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Examiners' Report
June 2015

GCE Chemistry 6CH04 01

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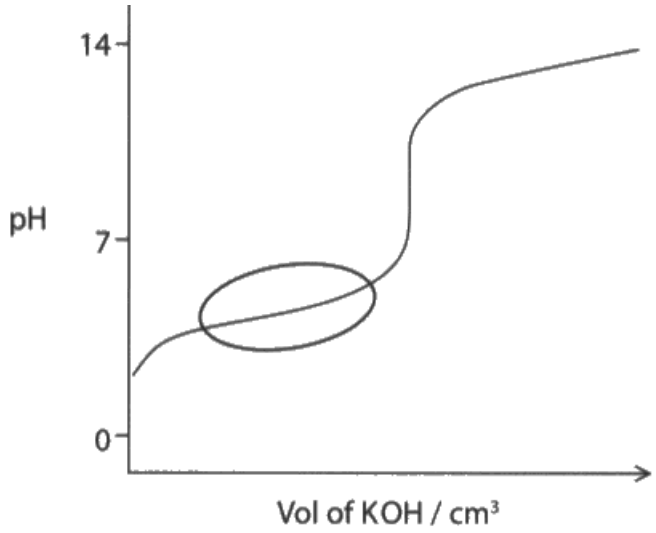
Introduction

The paper proved accessible to most candidates and provided them with the opportunity to demonstrate their knowledge and understanding of the key concepts in Unit 4. There was very little evidence of candidates having insufficient time to complete the paper. The mean score for the multiple-choice questions in Section A was 16/20. Questions 3, 10(c), 11(c) and 12(a) were found to be the most straightforward, whilst questions 4, 6(a), 6(b) and 12(b) were found to be the most demanding of the multiple-choice questions. Candidates attempted the calculation questions with confidence and the questions on kinetics and spectroscopy were well-answered by the majority of candidates. The questions requiring good quality of written communication (i.e. question 13(a)(i), 13(a)(ii) and question 16(b)) were found to be the most discriminating.

Question 13 (a) (i)



(a) *(i) Describe and explain the behaviour of the solution formed in the region circled on the sketch graph.

(3)

A buffer solution forms, which resists the change of pH when a small amount of alkali is added. The buffer consists of an a weak acid and a salt is produced. CH_3CH_2COOH ~~CH_3CH_2COOH~~ $\rightleftharpoons$ $CH_3CH_2COO^- + H^+$ $\Rightarrow$ Does not fully ionise

$CH_3CH_2COOK \rightleftharpoons CH_3CH_2COO^- + K^+$ $\Rightarrow$ Fully ionises

There is a high concentration of CH_3CH_2COOH and $CH_3CH_2COO^-$ as when the salt fully dissociates it pushes the position of equilibrium to the left so CH_3CH_2COOH is produce. When further OH^- is added they are neutralised by H^+ ions ($OH^- + H^+ \rightarrow 4H_2O$). This prevents an increase in pH.

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Examiner Comments

This response scored 2 out of 3 available marks.Mark 1 was awarded for the mention of 'buffer'.Mark 2 was awarded for identification of both CH_3CH_2COOH and $CH_3CH_2COO^-$ being present.Mark 3 (via the 2nd route) was not awarded. In discussion of the mode of action of the buffer solution on addition of OH^- ions, the candidate did not mention that the weak acid equilibrium shifts to the right on removal of the H^+ ions.

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Examiner Tip

Understand how a buffer solution works, in particular on addition of a small quantity of alkali (OHions).

(a) *(i) Describe and explain the behaviour of the solution formed in the region circled on the sketch graph.

(3)

In the region circled the solution acts like a buffer ~~buffer~~ solution. Some of the propanoic acid has reacted with the KOH to form propanoate ions. When small volumes of KOH are added the solution resists large changes in pH by the ~~CH3CO~~ CH_3CH_2COOH dissociating to $CH_3CH_2COO^-$ and H^+, the H^+ react will the OH^- neutralising it and keeping pH ~~relatively~~ constant for small ~~chan~~ additions of KOH. ↑ relatively So the increase in pH is less rapid than at the start.

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Examiner Comments

This response scored all 3 marks.

Scored mark 1 for the mention of 'buffer'. Scored mark 2 for the mention of both propanoic acid and propanoate ions being present. Scored mark 3 (via 1st route) as has mentioned that propanoic acid reacted with the potassium hydroxide and the word 'some' clearly implies that excess propanoic acid will be left over (in the buffer mixture).

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Examiner Tip

Be aware that there is a reservoir of both weak acid molecules and conjugate base ions present in the buffering mixture.

Question 13 (a) (ii)

*(ii) Explain why the pH at the equivalence point of this titration is greater than 7. **(3)**

The equivalence point is when an ~~equal amount~~ the amount added of alkali, from the burette is equal to the amount of acid in the flask. The alkali is a strong alkali and the acid is a weak acid. The alkali is more concentrated than the acid. More alkali is needed in order to reach the equivalence point. As alkalines have a higher pH, the equivalence point has a higher pH of around 9.

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Examiner Comments

This response gets only a 'rescue' mark for realising that the titration involves a weak acid and a strong alkali (or strong base). The initial concentrations (0.032 mol dm^{-3} for KOH and 0.024 mol dm^{-3} for CH_3CH_2COOH) are irrelevant.

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Examiner Tip

Be aware that the solution of a salt, such as potassium propanoate - formed from the neutralisation of a weak acid by a strong alkali - has a pH above 7. The salt undergoes hydrolysis as the propanoate ions accept protons from water molecules, forming hydroxide ions:

$CH_3CH_2COO^-(aq) + H_2O(l)$

$CH_3CH_2COOH(aq) + OH^-(aq)$

Question 13 (a) (iii)

(iii) By considering the amount of excess alkali remaining, calculate the pH of the solution formed when 40 cm^3 of 0.032 mol dm^{-3} potassium hydroxide solution has been added to 25.0 cm^3 of 0.024 mol dm^{-3} propanoic acid.

$K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6} at 298 K

(5)

$40cm^3$ of $0.032\ moldm^{-3}$ KOH

$0.032 = \frac{m}{\frac{40}{1000}}$

$m = 1.28 \times 10^{-3}$

$25cm^3$ of $0.024\ moldm^{-3}$ propanoic acid.

$0.024 = \frac{m}{\frac{25}{1000}}$ $m = 6 \times 10^{-4}$ moles.

$1.28 \times 10^{-3} - (6 \times 10^{-4}) = 6.8 \times 10^{-4}$ moles of KOH remaining.

$c = \frac{6.8 \times 10^{-4}}{\frac{65}{1000}} = 0.010461S$

$10^{-14} \div 0.010461S = 9.5588S8 \times 10^{-13}$

pH $= -\log(9.5588S8 \times 10^{-13})$

pH $= 12.02$

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Examiner Comments
This response was clearly set out and was awarded all 5 marks.

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Examiner Tip
Show every step in your calculation, as this candidate has done.

10.8

(iii) By considering the amount of excess alkali remaining, calculate the pH of the solution formed when 40 cm^3 of 0.032 mol dm^{-3} potassium hydroxide solution has been added to 25.0 cm^3 of 0.024 mol dm^{-3} propanoic acid.

$K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6} at 298 K

(5)

No of moles of propanoic acid = $\frac{25}{1000} \times 0.024$

$= 6 \times 10^{-4}$ mol

~~Mole ratio of $H^+ : OH^- = 1:1$~~

~~∴ no. of moles of $K_w = [H^+(aq)][OH^-(aq)]$~~

~~$[OH^-(aq)][H^+(aq)] = \frac{1.0 \times 10^{-14}}{6 \times 10^{-4}}$~~

~~$[OH^-(aq)] =$~~

No. of mole of KOH left = $\frac{40}{1000} \times 0.032 - \frac{25}{1000} \times 0.024$

$= 6.8 \times 10^{-4}$

$K_w = [H^+(aq)][OH^-(aq)]$

$[H^+(aq)] = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}}$

$[H^+(aq)] = 1.47 \times 10^{-11}$

$pH = -\log [H^+(aq)]$

$pH = 10.8$

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Examiner Comments

This response scored 4 out of 5 marks. By getting to 6.8 x 10^{-4} mol of excess KOH, marks 1 and 2 were secured. No mark 3 was awarded, however, as there had been no division by 0.065 dm^3 (i.e. the total volume of 65 cm^3, converted into dm^3). Mark 4 was awarded as a TE for the value of $[H^+(aq)]$, based on what the candidate thought was $[OH^-(aq)]$ and had correctly used the value of K_w (1.0 x 10^{-14} mol dm^{-3}, which must be used for the award of mark 4). Mark 5 was awarded, for a TE value of pH, correctly calculated, when based on the candidate's stated $[H^+(aq)]$.

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Examiner Tip

Get plenty of practice of calculations involving buffer solutions and their formation.

Question 13 (b)

(b) The student made the following statement:

'The pH of pure water is always 7.0'

Is the student correct? Use the following information to justify your answer.

- $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$
- $K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6} at 298 K
- ΔH is positive for the forward reaction in the equilibrium.

(3)

Yes because the dissociation for water is endothermic because ΔH is positive so an increased temperature would shift equilibrium to the right, but both $[OH^-]$ and $[H^+]$ increase together so overall the pH stays the same. Also $K_w = 1 \times 10^{-4}$ but $pK_w = 14$ so therefore $14 = p[OH^-] + p[H^+]$ both would have to be = to 7. $K_w = [H^+] * [OH^-]$.

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Examiner Comments

This scored the maximum of 1 mark (out of 3) for a 'yes' answer (i.e. an answer that agreed with the candidate's incorrect statement that 'the pH of pure water is always 7.0'). The mark was awarded for giving the correct direction of equilibrium shift (i.e. to the right) when the temperature is increased.

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Examiner Tip

Be aware that the criterion of pure water to be 'neutral' is that [H(aq)] = [OH$^-$(aq)], not necessarily that the pH = 7.0. At temperatures above 298

K, the pH falls below pH = 7.0, but the water does not become 'acidic'. As

K increases, [H(aq)] also increases. So the pH value decreases. The water remains neutral, however, as [H(aq)] = [OH(aq)] still applies.

(b) The student made the following statement:

'The pH of pure water is always 7.0'

Is the student correct? Use the following information to justify your answer.

- $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ fwd endo
- $K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6} at 298 K
- ΔH is positive for the forward reaction in the equilibrium.

(3)

No because K_w is affected by temperature. Therefore as $K_w = [OH^-][H^+]$, pure water, where $[OH^-] = [H^+]$, will be at a different concentration of H^+ ions therefore a different pH. As the forward reaction is endothermic, increasing the temperature would push the equilibrium to the right, to favour the forward reaction, therefore more H_2O will dissociate so there is a greater concentration of H^+ and OH^- ions. Therefore K_w must increase as the reaction is more product favoured. Therefore at higher temperatures, there is a larger concentration of H^+ ions as the dissociation of H_2O is no longer negligible or so small, therefore $-\log[H^+]$ will be more than 7. be more than

(Total for Question 13 = 14 marks)

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Examiner Comments

This response scored 1 mark for the correct direction in the shift of equilibrium position on increasing temperature. Mark 2 was awarded for stating that there would be a greater concentration of $H^+(aq)$ (and $OH^-(aq)$). No mark 3 was awarded, however, as this candidate had incorrectly stated that there was an increase in pH value. The candidate should have stated that pH decreases for the award of mark 3.

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Examiner Tip

Remember that as [H(aq)] increases, the pH decreases as pH = -log [H(aq)].

Question 14 (a)

(a) Outline a titrimetric method that could be used to measure the change in concentration of compound **A** with time. Compound **A** is an alkali, whereas compounds **B**, **C** and **D** are neutral.

(3)

at regular intervals take out samples of the reaction and allow them (quench) by putting in an ice bath. Then you can titrate the solution with a standard strong acid to find the number of moles of compound A using a suitable indicator in the equivalence range. then plot a graph of how the concentration of A varies with time

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Examiner Comments

This response scored all 3 available marks (the last 2 are via the 'EITHER' route in the Mark Scheme). Note, for the award of mark 3 here the term 'standard' equates to 'known concentration'.

A + B reacted together in titration, pipette samples of the reaction mixture at regular time intervals followed by quenching to stop further reaction. Plot Graph ln k and time. Acid titration

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Examiner Comments

This response scored 2 out of the available 3 marks. Mark 1 was awarded for mention of sampling at (regular) time intervals. Marking from the 'EITHER' route: Mark 2 was awarded for the mention of 'quenching' alone. Mark 3 was not awarded, however, as there was no mention of "acid of known concentration"/"standard solution of acid" (being used for the titration analysis).

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Examiner Tip

When answering questions on practical techniques, remember to include all essential details so that a feasible method is suggested.

Question 14 (b) (i)

(i) Explain how the graph confirms that the reaction is first order with respect to **A**.

(1)

The graph is a straight line so the gradient is constant. Therefore the rate is proportional to [A].

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Examiner Comments

This response scored the available mark. The answer mentioned the concept of proportionality between rate and [A] - see Mark Scheme. NOTE: JUST the statement: "The graph is a straight line, so the gradient is constant", alone, would not have scored the mark - again, please refer to the Mark Scheme.

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Examiner Tip

Zero order graphs of rate against concentration also produce a straight line, albeit it a horizontal one. Good, simple communication is required to explain why this is a first order relationship.

(i) Explain how the graph confirms that the reaction is first order with respect to **A**.

(1)

The graph forms a straight line

ResultsPlus
Examiner Comments

This response did not score the mark. There is insufficient detail - please see the Mark Scheme.

Question 14 (b) (ii)

(ii) Suggest an explanation, other than human error, for the two anomalous results circled on the graph.

(3)

When the concentration of A increases, more A reactions happen, the reaction is exothermic reaction and give out heat, the temperature of the mixture is increases and cause the increase in rate Then the anomalous results are measured.

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Examiner Comments

This response scored 2 marks out of 3. Mark 1 was awarded for the mention of '...increase in rate'. Mark 2 was awarded for mention of an 'exothermic reaction'. There was insufficient detail for mark 3 to have been awarded.

ResultsPlus
Examiner Tip

When considering practical situations, try to think of possible reasons for any systematic errors.

(ii) Suggest an explanation, other than human error, for the two anomalous results circled on the graph.

(3)

The rate increased due to the concentration of ~~B not being constant the of catalyst~~ B perhaps being lower because although it was in excess it may have decreased so the collisions between A and the catalyst increased so rate increased.

ResultsPlus
Examiner Comments

The first mark, being a stand-alone mark, was awarded for the "rate increased" statement. This mark was awarded, despite the rate increase being for the wrong reason. Mark 2 and mark 3 were not awarded.

ResultsPlus
Examiner Tip

Many reactions are exothermic and so systematic error will be significant, particularly at higher concentrations of reagents.

(ii) Suggest an explanation, other than human error, for the two anomalous results circled on the graph.

(3)

As the reaction is an exothermic one, as it progresses it increases the temperature of the surroundings by giving out energy. Therefore ~~as~~ if the starting concentration of A is greater the reaction will occur more vigorously and cause a greater increase in temperature of the mixture. As a result the rate would be recorded as larger than expected as the reactant molecules have on average a higher kinetic energy. This means a greater proportion of collisions are successful and so the rate of reaction increases.

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Examiner Comments

An excellent response, scoring all 3 available marks.

Mark 1 was awarded for the idea that the anomalous points are due to the rate being faster than expected.Mark 2 was awarded due to the mention of an exothermic reaction.Mark 3 was awarded via both the 'EITHER' and 'OR' routes in the Mark Scheme - this candidate has offered an explanation of increase in rate using collision theory in appropriate detail. The candidate has also (but was not required to do so) added a comment that the effect of the release of heat energy in the reaction is greater at higher concentrations of substance A.

Question 14 (c)

Experiment	Initial concentration / mol dm^{-3}			Initial rate / mol dm^{-3} s^{-1}
	A	**B**	**X**	
1	0.020	0.005	0.500	2.1×10^{-3}
2	0.040	0.005	0.500	4.2×10^{-3}
3	0.060	0.010	0.500	6.3×10^{-3}
4	0.080	0.010	0.250	4.2×10^{-3}

(i) Give **one** reason why obtaining these further data may be considered useful.

To identify whether the concentration of the other reagents effected the rate of reaction.

(ii) Deduce the rate equation for this reaction, explaining how you arrived at your answer.

(5)

rate = k [A] [X]

1st order with respect to [A] as when the concentration doubles, so does the rate 0 order with respect to [B] as when [A] triples ~~rate~~, the [X] remains the same and [B] doubles the rate tripleso [B] has no effect on the rate. First order with respect to [X] as when [A] x4, [B] remains the same and [X] halves the rate ~~[X]~~ doubles.

(iii) Use your answer from (c)(ii), and appropriate data from **Experiment 4**, to calculate the value of the rate constant, *k*. Include units in your answer.

(2)

rate = $k(0.02)(0.500)$

$\frac{2.1 \times 10^{-3}}{(0.02)(0.5)} = k.$

$k = 0.21 \ mol^{-1} dm^3 s^{-1}$

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Examiner Comments

Trait (c)(i) is correct. In (c)(ii), mark 1, mark 2, mark 3 and mark 4 were awarded. Mark 5 was not awarded as the candidate is comparing the data from experiments 1 and 4 and incorrectly stated that [B] remains constant (it doubles from experiment 1 to 4). For (c)(iii), the response was correct.

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Examiner Tip

Always check that kinetic data has been correctly compared from one experiment to another.

Experiment	Initial concentration / mol dm^{-3}			Initial rate / mol dm^{-3} s^{-1}
	A	B	X	
1	0.020	0.005	0.500	2.1×10^{-3}
2	0.040	0.005	0.500	4.2×10^{-3}
3	0.060	0.010	0.500	6.3×10^{-3}
4	0.080	0.010	0.250	4.2×10^{-3}

×4 ×3 ×2 ratio ×3 ×4

(i) Give **one** reason why obtaining these further data may be considered useful.

(1)

To see the overall order of reaction by finding the order in respect to B and X.

(ii) Deduce the rate equation for this reaction, explaining how you arrived at your answer.

(5)

order of A = 1
B = 0
X = 1

rate = k[A][X][B]^0

experiment 1 and 2. Concentration of A doubles, concentration of B and X is constant so change must be due to A, rate also doubles, order is 1 with respect to A. Experiment 1 and 3. A ×3 so rate must triple and B doubles but this has no effect on the rate so order of B is 0. Experiment 1 and 4. A is multiplied by 4 and B is doubled so rate must multiply by 4. X is halved in concentration and the rate is halved so the order in respect to X is 1.

(iii) Use your answer from (c)(ii), and appropriate data from **Experiment 4**, to calculate the value of the rate constant, *k*. Include units in your answer.

(2)

rate = k[A][X]

$k = \frac{rate}{[A][X]}$

$= \frac{4.2 \times 10^{-3}}{0.08 \times 0.250}$ $\frac{mol\,dm^{-3}\,s^{-1}}{mol^2\,dm^{-6}}$

= 0.21 $mol^{-1}\,dm^3\,s^{-1}$

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Examiner Comments

All traits, (c)(i), (c)(ii) and (c)(iii), were correct for this response - so the maximum marks of 1, 5 and 2 (respectively) were awarded for this candidate's response.

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Examiner Tip

This is a well set-out answer, with appropriate working shown to ensure that the units of the rate constant are correct.

Question 14 (d)

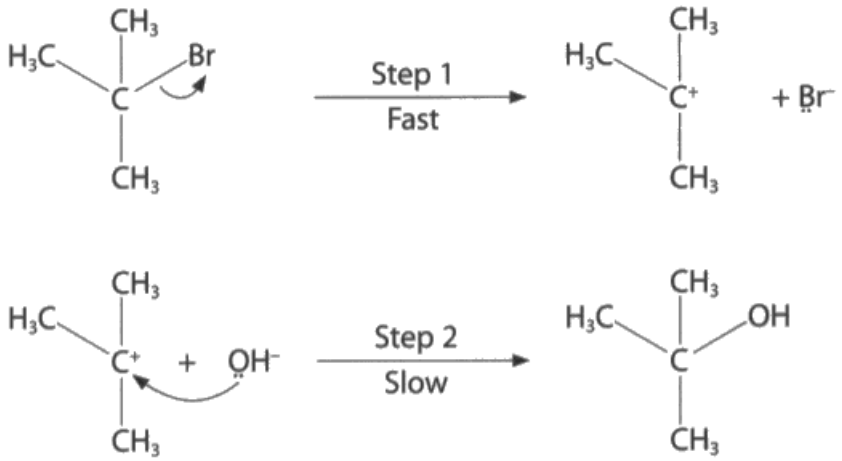
(d) A student carried out a similar investigation into the kinetics of the reaction between 2-bromomethylpropane and hydroxide ions. A summary of the student's findings is shown below.

Kinetics Investigation - Summary of Key Findings

Reaction is first order with respect to 2-bromomethylpropane

Suggested Mechanism

S_N2 - as two steps in process



Use your knowledge of the mechanism of nucleophilic substitution reactions to suggest one feature of the summary, including the student's mechanism, that you agree with and two features you think are incorrect.

(3)

One feature you agree with.

It is an S_N2 reaction because a tertiary carbocation is formed

Two features you think are incorrect.

~~I think that it is an S_N1 reaction not an S_N2~~ The reaction rate equation must have OH^- in as it is in the rate determining step. It should be second order w.r.t 2-bromomethyl propan

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Examiner Comments

This response scored 0 out of 3 marks. 'Correct feature' mark was not awarded for the statement made. No 'incorrect features' marks were awarded. The rate equation would not have OH^- ions in it, for what should be an S_N1 mechanism. Certainly, too, the reaction was not second order with respect to the reactant 2-bromomethylpropane.

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Examiner Tip

Make sure that you know the difference between S1 and S2 mechanisms.

One feature you agree with.

~~The mechanism~~ ~~Step 1 is~~

The way he drew the mechanism

Two features you think are incorrect.

~~Which of the 2 steps is the slow one & which is the fast~~

~~Could be more then 2 steps~~

Its an S_n1 mechanism if 2 steps

Step 1 is slow

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Examiner Comments

This answer did not score the 'correct feature' mark, as it only mentioned about the way the mechanism was drawn.Both of the 'incorrect features' marks, however, were awarded as follows:

correctly re-classifying the mechanism to S_N1

noting the fact that the first step should be the **slow** step.

One feature you agree with.

The reaction is first order with respect to 2-bromo methyl propane.

Two features you think are incorrect.

The 2 step mechanism is SN1 not SN2.

The first step is the slow step which is the rate detemining step which involves the 2-bromo methyl-propane.

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Examiner Comments

This scored the first mark as the candidate realised that the partial order with respect to 2-bromomethylpropane was first order. A further mark was awarded for realising that the mechanism drawn is, in fact, S_N1 and another mark for stating that 'the first step is the slow step'. So all 3 available marks were awarded.

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Examiner Tip

Thorough knowledge of reaction kinetics makes it easier to spot any errors in a suggested mechanism.

Question 15 (a)

(a) Explain **one** effect of an increase in pressure on the reaction in Step 1.

(2)

The rate of reaction increases because there are less moles of product than there are moles of reactants.

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Examiner Comments

Marking this response by the 'EITHER' or the 'OR' route (please refer to the Mark Scheme) scores only 1 mark. Ideas of kinetics and equilibria have been mixed up here. Mark 1 [by the 'EITHER' route] was awarded for the rate of reaction increase. Mark 2 was not awarded, as there was no reference to an increase in collision frequency on increasing the pressure.

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Examiner Tip

Try not to mix up kinetic ('how fast?') arguments with those relating to equilibria ('how far?').

(a) Explain **one** effect of an increase in pressure on the reaction in Step 1.

(2)

The increase in pressure will increase the rate of reaction because reactants are closer together so ~~more~~ liklihood of collisions is going to be higher so liklihood of them reacting will be higher.

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Examiner Comments

This response was marked via the 'EITHER' route (please refer to the Mark Scheme):

scored mark 1 for mention of a rate increase

mark 2 was not awarded as there was no reference to an increase in collision frequency or other acceptable alternative answer. 'Likelihood' of collisions was not sufficient as an alternative to mention of the 'frequency' of collisions.

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Examiner Tip

Make sure that you are fully conversant with collision theory.

Question 15 (b)

(b) The overall yield for this process is 79%.

Calculate the mass, in tonnes, of aspirin that would be formed from 2.5 tonnes of sodium phenoxide. Give your answer to **two** significant figures.

[Molar masses / g mol^{-1}: sodium phenoxide = 116; aspirin = 180]

(3)

moles $= \frac{2.5}{116} = \frac{5}{232}$

$\frac{5}{232} \times 0.79 = \frac{79}{4640}$

mass $= \frac{79}{4640} \times 180$

$= 3.06$ tonnes.

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Examiner Comments

This response scored 2 marks via the 'OR' route in the Mark Scheme:

mark 1 and mark 2 were awarded

mark 3 was not awarded, however, as the final answer is given to three (instead of the required two) significant figures.

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Examiner Tip

For calculation questions, always check whether a specified degree of accuracy is required for your final answer.

(b) The overall yield for this process is 79%.

Calculate the mass, in tonnes, of aspirin that would be formed from 2.5 tonnes of sodium phenoxide. Give your answer to **two** significant figures.

[Molar masses / g mol^{-1}: sodium phenoxide = 116; aspirin = 180]

(3)

mole of sodium phenoxide

$= \frac{2.5\,t}{116} = \frac{2500000\,g}{116}$

$= 21551.7$

mole of aspirin

$21551.7 \times 0.79 = 17025$

mass of aspirin

$17025 \times 180 = 3014655.172$

$= 3.1\,t$

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Examiner Comments

This answer scored 3 marks out of 3 (by the 'OR' route, see Mark Scheme). The final answer, if not read carefully, could be misinterpreted as being given as 3.2 tonnes. However, this candidate wrote the digit '1' in an unclear way, so had the benefit of the doubt.

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Examiner Tip

Write all digits legibly to avoid losing marks unnecessarily.

Question 15 (c)

(c) Classify the reaction type in Step 3 and suggest a suitable reagent.

(2)

Reaction type esterfication (condensation reaction)

Reagent CH_3COOH

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Examiner Comments

This response scored both the available marks. Mark 1 was awarded for 'esterification'. Note that we ignore the reference to a 'condensation reaction'. Mark 2 was awarded for CH_3COOH being identified as a correct reagent.

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Examiner Tip

Learn to classify appropriately all the organic reactions that you encounter.

(c) Classify the reaction type in Step 3 and suggest a suitable reagent.

(2)

Reaction type Esterification

Reagent CH_3COOH with conc H_2SO_4

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Examiner Comments

This answer scored both marks.Mark 1 was awarded for 'esterification'.Mark 2 was awarded for identification of CH_3COOH. Reference to the catalyst of conc H_2SO_4 was not essential for the award of this mark.

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Examiner Tip

Learn all reagents and conditions for organic reactions.

Question 16 (a) (i)

(a) (i) A solvent is added to the solid coffee grounds to dissolve the oil. Suggest how the oil is then obtained from this mixture.

(2)

The mixture is filtered to remove the solid coffee grounds. The solvent with the dissolved oil is heated and by fractional distillation and when the boiling point of the oil is reached it is distilled off and collected

ResultsPlus
Examiner Comments

This response scored mark 1 for 'filtered'. It was also awarded mark 2 for 'heated'/'fractional distillation' (either one would do). Also, importantly, these two steps were given in the right order.

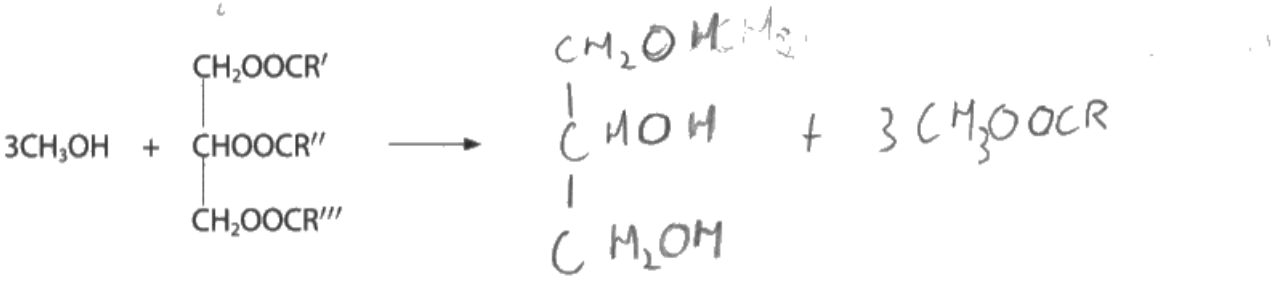
ResultsPlus
Examiner Tip

Always try to suggest feasible practical techniques by careful consideration of the physical states of the substances involved in the reaction process.

Question 16 (a) (ii)

(ii) Complete the equation below for the formation of a bio-diesel from the reaction of an oil with methanol.

(2)



ResultsPlus
Examiner Comments

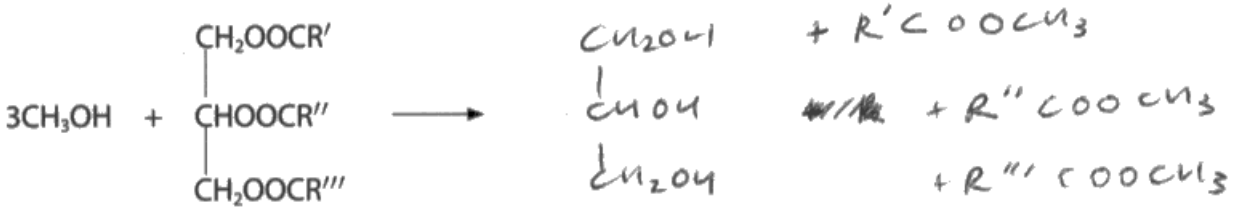
This response scored 1 out of 2 marks. Mark 1 was not awarded for the ester structure given, as there were R groups designated as R', R'' and R''' in this particular question. Mark 2 was awarded for the correct structure of propane-1,2,3-triol.

ResultsPlus
Examiner Tip

Be aware that trans-esterification is mentioned in the Unit 4 specification, in Topic 4.8 (Further organic chemistry), under heading 4(c)(iii) - carboxylic acid derivatives.

(ii) Complete the equation below for the formation of a bio-diesel from the reaction of an oil with methanol. alcohol produced

(2)



ResultsPlus
Examiner Comments

This response scored both available marks. Mark 1 was awarded for all three ester structures being correct. They are all given as per the Mark Scheme. Mark 2 was awarded for the correct structure of propane-1,2,3-triol.

Question 16 (a) (iii)

(iii) Suggest a suitable catalyst for the reaction in (a)(ii).

(1)

So NaOH

$CH_3COOCH_3 + CH_2CH_3 \rightarrow CH_3COOCH_2CH_3 + CH_3OH$

ResultsPlus
Examiner Comments

This response scored the mark for 'NaOH' as a suitable catalyst.

Question 16 (b)

*(b) Another source of oil for bio-diesel production is palm oil, obtained from the fruit of palm trees grown on large plantations across many tropical regions.

Consider **one** advantage and **one** disadvantage of each source to decide which oil may provide a potentially greener and more sustainable supply of bio-diesel.

(4)

• One advantage of using used coffee grounds is that it is using waste material that would be otherwise thrown away.
• A disadvantage is that it is would be expensive to produce the oil through using the solvents and potential harmful by-products
• An advantage of the palm trees is that they come from a sustainable source and are easily re-grown.
• A disadvantage is that it will use a lot of energy transporting the materials from tropical areas
• Use the coffee grounds as it uses up waste materials and uses less energy to produce

(Total for Question 16 = 9 marks)

ResultsPlus
Examiner Comments

This answer scored all 4 marks as follows:

Scored mark 1 - advantage of coffee grounds (uses waste material) Scored mark 2 - disadvantage of coffee grounds (expensive to use solvents) Scored mark 3 - advantage of palm oil (from sustainable resource, plants can be re-grown) Scored mark 4 - disadvantage of palm oil (cost of transporting it from tropical areas and this 'transport' mark has not already been credited for mark 2)

ResultsPlus
Examiner Tip

Try to structure your answers to more 'open-ended' questions in a clear and logical form.

*(b) Another source of oil for bio-diesel production is palm oil, obtained from the fruit of palm trees grown on large plantations across many tropical regions.

Consider **one** advantage and **one** disadvantage of each source to decide which oil may provide a potentially greener and more sustainable supply of bio-diesel.

(4)

One advantage of the palm trees is that it is a renewable resource and sustainable as trees can be grown easily and it is easier to obtain. A disadvantage is that land is being used up that could be used for food and also that a small amount may only be obtained from each fruit also must be flown/fossil fu
One advantage of coffee grounds is that it is pollut of air
easy to grow and transport which makes it sustain
and does not require tropical weather condition
machinary
A disadvantage is that is required to extract
it and grow it which would require energy from
e.g fossil fuels, this decrea its green aspect.

(Total for Question 16 = 9 marks)

ResultsPlus
Examiner Comments

This response scored 3 out of the 4 available marks as follows:- Scored mark 3 - advantage of palm oil (mentions both 'renewable' and 'sustainable' resource, plants can be re-grown) Scored mark 4 - disadvantage of palm oil (use of land) Did not score mark 1 - advantage of coffee grounds (the answers given are in the IGNORE section of the Mark Scheme) Scored mark 2 - disadvantage of coffee grounds (energy costs incurred)

ResultsPlus
Examiner Tip

It is always worth taking a few minutes to plan your answer to questions such as these, so that the advantages and disadvantages are clearly thought through beforehand.

Question 17 (a)

SECTION C

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

17 Adipic acid, $HOOC(CH_2)_4COOH$, is a dicarboxylic acid used in the production of polymers. It can be made by the reaction of buta-1,3-diene with carbon monoxide and water.

$$CH_2CHCHCH_2(g) + 2CO(g) + 2H_2O(l) \rightarrow HOOC(CH_2)_4COOH(s)$$

(a) (i) Use the Data Booklet to complete the table below.

(2)

	$CH_2CHCHCH_2(g)$	$CO(g)$	$H_2O(l)$	$HOOC(CH_2)_4COOH(s)$
$\Delta H_f^\ominus$ / kJ mol^{-1}	+109.9	-110.5	-285.8	–994.3
$S^\ominus$ / J mol^{-1} K^{-1}	278.7	197.6	69.9	250.0

(ii) Use data from the table to calculate the standard enthalpy change, in kJ mol^{-1}, when adipic acid is formed from buta-1,3-diene, carbon monoxide and water.

(2)

ΔH_{rxn}

$(-994.3) - [109.9 + (2 \times -110.5) + (2 \times -285.8)]$

$= -994.3 - (-682.7)$

$= -311.6$ kJ mol^{-1}

(iii) Use data from the table to calculate the standard entropy change of the system, in J mol^{-1} K^{-1}, when adipic acid is formed from buta-1,3-diene, carbon monoxide and water.

(2)

$\Delta S^\ominus_{sys} = S_{product} - S_{reactants}$

$= 250 - [278.7 + 2(197.6) + 2(69.9)]$

$= 250 - 813.7$

$= -563.7$ J mol^{-1} K^{-1}

(iv) Use your answers to (a)(ii) and (a)(iii) to calculate $\Delta S_{surroundings}$ and ΔS_{total} for the reaction at 298 K.

(3)

$\Delta S_{surr} = -\frac{\Delta H}{T} = \frac{-(-311.6)}{298} = +1.0456...$
$= +1.05 \text{ kJ mol}^{-1}$

$\Delta S_{total} = \Delta S_{surr} + \Delta S_{sys.}$
$= 1045.6 + (-563.7)$
$= 481.9 \text{ J mol}^{-1} \text{ K}^{-1}$

(v) It was suggested that **decreasing** the temperature of the reaction to less than 298 K would produce a greater yield of adipic acid.

Explain, in terms of the effect on ΔS_{system}, $\Delta S_{surroundings}$ and hence ΔS_{total}, whether this would be the case.

(3)

Since this is an exothermic reaction, decreasing temperature would increase the value of ΔS_{surr} making it more positive and hence when ΔS_{total} will be more positive and the reaction would be more spontaneous.

ResultsPlus
Examiner Comments

A well set-out response which was awarded full marks for parts 17(a)(i), (a)(ii), (a)(iii) and (a)(iv).2 marks out of 3, however, were awarded for (a)(v) as the fact that the entropy change of the system would remain unchanged on altering the temperature was not mentioned. The effect on the entropy change of the surroundings, and on the total entropy change of reaction, was correctly explained.

ResultsPlus
Examiner Tip

Set out all calculations in a logical form, showing each step.

(a) (i) Use the Data Booklet to complete the table below.

(2)

	$CH_2CHCHCH_2(g)$	$CO(g)$	$H_2O(l)$	$HOOC(CH_2)_4COOH(s)$
$\Delta H_f^{\ominus}$ / kJ mol^{-1}	+109.9	-110.5	-285.8	–994.3
$S^{\ominus}$ / J mol^{-1} K^{-1}	278.7	197.6	69.9	250.0

(ii) Use data from the table to calculate the standard enthalpy change, in kJ mol^{-1}, when adipic acid is formed from buta-1,3-diene, carbon monoxide and water.

(2)

$-682.7 + \Delta Hf = -994.3$

$\Delta H = -311.6 \text{ kJ mol}^{-1}$

(iii) Use data from the table to calculate the standard entropy change of the system, in J mol^{-1} K^{-1}, when adipic acid is formed from buta-1,3-diene, carbon monoxide and water.

(2)

Σ products $- \Sigma$ reactants

$= 250 - 2(69.9) - 2(197.6) - 278.7$

$= -563.7 \text{ J mol}^{-1}\text{K}^{-1}$

(iv) Use your answers to (a)(ii) and (a)(iii) to calculate $\Delta S_{surroundings}$ and ΔS_{total} for the reaction at 298 K.

(3)

$\frac{-\Delta H}{T} = \frac{-(-311.6) \times 1000}{298}$

$\Delta S_{surr} = +1045.6 \text{ J mol}^{-1}\text{K}^{-1}$

$\Delta S \text{ total} = -563.7 + 1045.6$

$= +481.9 \text{ J mol}^{-1}\text{K}^{-1}$

(v) It was suggested that **decreasing** the temperature of the reaction to less than 298 K would produce a greater yield of adipic acid.

Explain, in terms of the effect on ΔS_{system}, $\Delta S_{surroundings}$ and hence ΔS_{total}, whether this would be the case.

(3)

exothermic reaction, decrease of temperature would make $[-\Delta H/T]$ a larger value and $[\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}]$ so ΔS_{total} would also be larger. This suggests that the yield would increase.

ResultsPlus
Examiner Comments

17(a)(i) scored both marks - all four values from the Data Booklet are correct. Q17(a)(ii) scored 2 marks for the correct standard enthalpy change value. Q17(a)(iii) scored (2) both marks for the correct standard entropy change for the system. Q17(a)(iv) scored all 3 available marks: 2 marks for the correct working and value for the entropy change of the surroundings; then, 1 further mark for the subsequently correct total entropy change value. Q17(a)(v) scored 2 marks out of the 3 available: the larger entropy change of surroundings was implied - so scored mark 2 in the Mark Scheme. The reference to a larger total entropy change scored mark 3, the third scoring point. As the fact that the entropy change of the system remains unchanged, when the temperature is decreased, has not been mentioned, the first scoring point, mark 1, was not awarded.

ResultsPlus
Examiner Tip

Careful consideration of the units for enthalpy and entropy changes helps to secure full marks to questions such as these.

Question 17 (b)

(b) Infrared spectroscopy can be used to follow the progress of reactions. During the reaction to produce adipic acid, suggest **one** peak which diminishes and **one** peak which appears.

Use information from the Data Booklet to identify two such possible peaks, giving their wave numbers and the bonds involved.

(2)

the ~~1669 - 164~~ 1669 - 1645 peak diminishes which is the C=C bonds.

A 3300 - 2500 peak appears which belongs to the carboxylic acid O-H group bonds.

ResultsPlus
Examiner Comments

This response scored the 2 available marks.Mark 1 was awarded for the absorption in the region 1669 - 1645 (cm^{-1}); this is the first peak option in the Mark Scheme.Mark 2 - for 3300 - 2500 (cm^{-1}) - was awarded the mark for a peak that would appear (see ALLOW in the Mark Scheme).

ResultsPlus
Examiner Tip

Drawing out the structures of the reactants and products enables you to keep track on which bonds are present in the reactants and products of the reaction under consideration.

Question 17 (c)

(c) Adipic acid is used as an additive in some fruit jellies. Suggest what effect the adipic acid will have on the flavour of the jelly.

(1)

Sour taste.

ResultsPlus
Examiner Comments
This response scored the mark for the word 'sour'.

(c) Adipic acid is used as an additive in some fruit jellies. Suggest what effect the adipic acid will have on the flavour of the jelly.

(1)

The jelly would taste more acidic and sour.

ResultsPlus
Examiner Comments
The mark was awarded here, for the word 'sour'. Any references to just 'more acidity' did not gain credit.

Question 17 (d) (i)

(d) An organic compound, **Q**, is found to contain 49.3% carbon and 6.8% hydrogen by mass.

(i) Use these data to confirm its empirical formula is $C_3H_5O_2$.

(3)

49.3% C ÷ 12 = 4.1

6.8 H ÷ 1 = 6.8

43.9 O ÷ 16 = 2.74

moles = 4.1 : 6.8 : 2.74

100 - 49.3 - 6.8 = 43.9 O_2

$C_{16}H_{28}O_{11}$

ResultsPlus
Examiner Comments

This response scored 2 out of 3 marks. Mark 1 was awarded for the number 43.9(%). Mark 2 was awarded for the correct calculation of the mole ratio C:H:O (here given as 4.1 : 6.8 : 2.74). Mark 3 was not awarded, however, as the ratio 1.5 : 2.5 : 1 (for C:H:O respectively) was NOT stated.

ResultsPlus
Examiner Tip

Show all steps in calculation questions such as these.

(d) An organic compound, **Q**, is found to contain 49.3% carbon and 6.8% hydrogen by mass.

(i) Use these data to confirm its empirical formula is $C_3H_5O_2$. **(3)**

C / 49.3 → $\frac{49.3}{12}$ → 4.1083 → $\frac{4.1083}{2.74375}$ → 1.5 → 3

H / 6.8 → $\frac{6.8}{1}$ → 6.8 → $\frac{6.8}{2.74375}$ → 2.5 → 5

O / 43.9 → $\frac{43.9}{16}$ → 2.74375 → $\frac{2.74375}{2.74375}$ → 1 → 2

∴ $C_3H_5O_2$

ResultsPlus
Examiner Comments

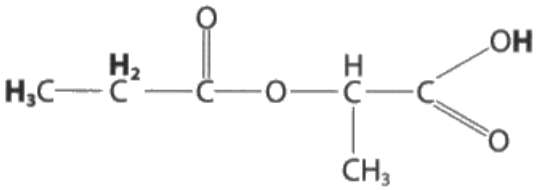
This response scored 3 out of 3 marks.
Mark 1 was awarded for deduction of the percentage by mass of oxygen as 43.9(%).
Mark 2 was awarded for the correct calculation of the mole ratio C:H:O. Mark 3 was awarded for 1.5 : 2.5 : 1 (for C:H:O respectively).

ResultsPlus
Examiner Tip

See how easy a well set-out calculation, such as this one, is to follow.

Question 17 (d) (ii)

(ii) The structure of **Q** is shown below.



The table below summarises some information about parts of the nmr spectrum of compound **Q**.

Use the Data Booklet, and your knowledge of splitting patterns, to complete the table with respect to the features of compound **Q** shown in bold.

(4)

Feature of compound **Q**	Chemical shift / ppm	Splitting pattern
CH_3	0.1 – 1.9	Doublet
CH_2	0·1 – 1·9	Triplet
COOH	10·0 – 12·0	singlet

ResultsPlus

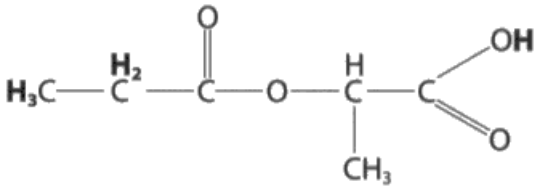
Examiner Comments

This response was awarded 1 out of the 4 available marks.

Mark 1 (for CH_3) was NOT awarded for 'doublet'. Mark 2 (for CH_2) was NOT awarded. The chemical shift range of 0.1 - 1.9 given was not completely within the required range of 1.7 - 3(.0).

Mark 3 (for CH_2) was NOT awarded for 'triplet'. Mark 4 (for OH) was awarded for the chemical shift range given as 10.0 - 12.0.

(ii) The structure of **Q** is shown below.



The table below summarises some information about parts of the nmr spectrum of compound **Q**.

Use the Data Booklet and your knowledge of splitting patterns, to complete the table with respect to the features of compound **Q** shown in bold.

(4)

Feature of compound **Q**	Chemical shift / ppm	Splitting pattern
CH_3	0.1 – 1.9	triplet
CH_2	0.1 – 1.9	quatet
COOH	10.0 – 12.0	singlet

ResultsPlus
Examiner Comments

This response was awarded 3 marks, out of a maximum of 4, as follows:

Mark 1 (for CH_3) was awarded for 'triplet'. Mark 2 (for CH_2) was NOT awarded. The chemical shift range of 0.1 - 1.9 is not within the required 1.7 - 3(.0) range.

Mark 3 (for CH_2) was awarded for 'quartet'. Mark 4 (for OH) was awarded for the chemical shift range 10.0 - 12.0.

ResultsPlus
Examiner Tip

Always check chemical shift ranges carefully.

Paper Summary

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

- read the question carefully
- try to frame your answer to a question whilst bearing in mind the number of marks available
- make sure you can write accurate balanced equations, one of the basic skills required by any advanced level candidate
- take care with units in calculations
- remember that this paper has a greater emphasis on applying knowledge and understanding in unfamiliar contexts than those at AS level.

Llywodraeth Cynulliad Cymru
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