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June 2024

IAL Chemistry WCH14 01

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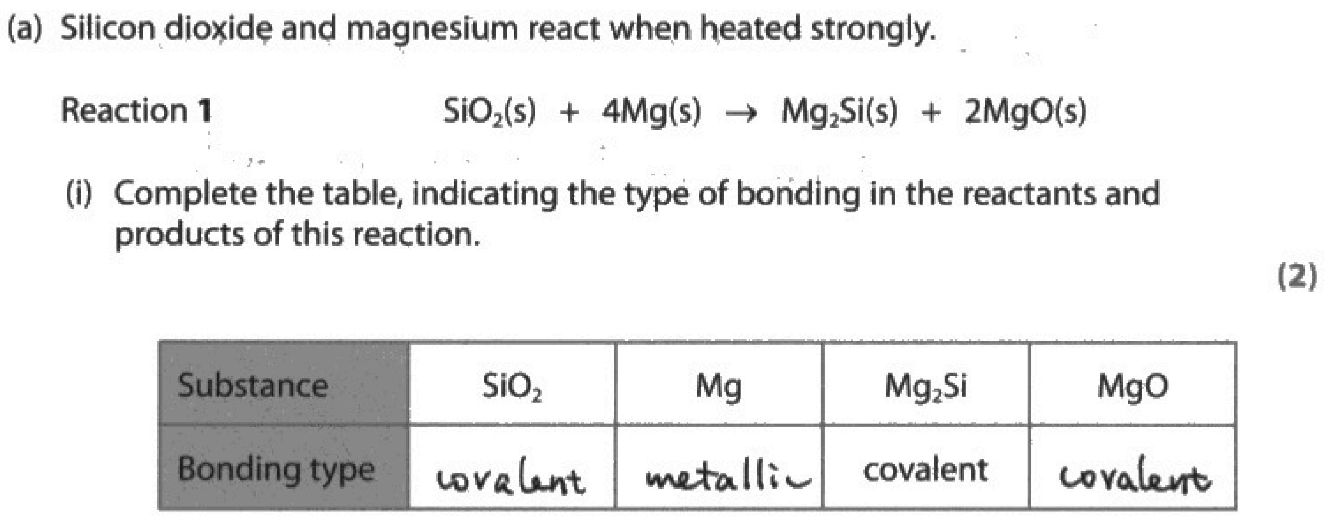
Introduction

Candidates overall found the paper accessible with very few questions that were frequently left blank in contrast to some papers on recent series. The most highly scoring questions typically involved familiar calculations or the straightforward recall of specification content; candidates found it much more challenging to apply their knowledge and understanding in an unfamiliar context. In particular many candidates did not know how to: determine two half-lives that were not consecutive; name a molecule with both an alkene and a carboxylic acid functional group; identify all possible isomers from a molecular formula; write the equation for the iodoform test; identify conjugate acid-base pairs; draw a titration curve for a diprotic acid with a base.

It was also apparent that many learners were lacking practical experience and would benefit from exposure to more practicals and demonstrations relating to the specification content.

Question 15 (a)(i)

Although a straightforward start to the paper, building on principles covered at GCSE, many candidates gave one or more incorrect bonding types.



(a) Silicon dioxide and magnesium react when heated strongly.

Reaction 1 $SiO_2(s) + 4Mg(s) \rightarrow Mg_2Si(s) + 2MgO(s)$

(i) Complete the table, indicating the type of bonding in the reactants and products of this reaction.

(2)

Substance	SiO_2	Mg	Mg_2Si	MgO
Bonding type	covalent	metallic	covalent	covalent

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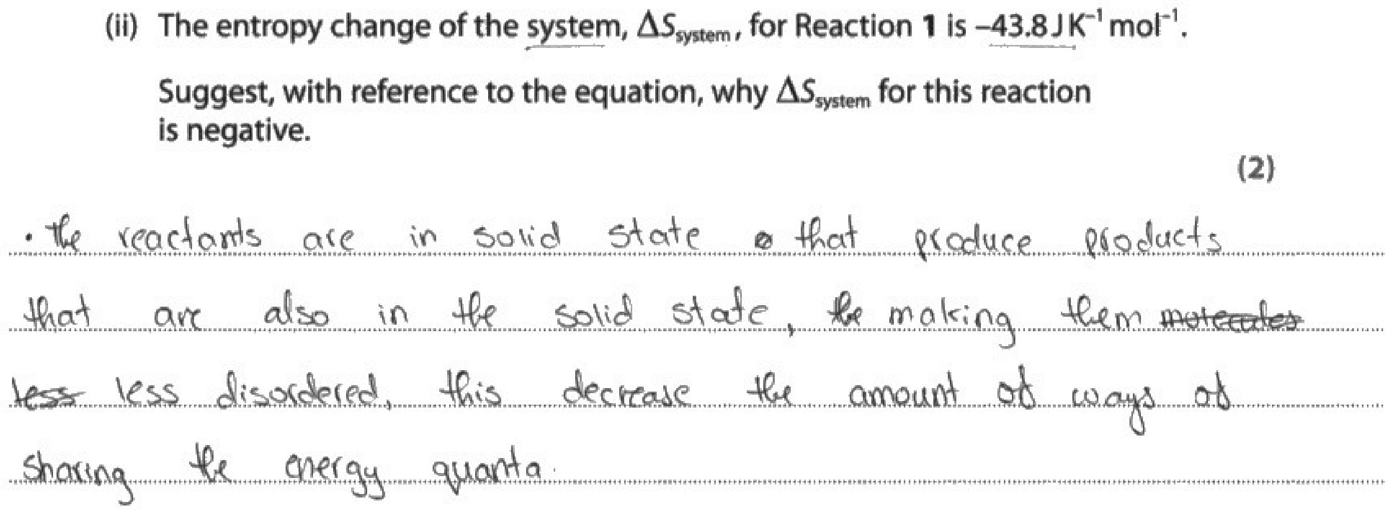
Examiner Comments

As here, it was not uncommon for the type of bonding in magnesium oxide to be given as covalent. Another common mistake was to identify silicon dioxide as ionic.

Question 15 (a)(ii)

Most candidates recognised that entropy decreased due to a decrease in the number of moles but far fewer gave a satisfactory indication of the meaning of the term entropy. A significant number tried to explain the change in terms of the entropies of the reactants and products but, as no data was provided, this was not a creditable approach.



(ii) The entropy change of the system, ΔS_{system}, for Reaction **1** is $-43.8\,J\,K^{-1}\,mol^{-1}$.

Suggest, with reference to the equation, why ΔS_{system} for this reaction is negative.

(2)

- the reactants are in solid state ~~o~~ that produce products that are also in the solid state, ~~the~~ making them ~~molecules~~ ~~less~~ less disordered, this decrease the amount of ways of sharing the energy quanta.

ResultsPlus
Examiner Comments

This candidate has recognised that entropy decreases due to a decrease in disorder but has incorrectly attributed this to the physical states rather than the decrease in moles.

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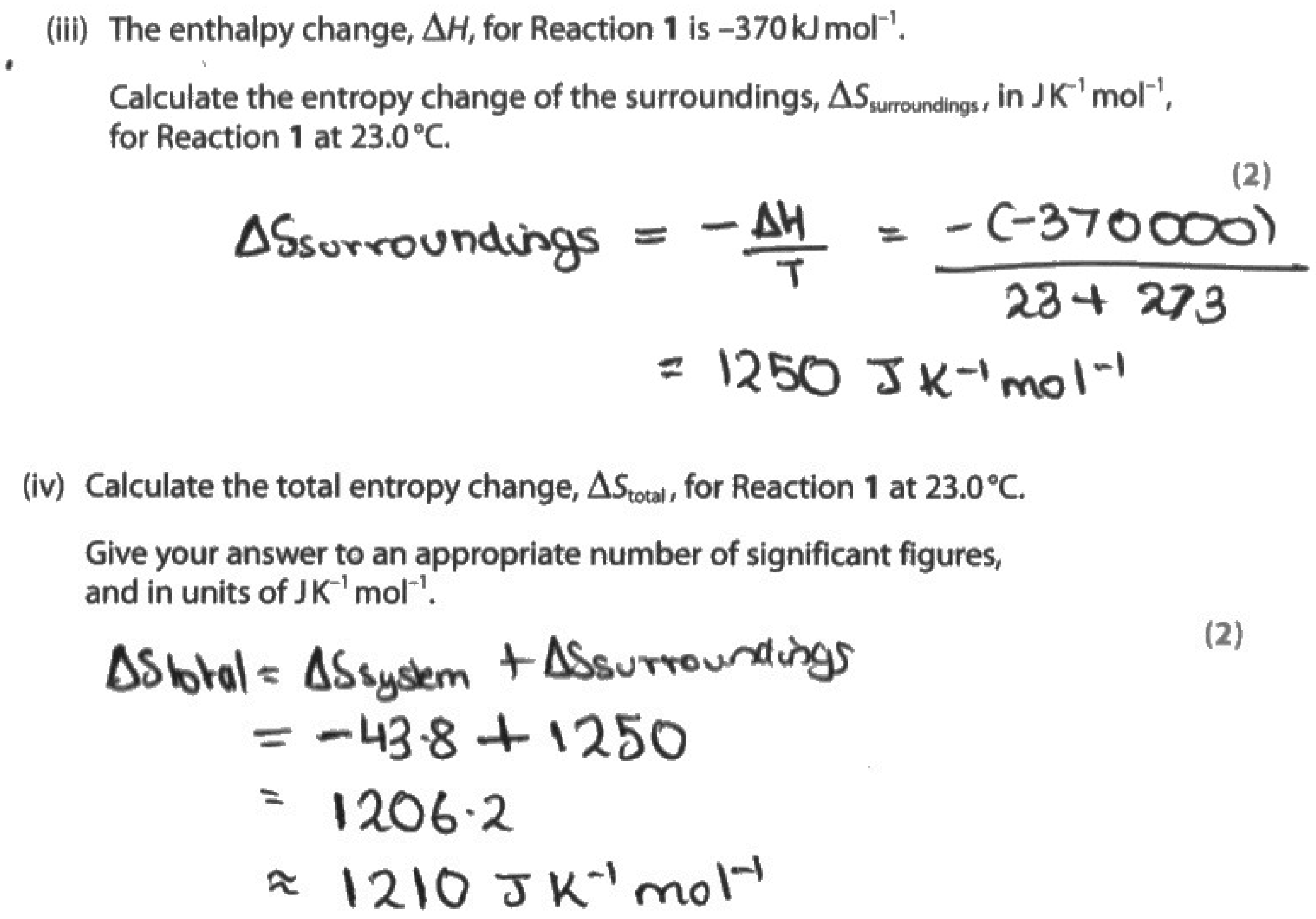
Examiner Tip

Entropy is most clearly expressed as a measure of the number of ways that energy can be distributed or the number of ways that particles can be arranged.

Question 15 (a)(iii-iv)

Candidates were well practised in their entropy calculations, however, many careless errors were seen, such as failing to convert the temperature from ° C to K or giving incorrect units, even though these were provided in the question. A large number did not score full marks in (a)(iv), usually for giving their answer to too many significant figures.



(iii) The enthalpy change, ΔH, for Reaction **1** is $-370\,\mathrm{kJ\,mol^{-1}}$.

Calculate the entropy change of the surroundings, $\Delta S_{\mathrm{surroundings}}$, in $\mathrm{J\,K^{-1}\,mol^{-1}}$, for Reaction **1** at 23.0 °C.

(2)

$$\Delta S_{\mathrm{surroundings}} = -\frac{\Delta H}{T} = \frac{-(-370000)}{23+273}$$

$$= 1250\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

(iv) Calculate the total entropy change, $\Delta S_{\mathrm{total}}$, for Reaction **1** at 23.0 °C.

Give your answer to an appropriate number of significant figures, and in units of $\mathrm{J\,K^{-1}\,mol^{-1}}$.

(2)

$$\Delta S_{\mathrm{total}} = \Delta S_{\mathrm{system}} + \Delta S_{\mathrm{surroundings}}$$

$$= -43.8 + 1250$$

$$= 1206.2$$

$$\approx 1210\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

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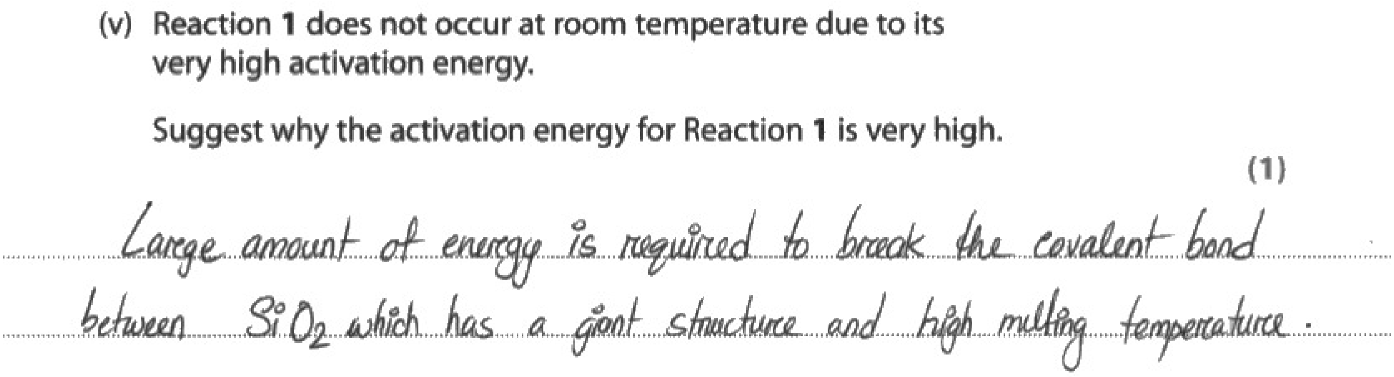
Examiner Comments

An excellent response to both (a)(iii) and (a)(iv) showing expressions, clear working and answers given to an appropriate number of significant figures with units.

Question 15 (a)(v)

Many missed the stimulus provided, stating that reactions between solids are slow. This is mainly due to a low collision frequency so did not explain why the activation energy for the reaction is high. A large number incorrectly thought that intermolecular forces, and not chemical bonds, needed to break for the reaction to happen. Some candidates missed the point of the question altogether and tried to regurgitate an answer from a previous mark scheme, for example stating that it was improbable for five particles to collide at once.



(v) Reaction **1** does not occur at room temperature due to its very high activation energy.

Suggest why the activation energy for Reaction **1** is very high.

(1)

Large amount of energy is required to break the covalent bond between SiO_2 which has a giant structure and high melting temperature.

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Examiner Comments

This response scored the mark for the clear idea that a lot of energy is needed to break the bonds in silicon dioxide. Although the high melting temperature is irrelevant, this statement is not incorrect so was ignored.

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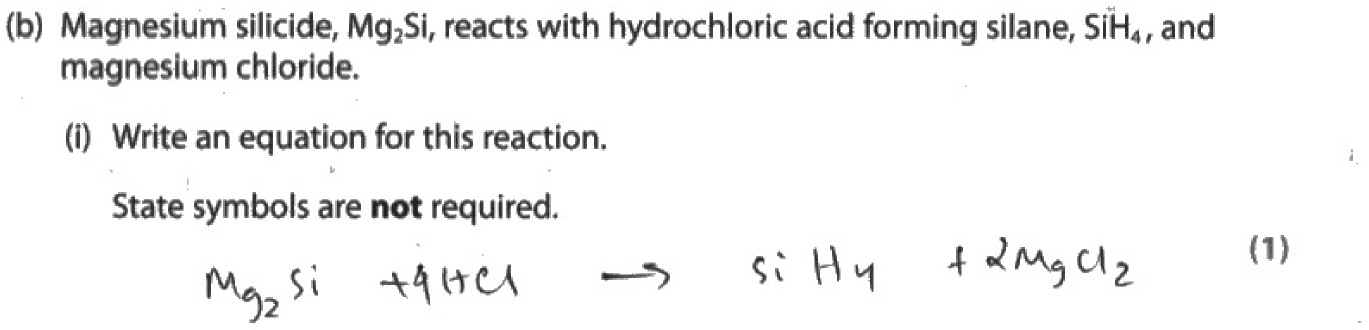
Examiner Tip

Try to avoid providing irrelevant information as any errors will usually be penalised.

Question 15 (b)(i)

Most candidates were able to generate the correct equation from the information provided. The most common mistakes arose from an incorrect formula for magnesium chloride.



(b) Magnesium silicide, Mg_2Si, reacts with hydrochloric acid forming silane, SiH_4, and magnesium chloride.

(i) Write an equation for this reaction.

State symbols are **not** required.

(1)

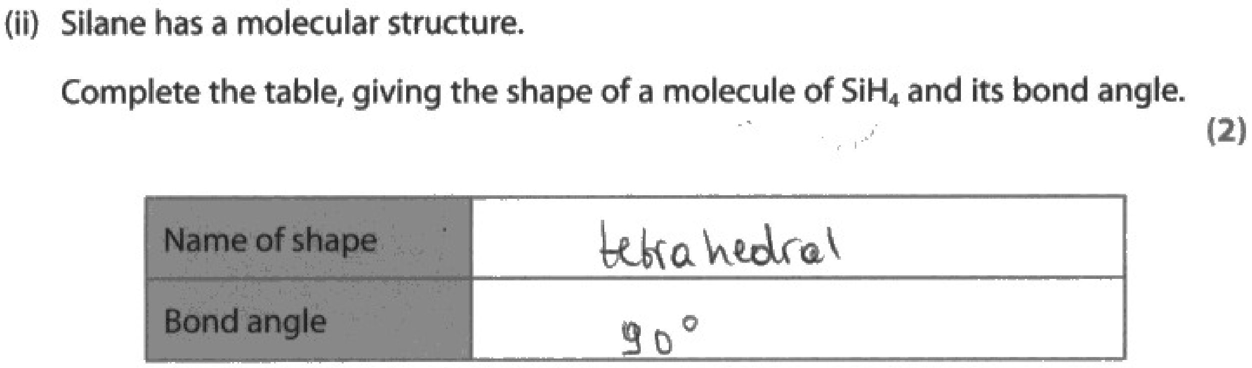
$Mg_2Si + 4HCl \rightarrow SiH_4 + 2MgCl_2$

ResultsPlus
Examiner Comments

A correct response.

Question 15 (b)(ii)

A well-answered question with many candidates knowing the correct shape and bond angle. Common mistakes were to give the angle as 90° and/or the shape as square planar. Some candidates were careless with their presentation, for example giving numbers that could have been interpreted as 109.5, 105.5 or 104.5.



(ii) Silane has a molecular structure.

Complete the table, giving the shape of a molecule of SiH_4 and its bond angle.

(2)

Name of shape	tetrahedral
Bond angle	90°

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Examiner Comments

The correct shape but an incorrect bond angle.

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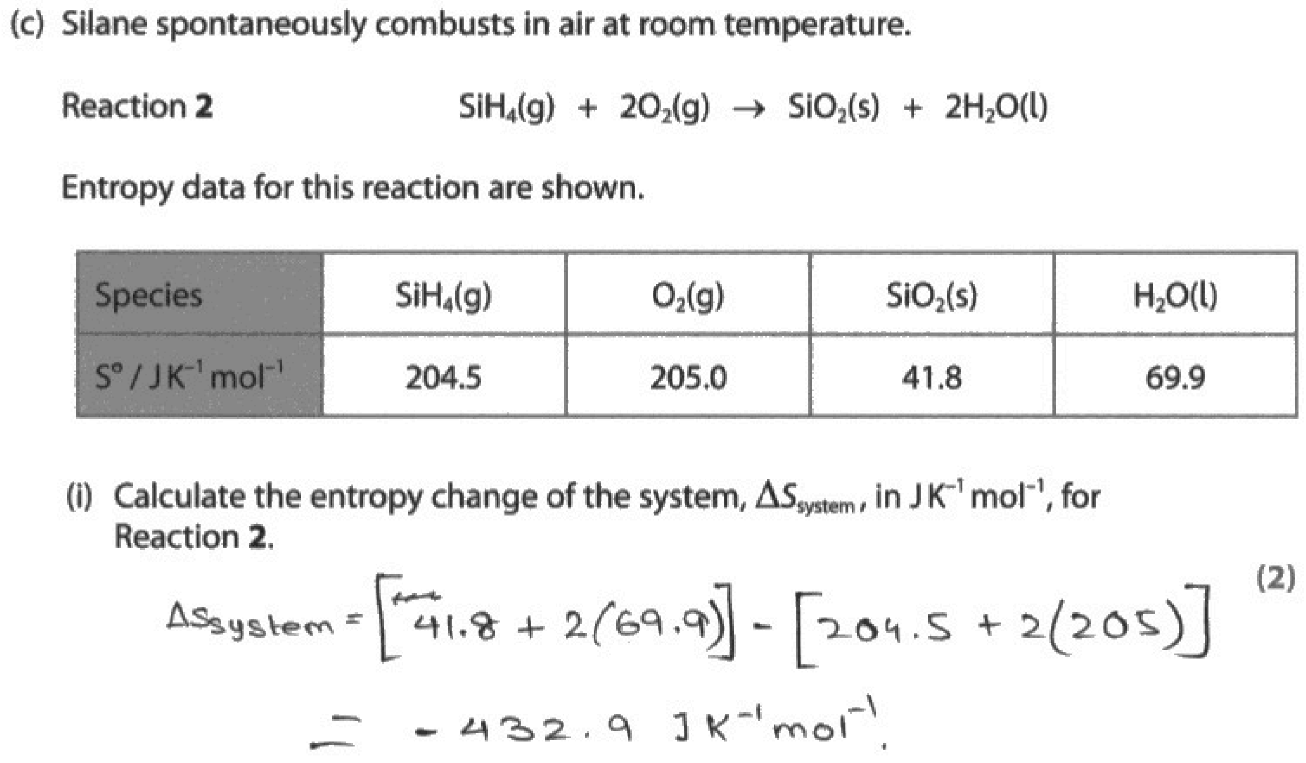
Examiner Tip

Draw analogies with familiar examples wherever possible, methane in this case.

Question 15 (c)(i)

Again, most candidates knew how to complete this entropy calculation. The most common mistakes included using incorrect numbers of moles or subtracting the products from the reactants.



(c) Silane spontaneously combusts in air at room temperature.

Reaction 2 $SiH_4(g) + 2O_2(g) \rightarrow SiO_2(s) + 2H_2O(l)$

Entropy data for this reaction are shown.

Species	$SiH_4(g)$	$O_2(g)$	$SiO_2(s)$	$H_2O(l)$
S° / J K^{-1} mol^{-1}	204.5	205.0	41.8	69.9

(i) Calculate the entropy change of the system, ΔS_{system}, in J K^{-1} mol^{-1}, for Reaction **2**.

(2)

$$\Delta S_{system} = [41.8 + 2(69.9)] - [204.5 + 2(205)]$$

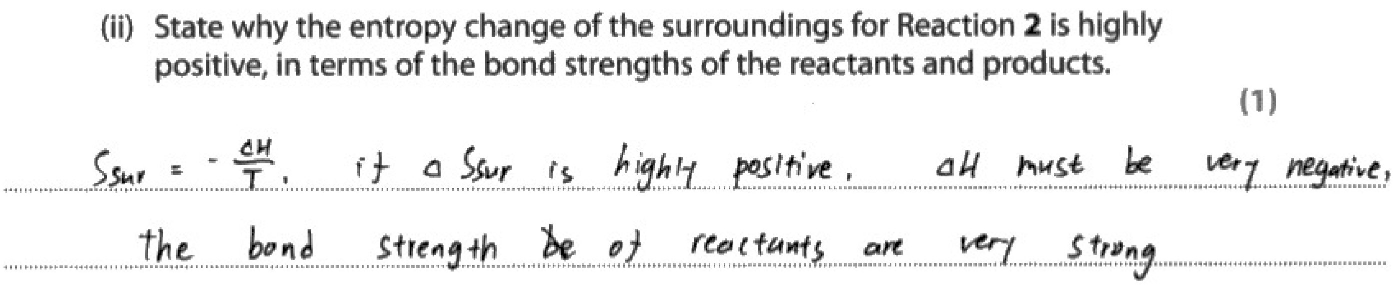
$$= -432.9 \text{ J K}^{-1}\text{mol}^{-1}.$$

ResultsPlus
Examiner Comments

A good response showing clear working. Best practice would also have stated the expression.

Question 15 (c)(ii)

Many candidates did not understand that this question was asking them to state why the reaction was exothermic, and to do so in terms of bond breaking and bond making.



(ii) State why the entropy change of the surroundings for Reaction **2** is highly positive, in terms of the bond strengths of the reactants and products.

(1)

$S_{sur} = -\frac{\Delta H}{T}$, if ΔS_{sur} is highly positive, ΔH must be very negative, the bond strength be of reactants are very strong

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Examiner Comments

This candidate has the right idea that the entropy change of the surroundings is positive due to the reaction being exothermic, but they do not understand this is because more energy is released from the bonds formed (than is needed to break bonds in the reactants).

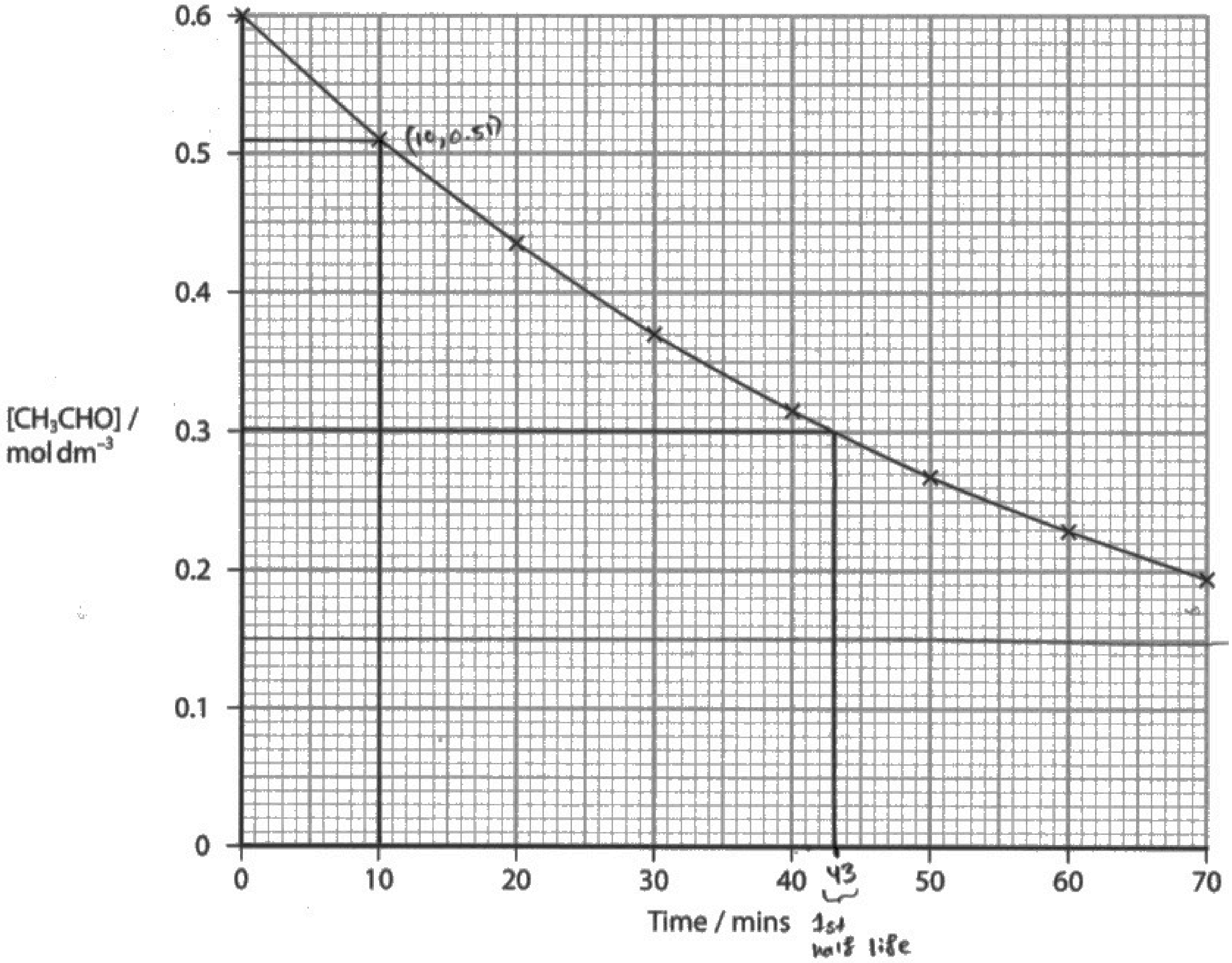
Question 16 (a)(i)

A surprisingly large proportion of candidates did not realise they needed to draw a tangent to the curve at $t = 0$ in order to determine the **initial** rate. Many used a single point from the curve or drew a tangent at a later time. Of those who drew a tangent, most knew how to determine the gradient but many did not pay attention to the units, giving a rate per minute and not per second.

16 This question is about the kinetics of the gas phase decomposition of CH_3CHO.

$$CH_3CHO \rightarrow CH_4 + CO$$

(a) A concentration-time graph for this reaction at 1000 K is shown.



(i) Calculate the initial rate of reaction, in **mol dm^{-3} s^{-1}**, at 1000 K.

You must show your working on the graph.

(3)

$$\text{rate} = \frac{0.51}{10 \times 60} = \underline{\underline{8.5 \times 10^{-4}}}\ \text{moldm}^{-3}\text{s}^{-1}$$

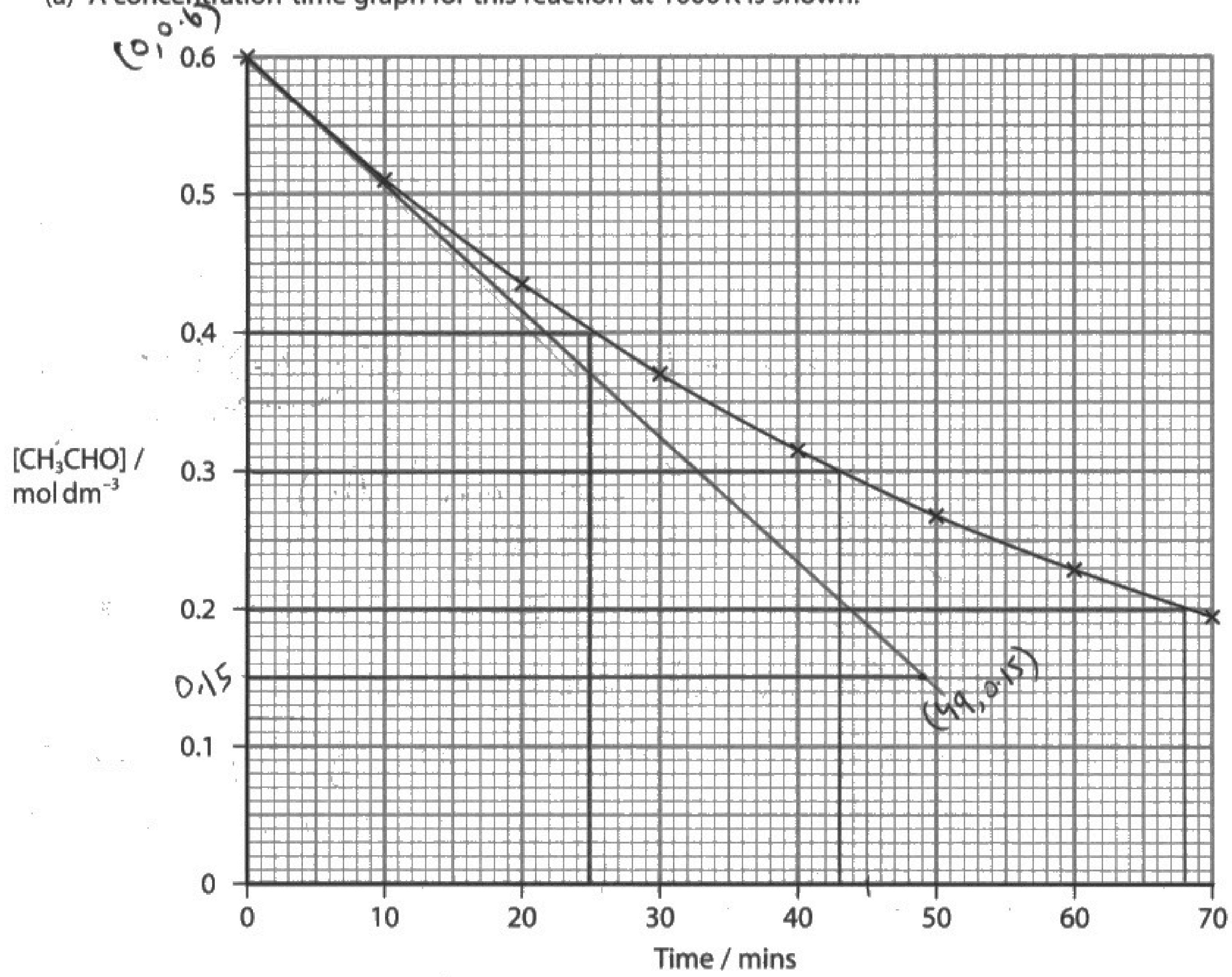
ResultsPlus
Examiner Comments

This candidate scored 1 mark only, for converting their "rate" from per minute to per second.

16 This question is about the kinetics of the gas phase decomposition of CH_3CHO.

$$CH_3CHO \rightarrow CH_4 + CO$$

(a) A concentration-time graph for this reaction at 1000 K is shown.



(i) Calculate the initial rate of reaction, in **mol dm^{-3} s^{-1}**, at 1000 K.

You must show your working on the graph.

(3)

$$\text{Rate} = \frac{\text{conc.}}{\text{volume}} = \text{gradient}$$

$$m = \frac{0.6 - 0.15}{0 - 49} = -\frac{9}{980}$$

$$\therefore 9.184 \times 10^{-3} \, \text{mol dm}^{-3} \text{s}^{-1}$$

(An)

ResultsPlus
Examiner Comments

This candidate has done everything but convert the rate from per minute to per second.

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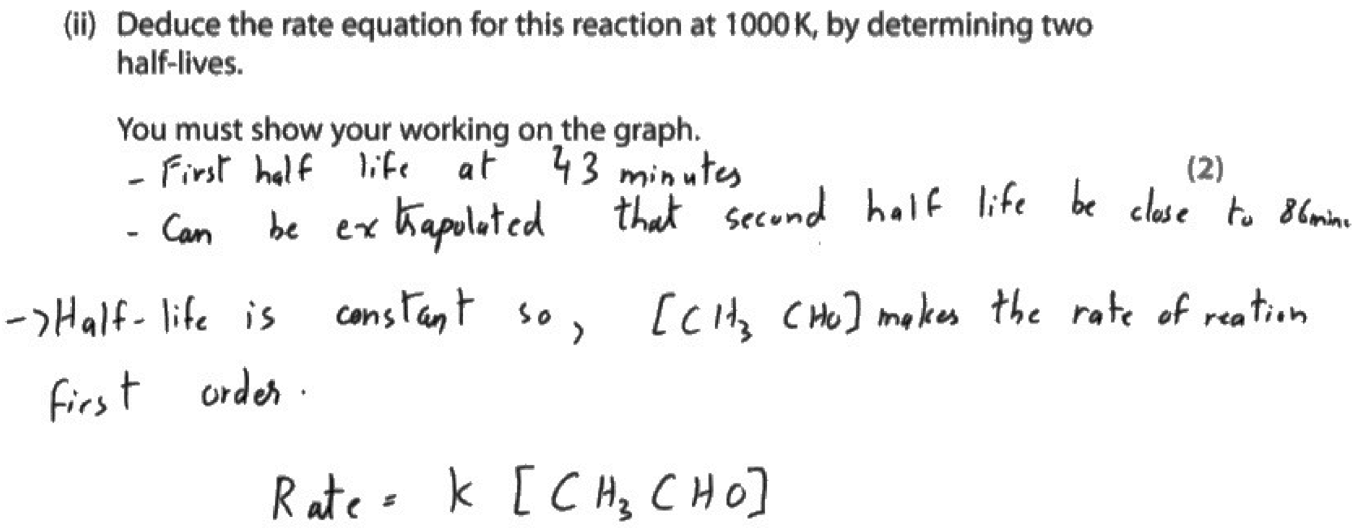
Examiner Tip

Always pay careful attention to units.

Question 16 (a)(ii)

The biggest hurdle in answering this question was that most candidates did not know how to determine two half-lives which are not consecutive. For a first order process, half-life is independent of the initial concentration so the time taken for any concentration to fall to half its original value (eg from 0.4 mol dm^{-3} to 0.2 mol dm^{-3}) could have been used. Of those who did know how to determine two half-lives, careless work was often seen, for example giving incorrect units or omitting the rate equation altogether.



(ii) Deduce the rate equation for this reaction at 1000 K, by determining two half-lives.

You must show your working on the graph.

(2)

- First half life at 43 minutes
- Can be extrapolated that second half life be close to 86mins

→ Half-life is constant so, $[CH_3CHO]$ makes the rate of reation first order.

Rate = $k[CH_3CHO]$

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Examiner Comments

Very many candidates, as here, did not know how to determine two half-lives that are not consecutive and simply guessed that the second half-life was equal to the first.

ResultsPlus
Examiner Tip

For a first order process, half-life is independent of the initial concentration.

(ii) Deduce the rate equation for this reaction at 1000 K, by determining two half-lives.

You must show your working on the graph.

(2)

1st half-life = 43 - 0 = 43 mins (from 0.6 $moldm^{-3}$ to 0.3 $moldm^{-3}$)

2nd half-life = 68 - 25 = 43 mins (from 0.4 $moldm^{-3}$ to 0.2 $moldm^{-3}$)

∴ The half-lives are constant

Thus the ~~rate~~ reaction is first order

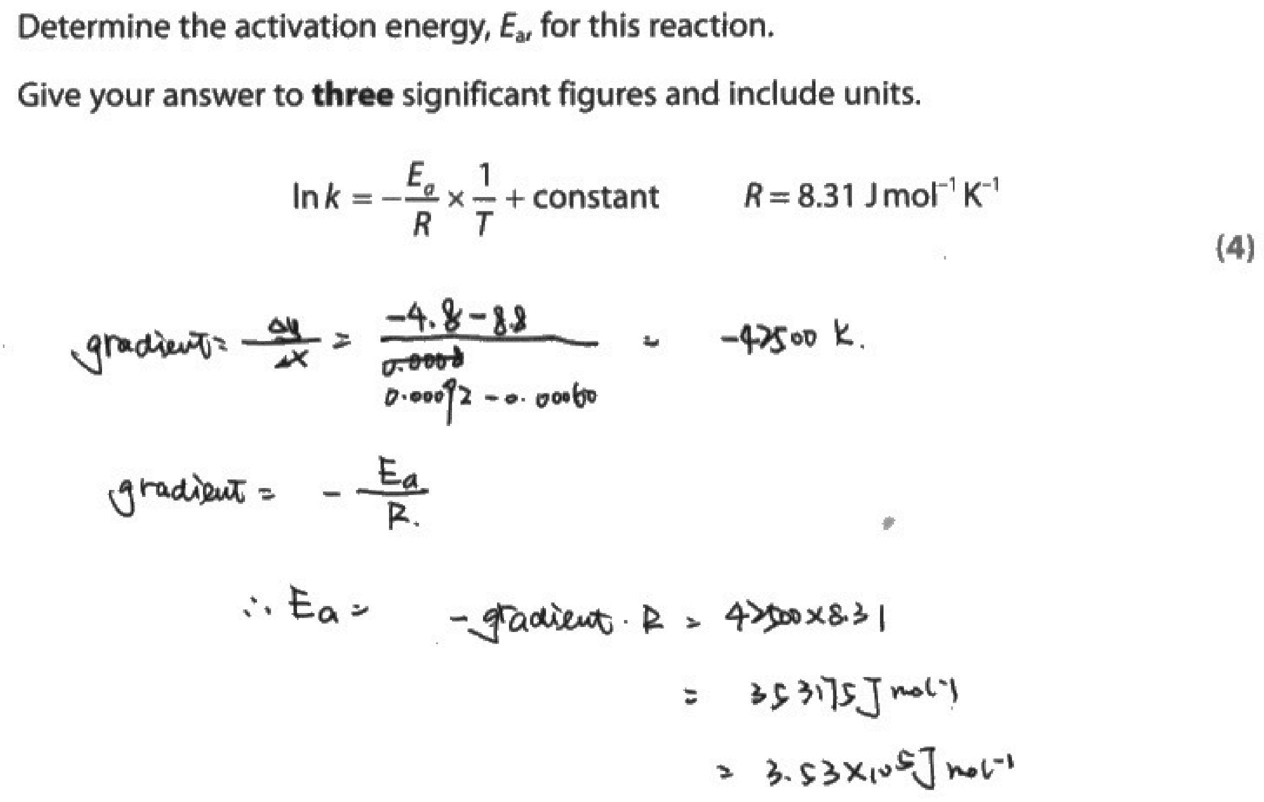
∴ rate = k·$[CH_3CHO]$

ResultsPlus
Examiner Comments

An excellent response receiving full credit.

Question 16 (b)

Those who knew how to determine activation energy from an Arrhenius plot scored well though many did not appear familiar with the process and tried to use a single point from the graph with the equation provided. A negative answer should have prompted candidates to check their working and far too many did not give their final answer to three significant figures, as instructed, and/or did not know the units of activation energy.



Determine the activation energy, E_a, for this reaction.

Give your answer to **three** significant figures and include units.

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

(4)

$$\text{gradient} = \frac{\Delta y}{\Delta x} = \frac{-4.8-8.8}{\cancel{0.0008}\ 0.00092 - 0.00060} \approx -42500\ \text{K}.$$

$$\text{gradient} = -\frac{E_a}{R}.$$

$$\therefore E_a = -\text{gradient} \cdot R = 42500 \times 8.31$$

$$= 353175\ \text{J mol}^{-1}$$

$$= 3.53 \times 10^5\ \text{J mol}^{-1}$$

ResultsPlus
Examiner Comments

An excellent response, showing a clear gradient determination and how the activation energy is calculated from this. The final answer is given to three significant figures, with units, as instructed.

Determine the activation energy, E_a, for this reaction.

Give your answer to **three** significant figures and include units.

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

(4)

$\frac{1}{1,700} = 5.88 \times 10^{-4}$

$T = 1,700$

$\ln 6 = -\frac{E}{8.31} \times \frac{1}{1,700}$

$13.296 = EA \times \frac{1}{1,700} =$

$EA = \underline{22\ 603.2}$

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Examiner Comments

It is not completely clear what this candidate is doing but it appears they are trying to use a single point from the graph along with the equation. They have ignored instruction and the final answer is neither given to three significant figures nor includes units.

ResultsPlus
Examiner Tip

Candidates should know that activation energy can be calculated from the gradient of an Arrhenius plot:

$E_a = -m \times R$

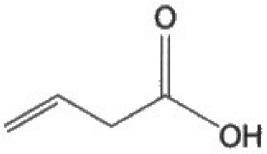
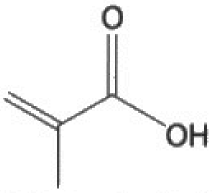
Activation energy should have a positive sign and units of kJ mol^{-1} (or J mol^{-1}).

Question 17 (a)(i)

Candidates found the naming of these – enoic acids challenging. Carboxylic acid functional groups should always be given the lowest possible locant number.

(i) Name the two structural isomers shown.

(2)

Isomer		
Name	but-1-enoic acid ~~but-1-ene oic acid~~	~~2-methyl but-1-en~~ 2-methyl prop-1-enoic acid

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Examiner Comments

A common mistake, as here, was to give the alkene functional group position 1 on the carbon chain.

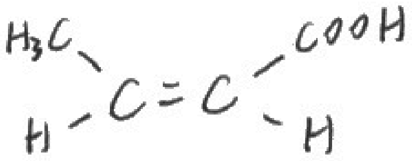
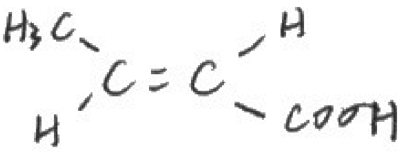
Question 17 (a)(ii-iii)

The structural isomers given in (a)(i) were a hint that the stereoisomers in (a)(ii) were geometric isomers of an – enoic acid, however, many tried without success to find a pair of optical isomers. Disappointingly, many candidates did not appear to know the basic principles of organic chemistry, for example that carbon forms four bonds. Once the – enoic acid isomers had been exhausted, the only possible option in (a)(iii) was a cyclic molecule; an answer reserved for the most able candidates.

(ii) The third structural isomer has two stereoisomers.

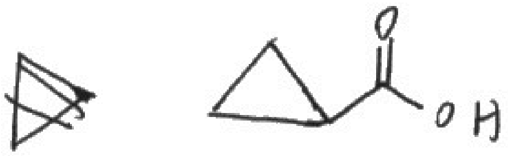
Draw these stereoisomers.

(2)

Stereoisomer **1**	Stereoisomer **2**
	

(iii) Draw the fourth structural isomer.

(1)



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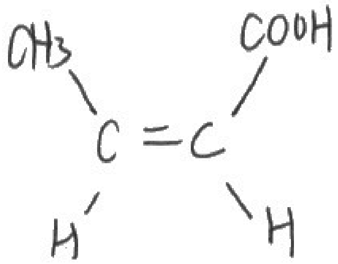
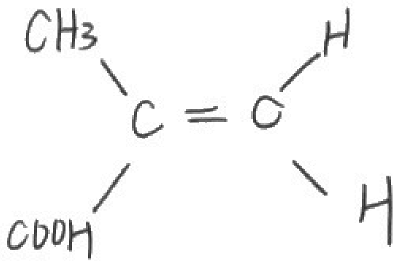
Examiner Comments

An excellent response showing the geometric isomers of but-2-enoic acid in (a)(ii) and cyclopropanecarboxylic acid in (a)(iii). Any types of structure were acceptable – a mixture of formulae are used here to good effect.

(ii) The third structural isomer has two stereoisomers.

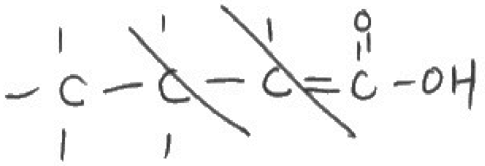
Draw these stereoisomers.

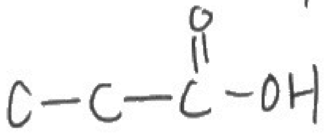
(2)

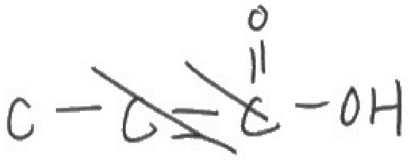
Stereoisomer 1	Stereoisomer 2
	

(iii) Draw the fourth structural isomer.

(1)







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Examiner Comments

This candidate has given two different structural isomers in (a)(ii). The right hand structure (2-methylpropenoic acid) was already given in (a)(i) and cannot have a stereoisomer as one of the carbons of the C=C is attached to the same group. The poor atom connectivity in the left hand structure was penalised.

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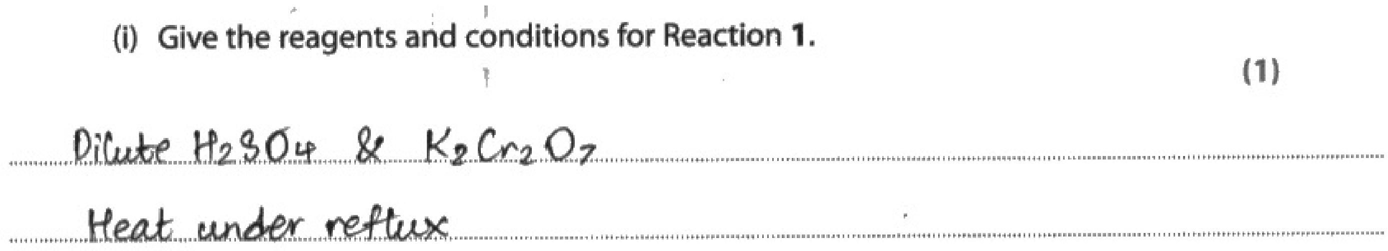
Examiner Tip

Be careful with atom connectivity when drawing organic structures as mistakes will usually be penalised.

Question 17 (b)(i)

The best responses identified both components of the oxidising agent as well as giving heating under reflux as the condition. Many candidates appeared to incorrectly think that sulfuric acid is a condition, for example a catalyst, as opposed to a reagent in the oxidation of alcohols. Centres should make learners aware that neither hydrochloric acid nor potassium manganate(VII) should be used in this reaction.



(i) Give the reagents and conditions for Reaction **1**.

(1)

Dilute H_2SO_4 & $K_2Cr_2O_7$

Heat under reflux

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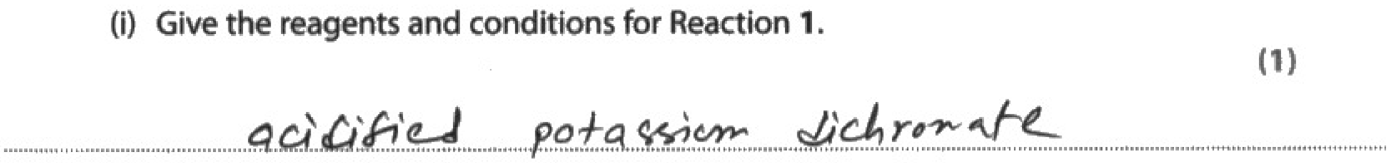
Examiner Comments

An excellent response giving two correct formulae for the reagents on the first line and the (essential) conditions on the second.



(i) Give the reagents and conditions for Reaction **1**.

(1)

acidified potassium dichromate

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Examiner Comments

This response would have been sufficient for the reagents had the conditions also been included.

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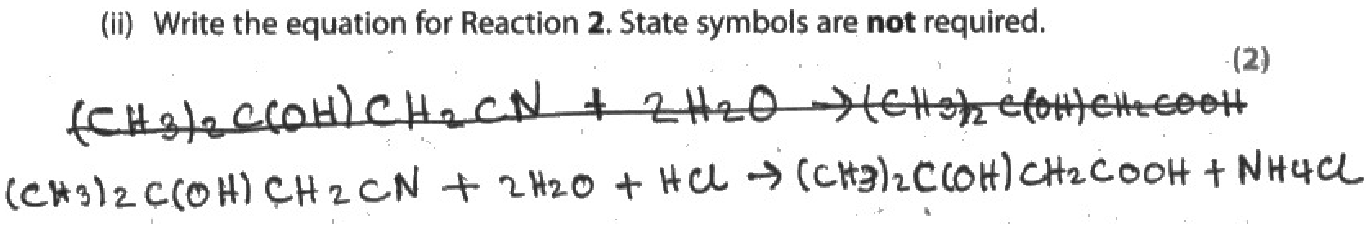
Examiner Tip

Candidates should be encouraged to use chemical formulae instead of names where allowed as this makes it easier to give a concise and accurate response.

Question 17 (b)(ii)

Despite being found to be a challenging question, it is encouraging that the equation for the hydrolysis of a nitrile was better known than in previous series. Common mistakes included omission of either water or hydrochloric acid and incorrect products such as HCN.



(ii) Write the equation for Reaction **2**. State symbols are **not** required.

(2)

~~$(CH_3)_2C(OH)CH_2CN + 2H_2O \rightarrow (CH_3)_2C(OH)CH_2COOH$~~

$(CH_3)_2C(OH)CH_2CN + 2H_2O + HCl \rightarrow (CH_3)_2C(OH)CH_2COOH + NH_4Cl$

ResultsPlus
Examiner Comments

An excellent response receiving full credit. The candidate has neatly crossed out and replaced their initial attempt.

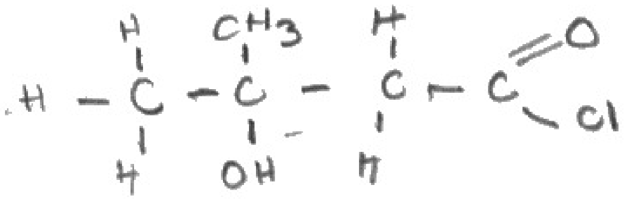
Question 17 (b)(iii)

The majority of candidates understood the reaction of the carboxylic acid functional group but failed to also consider the alcohol.

(iii) Give the structure of the organic product formed in Reaction **3**.

(2)

$(CH_3)_2C(OH)CH_2COCl$



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Examiner Comments

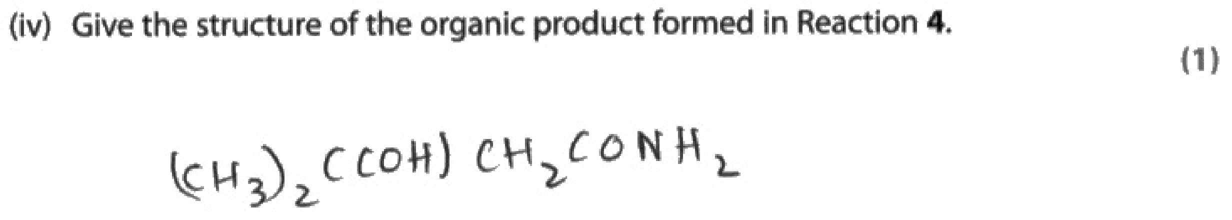
A typical response, recognising the conversion of the carboxylic acid group to an acyl chloride but neglecting the alcohol. The word "excess" alongside the PCl_5 reagent was a clue that more than one part of the molecule reacts, as was the number of marks available.

ResultsPlus
Examiner Tip

Be very careful if providing more than one type of structure as any mistakes will usually be penalised.

Question 17 (b)(iv)

Very few candidates recognised Reaction 4 as acid-base instead thinking that a primary amide was produced.



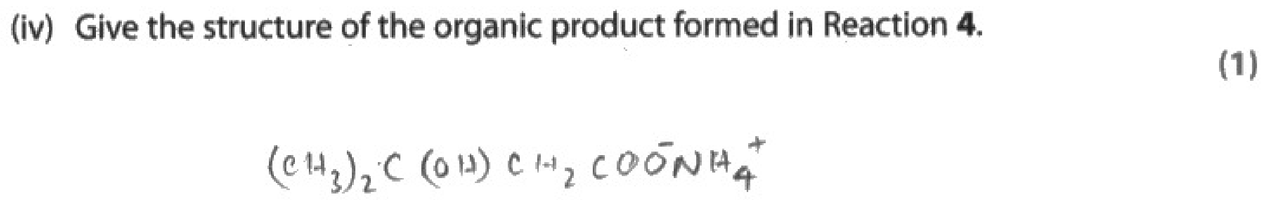
(iv) Give the structure of the organic product formed in Reaction **4**.

(1)

$(CH_3)_2C(OH)\ CH_2CONH_2$

ResultsPlus
Examiner Comments

As here, most candidates confused the carboxylic acid with an acyl chloride and gave a primary amide product.



(iv) Give the structure of the organic product formed in Reaction **4**.

(1)

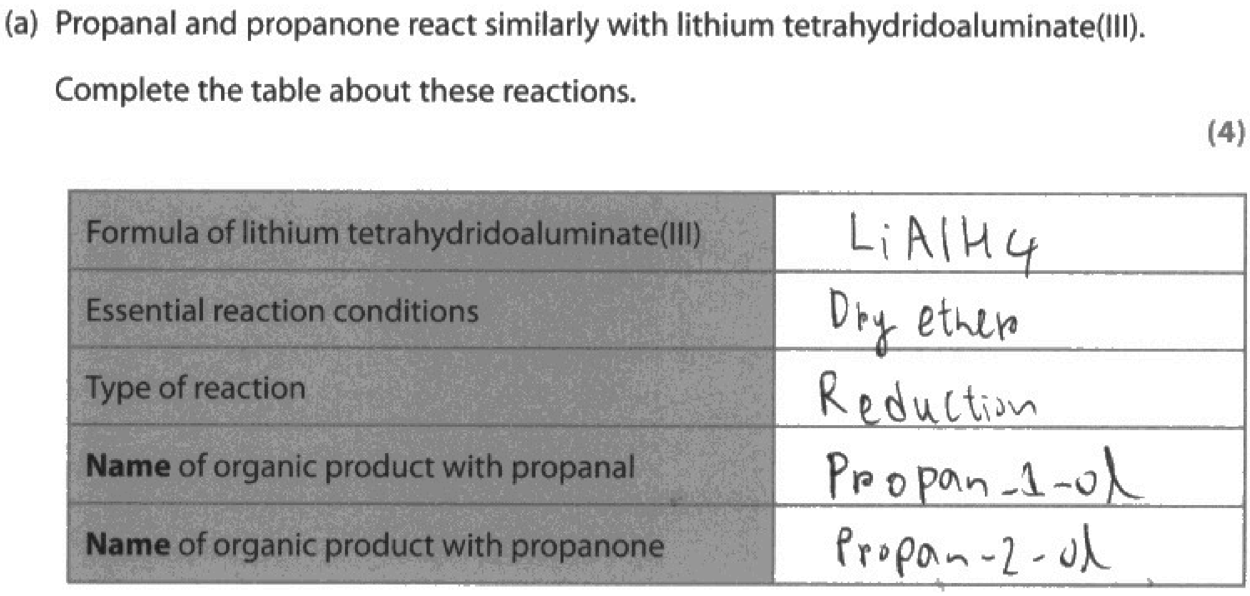
$(CH_3)_2C(OH)CH_2CO\bar{O}NH_4^+$

ResultsPlus
Examiner Comments

A rare correct response. The charges on the carboxylate and ammonium ions did not need to be shown.

Question 18 (a)

The reduction of carbonyls by lithium tetrahydridoaluminate(III) was well known though a common mistake was to give the product with propanal as just propanol, failing to indicate its primary nature.



(a) Propanal and propanone react similarly with lithium tetrahydridoaluminate(III).

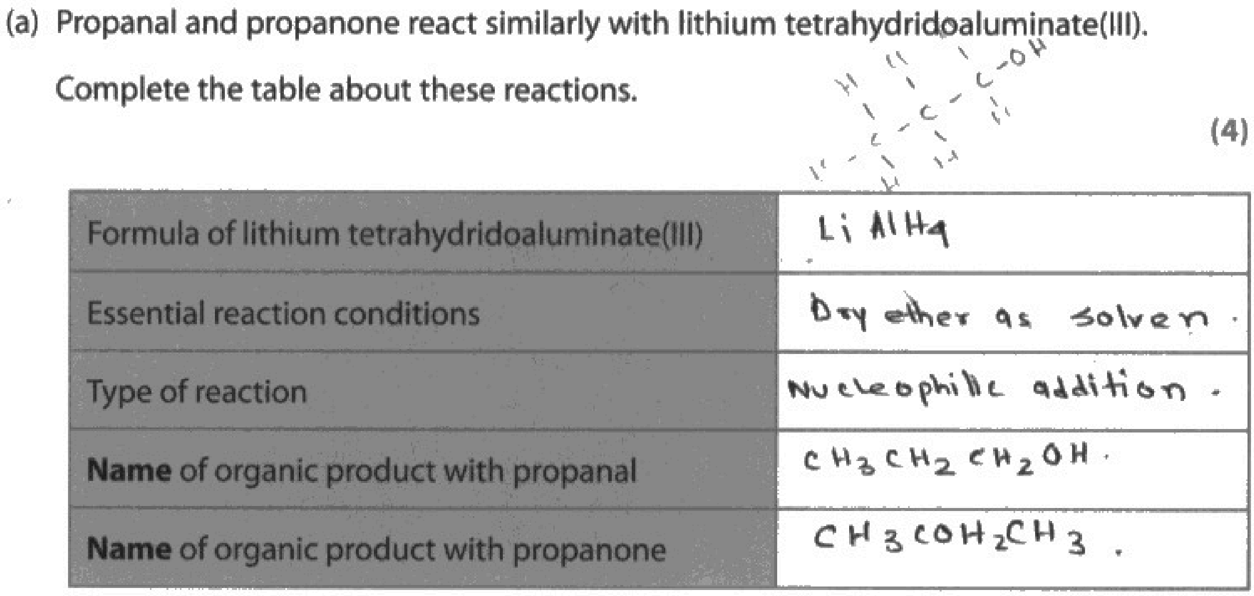
Complete the table about these reactions.

(4)

Formula of lithium tetrahydridoaluminate(III)	$LiAlH_4$
Essential reaction conditions	Dry ether
Type of reaction	Reduction
Name of organic product with propanal	Propan-1-ol
Name of organic product with propanone	Propan-2-ol

ResultsPlus
Examiner Comments

An excellent response scoring full marks.



(a) Propanal and propanone react similarly with lithium tetrahydridoaluminate(III).

Complete the table about these reactions.

(4)

Formula of lithium tetrahydridoaluminate(III)	$LiAlH_4$
Essential reaction conditions	Dry ether as solven.
Type of reaction	Nucleophilic addition.
Name of organic product with propanal	$CH_3CH_2CH_2OH$.
Name of organic product with propanone	$CH_3COH_2CH_3$.

ResultsPlus
Examiner Comments

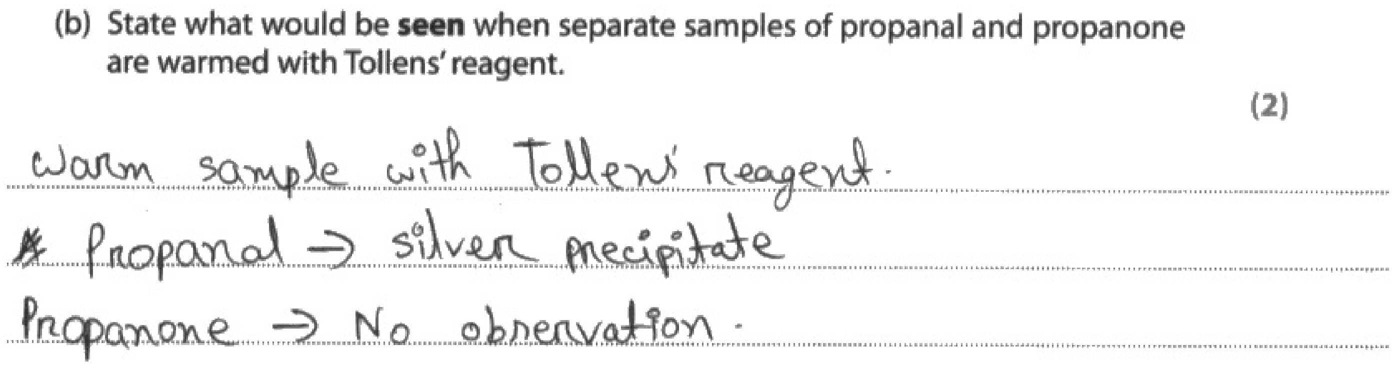
This candidate scored only 1 mark despite having a reasonable knowledge of the chemistry involved. While the reaction proceeds via a nucleophilic addition mechanism, the specification clearly identifies lithium tetrahydridoaluminate(III) as a reducing agent. They also failed to **name** the organic products (and gave an incorrect formula for propan-2-ol).

ResultsPlus
Examiner Tip

Read questions carefully, taking note of key instructions. The **names** of the organic products are clearly required.

Question 18 (b)

One of the highest scoring questions on the paper with most candidates knowing the effect of Tollens' reagent on aldehydes and ketones.



(b) State what would be **seen** when separate samples of propanal and propanone are warmed with Tollens' reagent.

(2)

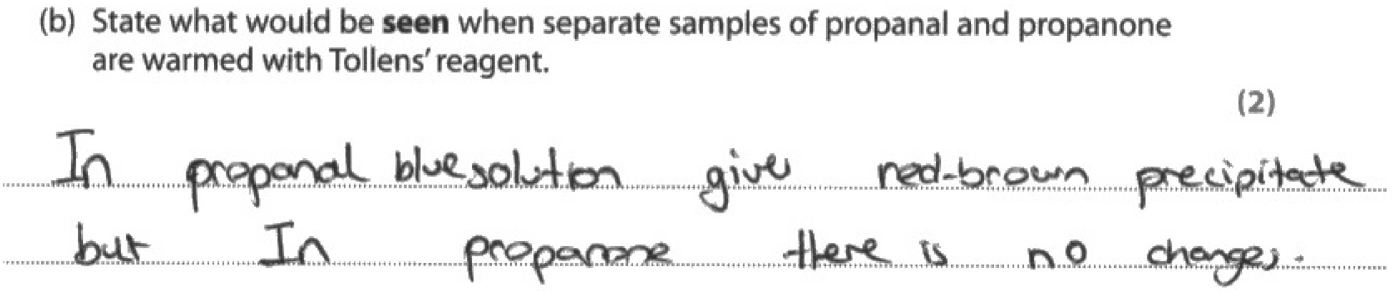
Warm sample with Tollens' reagent.

Propanal → silver precipitate

Propanone → No observation.

ResultsPlus
Examiner Comments

This candidate was awarded both marks despite the imprecision. The preferred observations are "silver mirror" and "no observable change" for propanal and propanone respectively.



(b) State what would be **seen** when separate samples of propanal and propanone are warmed with Tollens' reagent.

(2)

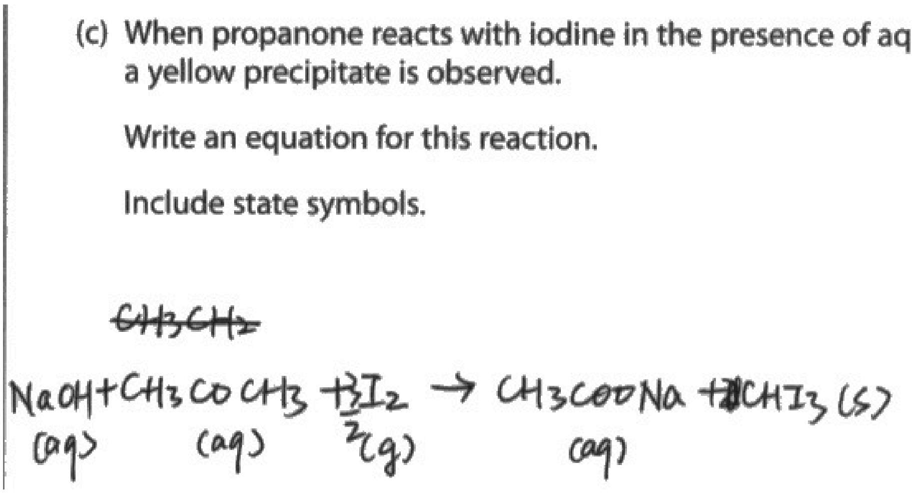
In propanal blue solution give red-brown precipitate but In propanone there is no changes.

ResultsPlus
Examiner Comments

Many candidates, as here, confused Tollens' reagent with Fehling's or Benedict's solution but were still able to score 1 mark for the observation with propanone.

Question 18 (c)

Very few candidates were able to demonstrate a sound knowledge of the equation for this reaction with the majority scoring 1 mark for the formula of the iodoform product. It was disappointing to see many of those who could identify the remaining species make careless mistakes with state symbols, even though much of the information required was provided in the question.



(c) When propanone reacts with iodine in the presence of aqueous sodium hydroxide, a yellow precipitate is observed.

Write an equation for this reaction.

Include state symbols.

(3)

$\cancel{CH_3CH_2}$

$NaOH + CH_3COCH_3 + \cancel{3}I_2 \rightarrow CH_3COONa + \cancel{2}CHI_3 (s)$

(aq) (aq) 2(g) (aq)

ResultsPlus
Examiner Comments

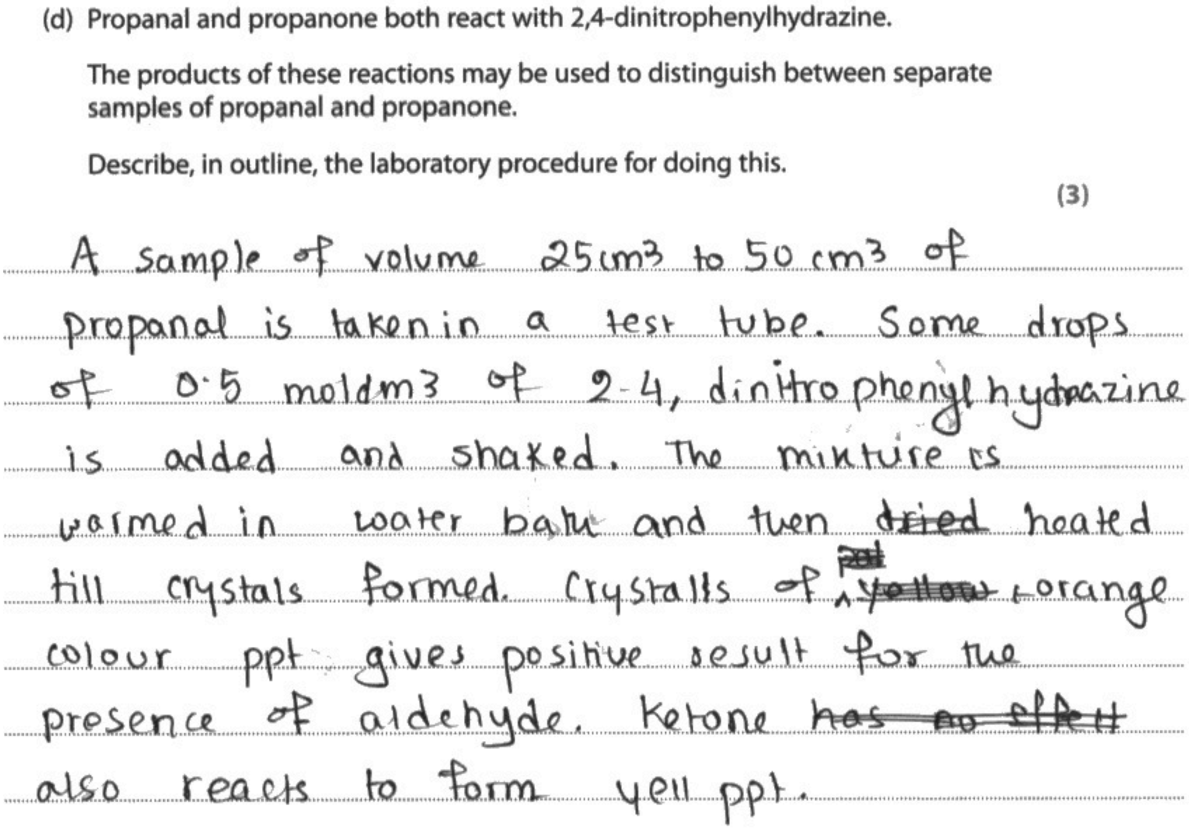
This candidate scored 2 marks for identifying iodoform and sodium ethanoate as two of the products.

ResultsPlus
Examiner Tip

Candidates should be able to write equations for all organic reactions on the specification unless explicitly stated otherwise.

Question 18 (d)

This question generated a wide range of candidate responses. Some gave far too much detail for the practical procedure, for example explaining the full process of recrystallisation, whereas others used insufficient terminology such as “collect” (for filter) or “crystallise” (for recrystallise). Many ignored the subject of the question, outlining how Fehling’s or Benedict’s solution or Tollens’ reagent could be used to distinguish between propanal and propanone. A lack of practical experience was commonplace, for example by those who suggested measuring the boiling (and not melting) temperatures of the derivatives.



(d) Propanal and propanone both react with 2,4-dinitrophenylhydrazine.

The products of these reactions may be used to distinguish between separate samples of propanal and propanone.

Describe, in outline, the laboratory procedure for doing this.

(3)

A sample of volume 25cm3 to 50 cm3 of propanal is taken in a test tube. Some drops of 0·5 moldm3 of 2-4, dinitro phenyl hydrazine is added and shaked. The mixture is warmed in water bath and then ~~dried~~ heated till crystals formed. Crystalls of ~~red~~ ~~yellow~~ orange colour ppt gives positive result for the presence of aldehyde. Ketone ~~has no effect~~ also reacts to form yell ppt.

ResultsPlus Examiner Comments

This candidate is clearly lacking practical experience and seems to think that the colour of the precipitate can be used to distinguish between the carbonyl compounds.

ResultsPlus Examiner Tip

Candidates should be encouraged to perform practical procedures when possible and shown video clips when not.

(d) Propanal and propanone both react with 2,4-dinitrophenylhydrazine.

The products of these reactions may be used to distinguish between separate samples of propanal and propanone.

Describe, in outline, the laboratory procedure for doing this.

(3)

→ Add 2,4-DNPH to test tubes, each containing equal volumes of propanal and propanone.

→ Allow precipitate to be form, filter the solution to get precipitate.

→ Recrystalise the precipitate and then ~~re~~ heat samples to find the melting point of each.

→ Compare values obtained with values from the data booklet to distinguish propanal and propanone.

ResultsPlus
Examiner Comments

A model answer, receiving full credit, with just the right level of detail.

ResultsPlus
Examiner Tip

An outline procedure requires the basic details only. Precise details such as volumes and concentrations of solutions are **not** required.

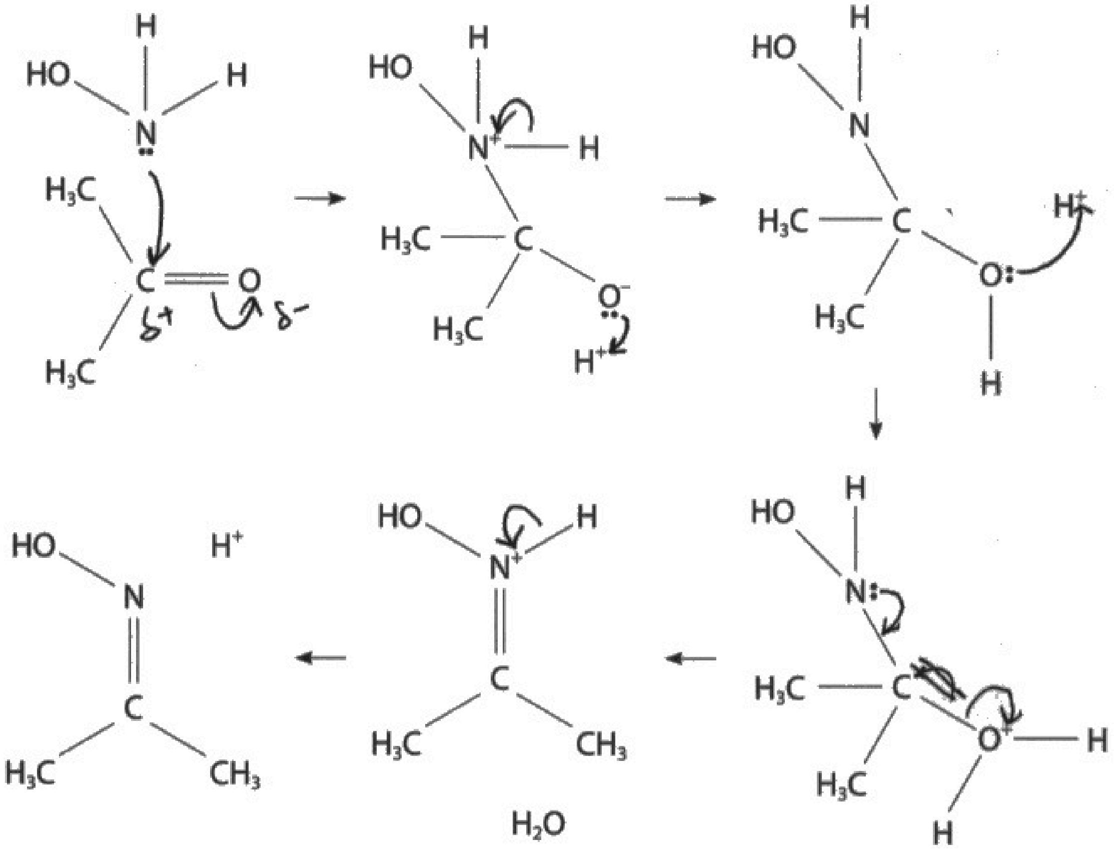
Question 18 (e)

The key to scoring well in this question was to understand where bonds were forming and breaking and to consider how electron pairs needed to move to effect this. Despite the instructions requiring the addition of curly arrows only, many candidates added incorrect charges and/or unnecessary dipoles. It was commonplace for curly arrows to go in the wrong direction, for example from H^+ ions to O lone pairs or from N – H bonds to H atoms. Candidates need to more carefully consider where electron pairs are located as well as the products that will be formed by their movement.

(e) Propanone, CH_3COCH_3, reacts with hydroxylamine, NH_2OH, under mildly acidic conditions.
The first stage of the reaction is a nucleophilic addition.

Add curly arrows to complete the mechanism for this reaction.

(4)



ResultsPlus
Examiner Comments

An excellent response scoring full marks. Note that each curly arrow is precise in its origin and terminus, clearly indicating the movement of electron pairs and the formation and breaking of bonds.

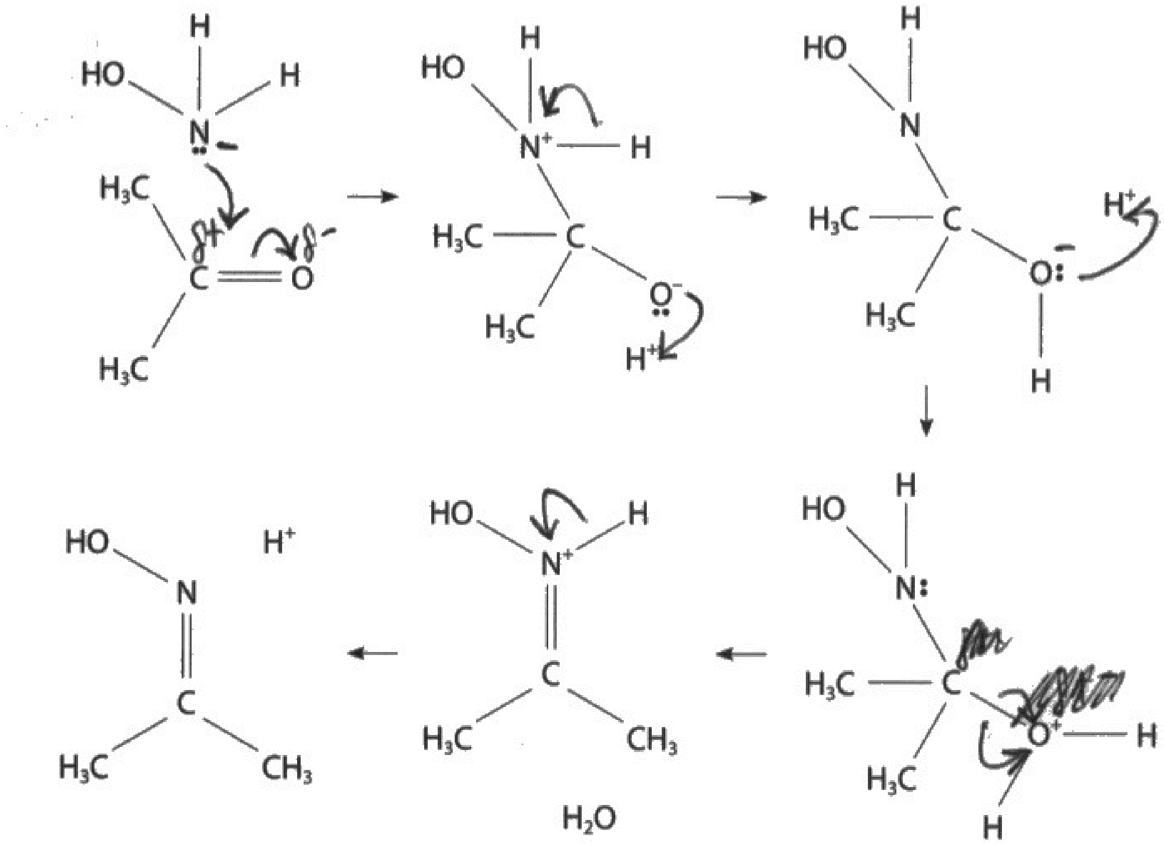
ResultsPlus
Examiner Tip

In an unfamiliar mechanism such as this, it is important to understand where bonds have been both formed and broken.

(e) Propanone, CH_3COCH_3, reacts with hydroxylamine, NH_2OH, under mildly acidic conditions.
The first stage of the reaction is a nucleophilic addition.

Add curly arrows to complete the mechanism for this reaction.

(4)



ResultsPlus
Examiner Comments

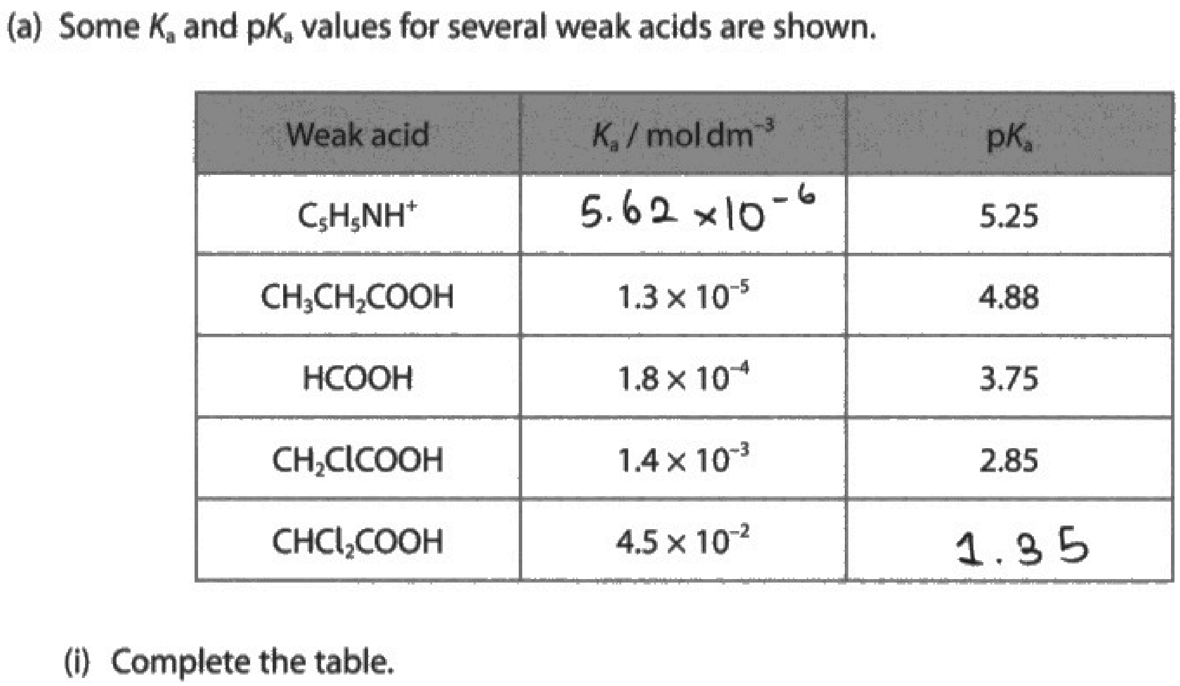
This response was awarded 2 marks. The candidate has added some spurious charges and the dipole on the C=O bond is blocking the intended trajectory of the first curly arrow.

ResultsPlus
Examiner Tip

Read questions carefully to see what is required. Curly arrows only needed to be added in this case.

Question 19 (a)(i)

The majority of candidates knew how to calculate the K_a and pK_a values, but a significant number incorrectly rounded their answers or were inconsistent in their use of significant figures.



(a) Some K_a and pK_a values for several weak acids are shown.

Weak acid	K_a / mol dm^{-3}	pK_a
$C_5H_5NH^+$	5.62×10^{-6}	5.25
CH_3CH_2COOH	1.3×10^{-5}	4.88
$HCOOH$	1.8×10^{-4}	3.75
$CH_2ClCOOH$	1.4×10^{-3}	2.85
$CHCl_2COOH$	4.5×10^{-2}	1.35

(i) Complete the table.

ResultsPlus
Examiner Comments

This candidate understood how to calculate the missing values but did not give the K_a value to two significant figures in keeping with the data provided.

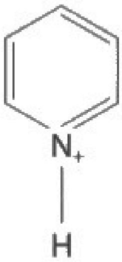
ResultsPlus
Examiner Tip

When considering significant figures, always be consistent with the data provided.

Question 19 (a)(ii)

Although most candidates knew what they were trying to achieve, many gave insufficient consideration to charge and failed to appreciate the conjugate base would be a neutral species. A significant number also thought that the ring contained six carbon atoms, despite the formula of the acid being given in the question.

(ii) The structure of $C_5H_5NH^+$ is shown.



Write the K_a expression for this weak acid.

(1)

$$ka = \frac{[H^+][C_6H_5N]}{[C_6H_5NH^+]}$$

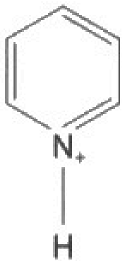
ResultsPlus
Examiner Comments

This candidate has not considered the nitrogen as part of the ring, giving an incorrect number of carbon atoms.

ResultsPlus
Examiner Tip

It can be helpful to number the carbon atoms on organic structures, particularly with skeletal formulae.

(ii) The structure of $C_5H_5NH^+$ is shown.



Write the K_a expression for this weak acid.

(1)

$$Ka = \frac{[C_5H_5N^-][H^+]}{[C_5H_5NH^+]}$$

$$C_5H_5NH^+ \rightleftharpoons C_5H_5N^- + H^+$$

ResultsPlus
Examiner Comments

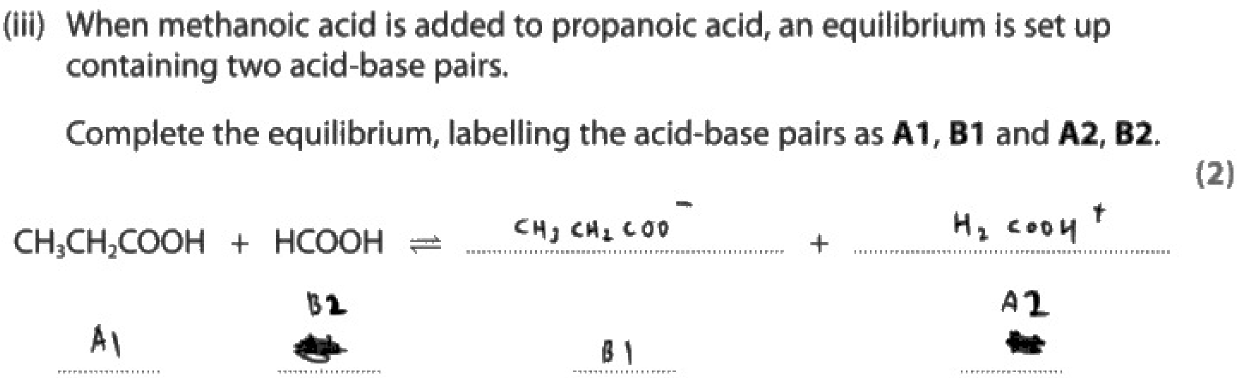
A common mistake was to put a negative charge on the conjugate base of the acid.

ResultsPlus
Examiner Tip

Always check that charge balances when writing equations.

Question 19 (a)(iii)

Candidates were supposed to use the K_a/ pK_a data from the table to identify methanoic acid as the stronger acid though this was missed by many. A significant number were also unable to correctly show the transfer of a proton from one molecule to the other, for example showing a positive charge on each of the products. It was evident that many candidates were not well practised in the labelling of conjugate acid-base pairs, which was often poorly done.



(iii) When methanoic acid is added to propanoic acid, an equilibrium is set up containing two acid-base pairs.

Complete the equilibrium, labelling the acid-base pairs as **A1**, **B1** and **A2**, **B2**.

(2)

$$CH_3CH_2COOH + HCOOH \rightleftharpoons CH_3CH_2COO^- + H_2COOH^+$$

A1 B2 B1 A2

ResultsPlus
Examiner Comments

This candidate was not able to use the data in the table to correctly identify the stronger acid. However, they were awarded the mark, with transferred error, for the labelling of the conjugate acid-base pairs, despite their unconventional formula for the protonated methanoic acid.

Question 19 (a)(iv)

Most were able to show how the pH values had been calculated but candidates found it much more challenging to use the assumptions to explain the differences between the measured and calculated values. It was a common approach to simply restate the assumptions, rather than question their validity, and many thought that dissociation of water meant the first assumption was partly responsible for any differences. A good proportion of candidates realised that the equilibrium concentration of the acids would be lower than the initial values, and that this was due to acid dissociation. Far fewer were able to express that this meant the concentrations of the acids would be overestimated in the calculations, leading to erroneously high hydrogen ion concentrations and lower pH values. Although not prompted to do so, it was expected that candidates would comment on the greater difference between measured and calculated pH values for dichloroethanoic acid but very few did this or attempted to compare the strength of the two acids.

Discuss the differences between the student's measured and calculated pH values.

(6)

In your answer, you should

- show how the student calculated their pH values

  [$K_a(CH_2ClCOOH) = 1.4 \times 10^{-3}\,mol\,dm^{-3}$;
  $K_a(CHCl_2COOH) = 4.5 \times 10^{-2}\,mol\,dm^{-3}$]

- explain, with reference to the assumptions made, why there is a difference between the calculated and measured pH values

- suggest why the measured pH values are higher than the calculated pH values.

$K_a = \frac{[H^+][A^-]}{[HA]}$, $[H^+] = [A^-]$

for $CH_2ClCOOH$: $[H^+]_A = \sqrt{K_{a_A} \times [HA]} = \sqrt{1.4 \times 10^{-3} \times 0.05} = 8.37 \times 10^{-3}$ moldm^{-3}

$pH_A = -\log[H^+] = 2.077$

for $CHCl_2COOH$: $[H^+]_B = \sqrt{K_{a_B} \times [HA]} = \sqrt{4.5 \times 10^{-2} \times 0.05} = 0.0474$ moldm^{-3}

$pH_B = -\log[H^+]_B = 1.323$

in real condition : $[HA]_{initial}$ will higher than $[HA]$ equilibrium because HA will dissociate and moles of HA will decrease. then $c = \frac{n}{V}$, concentration decrease when calculating pH

$pH = -\log_{10}(\sqrt{Ka \times [HA]})$

~~#~~ [HA] initial ~~is~~ > [HA] equilibrium

So $\sqrt{Ka \times [HA]}$ will decrease

therefore, pH will ~~be~~ increase, that's why the measured pH values are higher than the calculated pH values

dissociation of HA => ~~HA →~~ $HA \rightleftharpoons$ ~~H~~ $H^+ + A^-$

ResultsPlus
Examiner Comments

This candidate has used the prompts to create a clear and concise response, which scored 5 marks. Their only omission is a comparison of acid strength, which candidates were expected to consider as a result of the greater difference between measured and calculated pH values for dichloroethanoic acid.

Discuss the differences between the student's measured and calculated pH values.

(6)

In your answer, you should

- show how the student calculated their pH values

  [$K_a(CH_2ClCOOH) = 1.4 \times 10^{-3}\ mol\ dm^{-3}$;
  $K_a(CHCl_2COOH) = 4.5 \times 10^{-2}\ mol\ dm^{-3}$]

- explain, with reference to the assumptions made, why there is a difference between the calculated and measured pH values

- suggest why the measured pH values are higher than the calculated pH values.

$pH = -\log_{10}\sqrt{1.4 \times 10^{-3} \times 0.05}$

$= 2.077 = 2.08$ $(CH_2ClCOOH)$

$pH_{(CH_2Cl_2COOH)} = -\log_{10}\sqrt{4.5 \times 10^{-2} \times 0.05}$

$= 1.32$

There could be impurities in the beaker the student measured the pH in.

The temperature at which the student measured the pH must be ~~greater~~ lower than room temperature.

At greater temperature acid dissociation increases, so there are more H+ ions.

As student measured in lower temperature, acid dissociation is decreases, number of H+ ions decreases, so concentration of H+ ion decreases, so pH increases.

Calculated pH values are for standard conditions and room temperature.

ResultsPlus
Examiner Comments

This response scored 2 marks for showing how the pH values were calculated. Although acid dissociation is stated as a cause of the difference between the measured and calculated pH values, this has been incorrectly linked to temperature and so no marks for structure and lines of reasoning were awarded.

Question 19 (b)

In general, candidates did not seem familiar with a titration curve for a diprotic acid with a base. Many did not appreciate that there would be two vertical sections or know how to use the data to identify the volume of sodium hydroxide at each equivalence point. The partial curve was supposed to provide a prompt that the pK_a values relate to the pH at the half-equivalence point, but this was either not known or missed by most.

(b) 4-Hydroxybenzoic acid, HOC_6H_4COOH, is a diprotic acid, which dissociates in two stages. Each stage has a different pK_a value.

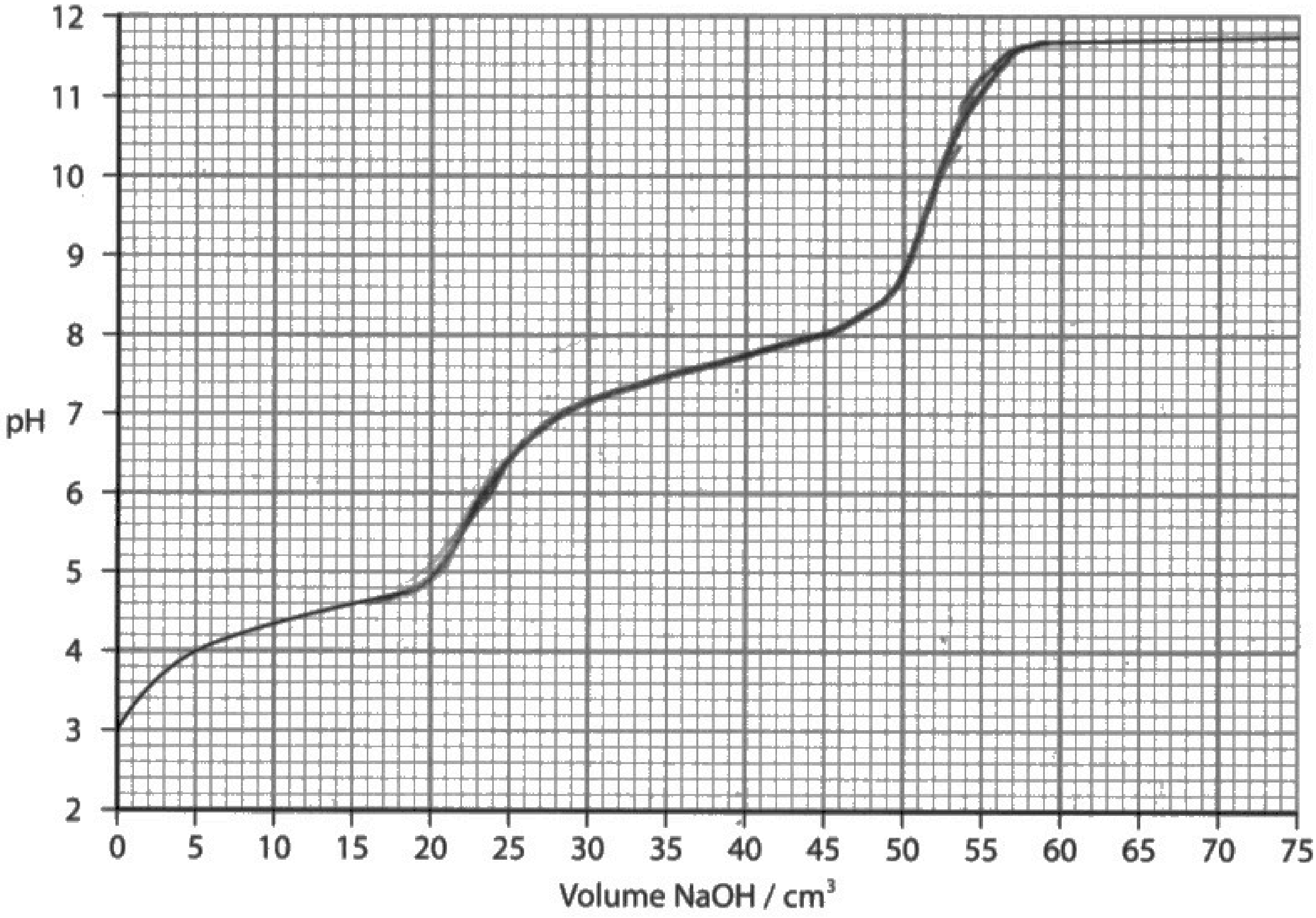
Stage 1 $HOC_6H_4COOH \rightleftharpoons H^+ + HOC_6H_4COO^-$ $pK_{a1} = 4.5$

Stage 2 $HOC_6H_4COO^- \rightleftharpoons H^+ + {}^-OC_6H_4COO^-$ $pK_{a2} = 9.3$

In a titration, 75.0 cm^3 of 0.025 mol dm^{-3} NaOH was added to 25.0 cm^3 of 0.025 mol dm^{-3} HOC_6H_4COOH.

Complete the titration curve.

(3)



ResultsPlus
Examiner Comments

Although this candidate appears to know the general shape of a titration curve for a diprotic acid with a base, their response did not receive any credit. The "vertical" sections slope heavily and have no true vertical section and the pH at the half-equivalence point (between the first and second deprotonations) is much lower than the second pK_a value of 9.3.

(b) 4-Hydroxybenzoic acid, HOC_6H_4COOH, is a diprotic acid, which dissociates in two stages. Each stage has a different pK_a value.

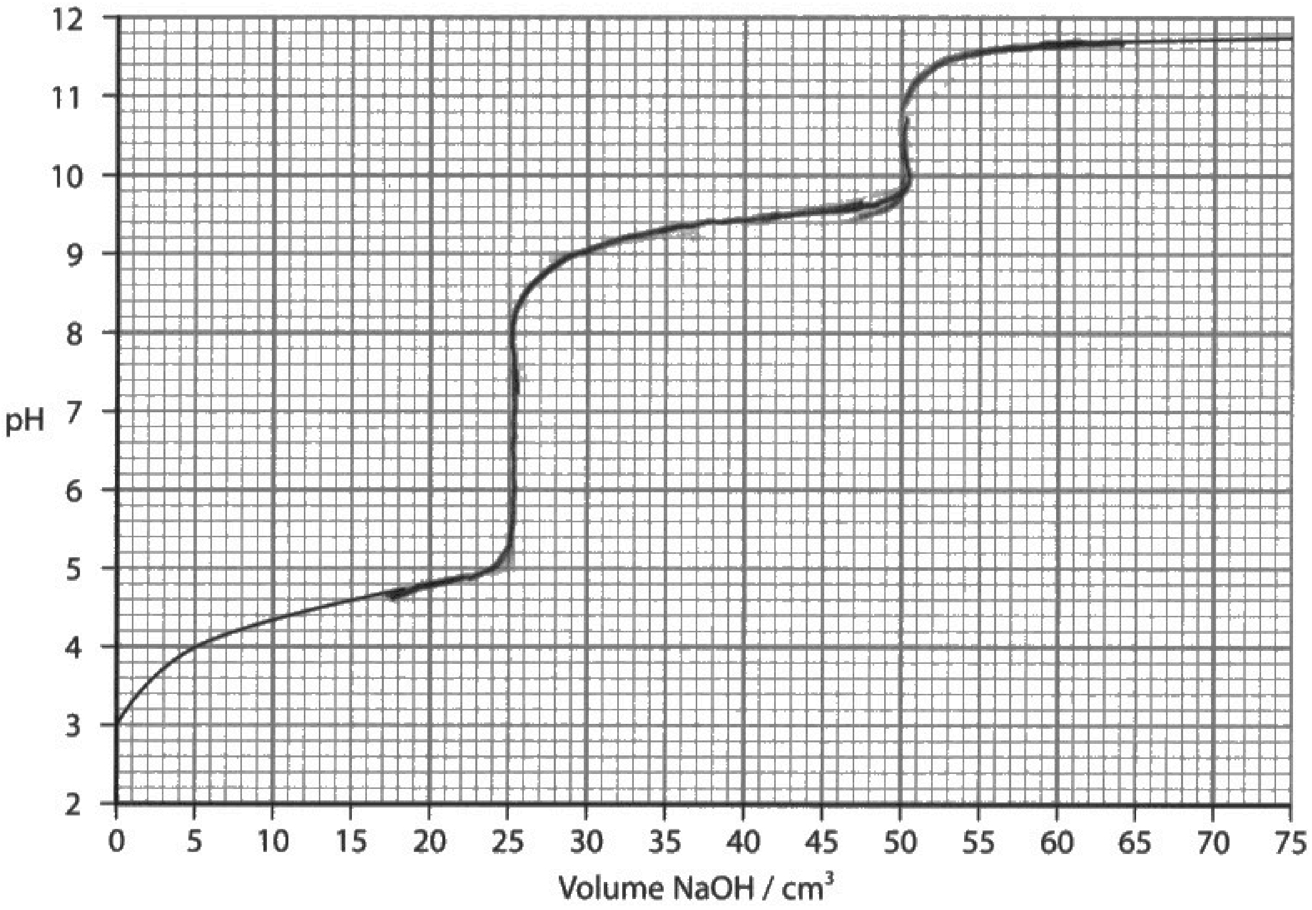
Stage 1 $HOC_6H_4COOH \rightleftharpoons H^+ + HOC_6H_4COO^-$ pK_{a1} = 4.5

Stage 2 $HOC_6H_4COO^- \rightleftharpoons H^+ + {}^-OC_6H_4COO^-$ pK_{a2} = 9.3

In a titration, 75.0 cm^3 of 0.025 mol dm^{-3} NaOH was added to 25.0 cm^3 of 0.025 mol dm^{-3} HOC_6H_4COOH.

Complete the titration curve.

(3)

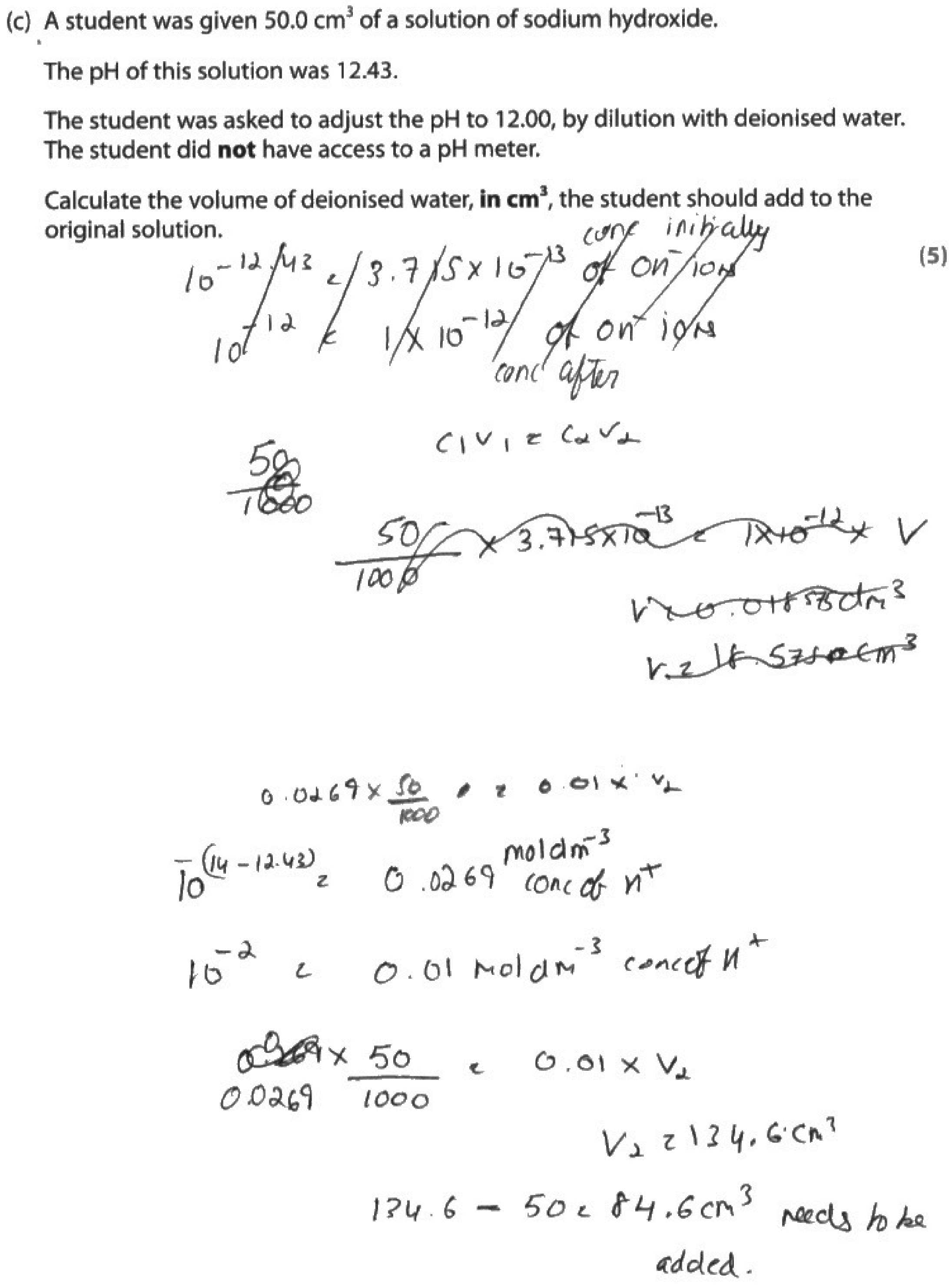


ResultsPlus Examiner Comments

An excellent response scoring all 3 marks.

Question 19 (c)

This was a challenging and unfamiliar pH calculation with which to end the paper and it was encouraging to find a good proportion of correct answers with candidates finding a surprising number of successful approaches. Some were unsurprisingly lost and it was not uncommon to find responses using data from the previous question, which was completely unrelated.



(c) A student was given 50.0 cm³ of a solution of sodium hydroxide.

The pH of this solution was 12.43.

The student was asked to adjust the pH to 12.00, by dilution with deionised water.
The student did **not** have access to a pH meter.

Calculate the volume of deionised water, **in cm³**, the student should add to the original solution.

(5)

conc initially

~~$10^{-12.43} = 3.715 \times 10^{-13}$ of OH^- ions~~

~~$10^{-12} = 1 \times 10^{-12}$ of OH^- ions~~

conc after

$C_1V_1 = C_2V_2$

~~$\frac{50}{1000}$~~

~~$\frac{50}{1000} \times 3.715 \times 10^{-13} = 1 \times 10^{-12} \times V$~~

~~$V = 0.01858 dm^3$~~

~~$V = 18.5750 cm^3$~~

$0.0269 \times \frac{50}{1000} = 0.01 \times V_2$

$10^{-(14-12.43)} = 0.0269$ moldm⁻³ conc of H^+

$10^{-2} = 0.01$ moldm⁻³ conc of H^+

$0.0269 \times \frac{50}{1000} = 0.01 \times V_2$

$V_2 = 134.6 cm^3$

$134.6 - 50 = 84.6 cm^3$ needs to be added.

ResultsPlus
Examiner Comments

A valid approach using pOH and the dilution equation, $c_1v_1 = c_2v_2$.

Full marks were awarded.

(c) A student was given 50.0 cm³ of a solution of sodium hydroxide.

The pH of this solution was 12.43.

The student was asked to adjust the pH to 12.00, by dilution with deionised water.
The student did **not** have access to a pH meter.

Calculate the volume of deionised water, **in cm³**, the student should add to the original solution.

(5)

c =

~~pH =~~

$[H^+] = 10^{-12.43}$

$= 3.718 \times 10^{-13}$

$K_w = [OH][H^+]$

$1 \times 10^{-14} = [OH][3.715 \times 10^{-13}]$

$[OH] = 0.0269$

adding ~~salt~~ NaOH

$n = \frac{0.025 \times 50}{1000}$

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

acid

$n = \frac{25 \times 0.025}{1000}$

$= 6.25 \times 10^{-4}$

excess acid

$1.875 \times 10^{-3} - 6.25 \times 10^{-4}$

$= 1.25 \times 10^{-3}$

salt

$n = \frac{0.025 \times 75}{1000}$

$= 1.875 \times 10^{-3}$

75 + 50 =

$HOC_6H_4COOH + NaOH -$

$c = \frac{1.875 \times 10^{-3} \times 1000}{125}$

$= 0.015$

ResultsPlus
Examiner Comments

This candidate has used data from the previous question despite parts (b) and (c) being completely unrelated. They were, however, awarded 1 mark for calculating the hydroxide ion concentration at pH 12.43.

ResultsPlus
Examiner Tip

Always consider the context of a question.

Paper Summary

Based on their performance on this paper, candidates should:

- read questions carefully, use the stimulus provided and follow instructions
- present their working to unstructured calculations clearly and consider sign, units and significant figures
- try to link questions in an unfamiliar context to their knowledge of the specification
- practise drawing tangents and determining half-lives
- practise naming organic compounds and drawing isomers
- learn the equation for the iodoform test
- try to better understand the movement of electron pairs in reaction mechanisms
- practise identifying conjugate acid-base pairs
- practise drawing and interpreting titration curves for diprotic acids with bases
- practise unfamiliar pH calculations.

Grade boundaries

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