledged in the majority of answers. In (c)(ii), the idea that the same bond has a slightly different bond energy depending on the environment in which it is found was often overlooked.

(c) (i) Identify which bonds are broken and which bonds are made in the esterification reaction.

(2)

Bonds broken:

O–H and C–O

Bonds made:

C–O and O–H

(ii) Explain why ΔH for this reaction is not **exactly** zero.
(A calculation is not required.)

(1)

The reaction is slightly endothermic as the O–H bonds made are both to the same Oxygen So the energy regained is lower than from breaking two separate O–H

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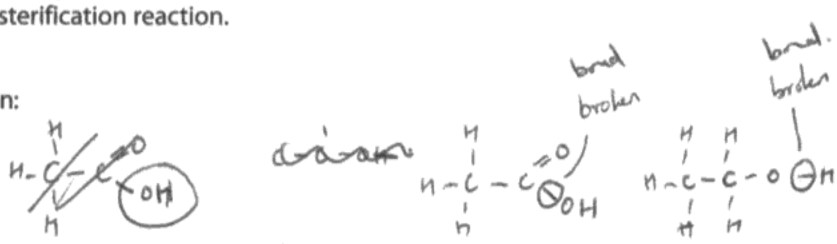
Examiner Comments

The answer to (c)(i) scores both marks for the correct bonds being broken (first mark) and then made (second mark).
No mark is awarded for the response to (c)(ii).

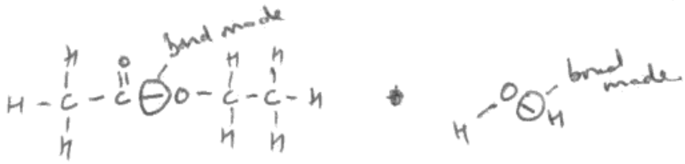
(c) (i) Identify which bonds are broken and which bonds are made in the esterification reaction.

(2)

Bonds broken:



Bonds made:



(ii) Explain why Δ*H* for this reaction is not **exactly** zero.
(A calculation is not required.)

(1)

The enthalpy required to break the bonds is slightly higher than the enthalpy required to make the bonds.

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Examiner Comments

In (c)(i), both marks are awarded. The annotations clearly show the correct bonds that are broken (one mark) and the correct bonds that are made (another mark). In (c)(ii), however, the reasoning is incorrect so no mark was awarded.

Question 17 (d) (i)-(ii)

Topic 4.5(f) of the specification requires candidates to be able to recall the relationship ΔS_{total} = Rln*K*, yet this expression was often not seen in answers to (d)(i). However, this did not prevent many candidates from subsequently achieving full marks for (d)(ii). The most common reason for losing one of the three available marks in (d)(ii) was for omitting to state that $\Delta S_{surroundings}$ (or $-\Delta H$ /T) was zero, rather than stating just that it was 'constant'.

(d) (i) State the relationship between ΔS_{total} and the equilibrium constant, *K*, of a reaction.

(1)

ΔS_{total} : R ln K

*(ii) Use entropy considerations and your answer to (d)(i) to predict any effect of an increase in temperature on the value of the equilibrium constant of a reaction for which ΔH is zero. Assume that ΔS_{system} does not change with temperature.

(3)

ΔS_{total} is positively proportional to the equilibrium constant K. However as the ΔH is zero the effect of temperature will be nothing as the value for $\Delta S_{surroundings}$ will always be zero even if the temperature in the reaction changes. As ΔS_{system} doesn't change temperature will have no effect.

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Examiner Comments

In (d)(i), the expression is correct so the mark is awarded. In (d)(ii), the first scoring point is addressed as it is stated that $\Delta S_{surroundings}$ is zero. The second scoring point, however, is not awarded as there is no reference to ΔS_{total} remaining constant. However, the "temperature will have no effect" implies, from the wording of the question, that *K* remains unchanged, so this mark is awarded. So, two marks out of three were given overall for this part.

(d) (i) State the relationship between ΔS_{total} and the equilibrium constant, *K*, of a reaction.

(1)

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

when $R = 8.31$. (constant)

*(ii) Use entropy considerations and your answer to (d)(i) to predict any effect of an increase in temperature on the value of the equilibrium constant of a reaction for which ΔH is zero. Assume that ΔS_{system} does not change with temperature.

(3)

$\Delta H = 0$, then $\Delta S_{surroundings} = 0$. ~~so~~ $\Delta S_{surroundings} = \frac{-\Delta H}{T}$ so equals $\frac{0}{temperature}$ so equals 0. If ΔS_{system} remains constant, ΔS_{total} will not change when the temperature is increased. This means K will not increase or decrease (no change) and so equilibrium will not shift.

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Examiner Comments

In (d)(i), the expression scores the mark available. In (d)(ii), all three scoring points were addressed, so three marks were awarded. Firstly, the answer states that $\Delta S_{surroundings}$ is zero. Secondly, the answer states that ΔS_{total} does not change. Thirdly, it correctly states that, as a consequence, there is no effect on *K*.

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Examiner Tip

Learn to set out arguments in a logical and well-structured format.

Question 17 (e)

Part (e)(i) was, in general, answered correctly. On occasions, the formula of ethanoyl chloride was incorrectly given as "CH_3COOCl". Also, water was sometimes mistakenly identified as the co-product of the reaction to form the ester instead of hydrogen chloride. In (e)(ii), some candidates seemed unaware as to how to draw a skeletal formula and so drew the displayed formula of ethyl ethanoate instead. In (e)(iii), the $-NH_2$ group was often written in an 'undisplayed' way, instead of showing all the atoms and all the bonds involved.

(e) An alternative method for preparing ethyl ethanoate is to react ethanoyl chloride with ethanol.

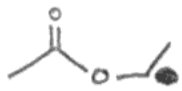
(i) Give the equation for the reaction.

(1)

$CH_3COCl + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + HCl$

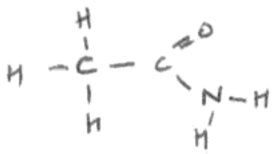
(ii) Draw the **skeletal** formula of ethyl ethanoate.

(1)



(iii) Ethanoyl chloride also reacts with concentrated ammonia. Draw the **displayed** formula of the organic product of this reaction.

(1)



ResultsPlus
Examiner Comments

Part (e)(i) is correct, despite the slightly unclear presentation. The skeletal formula is correct in (e)(ii), as is the displayed formula in (e)(iii).

(e) An alternative method for preparing ethyl ethanoate is to react ethanoyl chloride with ethanol.

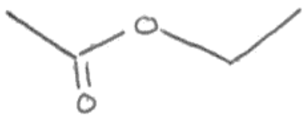
(i) Give the equation for the reaction.

(1)

$CH_3COCl_{(l)} + CH_3CH_2OH_{(l)} \rightarrow CH_3COOCH_2CH_{3(l)} + HCl$

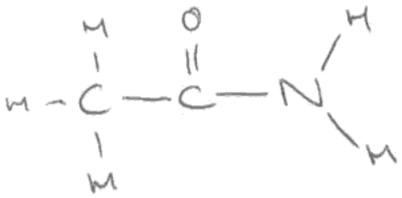
(ii) Draw the **skeletal** formula of ethyl ethanoate.

(1)



(iii) Ethanoyl chloride also reacts with concentrated ammonia. Draw the **displayed** formula of the organic product of this reaction.

(1)



ResultsPlus

Examiner Comments

In (e)(i), the state symbol after the HCl is missing but the mark for the equation is still awarded.

In (e)(ii), the skeletal formula is correct. In (e)(iii), the displayed formula is correct and the mark is awarded.

Question 17 (f) (i)

This part was very well-answered, with the equation for the reaction to form the alcohol and the sodium salt of the carboxylic acid well-known for the alkaline hydrolysis reaction given.

(f) (i) Complete the equation below for the alkaline hydrolysis of ethyl ethanoate using sodium hydroxide. State symbols are **not** required.

(1)

$CH_3COOCH_2CH_3 + NaOH \rightarrow CH_3COO^-Na^+ + CH_3CH_2OH$

ResultsPlus
Examiner Comments

This answer was awarded the mark available.

ResultsPlus
Examiner Tip

Learn the equations for all the major organic chemistry reactions encountered in the specification.

(f) (i) Complete the equation below for the alkaline hydrolysis of ethyl ethanoate using sodium hydroxide. State symbols are **not** required.

(1)

$CH_3COOCH_2CH_3 + NaOH \rightarrow CH_3COO^- Na^+ + CH_3CH_2OH$

ResultsPlus
Examiner Comments

A correct answer, with the ionic charges shown on the ions in the sodium ethanoate. These charges, however, were not required for the mark to be awarded.

Question 17 (f) (ii)

Many candidates were aware that the alkaline hydrolysis of an ester is not an equilibrium reaction, whereas the acid hydrolysis is reversible and so does not go to completion.

(f) (i) Complete the equation below for the alkaline hydrolysis of ethyl ethanoate using sodium hydroxide. State symbols are **not** required.

(1)

$CH_3COOCH_2CH_3$ + NaOH → $CH_3COO^-Na^+$ + CH_3CH_2OH

(ii) Explain why the reaction in (f)(i) gives a better yield of the alcohol compared with acid hydrolysis of the ethyl ethanoate.

(1)

The reaction goes to ~~eq~~ completion without producing an equilibrium mixture

ResultsPlus

Examiner Comments

This correct response scored the mark available.

salt of carboxylic acid

(f) (i) Complete the equation below for the alkaline hydrolysis of ethyl ethanoate using sodium hydroxide. State symbols are **not** required.

(1)

$CH_3COOCH_2CH_3$ + NaOH → CH_3CH_2OH + $CH_3COO^-Na^+$

(ii) Explain why the reaction in (f)(i) gives a better yield of the alcohol compared with acid hydrolysis of the ethyl ethanoate.

(1)

The reaction above goes to completion, as opposed to the acid hydrolysis which is a reversible reaction. This results in the above reaction have a greater yield.

ResultsPlus

Examiner Comments

This candidate has answered the question in a clear and succinct way.

Question 18 (a)

In (a)(i), deriving the order with respect to hydrogen ions presented few problems for candidates. The question specifically required candidates, however, to state the experiment numbers that they had used but many failed to do so.

Calculating the order with respect to bromide ions proved far more challenging. Those who used the data from experiments 1 and 3 generally fared better than those who attempted to process the data from experiments 2 and 3. The fact that more than one reagent concentration had been changed provided considerable stretch and challenge to candidates. Many in the end decided, incorrectly, that the order with respect to bromide ions was zero, despite noticing that altering its concentration affected the rate of reaction.

Parts (a)(ii) and (a)(iii) usually correctly followed on from the orders deduced in (a)(i), although sometimes the units of the rate constant were overlooked in answers to (a)(iii).

18 Bromate(V) ions, BrO_3^-, oxidize bromide ions, Br^-, in the presence of dilute acid, H^+, as shown in the equation below.

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

Three experiments were carried out using different initial concentrations of the three reactants.

The initial rate of reaction was calculated for each experiment.

The results are shown in the table below.

Experiment number	$[BrO_3^-(aq)]$ / mol dm^{-3}	$[Br^-(aq)]$ / mol dm^{-3}	$[H^+(aq)]$ / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
1	0.050	0.25	0.30	1.68×10^{-5}
2	0.050	0.25	0.60	6.72×10^{-5}
3	0.15	0.50	0.30	1.01×10^{-4}

*(a) (i) This reaction is first order with respect to $BrO_3^-(aq)$. State, with reasons, including appropriate experiment numbers, the order of reaction with respect to

(5)

$H^+(aq)$ Consider Experiments 1 and 2, $[H^+]$ multiplies by factor of 2^1. $[Br^-]$ and $[BrO_3^-]$ stays constant. Rate multiplies by 2^2. So its second order

$Br^-(aq)$ Consider, Experiments 1 and 3. The $[Br^-]$ increases by factor of 2^1. $[H^+]$ concentration remain constant. $[BrO_3^-]$ multiplies by 3^1. Rate increases by factor of 6, $[BrO_3^-]$ order is first so, eliminating its effect rate increases by 2^1. So, its 1 order with $[Br^-]$.

(ii) Write the rate equation for the reaction.

(1)

Rate = k $[BrO_3^-][H^+]^2[Br^-]$

(iii) Use the data from experiment 1 and your answer to (a)(ii) to calculate the value of the rate constant. Include units in your answer.

(3)

Using data from experiment 1,

$1.68 \times 10^{-5} = k \times 0.05 \times 0.3^2 \times 0.25$

$k = \frac{1.68 \times 10^{-5}}{0.05 \times 0.3^2 \times 0.25} = 0.0149 \text{ mol}^{-3} \text{dm}^9 \text{s}^{-1}$

ResultsPlus
Examiner Comments

This answer was well set-out, with experiment numbers included as required by the wording of the question in (a)(i).

ResultsPlus
Examiner Tip

Always read the question carefully and include all the detail required in your answer. For example, experiment numbers were asked for in (a)(i) and the units of the rate constant in (a)(iii).

18 Bromate(V) ions, BrO_3^-, oxidize bromide ions, Br^-, in the presence of dilute acid, H^+, as shown in the equation below.

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

Three experiments were carried out using different initial concentrations of the three reactants.

The initial rate of reaction was calculated for each experiment.

The results are shown in the table below.

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2	0.050	0.25	0.60	6.72×10^{-5}
3	0.15	0.50	0.30	1.01×10^{-4}

×3

1.68×10^{-5} ×3 $= 5.04 \times 10^{-5}$ ×2

*(a) (i) This reaction is first order with respect to $BrO_3^-(aq)$. State, with reasons, including appropriate experiment numbers, the order of reaction with respect to

* and other concentration are constant

(5)

$H^+(aq)$

Second order because as $[H^+]$ ~~does~~ increases by a factor of 2 from 0.30 moldm^{-3} to 0.6 moldm^{-3},* rate increases by a factor of 4; from 1.68×10^{-5} moldm^{-3}s^{-1} to 6.72×10^{-5} moldm^{-3}s^{-1}.

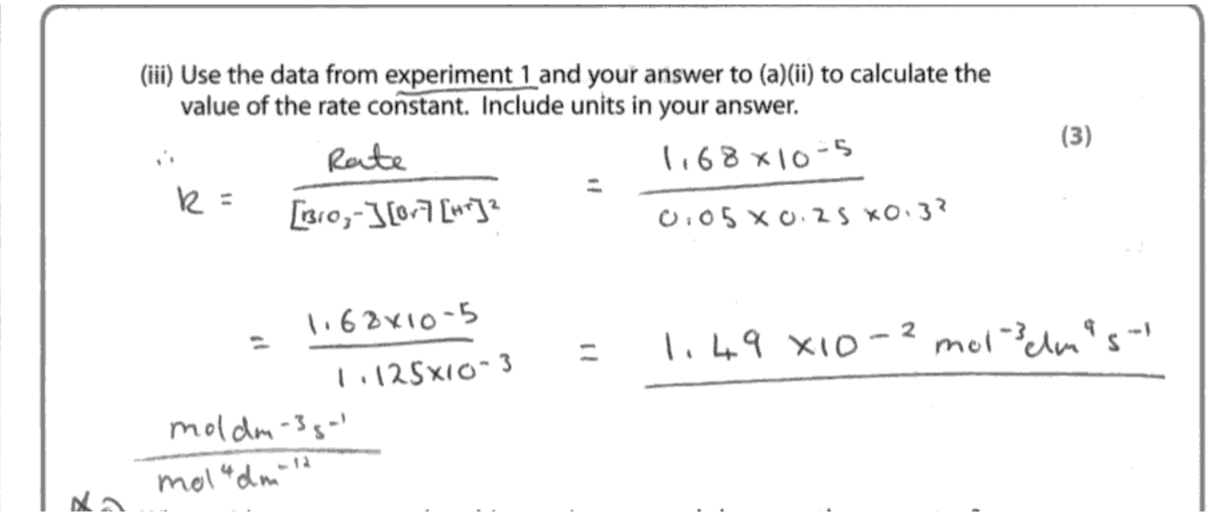
$Br^-(aq)$

First order because as $[BrO_3^-]$ increases by a factor of 3, (0.05 to 0.15 moldm^{-3}), Rate must increase by a factor of 3 (as it is 1st order), so rate is 5.04×10^{-5} moldm^{-3}s^{-1}. Then, rate must double to get to 1.01×10^{-4} moldm^{-3}s^{-1}, as $[Br^-]$ doubles from 0.25 to 0.5 moldm^{-3}, so rate is directly proportional to $[Br^-]$.

(ii) Write the rate equation for the reaction.

(1)

$$Rate = k[BrO_3^-][Br^-][H^+]^2$$



(iii) Use the data from experiment 1 and your answer to (a)(ii) to calculate the value of the rate constant. Include units in your answer.

(3)

$$\therefore k = \frac{\text{Rate}}{[BrO_3^-][Br^-][H^+]^2} = \frac{1.68 \times 10^{-5}}{0.05 \times 0.25 \times 0.3^2}$$

$$= \frac{1.68 \times 10^{-5}}{1.125 \times 10^{-3}} = 1.49 \times 10^{-2}\ mol^{-3} dm^{9} s^{-1}$$

$$\frac{mol\ dm^{-3} s^{-1}}{mol^4 dm^{-12}}$$

ResultsPlus

Examiner Comments

This is a good answer, except that the experiment numbers were not given in (a)(i) so a mark was lost. This omission was only penalised once.

Question 18 (b)

The answers to (b) followed on from the rate equation deduced in (a)(ii). Those candidates who had deduced incorrectly that the order with respect to bromide ions was zero could score the mark by suggesting that bromide ions did not appear in the rate-determining step. The key point for those who had earlier derived the correct orders with respect to hydrogen ions and bromide ions was that the number of particles in the rate-determining step did not match those in the equation for the reaction. It followed that the reaction, therefore, must proceed in more than one step.

(b) What evidence suggests that this reaction proceeds by more than one step?

(1)

There are 3 reactants involved in the equation ~~by 0~~ but only 2 ~~?~~ reactants appear in the rate ~~determinat~~ equation.

ResultsPlus

Examiner Comments

The mark was awarded as this conclusion follows on from an answer of order = 0 with respect to Br^- ions in (a)(i).

(b) What evidence suggests that this reaction proceeds by more than one step?

(1)

Because the reaction has three substances in the rate equation.

ResultsPlus

Examiner Comments

This answer did not score the mark as there are indeed three substances in the correct rate equation and there are also three substances in the balanced equation for the reaction. The fact that the numbers of the particles is different in these two equations is the important point missing from this answer.

ResultsPlus

Examiner Tip

Chemical reactions such as these have to occur in more than one step as it is statistically impossible for all 12 reacting species to collide simultaneously!

Question 18 (c)

In (c), many candidates sketched graphs that showed either a decrease or no change in concentration of bromine with time, despite being told in the question that bromine was a product. Others confused bromide ions with bromine molecules. The majority of candidates realised that a gradient had to be calculated, but relatively few mentioned that it would be that of a tangent drawn at t=0.

(c) The initial rate of reaction was obtained from measurements of the concentration of bromine at regular time intervals. How is the **initial** rate of formation of bromine calculated from a concentration-time graph?

(2)

Calculated from the gradient of a concentration-time graph.

ResultsPlus

Examiner Comments

This response scored the first mark only as no mention was made of drawing a tangent to the curve at t=0.

(c) The initial rate of reaction was obtained from measurements of the concentration of bromine at regular time intervals. How is the **initial** rate of formation of bromine calculated from a concentration-time graph?

(2)

On the graph draw a tangent with the data going through the origin. Then work out the gradient of the tangent, which is $\frac{\Delta y}{\Delta x}$.

ResultsPlus

Examiner Comments

This answer has mentioned that a tangent has to be drawn at t=0 and its gradient calculated.

Question 19 (a)

Part (a)(i) was well-answered, with the method of how to calculate the empirical formula from percentage by mass data familiar to almost all candidates. In (a)(ii), candidates did not explain how information from the mass spectrum had enabled them to deduce that the molar mass of compound **X** was 88 g mol^{-1}.

19 An organic compound, **X**, was analyzed in a laboratory.

(a) Compound **X** was found to have the following percentage composition by mass:

carbon, C = 54.5%

hydrogen, H = 9.1%

oxygen, O = 36.4%

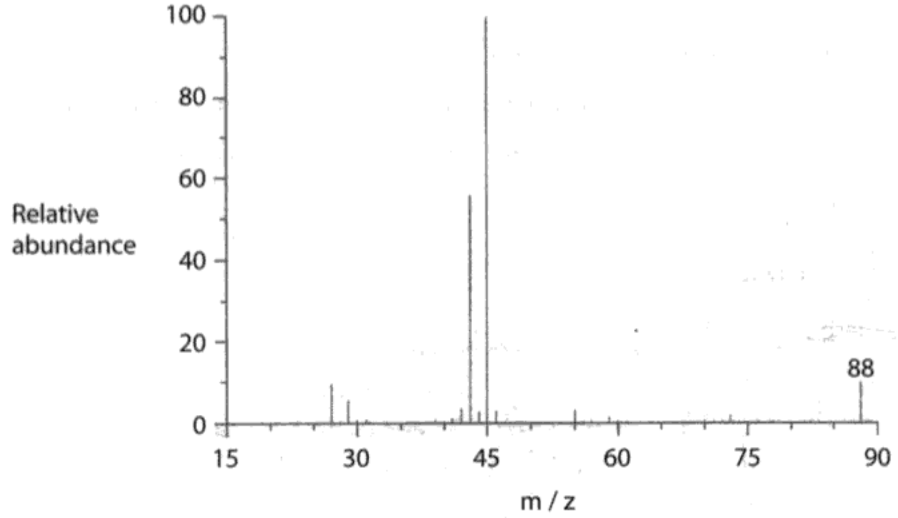
(i) Use these data to calculate the empirical formula of compound **X**, showing your working.

(2)

	C	H	O
m	54.5	9.1	36.4
RMM	12	1	16
n	4.5416	9.1	2.275
ratio	1.99	4	1

C_2H_4O

(ii) The mass spectrum of **X** is shown below.



Use your answer to (a)(i), and the mass spectrum of **X**, to show that the molecular formula of compound **X** is $C_4H_8O_2$.

(2)

Empirical formula molar mass is 44. Molecular ~~mass~~ formula molar mass is the last peak with high m/z ratio on mass spectrum x. which is 88. ∴ It's twice the emperical formula ∴ $C_4H_8O_2$

ResultsPlus
Examiner Comments

Parts (a)(i) and (a)(ii) are both correct, so two marks were awarded for each part. In (a)(ii), reference has been made to the mass spectrum to justify the use of 88 g mol^{-1} for the molar mass of **X**.

19 An organic compound, **X**, was analyzed in a laboratory.

(a) Compound **X** was found to have the following percentage composition by mass:

carbon, C = 54.5%

hydrogen, H = 9.1%

oxygen, O = 36.4%

(i) Use these data to calculate the empirical formula of compound **X**, showing your working.

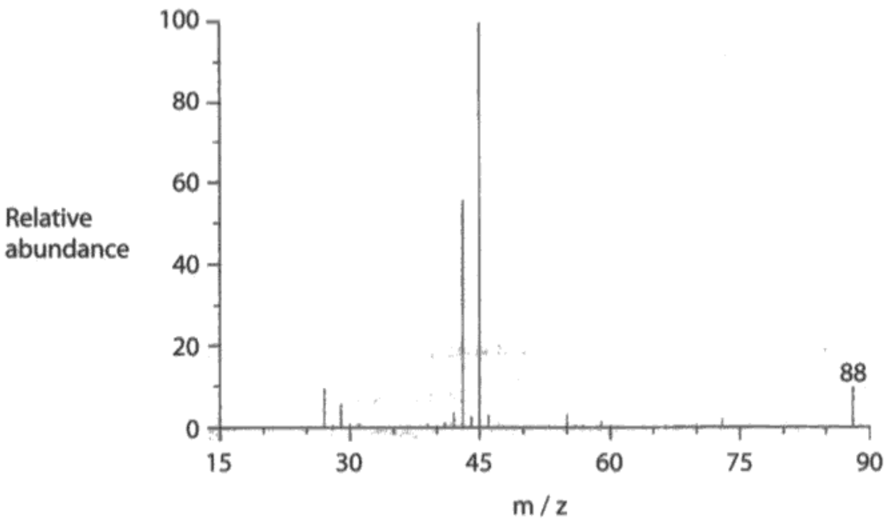
(2)

$C = \frac{54.5}{12} = 4.542$ $H = \frac{9.1}{1} = 9.1$ $O = \frac{36.4}{16} = 2.275$

$C = \frac{4.542}{2.275} = 2$ $H = \frac{9.1}{2.275} = 4$ $O = \frac{2.275}{2.275} = 1$

∴ empirical formula of X is C_2H_4O

(ii) The mass spectrum of **X** is shown below.



Use your answer to (a)(i), and the mass spectrum of **X**, to show that the molecular formula of compound **X** is $C_4H_8O_2$.

(2)

$C_2H_4O \times 2 = 2C_2H_4O = C_4H_8O_2$

$Mr\,(C_4H_8O_2) = (4 \times 12) + (8 \times 1) + (2 \times 16)$
$= 48 + 8 + 32$
$= 88$ which is the last peak on the mass spectrum

ResultsPlus
Examiner Comments

This answer obtained maximum credit as all deductions have been fully explained.

Question 19 (b)

In (b), most candidates correctly assigned the bonds to the infrared frequencies given, although some quoted the N-H bond despite the molecular formula $C_4H_8O_2$ having being given in (a)(ii).

(b) The infrared spectrum of **X** has a broad peak at approximately 3500 cm^{-1} and a sharp peak at approximately 1700 cm^{-1}. Identify the **bond** responsible for the peak at

(2)

3500 cm^{-1} O-H

1700 cm^{-1} C=O

ResultsPlus

Examiner Comments

Both bonds were correctly identified, so two marks were awarded here.

Question 19 (c)

The answers to (c)(i) were generally good. Many candidates commented upon the absence of an aldehyde group from the negative result of the test with Tollens' reagent. The presence of the alcohol functional group was often noted, although this was seldom followed up by a comment about which class of alcohol group (primary or secondary) could be present in the molecule. A surprising number of candidates interpreted the statement in the question that "**X** is a neutral organic compound" as meaning that "**X** has an equal number of positive and negative charges" rather than using it as information to deduce that **X** was not a carboxylic acid. Marks were lost in (c)(ii) by not giving the names of the functional groups as required by the question.

(c) (i) Some chemical information about compound **X** is given below.

- **X** is a neutral organic compound.
- **X** has no effect on Tollens' reagent.
- **X** turns hot acidified potassium dichromate(VI) solution from orange to green.

What does each of these three pieces of information suggest about the nature of **X**?

(4)

X contains no COOH group

X is not an aldehyde ∴ a ketone

X can oxidised

(ii) Use your answers to parts (b) and (c)(i) to name the two functional groups present in **X**.

(1)

Alcohol ~~OH~~, ketone

ResultsPlus

Examiner Comments

In (c)(i), one mark for 'no COOH group' and a second mark for 'not an aldehyde' were awarded. In (c)(ii), the answer is correct so one mark was scored.

(c) (i) Some chemical information about compound **X** is given below.

$C_4H_8O_2$

- **X** is a neutral organic compound.
- **X** has no effect on Tollens' reagent.
- **X** turns hot acidified potassium dichromate(VI) solution from orange to green.

What does each of these three pieces of information suggest about the nature of **X**?

(4)

If X is neutral it does't have a COOH group
If X has no effect on tollens it doesn't have an aldehyd CHO group.
If X turns hot acidified pottassium dichromate solution orange to green, it can be oxidised so cannot have a ketone group (RCOR)

(ii) Use your answers to parts (b) and (c)(i) to name the two functional groups present in **X**.

(1)

O–H and C=O

ResultsPlus
Examiner Comments

The answer to (c)(i) scores two marks. The first mark is for "...doesn't have a COOH group" and the second mark for "... doesn't have an aldehyde group". The presence of an alcohol group in a molecule of **X** has not been considered, however. No mark is given for (c)(ii) as names have not been given in the answer.

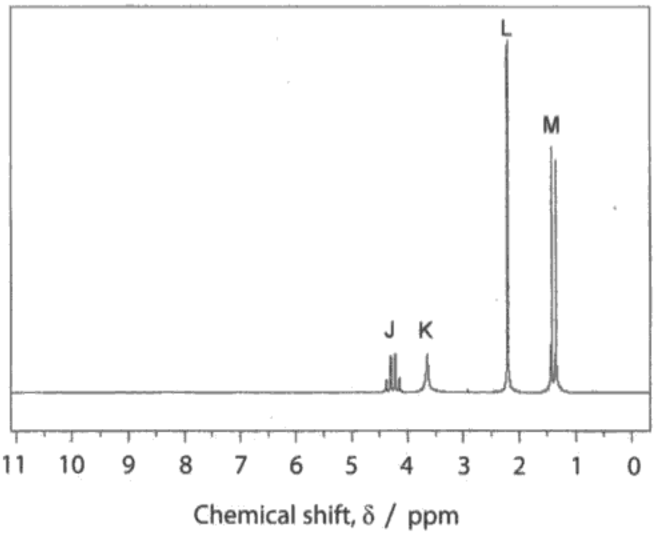
ResultsPlus
Examiner Tip

Read the question carefully. In (c)(ii), the names of the two functional groups are required, not their formulae.

Question 19 (d)

Answers to (d) varied greatly. Some candidates seemed to have little difficulty in obtaining all seven marks, especially if they had taken into account their answers to (b) and (c). It was also helpful when candidates neatly annotated a drawing of the displayed formula for **X** with labels of the letters of the peaks arising from the hydrogen atoms in each environment. Other candidates found it difficult to interpret the nmr spectrum and included functional groups in their suggested structures for **X** that had been discounted in earlier answers to (c) (i). A small number of candidates just drew out a correct structural formula for **X** without any further explanation or justification.

*(d) The high resolution proton nmr spectrum of **X** is shown below.



The relative number of protons causing the peaks shown are: J = 1, K = 1, L = 3 and M = 3.

Use the information above to determine the structural formula of **X**.

In your answer, you should refer to the number of peaks, their relative sizes and their splitting patterns.

(7)

This nmr spectrum shows 4 peaks, illustrating that X contains 4 different hydrogen environments. The relative sizes are 1, 1, 3 and 3, which illustrates the number of hydrogens in each environment. Peak K shows no splitting, illustrating that it is caused by a hydrogen from an -OH group. Peak J represents 1 hydrogen, and is a quartet, illustrating that this hydrogen has 3 adjacent to it. Finally, L and M both represent 3 hydrogens each in 2 methyl groups.

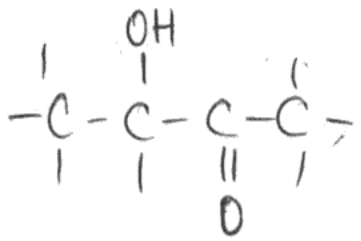
L shows no splitting, illustrating it has no adjacent hydrogens - other side of a C=O bond. M is split into 2 - the effect of 1 adjacent hydrogen. the hydrogen that caused peak K.

It is ~~$CH_3CH(OH)COCH_3$~~

↳ $CH_3CH(OH)COCH_3$

(Total for Question 19 = 18 marks)

TOTAL FOR SECTION C = 18 MARKS
TOTAL FOR PAPER = 90 MARKS

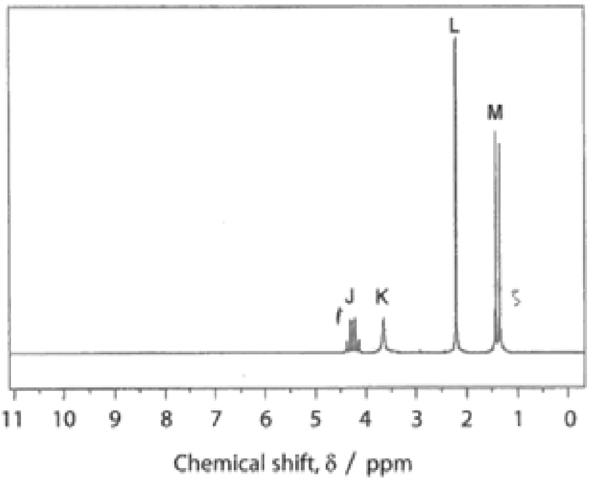


ResultsPlus
Examiner Comments

For this candidate's response, the seven marks available for this question are awarded as follows:

Four different hydrogen environments are mentioned (1)
The correct structure for **X** is given (1)
Peak K is identified as the OH peak (1)
The (n+1) rule is applied to peak J (1)
Peak J is due to the hydrogen atom next to the CH_3 group (1)
The absence of splitting for Peak L is mentioned (1)
Peak L is due to the CH_3 group adjacent to the C=O bond (1)

*(d) The high resolution proton nmr spectrum of **X** is shown below.

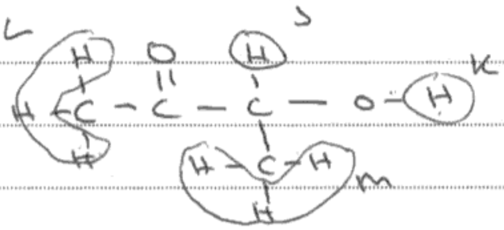


The relative number of protons causing the peaks shown are: J = 1, K = 1, L = 3 and M = 3.

Use the information above to determine the structural formula of **X**.

In your answer, you should refer to the number of peaks, their relative sizes and their splitting patterns.

(7)



- 4 hydrogen environment in the spectrum which is consistent with my structure.
- Their sizes indicate the number of hydrogen atoms present in the environment which is consistent with my structure.
- no splits with L and K since there are no hydrogen atoms neighbouring that environment. J is a quartet which means there are three H atoms adjacent to the carbon bonded to it. M is a doublet which means a single hydrogen atom adjacent to the carbon bonded to it
- structure is consistent

(Total for Question 19 = 18 marks)

ResultsPlus Examiner Comments

This is a fully correct response and scored seven marks.

ResultsPlus Examiner Tip

Note how the use of an annotated displayed formula greatly enhances the clarity of the answer.

Paper Summary

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

- Make sure you read the question through carefully - more than once if necessary.
- In questions that require the use of several pieces of information in the answer make sure you address the requirements of the question in full.
- Show all the steps in your answers to calculations.
- In calculations ensure that you give your final answer to an appropriate number of significant figures making sure your rounding is correct.
- Make sure you are totally familiar with the data book and its contents and that you can find information you need quickly and accurately.

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