Examiners' Report
June 2019

IAL Chemistry WCH04 01

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June 2019
Publications Code WCH04_01_1906_ER

Introduction

The majority of candidates were very well prepared for the examination. High marks were recorded, displaying the quality of learning and teaching which took place prior to examinations. Many candidates demonstrated a sound knowledge of the specification and showed this in their explanations and descriptions. A minority of candidates found the questions challenging and need to express their understanding of Chemistry more clearly. The calculations were generally well attempted, with the main errors being made were significant figures. There were no reports of candidates running out of time and the majority attempted the last question.

Section A

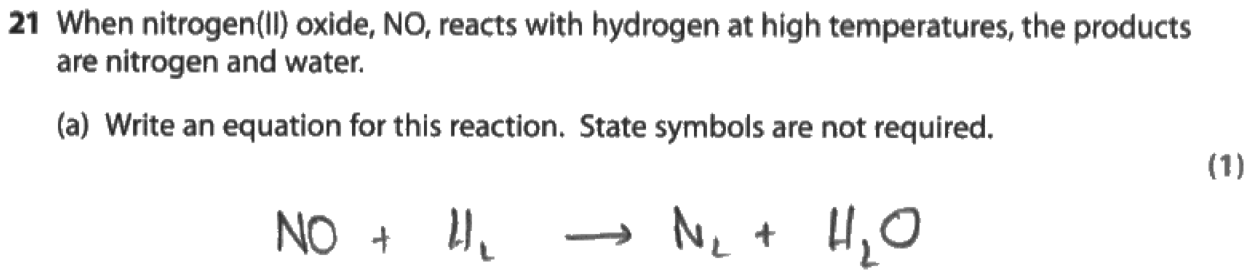
The mean mark on the multiple choice questions was 14.

The highest scoring questions were Q06 (Brønsted-Lowry acids), Q14 (forming ethanoyl chloride), Q15 (forming an amide) and Q12 (expression for $R\ln K$). Over 85% of candidates chose the correct answers for these items.

The least accessible question was Q19 (transesterification). Here, candidates' answers were spread evenly across the distractors and only 29% chose the correct answer. Q09 (relative pH of compounds), Q07 (choosing an indicator) and Q05 (signs for entropy) also presented difficulties for the candidates.

Question 21 (a)

This question presented little challenge to most candidates, however, some incorrect balancing was occasaionally seen. The most common reason for not gaining the mark was forgetting to balance the elements on both sides. Forgetting to balance the elements on both sides proved to be the most common mistake, resulting in failure to achieve the mark.



21 When nitrogen(II) oxide, NO, reacts with hydrogen at high temperatures, the products are nitrogen and water.

(a) Write an equation for this reaction. State symbols are not required.

(1)

$NO + H_2 \rightarrow N_2 + H_2O$

ResultsPlus
Examiner Comments

This response does not gain credit as the equation is not balanced.

ResultsPlus
Examiner Tip

Always ensure that your equations are balanced.

$NO + H_2 \longrightarrow \frac{1}{2}N_2 + H_2O$

ResultsPlus
Examiner Comments

This response scores one mark as multiples are acceptable.

ResultsPlus
Examiner Tip

Always leave space before the species in an equation for balancing.

Question 21 (b) (c)

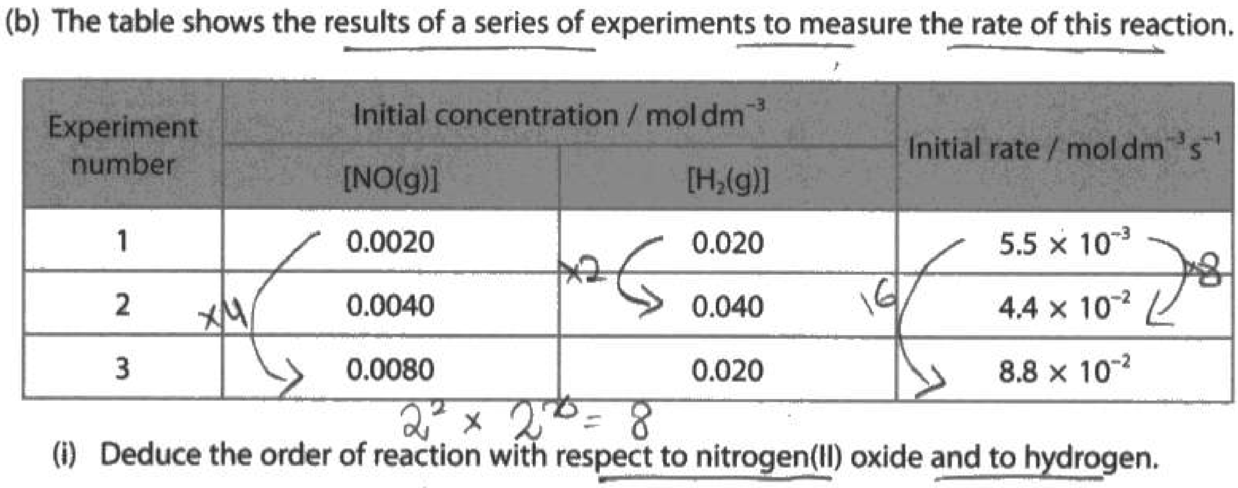
This question proved to be a challenge for some candidates and a wide range of marks were seen.

In (b)(i) candidates were required to deduce the orders of reaction, using the data to explain their reasoning. Correct orders alone scored 1, however if these were incorrect, candidates could still gain explanation marks. Most candidates were able to conclude the order of reaction for NO and form an explanation, though they found hydrogen more challenging. For the final mark, candidates were required to use the concentrations of both NO and H_2 in their reasoning.

A transfer error (TE) was given from the orders in (b)(i) to the rate equation in (b)(ii) so most candidates gained this mark. A further TE was awarded from the rate equation to the value of k and its units so it was usually algebraic errors that led to a loss of marks in (b)(ii).

Q21(b)(iii) had few correct responses. Many candidates explained the rate determining step as being a slow step here.

Part (c) also presented difficulties. Common errors included using two hydrogens in their suggested equation, and failing to use the N_2O_2 given in the question or reproducing the equation from Q21(a). This led to a great deal of confusion in the justifications. There appears to be a misconception among candidates that the rate equation describes the exact species involved in the rate determining step, rather than the comparative ratio of each reactant in the rate determining step as a result of all previous steps up to that reaction.



(b) The table shows the results of a series of experiments to measure the rate of this reaction.

Experiment number	Initial concentration / mol dm^{-3}		Initial rate / mol dm^{-3} s^{-1}
	[NO(g)]	[H_2(g)]	
1	0.0020	0.020	5.5×10^{-3}
2	0.0040	0.040	4.4×10^{-2}
3	0.0080	0.020	8.8×10^{-2}

x4

x2

16

x8

$2^2 \times 2^b = 8$

(i) Deduce the order of reaction with respect to nitrogen(II) oxide and to hydrogen.

Order with respect to NO Second order

Order with respect to H_2 First order

Justification From experiment 1 to 3, when [NO(g)] is quadrapled, the initial Rate of Reaction increases by 16 times ($2^4=16$). [H_2(g)] is constant. From experiment 1 to 2, [NO] doubles and so does [H_2] while initial Rate increases by 8 times. $2^2 \times 2^x = 8$

Thus, x is 1st order. $2^x = 8 \div 2^2 = 2$

$x = 1$

ResultsPlus

Examiner Comments

This answer scores three for part (i) and shows how annotating their tables can aid candidates' answers when calculating orders of reaction.

ResultsPlus

Examiner Tip

Make full use of the material given in the question. Annotate tables and graphs.

Underlining is a great way to bring focus to your answer.

(i) Deduce the order of reaction with respect to nitrogen(II) oxide and to hydrogen.

Justify your answers by referring to data from the table.

(3)

Order with respect to NO 2

Order with respect to H_2 1

Justification From 1—>3 when the Concentration of NO is quadrupled, initial rate increases by a factor of 16, therefore second order wrt [NO]

From 1—>2

$$[NO]^2[H_2]^x = \frac{4.4\times10^{-2}}{5.5\times10^{-3}}$$

$$4[H_2]^x = 8$$

$$[H_2]^x = 2$$

$$[2]^x = 2 \quad x = 1$$

Hence 1st order wrt $[H_2]$

(ii) Write the rate equation for the reaction.

(1)

$$rate = k[NO]^2[H_2]$$

(iii) Calculate the value of the rate constant and give its units.

(2)

$$5.5\times10^{-3} = k[0.002]^2[0.02]$$

$$\frac{mol\,dm^{-3}s^{-1}}{(mol\,dm^{-3})^3}$$

$$k = \underline{\underline{68750\,dm^{24}\,mol^{-2}s^{-1}}}$$

$$68750\,dm^{24}mol^{-2}s^{-1}$$

(c) There is more than one step in the reaction mechanism.

(i) Suggest why the reaction is unlikely to take place in a single step.

(1)

This is because the rate equation does not have the same order as the overall equation moles.

(ii) The first step of a three-step reaction mechanism is shown.

$$2NO(g) \rightarrow N_2O_2(g)$$

The second step of the mechanism is the rate determining step.

Suggest an equation for the rate determining step.

Justify your suggestion.

(2)

Second step : $N_2O_2 + H_2 \longrightarrow H_2O + N_2O$

The second step will be as shown and the rate equation should be $K[NO]^2[H_2]$ as N_2O_2 is an intermediate species and will not appear in the rate equation but the NO appears in the rate equation as it is responsible to produce N_2O_2. In the third step N_2O reacts further with H_2 to form N_2 and H_2O.

ResultsPlus
Examiner Comments

This candidate scored three marks having illustrated a concise method for part (i). This is a concise way to express their understanding of the orders of reaction.

The rate equation is correctly written for (ii) but the units are incorrect in (iii) so only one mark can be awarded here.

The answer in (c)(i) does not gain credit as it is not clearly expressed; although their reasoning is close to a correct answer.

The candidate scored two on part (c)(ii) which was quite unusual. The equation is a good suggestion and the explanation links the first step to the overall equation and the rate equation. Though the words from the mark scheme are not stated per se, the candidate's understanding is clear.

ResultsPlus
Examiner Tip

Double check your units on each answer.

Practise working out units for k for rate equations with different orders of reaction.

(c) There is more than one step in the reaction mechanism.

(i) Suggest why the reaction is unlikely to take place in a single step.

(1)

It requires collision between more than two molecules at the same time for the reaction to take place in a single step.

(ii) The first step of a three-step reaction mechanism is shown.

$$2NO(g) \rightarrow N_2O_2(g)$$

The second step of the mechanism is the rate determining step.

Suggest an equation for the rate determining step.

Justify your suggestion.

(2)

$$N_2O_2(g) + H_2(g) \longrightarrow N_2O(g) + H_2O(g)$$

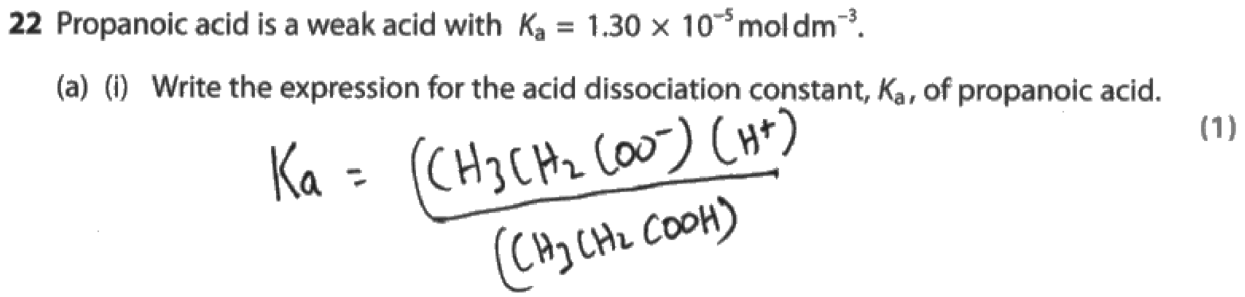
~~Because~~ From the rate equation, it is known that H_2 takes part in the rate determining step, ~~Because~~ so the rate determining step should be a reaction between the product in the first step and H_2.

ResultsPlus
Examiner Comments

This is an example of an answer which gained credit for (c)(i). Alhough the candidate does not state that it will be three molecules, "more than two" is sufficient.

Question 22 (a) (i)

Most candidates gained credit on this question with only the occasional use of curved brackets or use of ethanoic acid and ethanoate losing marks. A few candidates wrote the equation for the reaction rather than a K_a expression.



22 Propanoic acid is a weak acid with $K_a = 1.30 \times 10^{-5}\ \text{mol dm}^{-3}$.

(a) (i) Write the expression for the acid dissociation constant, K_a, of propanoic acid.

(1)

$$Ka = \frac{(CH_3CH_2COO^-)(H^+)}{(CH_3CH_2COOH)}$$

ResultsPlus
Examiner Comments

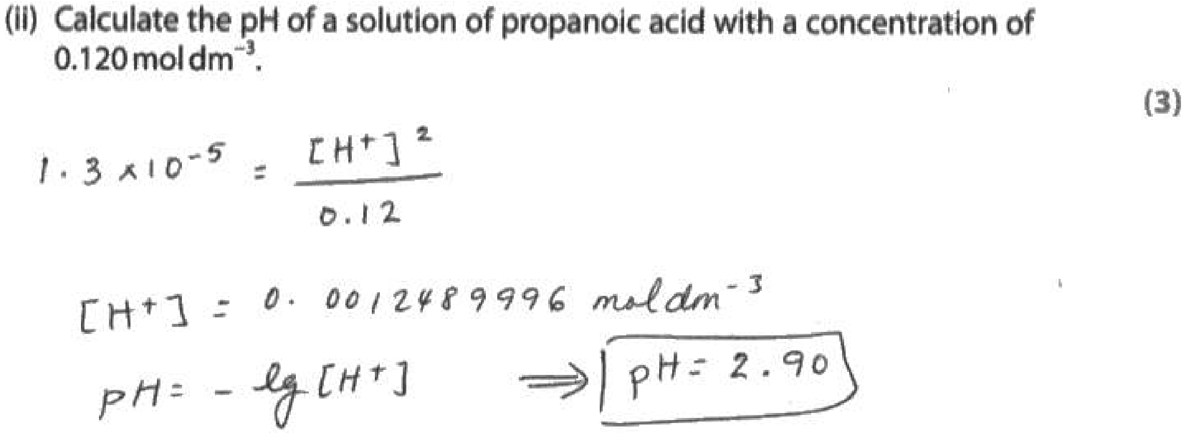
This candidate did not gain a mark as their brackets are curved instead of square.

ResultsPlus
Examiner Tip

Practise writing out equilibrium constants using correct notation: K_c and K_a must have square brackets for concentrations.

Question 22 (a) (ii)

This question was well answered by candidates of all abilities. Occasionally, candidates forgot to find the square root, not gaining a mark, however, the vast majority gained all three marks.



(ii) Calculate the pH of a solution of propanoic acid with a concentration of 0.120 mol dm^{-3}.

(3)

$$1.3 \times 10^{-5} = \frac{[H^+]^2}{0.12}$$

$$[H^+] = 0.0012489996 \text{ moldm}^{-3}$$

$$pH = -\lg[H^+] \Rightarrow \boxed{pH = 2.90}$$

ResultsPlus
Examiner Comments

This response scored three and clearly shows all of the steps in the candidate's answer.

ResultsPlus
Examiner Tip

Emphasising your final answer is helpful to examiners.

(3)

b $[H^+] = \sqrt{1.30 \times 10^{-5} \times 0.120}$

$[H^+] = 1.25 \times 10^{-3}$

$pH = -\log_{10}(1.25 \times 10^{-3})$

$= 3$

ResultsPlus
Examiner Comments

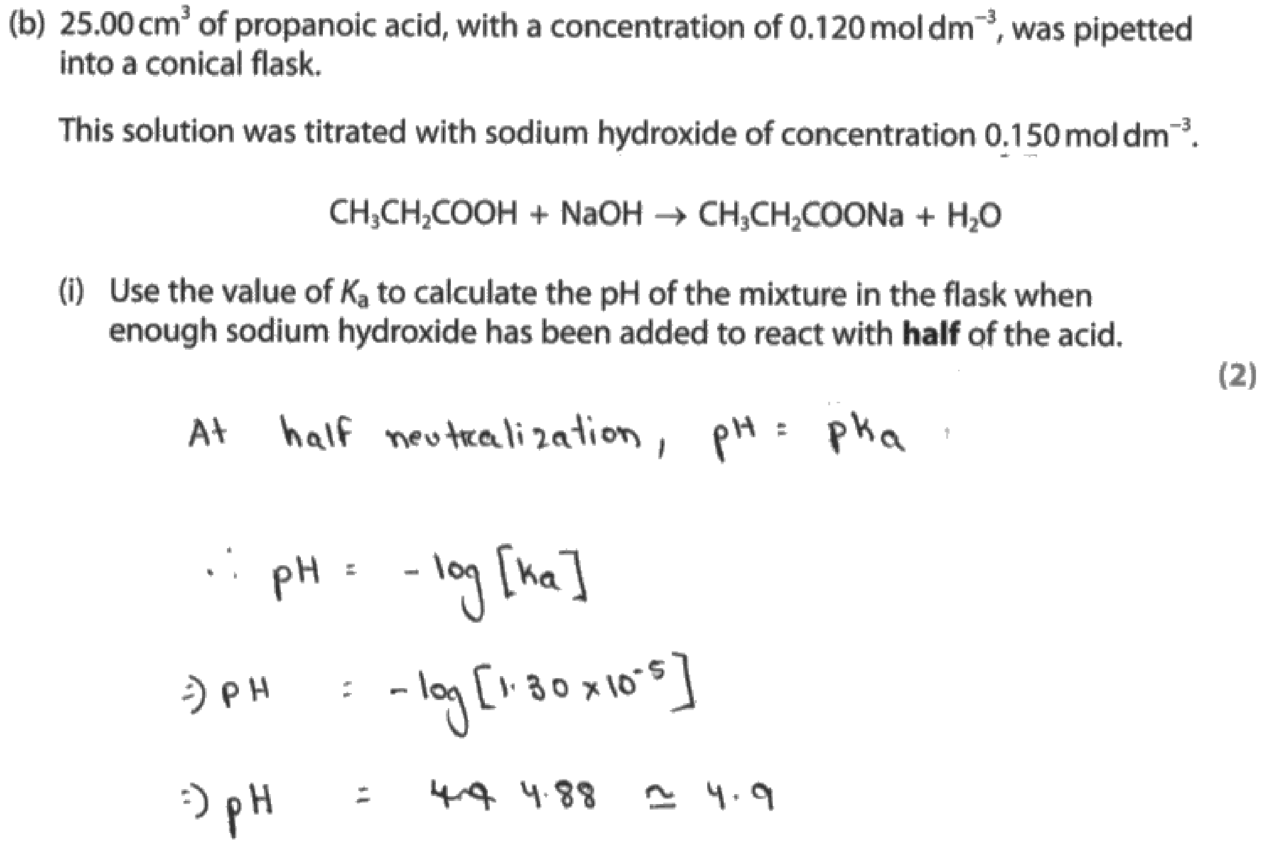
This candidate only scored two marks. Although their working is correct, their final answer is rounded to one significant figure and so is over truncated.

ResultsPlus
Examiner Tip

Never give answers to 1 significant figure, use the numbers in the question to help you decide how many you should use.

Question 22 (b) (i)

This was anticipated to be a straight-forward calculation for candidates, however, many failed to realise that the pH would be the pK_a and failed to achieve any marks. No TE was awarded here so candidates who performed long calculations using the concentrations of the solutions did not gain credit. A pH of 4.98 was a very common incorrect answer.



(b) 25.00 cm^3 of propanoic acid, with a concentration of 0.120 mol dm^{-3}, was pipetted into a conical flask.

This solution was titrated with sodium hydroxide of concentration 0.150 mol dm^{-3}.

$$CH_3CH_2COOH + NaOH \rightarrow CH_3CH_2COONa + H_2O$$

(i) Use the value of K_a to calculate the pH of the mixture in the flask when enough sodium hydroxide has been added to react with **half** of the acid.

(2)

At half neutralization, pH = pKa

$\therefore$ pH = $-\log[Ka]$

$\Rightarrow$ pH = $-\log[1.30 \times 10^{-5}]$

$\Rightarrow$ pH = ~~4.9~~ 4.88 $\simeq$ 4.9

ResultsPlus
Examiner Comments

This answer is succinct and clear, scoring both marks.

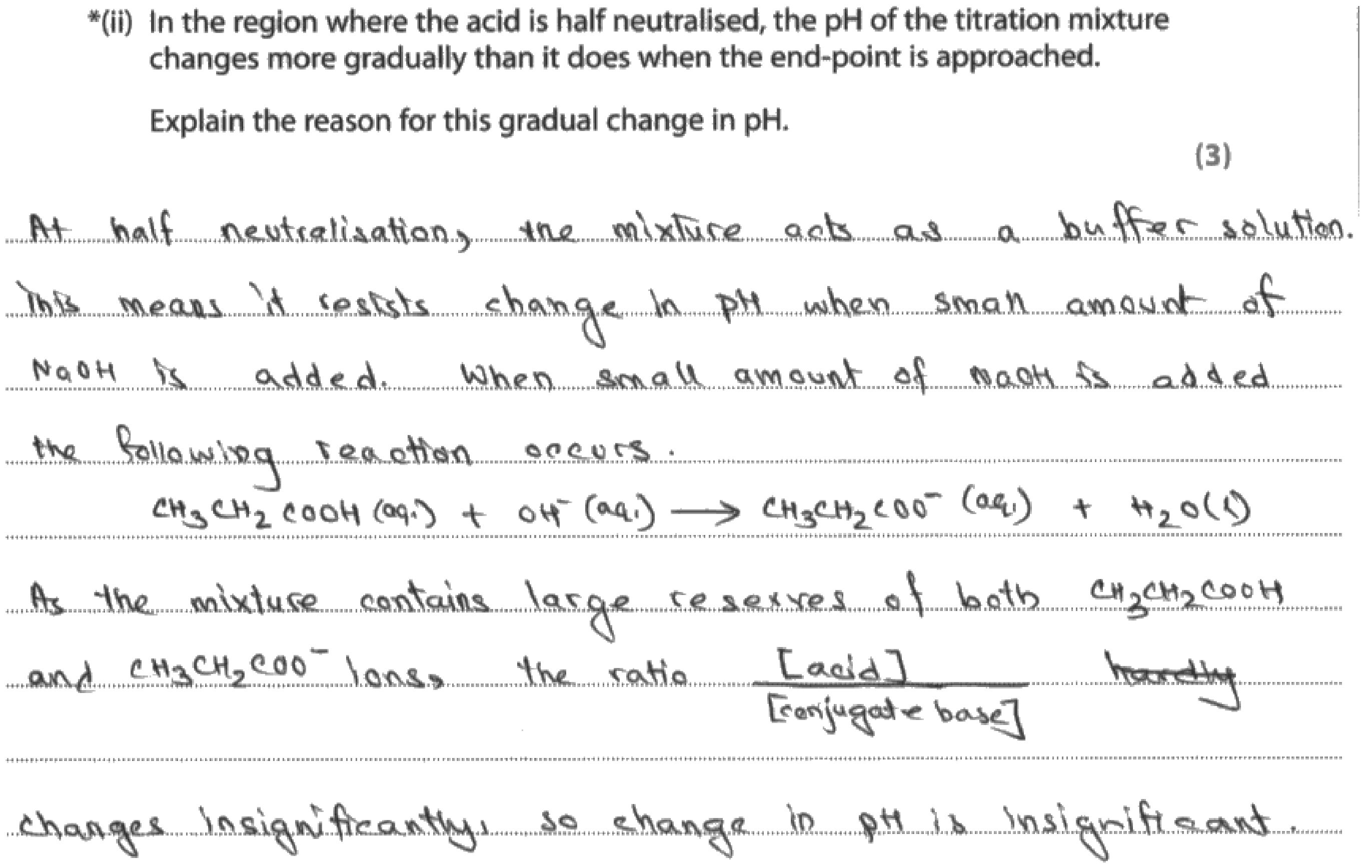
ResultsPlus
Examiner Tip

Use the space provided on the paper as a guide; a long calculation will be given over a half a page to allow for your workings.

Question 22 (b) (ii)

This question was not answered clearly by many candidates. Usually the second marking point was awarded, as several options were available, but a lack of precision often meant that the first mark was not merited. Many candidates wrote about the acid and conjugate base being in excess which did not achieve credit for mark point one.

Only the most able candidates mentioned the ratio of propanoic acid and propanoate although some stated that it remained constant, which negated the mark.



*(ii) In the region where the acid is half neutralised, the pH of the titration mixture changes more gradually than it does when the end-point is approached.

Explain the reason for this gradual change in pH.

(3)

At half neutralisation, the mixture acts as a buffer solution. This means it resists change in pH when small amount of NaOH is added. When small amount of NaOH is added the following reaction occurs.

$$CH_3CH_2COOH(aq) + OH^-(aq) \longrightarrow CH_3CH_2COO^-(aq) + H_2O(l)$$

As the mixture contains large reserves of both CH_3CH_2COOH and $CH_3CH_2COO^-$ ions, the ratio $\frac{[acid]}{[conjugate\ base]}$ ~~hardly~~ changes insignificantly, so change in pH is insignificant.

Examiner Comments

This is an excellent answer, scoring three marks.

Examiner Tip

Include relevant equations in your explanations.

The region is known as the buffer region. It resists p^H change when small amount of H^+ and OH^- is added to large amount of acid and base.

When H^+ ion is added $CH_3CH_2CH_2COO^- + H^+ \rightarrow CH_3CH_2CH_2COOH$

When OH^- ion is added $CH_3CH_2CH_2COOH + OH^- \rightarrow CH_3CH_2CH_2COO^- + H_2O$. Since only small amount of H^+ and OH^- ions are added, the p^H change is so small that it is considered negligible and hence the graph of titration mixture changes more gradually.

ResultsPlus
Examiner Comments

This answer scored one for the explanation of the buffer region resisting a change in pH.

The "large amounts of acid and base" omits the "conjugate".

The equations given here are for butanoic acid.

There is no reference to the ratio of propanoic acid and propanoate.

ResultsPlus
Examiner Tip

Carefully check the number of carbons when writing shortened structural formulae.

Question 22 (b) (iii)

This question was answered well. The calculation was well done and marks were only very occasionally not awarded for incorrect or absent units.

(iii) Calculate the minimum volume of sodium hydroxide required to react with **all** of the propanoic acid.

(2)

~~A_1~~ $V_1C_1 = V_2C_2$

$\Rightarrow \frac{25}{1000} \times 0.120 = V_2 \times 0.150$

$\Rightarrow V_2 =$ ~~0.2~~ $0.02\ dm^3$

$= 20\ cm^3$

$\therefore$ $20\ cm^3$ of NaOH is required to react with all CH_3CH_2COOH.

ResultsPlus
Examiner Comments

This response scored two marks.

ResultsPlus
Examiner Tip

Setting your calculations out neatly allows examiners to follow your steps easily.

$0.12 \times \frac{25}{1000} = 0.150 \times V$

$V = 0.02$

ResultsPlus
Examiner Comments

This response scored one mark for its workings but has not included units for the second mark.

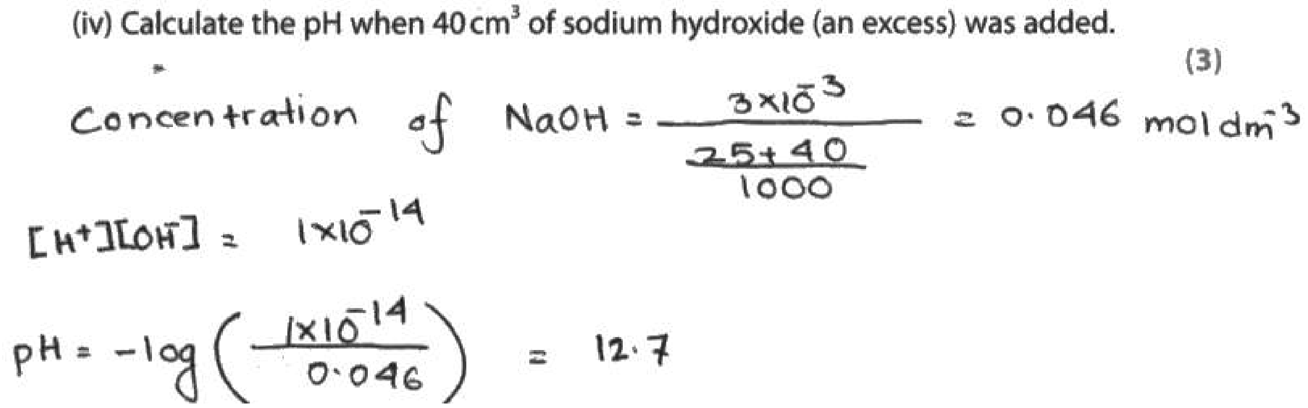
ResultsPlus
Examiner Tip

Always include units in your answers.

Question 22 (b) (iv)

The modal mark for this question was one with candidates often misunderstanding the total volume of solution. Transfer errors were available but answers had to be alkaline and to at least 1 decimal place.

Some candidates used their answer to part (iii) to calculate the pH which was acceptable.



(iv) Calculate the pH when 40 cm^3 of sodium hydroxide (an excess) was added.

(3)

Concentration of NaOH = $\dfrac{3\times10^{-3}}{\frac{25+40}{1000}}$ = 0.046 mol dm^{-3}

$[H^+][OH^-]$ = 1×10^{-14}

pH = $-\log\left(\dfrac{1\times10^{-14}}{0.046}\right)$ = 12.7

ResultsPlus
Examiner Comments

This candidate scores all three marks and used the K_w route.

ResultsPlus
Examiner Tip

Start each step of a calculation on a new line.

(3)

$n(NaOH) = CV = 0.15 \times 0.04 = 6 \times 10^{-3}$ mol.

$n(CH_3CH_2COOH) = 3 \times 10^{-3}$ mol

$n(OH^- \text{ remained}) = (6-3) \times 10^{-3} = 3 \times 10^{-3}$ mol

$$pH = pkw - pOH = 14 - p\frac{3 \times 10^{-3}}{0.04 + 0.025}$$

$$= 12.664 \ldots \approx 12.7$$

ResultsPlus
Examiner Comments

This is an alternative route to the mark scheme, using the answer to (b)(iii) via pOH. This response scored all three marks and is clearly laid out.

ResultsPlus
Examiner Tip

Writing down your intermediate steps will allow you to gain credit if you make an arithmetic error.

Question 22 (c)

This question was poorly answered.

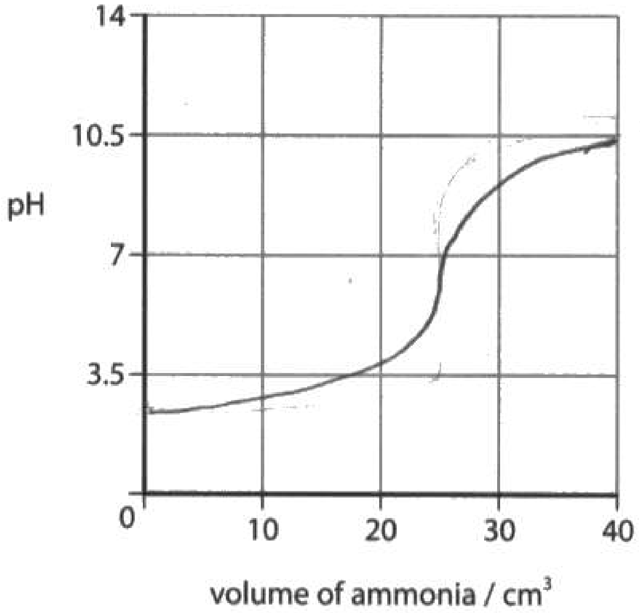
For (c)(i), the curve was not expected to start too low or end too high for the first mark. The second mark was given for the inflection passing through 7 at about 25cm^3. Frequently, candidates' curves passed through pH 7 at 20cm^3 - in the middle of the grid. If candidates started at an alkaline pH and ended at an acid, they could still gain the second mark. Some candidates plotted graphs for diprotic acids which could not gain credit, or drew lines for strong acid, strong, base or both. Many candidates did not appreciate that ammonia is a weak base. Obvious verticals negated the second mark.

The most frequently seen answer for (c)(ii) was "no vertical region". This was not an accepted answer and credit was only given for gradual changes in pH or indicator colour.

(c) In another titration, a solution of aqueous ammonia with a concentration of 0.120 mol dm^{-3} was added to 25.00 cm^3 propanoic acid with a concentration of 0.120 mol dm^{-3}.

(i) Sketch the shape of the titration curve on the grid.

(2)



(ii) Explain why an indicator **cannot** be used to determine the end-point of this reaction.

(1)

The pH change is so gradual for weak acid-base ~~tit~~ titration that ~~the~~ no sudden colour is noticed.

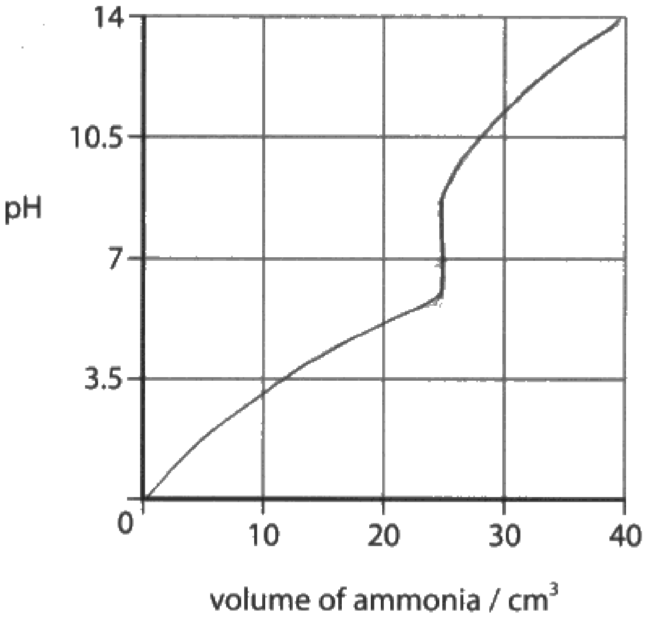
ResultsPlus
Examiner Comments

This graph scored both available marks.

The explanation also scored a mark.

ResultsPlus
Examiner Tip

Carefully rub out any misplaced lines on graphs or clearly label the line you want to be marked.



(ii) Explain why an indicator **cannot** be used to determine the end-point of this reaction.

(1)

Because the colour change at the end point is too gradual.

ResultsPlus
Examiner Comments

This graph cannot gain any credit as it starts too low and ends too high for mark point one.

There is an obvious vertical section which negates mark point two.

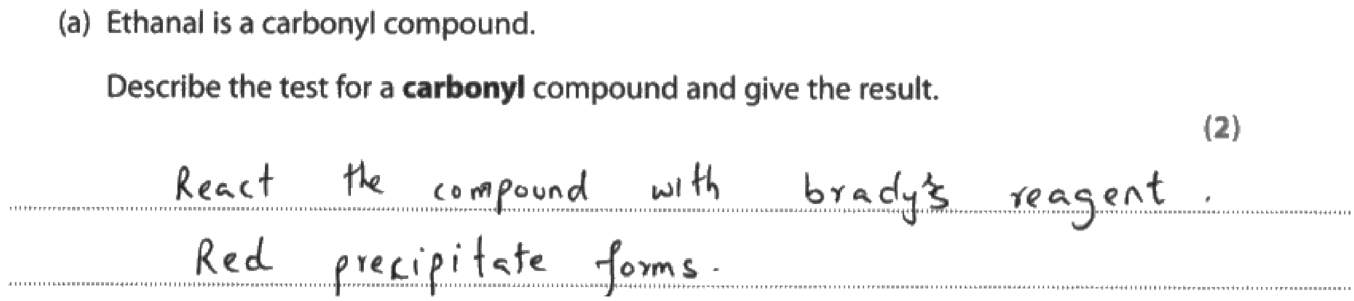
Despite the incorrect graph the candidate scored a mark for their explanation.

ResultsPlus
Examiner Tip

Consider the pH of the acid and alkali before you start to draw a pH curve for a titration. Consider the concentrations given in the question when you choose the volume at which neutralisation will occur.

Question 23 (a)

This question was answered well, with most candidates scoring full marks. A wide range of colours for the precipitate were seen and any in the yellow-orange-red part of the spectrum were accepted. Crystals and solid were allowed as alternatives to precipitate.



(a) Ethanal is a carbonyl compound.

Describe the test for a **carbonyl** compound and give the result.

(2)

React the compound with brady's reagent.

Red precipitate forms.

ResultsPlus
Examiner Comments

This response scores two marks.

ResultsPlus
Examiner Tip

Short sentences can show a clear understanding.

Fehling's solution.

~~Turns~~ Solution turns from blue to red brown.

ResultsPlus
Examiner Comments

This response does not gain credit as the candidate has not stated that a precipitate will form with the Fehling's solution. Only one mark was available for the use of Fehling's or Tollen's as the question emphasises that the test should work for all carbonyl compounds, not just aldehydes.

ResultsPlus
Examiner Tip

Include all observations in your answers, not just colour changes.

Question 23 (b)

This question did not cause any problems for most candidates. Many added the conditions "in dry ether" which was not required and was ignored (although aqueous solution would have negated the mark). Both names and formulae were seen. Some responses confused the numbers for aluminium and hydrogen in the formula which lost the mark, but phonetic spellings of the names were allowed.

(b) Identify, by name or formula, the reagent needed to carry out Reaction **A**.

(1)

$LiAlH_4$ in dry ether.

ResultsPlus
Examiner Comments

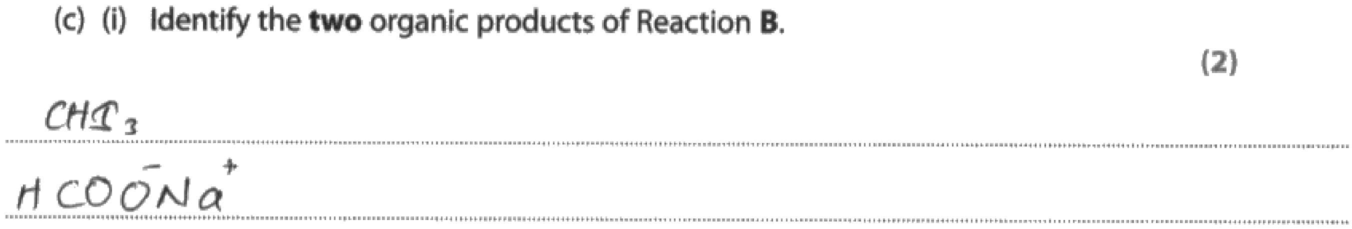
This response scored one mark.

ResultsPlus
Examiner Tip

Remember that incorrect conditions could negate your mark so check whether conditions are required in the question.

Question 23 (c) (i)

Most candidates gained one mark here. Common reasons failing to achieve the second mark included; giving sodium ethanoate instead of methanoate (or ethanoic acid instead of methanoic acid) and confusing the numbers of hydrogen and iodine atoms in iodoform. If names and formulae were given, then both had to be correct in order to earn the mark, however, very few candidates stated the names of the compounds.



(c) (i) Identify the **two** organic products of Reaction **B**.

(2)

CHI_3

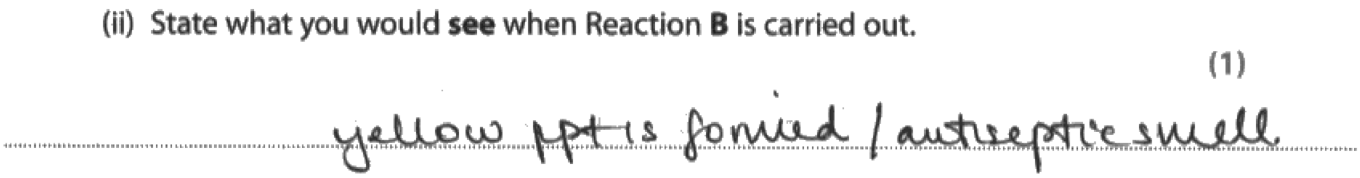
$HCO\overset{-}{O}Na^{+}$

ResultsPlus
Examiner Comments

This response scored both marks, the charges on the sodium methanoate were allowed.

Question 23 (c) (ii)

The majority of candidates gained a mark here with only a few forgetting that a precipitate was formed. A "yellow solution" did not gain credit. Occasionally, white precipitates was seen but not credited.



(ii) State what you would **see** when Reaction **B** is carried out.

(1)

yellow ppt is formed / antiseptic smell

ResultsPlus
Examiner Comments

This response gained a mark for the inclusion of yellow precipitate. The antiseptic smell is ignored.

ResultsPlus
Examiner Tip

Read the questions carefully, especially words in bold.

Question 23 (d) (i)

Over 70% of candidates achieved this mark with the most common incorrect response being "nucleophilic substitution". Phonetic spellings were allowed. Heterolytic was ignored but homolytic was rejected.

(d) (i) Name the reaction type and mechanism that occurs in Reaction **C**.

(1)

Nucleophilic ~~Substitution~~ Addition.

ResultsPlus
Examiner Comments

This candidate scored one mark after changing their mind.

ResultsPlus
Examiner Tip

Incorrect answers should be clearly crossed out when new responses are added

Question 23 (d) (ii)

Mechanisms were generally well drawn and understood and most candidates gained three marks.

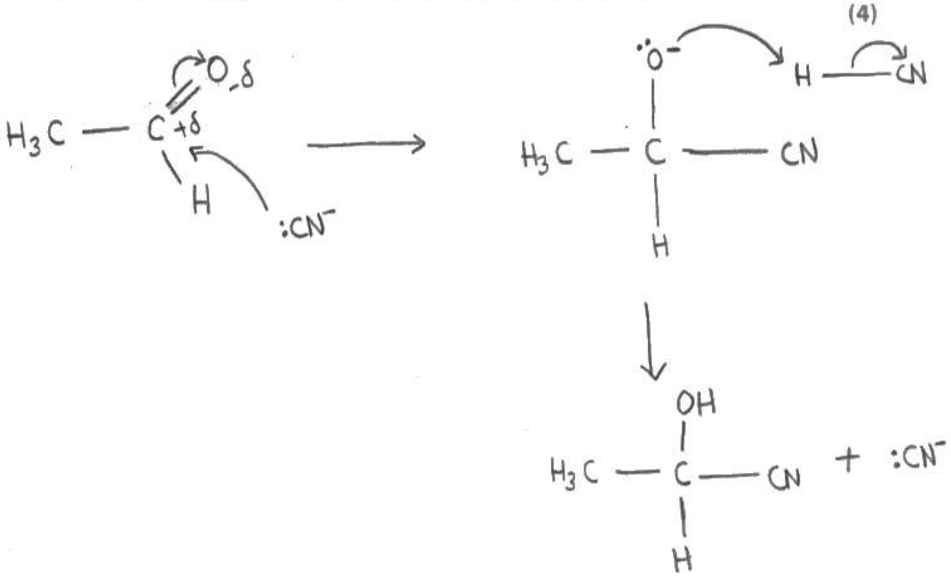
Common errors included:

- no charge on the cyanide ion
- forgetting the partial charges on the carbonyl carbon and oxygen
- putting a lone pair on the cyanide nitrogen instead of the carbon
- drawing a transition state intermediate with dashed bonds
- omitting the second arrow from the H—CN bond to the CN.

(ii) Draw the mechanism for Reaction **C**.

Include curly arrows, and all the relevant dipoles and lone pairs.

(4)



ResultsPlus
Examiner Comments

This response scored four marks, the +δ and –δ were allowed.

ResultsPlus
Examiner Tip

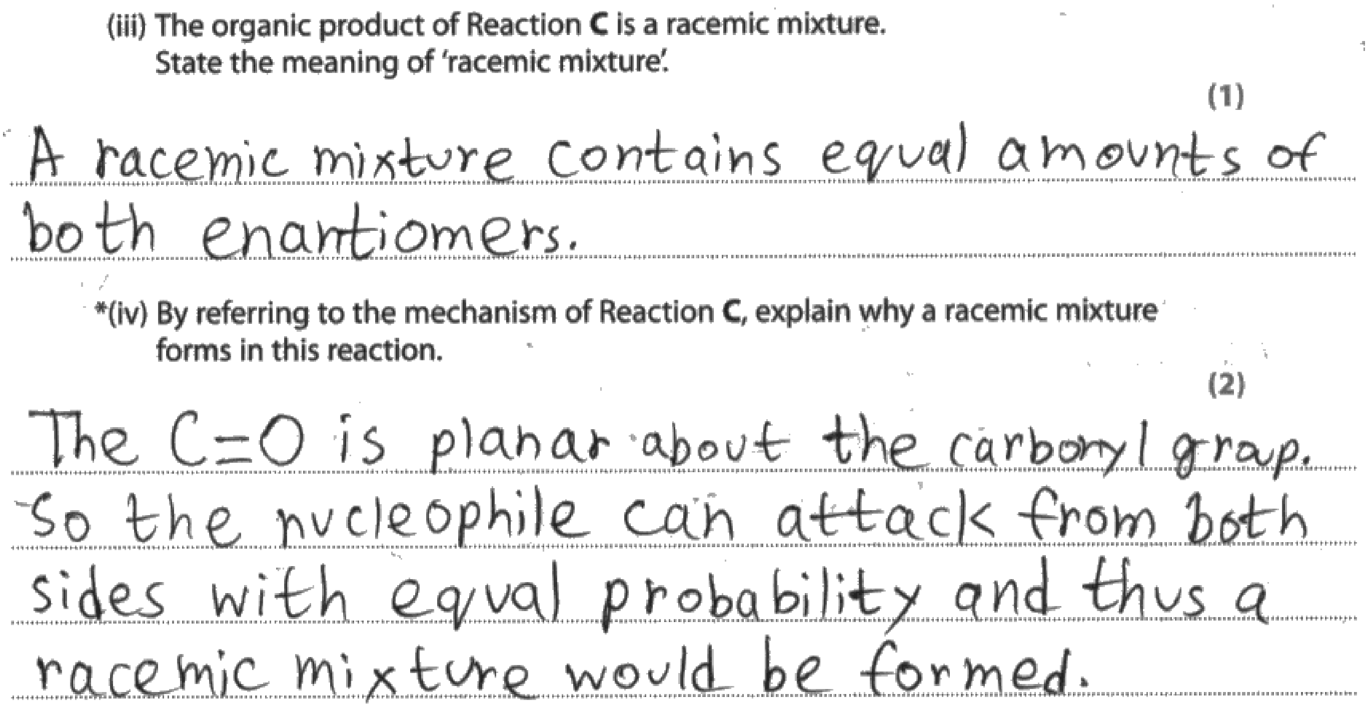
Drawing longer bonds on mechanisms gives you lots of space for annotations

Question 23 (d) (iii) - (iv)

The majority of candidates stated what a racemic mixture was but the explanation of the mechanism posed more of a challenge.

A variety of descriptors were allowed for part (iii) and these are given on the mark scheme. Some candidates chose to write about racemic mixtures not rotating plane polarised light which was unanticipated.

In Q23(d)(iv) the first mark was frequently lost for the statement "ethanal is a planar molecule". A variety of language options were deemed acceptable for the second mark, "above and below", "top and bottom", "from either side" or "from both sides" and "CN^-", "cyanide ion" or "nucleophile" but some candidates discussed the carbocation or intermediate being attacked rather than the aldehyde group which negated the mark.



(iii) The organic product of Reaction **C** is a racemic mixture.
State the meaning of 'racemic mixture'.

(1)

A racemic mixture contains equal amounts of both enantiomers.

*(iv) By referring to the mechanism of Reaction **C**, explain why a racemic mixture forms in this reaction.

(2)

The C=O is planar about the carbonyl group. So the nucleophile can attack from both sides with equal probability and thus a racemic mixture would be formed.

ResultsPlus
Examiner Comments

This is a great answer, gaining full marks in both parts.

The compound is planar about the carbonyl group, so the :CN⁻ has an equal chance to attack the carbocation from both sides, which forms equal amounts of two enantiomers.

ResultsPlus
Examiner Comments

Mentioning a carbocation which is not present in the mechanism does not score a mark.

ResultsPlus
Examiner Tip

Refer back to your mechanism if you are instructed to do so in the item.

(iii) The organic product of Reaction **C** is a racemic mixture.
State the meaning of 'racemic mixture'.

(1)

Racemic mixture is ~~the~~ an equimolar mixture of enantiomers which is optically active.

*(iv) By referring to the mechanism of Reaction **C**, explain why a racemic mixture forms in this reaction.

(2)

The reaction site is a trigonal planar structure and nucleophile CN^- ions attacks the ethanal equally from both above and below the plane producing equimolar enantiomers that rotate the plane of plane-polarised light in opposite directions and effect gets cancelled out.

(Total for Question 23 = 14 marks)

ResultsPlus
Examiner Comments

There are many ways to answer both parts of this item.

"Equimolar mixture of enantiomers" was fine here. The "optically active" was ignored, as it is not required by the question. It is not clear here if the candidate is referring to the enantiomer or the racemic mixture.

Here the candidate refers to the shape of the structure and the cyanide ion attacking from above and below. The candidate then unnecessarily clarifies the optical rotation of a racemic mixture.

ResultsPlus
Examiner Tip

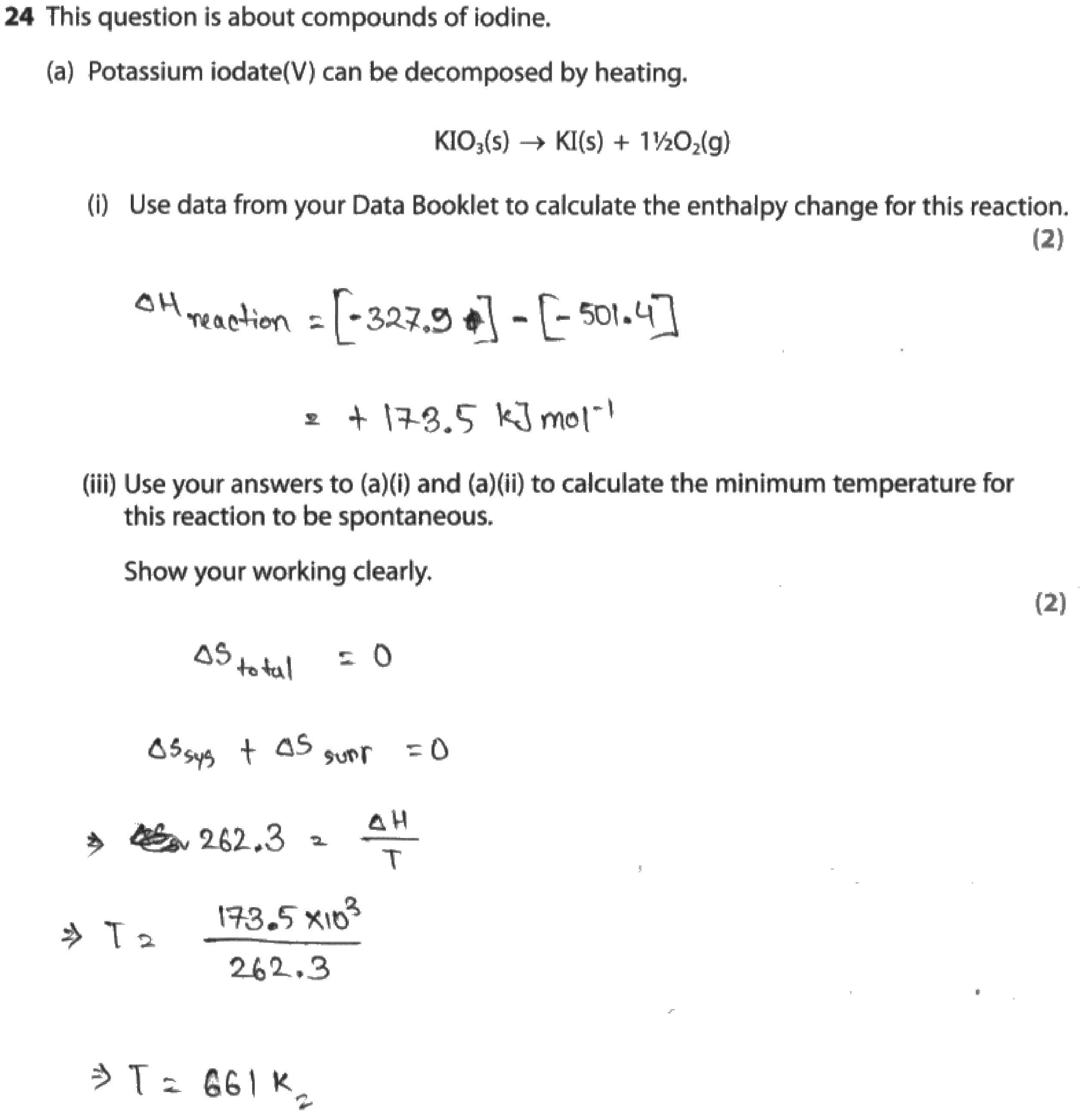
Do not add unnecessary details to your answers.

Question 24 (a) (i) - (iii)

Transfer errors were available here from both part (i) and part (ii) into part (iii). This allowed many candidates to gain credit and resulted in 4 being the mean mark.

In both part (i) and part (ii) credit was given for using the correct values from the data booklet and the vast majority of candidates transcribed these correctly to gain one mark in each part. The calculations proved trickier especially as each second mark could be lost for incorrect units. In part (ii) the most frequently seen incorrect answer was 57.3, when the entropy value for oxygen had not been multiplied by three.

In part (iii) a common error was to forget to multiply the ΔH found in part (i) by 1000 which led to some very low temperatures! Using or stating the principle gained a mark here which benefitted the less able candidates, some of whom ended up with minus temperatures in Kelvin.



24 This question is about compounds of iodine.

(a) Potassium iodate(V) can be decomposed by heating.

$$KIO_3(s) \rightarrow KI(s) + 1\tfrac{1}{2}O_2(g)$$

(i) Use data from your Data Booklet to calculate the enthalpy change for this reaction.

(2)

$\Delta H_{reaction} = [-327.9] - [-501.4]$

$= +173.5\ kJ\ mol^{-1}$

(iii) Use your answers to (a)(i) and (a)(ii) to calculate the minimum temperature for this reaction to be spontaneous.

Show your working clearly.

(2)

$\Delta S_{total} = 0$

$\Delta S_{sys} + \Delta S_{surr} = 0$

$\Rightarrow 262.3 = \frac{\Delta H}{T}$

$\Rightarrow T = \frac{173.5 \times 10^3}{262.3}$

$\Rightarrow T = 661\ K_2$

ResultsPlus
Examiner Comments

This response highlights a common mistake made by a more able candidate. They correctly calculated the enthalpy and entropy but then forgot to round up their answer to three significant figures when giving the temperature. As ΔG and/or ΔS_{total} would be positive.

ResultsPlus
Examiner Tip

Remember to round up answers if you are reducing the number of significant figures.

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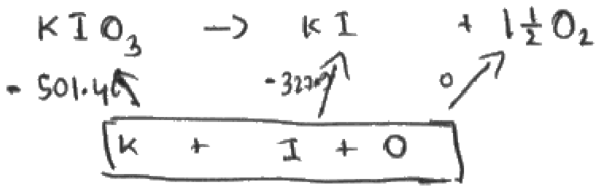


$\Delta H - 501.4 = -327.9 + 0$

$\Rightarrow \Delta H = -327.9 + 501.4$

$\therefore \Delta H = +173.5$ KJ mol^{-1}

(ii) Calculate the standard entropy change of the system, $\Delta S^{\ominus}_{system}$.

[The standard molar entropy of $\frac{1}{2}O_2(g)$ is 102.5 J mol^{-1} K^{-1}]

(2)

$\Delta S^{\ominus}_{system} = \Sigma p - \Sigma r$

$= 106.3 + (1.5 \times 102.5) - 151.5$

$= + 108.55$ J mol^{-1} K^{-1}

(iii) Use your answers to (a)(i) and (a)(ii) to calculate the minimum temperature for this reaction to be spontaneous.

Show your working clearly.

(2)

$$\Delta S^{\theta}_{\text{surrounding}} = -\frac{\Delta H}{T}$$

$$\Rightarrow \cancel{-}108.55 = \cancel{-}\frac{173.5 \times 1000}{T}$$

$$\Rightarrow \quad T = \frac{173.5 \times 1000}{108.55}$$

$$= 1598.3 \text{ k.}$$

ResultsPlus
Examiner Comments

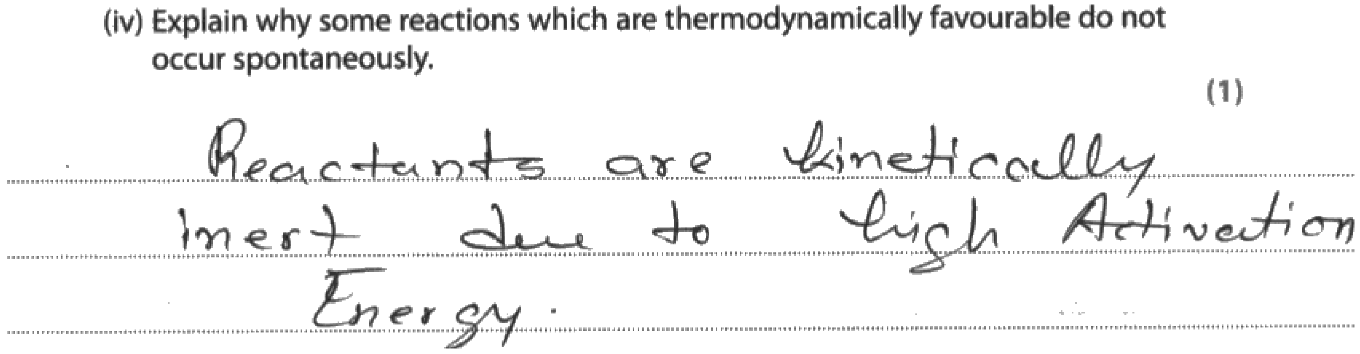
This response highlights how an incorrect calculation of entropy does not necessarily have to lead the loss of marks in the calculation in part (iii). This response only scores 1 in part (ii) but achieves all other available marks.

ResultsPlus
Examiner Tip

Follow through all calculations to the end, even if your answer seems wrong; you may gain some marks for your approach.

Question 24 (a) (iv)

Nearly two thirds of candidates achieved this mark. References to temperature were rejected without mention of activation energy.



(iv) Explain why some reactions which are thermodynamically favourable do not occur spontaneously.

(1)

Reactants are kinetically inert due to high Activation Energy.

ResultsPlus
Examiner Comments

This response scored a mark as the candidate continued on to mention activation energy. "Reactants are kinetically inert" alone would not have been sufficient for the mark.

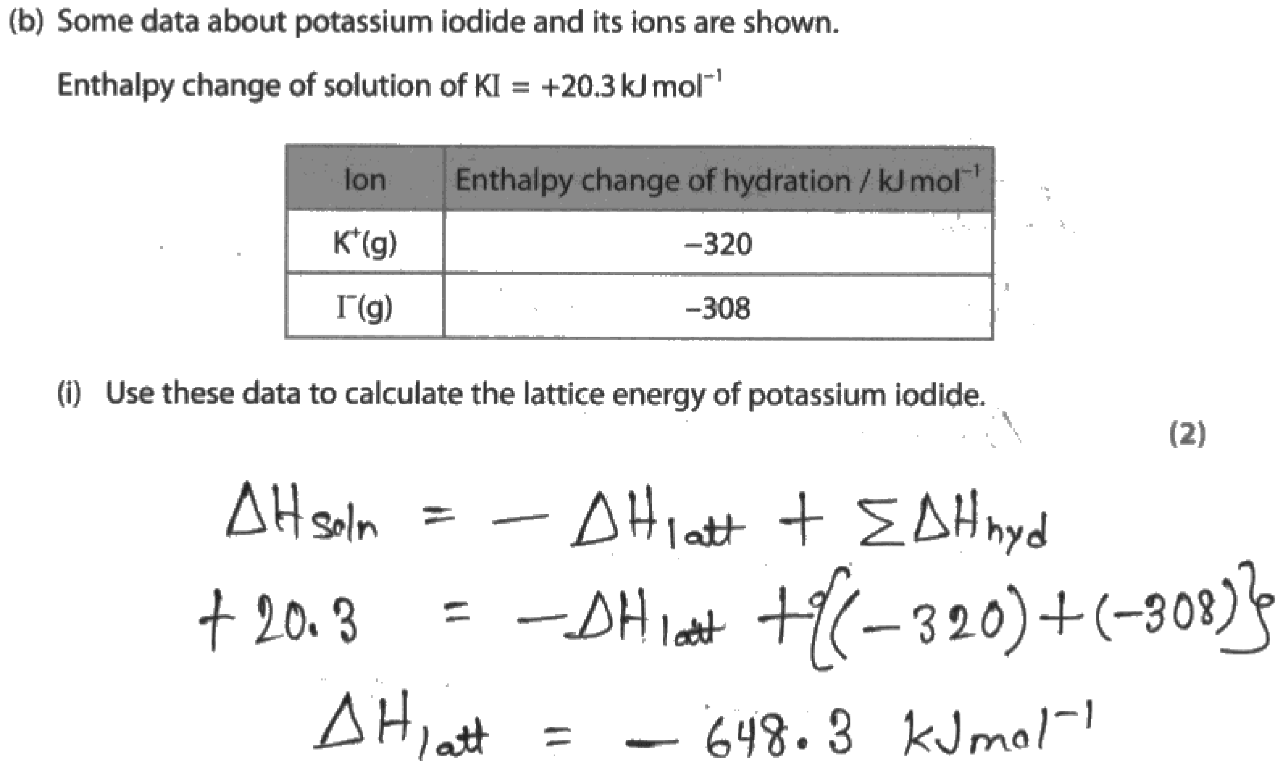
ResultsPlus
Examiner Tip

Fully explain your answers.

Question 24 (b) (i)

Many candidates showed limited working on this question but still scored both marks.

If no other mark was awarded then -608 or +648 could score 1.



(b) Some data about potassium iodide and its ions are shown.

Enthalpy change of solution of KI = +20.3 kJ mol^{-1}

Ion	Enthalpy change of hydration / kJ mol^{-1}
$K^+(g)$	−320
$I^-(g)$	−308

(i) Use these data to calculate the lattice energy of potassium iodide.

(2)

$$\Delta H_{soln} = -\Delta H_{latt} + \Sigma \Delta H_{hyd}$$

$$+20.3 = -\Delta H_{latt} + \{(-320) + (-308)\}$$

$$\Delta H_{latt} = -648.3 \text{ kJmol}^{-1}$$

ResultsPlus
Examiner Comments

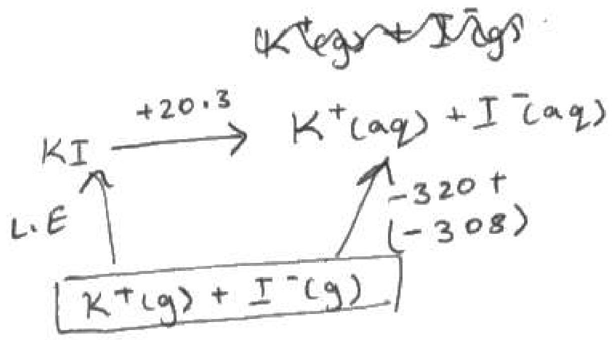
This candidate has written a correct equation for mark one and performed the calculation for mark two.

ResultsPlus
Examiner Tip

Showing all your working can help you get the sign for your answer correct.

(i) Use these data to calculate the lattice energy of potassium iodide.

(2)



$$L.E = -320 - 308 - 20.3$$

$$= -648.3 \text{ kJmol}^{-1}$$

ResultsPlus
Examiner Comments

This candidate has constructed a labelled cycle which gains mark one.

The calculation gives the correct answer for mark two.

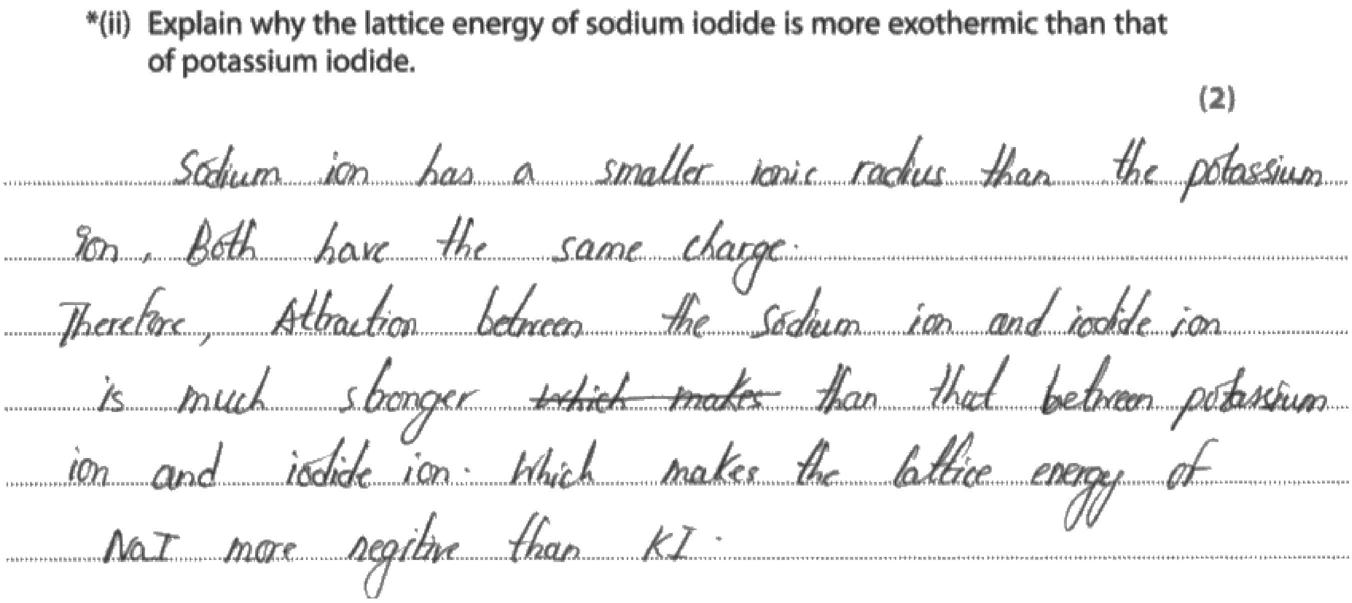
ResultsPlus
Examiner Tip

Drawing out energy cycles can help you construct your calculation

Question 24 (b) (ii)

Most candidates were able to state that the sodium ion is smaller than the potassium ion. Some candidates failed to gain mark two by describing endothermic reactions breaking the lattice or referring to the relative covalency of the compound.

A small number of candidates neglected to use the word "ion" (or give the formula) so could not gain any credit.



***(ii) Explain why the lattice energy of sodium iodide is more exothermic than that of potassium iodide.**

(2)

Sodium ion has a smaller ionic radius than the potassium ion. Both have the same charge.
Therefore, Attraction between the sodium ion and iodide ion is much stronger ~~which makes~~ than that between potassium ion and iodide ion. Which makes the lattice energy of NaI more negitive than KI.

ResultsPlus
Examiner Comments

This response scores full marks. The difference in the ionic radii is described for the first mark and the attraction between the pairs of ions is compared for the second mark.

ResultsPlus
Examiner Tip

Be careful when describing bonds breaking or forming in terms of energy being absorbed or released.

- K^+ has larger size and radius than that of Na^+.
- So, less energy is required to break the K-I bond.

ResultsPlus
Examiner Comments

This response highlights a common error; where the lattice breaking energy is discussed rather than the lattice energy.

ResultsPlus
Examiner Tip

Revise the definitions of the different terms for enthalpy cycles.

Question 25 (a) (iii)

Scores for this question were quite polarised, with many candidates scoring two or zero marks. Where candidates stated that the reaction was endothermic, they could still be awarded the second mark if they continued with their line of reasoning, however, this rarely occurred.

(iii) The value of K_p is greater when the reaction is carried out at a **lower** temperature.

Use this information to deduce the sign of $\Delta S_{surroundings}$ for the forward reaction.

Give your reasoning.

(2)

When temperature decreases, kp increases.

$Kp \propto \Delta S_{total}$

$\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding}$. ΔS_{system} is constant.

kp increases, so ΔS_{total} increases, so $\Delta S_{surrounding}$ increases.

So, $\Delta S_{surrounding}$ is positive. $\Delta S_{surrounding} = -\frac{\Delta H}{T}$

ResultsPlus

Examiner Comments

This response scored one as the candidate has not mentioned the sign for the enthalpy, the progress of the reaction, or stated that the reaction is exothermic. The fact that K_p increases is given in the question, therefore, information other than this must be required for the second mark to be awarded.

ResultsPlus

Examiner Tip

Don't waste time rewriting the question.

The reaction is exothermic, because when the temperature is reduced, the yield of CH_3OH is increased. $\Delta S_{surrounding} = -\frac{\Delta H}{T}$, So, $\Delta S_{surrounding}$ is positive.

ResultsPlus
Examiner Comments

This is an example of a perfect answer, scoring both marks.

ResultsPlus
Examiner Tip

Try to structure your answers to clearly explain your reasoning.

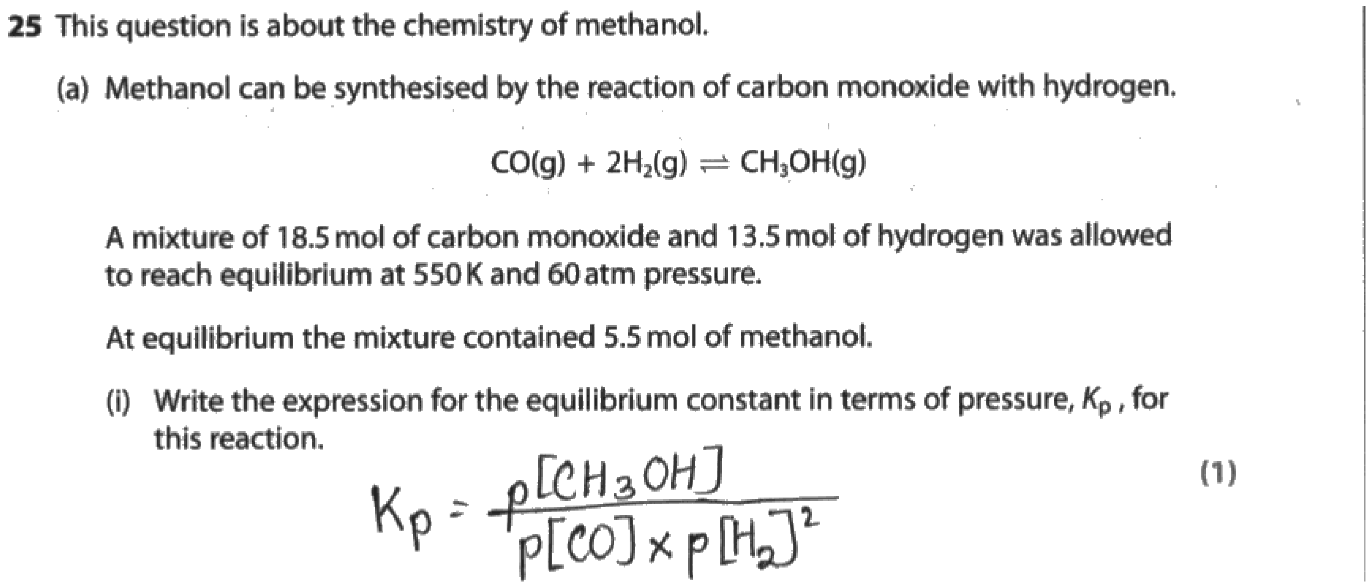
Question 25 (a) (i) - (ii)

The mean mark for this question was four out of the six available.

Most candidates could write the correct K_p expression and transfer errors on incorrect expressions were allowed in part (ii). Occasional upside-down expressions were seen but most marks for part (i) were lost by the use of square brackets.

Candidates who did not arrive at the correct final answer still usually scored three marks for part (ii) as transfer errors were allowed throughout. The most common error was in calculating the partial pressures; this was sometimes from incorrect moles at equilibrium, by dividing an incorrect number of total moles, or from finding the wrong total volume. The calculated partial pressures were usually substituted correctly into the K_p expression and a value was calculated. Some candidates expressed the units as $mol^2\ dm^6$, which did not gain the final mark.

Truncation of answers during intermediate steps was ignored except when 1SF was used. 8.30×10^{-3} was allowed as a final answer but not 8.3×10^{-3}. Some candidates ignored the instruction about significant figures and units.



25 This question is about the chemistry of methanol.

(a) Methanol can be synthesised by the reaction of carbon monoxide with hydrogen.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

A mixture of 18.5 mol of carbon monoxide and 13.5 mol of hydrogen was allowed to reach equilibrium at 550 K and 60 atm pressure.

At equilibrium the mixture contained 5.5 mol of methanol.

(i) Write the expression for the equilibrium constant in terms of pressure, K_p, for this reaction. **(1)**

$$K_p = \frac{p[CH_3OH]}{p[CO] \times p[H_2]^2}$$

ResultsPlus
Examiner Comments

This candidate does not gain credit for their K_p expression as they have used square brackets.

ResultsPlus
Examiner Tip

Practice writing out K_p expressions for different gaseous equilibria.

(i) Write the expression for the equilibrium constant in terms of pressure, K_p, for this reaction.

(1)

$$K_p = \frac{P_{CH_3OH(g)}}{P_{CO(g)} \times (P_{H_2})^2_{(g)}}$$

(ii) Calculate the number of mol of carbon monoxide and hydrogen remaining at equilibrium.

Hence calculate the value of K_p at 550 K.

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

(5)

	CO	H_2	CH_3OH
initially (mol)	18.5	13.5	0

mole no of CO unreacted at equilibrium $= 18.5 - 5.5 = 13$ mol

mole no. of H_2 unreacted at equilibrium $= 13.5 - (5.5 \times 2) = 2.5$ mol

$$K_c = \frac{\frac{5.5}{21} \times 60}{\left(\frac{13}{21} \times 60\right) \times \left(\frac{2.5}{21} \times 60\right)^2} = 8.29 \times 10^{-3}\ \text{atm}^{-2}$$

ResultsPlus
Examiner Comments

This candidate gained full credit for both parts.

"P"s, in all capitals or lower case, were accepted in the expression.

The candidate has the correct answer for part (ii) to three significant figures and has included the units.

ResultsPlus
Examiner Tip

Show all steps in your calculations.

Question 25 (b) (i) - (iv)

A variety of functional groups were stated for part (i) which then led to confusion when drawing the final structure. Similarly, those that chose their mass spectrometer peak in part (ii) as a propyl fragment found themselves in difficulty when it came to drawing the structure. C=O was a very common incorrect answer as a functional group; this was not allowed as the structure contained a ketone and not an aldehyde.

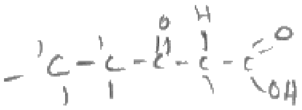
Some candidates gained credit for stating that there were four proton environments but continued to draw a structure with a different number of labelled proton environments. A correctly labelled diagram could gain all four marks for part (iii) as long as the splitting patterns were explained.

A transfer error was awarded from part (iii) to part (iv) so the corresponding acid to the drawn structure could gain credit. The main reason for a loss of marks here was due to candidates neglecting to balance the equation with a molecule of water.

The mean mark for this question was five out of the nine available.

(b) An organic compound, **P**, has the molecular formula $C_5H_8O_3$.

A molecule of **P** has a carbon chain that is **not** branched, and contains **two** different functional groups.

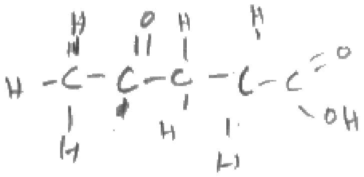


(i) **P** reacts with sodium carbonate solution, forming bubbles of a colourless gas. There is no colour change when **P** is warmed with a mixture of potassium dichromate(VI) and sulfuric acid.

Use all the information provided to identify, by name or formulae, the **two** functional groups present in **P**.

(2)

Ketone and carboxylic acid.



(ii) The mass spectrum of **P** has a strong peak at *m* / *e* = 43.

Suggest the structural formula of the fragment causing this peak.

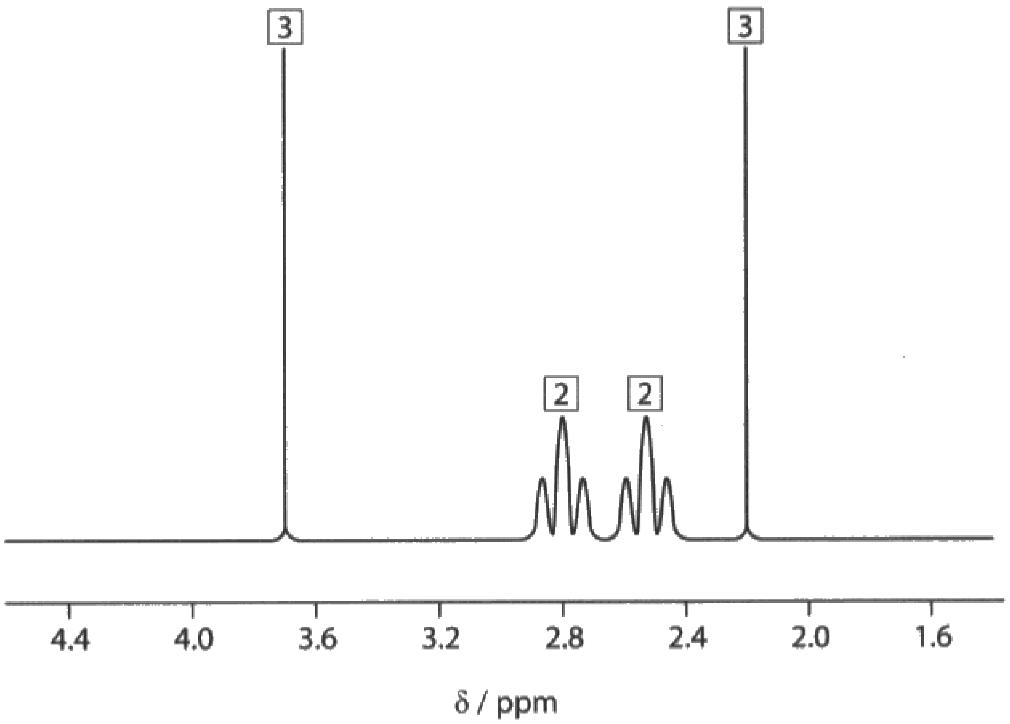
(1)

$CH_3C{=}O^+$

*(iii) When **P** is heated with methanol, in the presence of dilute sulfuric acid, a pleasant smelling compound, **Q**, is formed.

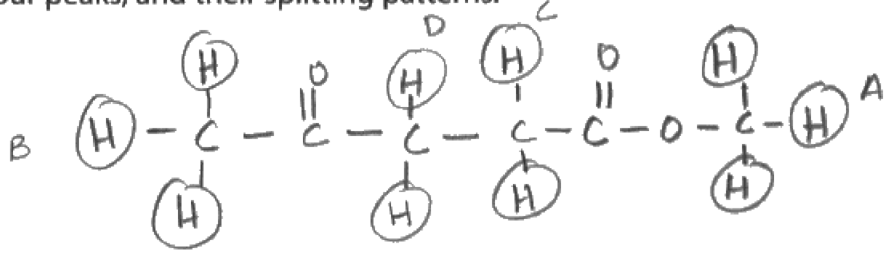
The **high resolution** proton nmr spectrum of **Q** is shown.

The numbers show the relative areas of the peaks.



Draw the structure of **Q**. Justify your answer by considering the relative areas of the four peaks, and their splitting patterns.

(4)



Here, due to peak A, there will be a singlet since no adjacent carbon is present. Area B will also give a singlet since the adjacent carbon has no hydrogen. Area C and Area D will give a triplet ~~since~~ since both the carbon atoms are attached to ~~ado~~ adjacent carbon atom containing two hydrogen atoms. The splitting ~~patten~~ pattern will follow (n+1) rule.

ResultsPlus
Examiner Comments

This response gained full marks for all sections.

The functional groups are correctly identified.

The mass spectrometer fragment is worthy of credit.

In part (iii) the structure has been correctly drawn and labelled to justify the reasoning.

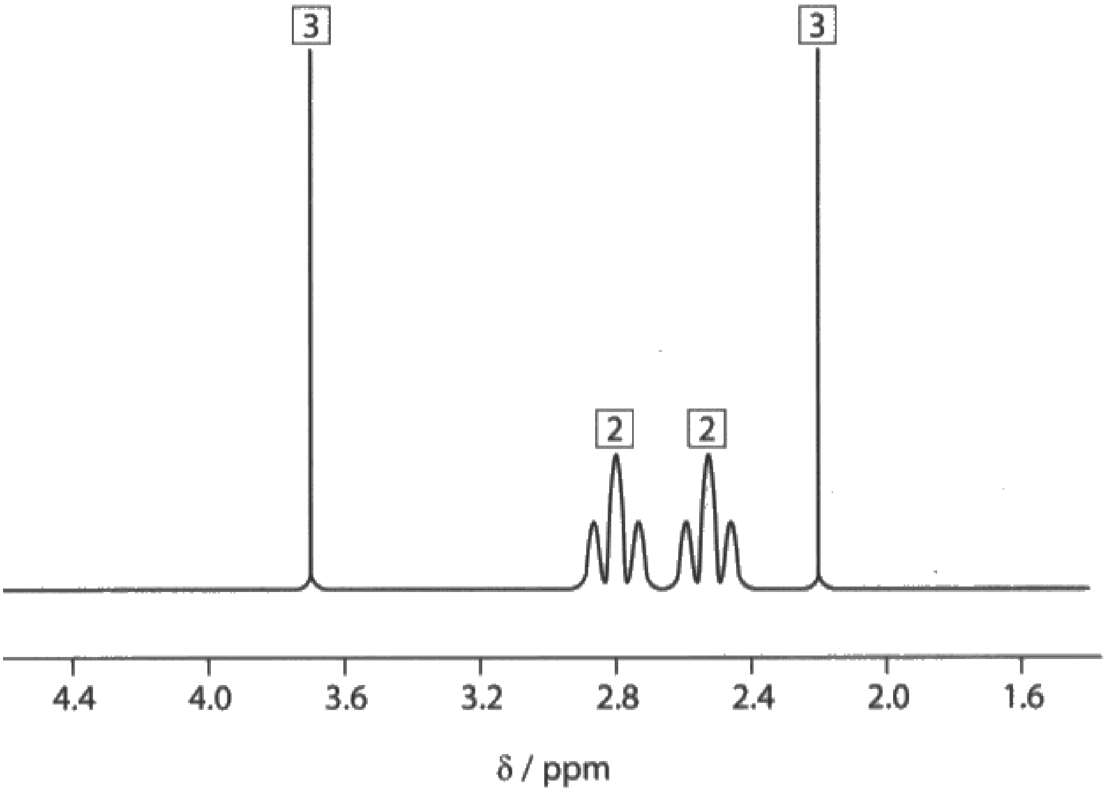
ResultsPlus
Examiner Tip

Labelling diagrams is a great way to show your understanding.

*(iii) When **P** is heated with methanol, in the presence of dilute sulfuric acid, a pleasant smelling compound, **Q**, is formed.

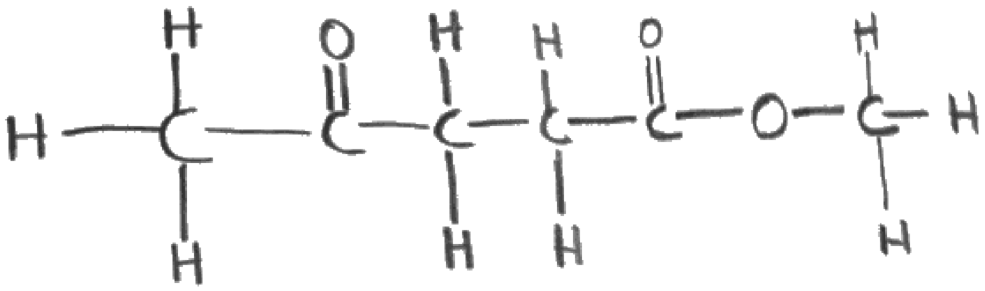
The **high resolution** proton nmr spectrum of **Q** is shown.

The numbers show the relative areas of the peaks.



Draw the structure of **Q**. Justify your answer by considering the relative areas of the four peaks, and their splitting patterns.

(4)



There are four different proton environments. Structure of Q contains two singlets and two triplets. Relative areas under the peak of Q have ratio 3:2:2:3.

(iv) Write an equation using structural formulae to show the reaction of **P** with methanol in the presence of dilute sulfuric acid to form **Q**.

(2)

$CH_3COCH_2CH_2COOH + CH_3OH \longrightarrow CH_3COCH_2CH_2COOCH_3 + H_2O$

ResultsPlus
Examiner Comments

This response achieved two marks on part (iii). The structure is correct and the candidate has identified that there are four proton environments but there is no attempt to consider the splitting patterns either by annotation of the structure or in prose.

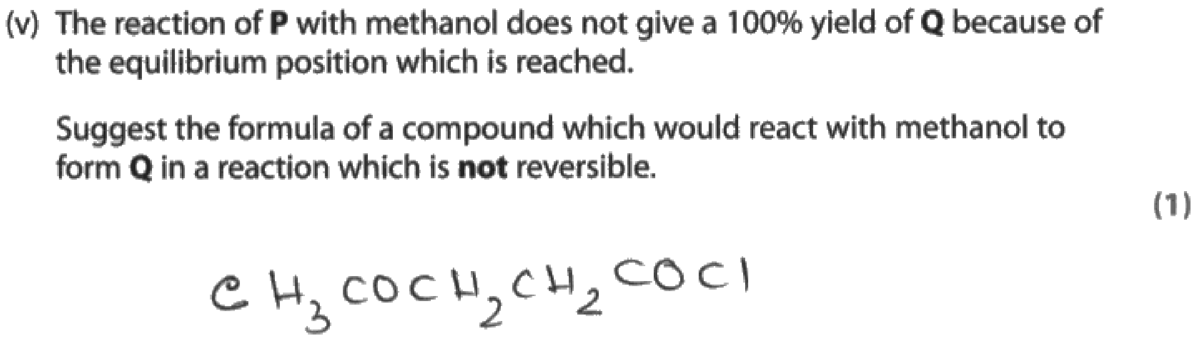
The response to part (iv) gains both marks. The acid given is consistent with the structure given in part (iii) and the equation has been balanced.

ResultsPlus
Examiner Tip

Always check your equations are balanced

Question 25 (b) (v)

Any acyl chloride was credited here, whether it was written as a name, displayed or illustrated as skeletal formulae. Molecular formulae were ignored as they do not allow the structure to be seen. There were a few answers in which candidates had drawn an acid or had written the functional group as —COOCl.



(v) The reaction of **P** with methanol does not give a 100% yield of **Q** because of the equilibrium position which is reached.

Suggest the formula of a compound which would react with methanol to form **Q** in a reaction which is **not** reversible.

(1)

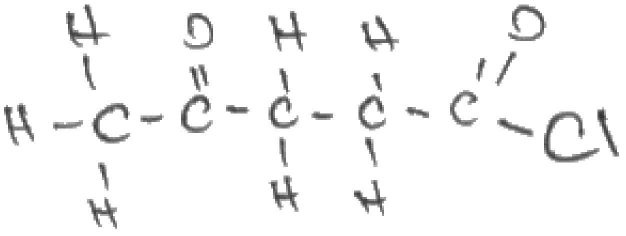
$CH_3COCH_2CH_2COCl$

ResultsPlus
Examiner Comments

This response scored one as a shortened structural formula is enough to show the acyl chloride.

ResultsPlus
Examiner Tip

Practice drawing organic molecules using different types of formulae and structures.



Examiner Comments

This response scored one as the candidate has drawn the formula of an acyl chloride. This matches the structure asked for earlier in the question but the system used for marking meant that examiners could not see the items above so any acyl chloride was accepted.

Examiner Tip

Do not give a molecular formula unless this is specifically requested.

Paper Summary

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

- read the questions carefully, underlining or highlighting key words. Use this to successfully structure answers
- record answers for calculations to appropriate numbers of significant figures, using values stated in the question as a guide
- always give units with the answer
- practise deducing and explaining the orders of reactions from rates data
- practise sketching the pH titration curves for different concentrations and types of acids and alkalis and use the data booklet to choose appropriate indicators
- practise explaining splitting patterns for different organic molecules and be able to predict the observations for molecules in different chemical tests.

Grade Boundaries

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