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Examiners' Report
January 2011

GCE Chemistry 4 6CH04 01

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Introduction

It was pleasing to see many scripts of a very good standard. Nearly all candidates completed the paper, with many writing extensively on the final question. However, the paper did prove to be long and demanding for a proportion of the candidates who clearly were under time pressure. Some answers were difficult to follow, and candidates need practice in expressing clear, legible and well-reasoned arguments, which are focussed on the question so that time spent on them is not wasted.

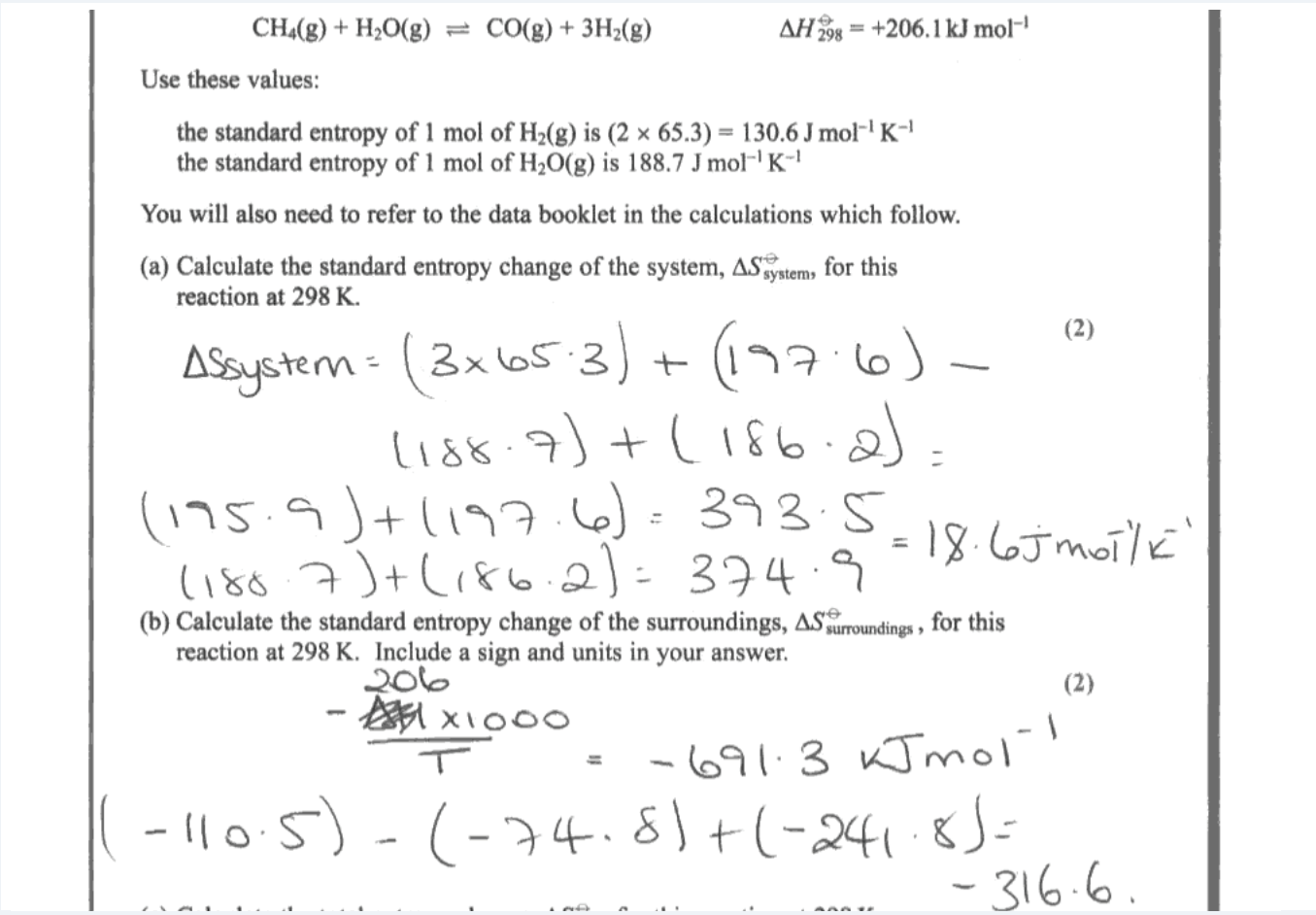
This paper involves selecting data from the data booklet, and familiarity with using this booklet would also help to save time in the examination.

Questions involving calculations were well done, but knowledge of organic reactions was less good, and the reasons for carrying out a rate experiment in a particular way were poorly understood.

Question 17(a-c)

It appears only a tiny minority of candidates did not have a data booklet, and most found the correct data for (a), though a few used enthalpy values, or added the values for the individual elements in each compound. The relationship between the entropy change in the surroundings and enthalpy was well known, but common errors were to miss the negative sign or the units in the answer.

In (c) a few candidates subtracted the values in (a) and (b) to find the total entropy change instead of adding them, and those who added the entropy values based on joules in (a) to the value based on kilojoules in (b) did not get the first mark. It was well known that the reaction was not spontaneous because the value of the total entropy change was negative.



$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$ $\Delta H^{\ominus}_{298} = +206.1\,kJ\,mol^{-1}$

Use these values:

the standard entropy of 1 mol of $H_2(g)$ is $(2 \times 65.3) = 130.6\,J\,mol^{-1}\,K^{-1}$
the standard entropy of 1 mol of $H_2O(g)$ is $188.7\,J\,mol^{-1}\,K^{-1}$

You will also need to refer to the data booklet in the calculations which follow.

(a) Calculate the standard entropy change of the system, $\Delta S^{\ominus}_{system}$, for this reaction at 298 K.

(2)

ΔSsystem = (3x65·3) + (197·6) −
(188·7) + (186·2) =
(195·9) + (197·6) = 393·5 = 18·6 J mol⁻¹ K⁻¹
(188·7) + (186·2) = 374·9

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

(2)

$-\frac{206}{T} \times 1000 = -691.3\ kJ\,mol^{-1}$

(−110·5) − (−74·8) + (−241·8) =
−316·6.

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

Explain why this value shows that the reaction is not spontaneous at this temperature.

(2)

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

$\Delta S_{total} = (374.9) + (-316.6) = +58.3$ kJ mol^{-1} K^{-1}

As the reaction is endothermic, and is kinetically stable at room temperature.

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Examiner Comments

In (a) the correct data has been found scoring the first mark but the calculation is incorrect. The enthalpy change should not be rounded in (b) before doing the calculation, and the units are incorrect. Then a second incorrect calculation follows, which would disallow the mark if the first calculation had scored it.

In (c) values stated to be in kilojoules should not be added to values in joules. The final explanation does not answer the question as it does not refer to the value of the total entropy change.

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Examiner Tip

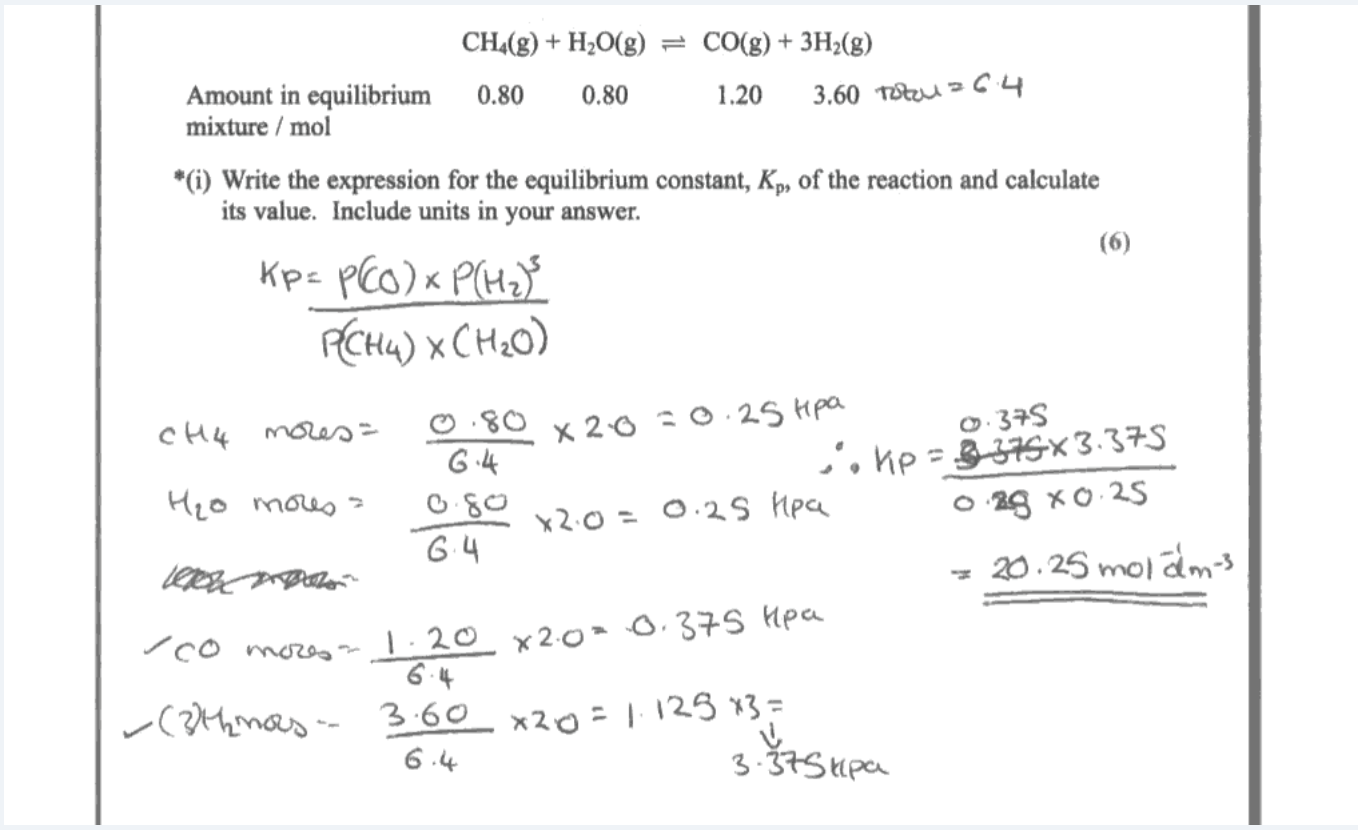
Enthaply changes are usually quoted in kJ mol^{-1} and entropy changes are usually in Jmol-1K^{-1}. Values must be converted to the same units before adding them.

Question 17(d)(i-iii)

This unstructured calculation was very well done.

Only a few candidates treated it as a K_c calculation. Some included square brackets when writing the expression for K_p but then calculated partial pressures correctly. The most common errors were in calculating the total number of moles present, and in dealing with the three hydrogen molecules by multiplying partial pressure by three instead of cubing it. There were also some errors in rounding values of mole fractions and in deducing the units. Calculating the total entropy change in (d)(ii) was a simple exercise, but rearranging the equation to find the temperature in (d)(iii) was more difficult.

A significant number of candidates did not convert the enthalpy change to joules here and got an answer of about 1K. Attention to detail would have suggested that this was wrong, and that a factor of 1000 was missing somewhere.



$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

Amount in equilibrium mixture / mol	0.80	0.80	1.20	3.60	total = 6.4

*(i) Write the expression for the equilibrium constant, K_p, of the reaction and calculate its value. Include units in your answer.

(6)

$$K_p = \frac{p(CO) \times p(H_2)^3}{p(CH_4) \times (H_2O)}$$

CH_4 moles $= \frac{0.80}{6.4} \times 2.0 = 0.25$ kPa

H_2O moles $= \frac{0.80}{6.4} \times 2.0 = 0.25$ kPa

CO moles $= \frac{1.20}{6.4} \times 2.0 = 0.375$ kPa

(3)H_2 moles $= \frac{3.60}{6.4} \times 2.0 = 1.125 \times 3 =$ 3.375 kPa

$\therefore K_p = \frac{0.375 \times 3.375}{0.25 \times 0.25}$

$= 20.25$ mol^{-2} dm^{-3}

(ii) The total entropy change in J mol^{-1} K^{-1} is related to the equilibrium constant by the equation

$$\Delta S^{\ominus}_{total} = R \ln K_p \quad \text{or} \quad \Delta S^{\ominus}_{total} = 2.3R \log K_p$$

Calculate the total entropy change at the temperature of the reaction.

[R = 8.31 J mol^{-1} K^{-1}]

(1)

$2.5 \times 8.31 \log(20.25) =$ ~~220~~ 24.96970155

$+ 25$ J mol^{-1} K^{-1}

(iii) Calculate the temperature at which this equilibrium is reached using your answer to (ii) for $\Delta S^{\ominus}_{total}$. Assume that ΔH is still +206.1 kJ mol^{-1} and that $\Delta S^{\ominus}_{system}$ = +225 J K^{-1} mol^{-1}. (This is not the same as the value for $\Delta S^{\ominus}_{system}$ calculated in (a) which is at 298 K.)

(2)

$\Delta S_{system}^{\ominus} = +225$ $-\Delta H = +206.1$

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Examiner Comments

This candidate did not know how to find the partial pressure of the hydrogen as there were three moles of it. The total number of moles is correct and the use of the total pressure is also correct. The units of the equilibrium constant are wrong. The value of the total entropy change follows from (i), but having calculated this, the entropy change of the surroundings should have been calculated in (iii) and hence the temperature of the reaction.

$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

Amount in equilibrium mixture / mol	0.80	0.80	1.20	3.60

*(i) Write the expression for the equilibrium constant, K_p, of the reaction and calculate its value. Include units in your answer. (6)

$$K_p = \frac{P(CO)P(H_2)^3}{P(CH_4)P(H_2O)}$$

$CH_4 + H_2O \rightleftharpoons CO + 3H_2O$

equilib moles: 0.8 0.8 1.2 3.6

0.8+0.8 +1.2+3.6 = 6.4

mole fraction: $\frac{0.8}{6.4}$ $\frac{0.8}{6.4}$ $\frac{1.2}{6.4}$ $\frac{3.6}{6.4}$

= 0.125 0.125 0.1875 0.5625

(2atm) ÷ 2: = 0.0625 0.0625 0.09375 0.28125

$$K_p = \frac{0.09375 \times (0.28125)^3}{0.0625 \times 0.0625}$$

$= 0.53393 = 0.534 \text{ atm}^2$

(ii) The total entropy change in J mol^{-1} K^{-1} is related to the equilibrium constant by the equation

$\Delta S^{\ominus}_{total} = R \ln K_p$ or $\Delta S^{\ominus}_{total} = 2.3R \log K_p$

Calculate the total entropy change at the temperature of the reaction.

[$R = 8.31$ J mol^{-1} K^{-1}] (1)

$\Delta S^{\ominus}_{total} = -R \ln K_p$

$= 8.31 \ln(0.534)$

$= -5.21 \text{ J mol}^{-1}$

(iii) Calculate the temperature at which this equilibrium is reached using your answer to (ii) for $\Delta S^{\ominus}_{total}$. Assume that ΔH is still +206.1 kJ mol^{-1} and that $\Delta S^{\ominus}_{system}$ = +225 J K^{-1} mol^{-1}. (This is not the same as the value for $\Delta S^{\ominus}_{system}$ calculated in (a) which is at 298 K.)

(2)

$\Delta S^{\ominus}_{total} = \Delta S^{\ominus}_{system} + \Delta S^{\ominus}_{surr}$

$-5.21 = 225 + -\frac{\Delta H}{T}$

$-5.21 = 225 - \frac{206.1 \times 10^3}{T}$

$-230.21 = -\frac{206.1 \times 10^3}{T}$

$T = \frac{206.1 \times 10^3}{230.21}$

$T = 895.27\text{K}$

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Examiner Comments

This answer made errors in (i) and (ii), calculating the total entropy change as -5.21, but earns full marks in (iii) by using the value correctly.

Question 17(e)

*(e) Use the magnitude and signs of the entropy changes to explain the effect of a temperature increase on the equilibrium constant of this endothermic reaction.

(2)

ΔH is positive for the endothermic reaction. $\Delta S^{\ominus}_{total}$ is negative so reaction is not spontaneous at 298K. $\Delta S^{\ominus}_{system}$ is positive and $\Delta S^{\ominus}_{surr}$ is negative. An increase in temperature causes $\Delta S^{\ominus}_{surr}$ to become less negative causing the value of $\Delta S^{\ominus}_{total}$ to increase. The value of the equilibrium constant Kp increases with an increase in temperature of an endothermic reaction.

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Examiner Comments

This scores the first mark, though the candidate could have saved time by starting the answer on the fourth line. The total entropy change is not linked to the equilibrium constant for the second mark.

*(e) Use the magnitude and signs of the entropy changes to explain the effect of a temperature increase on the equilibrium constant of this endothermic reaction.

(2)

Because the reaction is endothermic an increase in temperature would shift the equilibrium to the right which would cause more product to be formed. Because the entropy change is very negative this effect will be quite large and because there is more product formed Kp will increase as there will be a larger number on the top of the equation.

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Examiner Comments

This answer does not explain the effect of temperature increase on the entropy change, or the relationship of total entropy change and equilibrium constant, so scores no marks.

Question 18(a)

The calculation of the pH of a strong acid was straightforward for most candidiates.

Question 18(b-c)

The calculations were well done in this question. In (b)(i) a few answers gave the approximation for K_a but the complete expression was required. There were occasional errors in the chemical equation in (c)(i) such as missing oxygen atoms. Many calculations in (c)(ii) were correct, the main error being a lack of understanding that in a mixture of an acid and a base the concentration of H^+ ions is not equal to the concentration of the ions from the salt. Only a few candidates used the log method in their calculation.

In (c)(iii) most candidates realised that a buffer had formed. However many referred to hydroxide ions combining with propanoate ions, or even with sodium ions. Others said there was a large reservoir of hydrogen ions which neutralised the added alkali. It was also common to say, correctly, that hydroxide ions combine with hydrogen ions, but then continue to say that "the equilibrium then moves to the right" without specifying that the equilibrium in question was the dissociation of propanoic acid.

The titration curves in (c)(iv) were usually close to the correct shape with a vertical section at 25 cm^3. However, many looked more like curves from the titration of a strong acid with a strong base, as the vertical section was much too long, and others looked like weak acid/ weak base curves.

The comment made about bromocresol green in (c)(v) had to be consistent with the curve drawn. Although candidates appeared able to locate the correct data concerning bromocresol green some omitted to state this data. Others failed to give an appropriate reason why it was an unsuitable indicator, referring to equivalence without stating that the indicator range must coincide with the region where the pH of the titration curve changes sharply.

A very large number of candidates used the term "equivalence point" when they probably meant the vertical section of the graph. A common misunderstanding was that the mid-range of the indicator must coincide with the equivalence point. This would mean that, for example, phenolphthalein could not be used in strong acid / strong base titration because its pK_{in} of about 9 is very different from the pH at the endpoint, 7. Also the equivalence point of a weak acid / weak base titration cannot be detected with an indicator whose range includes the value because there is no sharp change in pH at this point. The question could also have been answered in terms of pK_{in} values, though very few candidates did it this way.

(b) Propanoic acid, CH_3CH_2COOH, is a weak acid with $K_a = 1.3 \times 10^{-5}$ mol dm^{-3} at 25 °C.

(i) Write the expression for K_a for propanoic acid.

(1)

$$K_a = \frac{[CH_3CH_2COO^-][H^+]}{[CH_3CH_2COOH]}$$

(ii) Calculate the pH of 0.25 mol dm^{-3} propanoic acid at 25 °C.

(2)

$$(1.3 \times 10^{-5}) = \frac{0.25\,[H^+]}{0.25}$$

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

$$-\log(1.3 \times 10^{-5}) = 4.9$$

(c) During a titration, 10 cm^3 0.10 mol dm^{-3} sodium hydroxide was added to 10 cm^3 of 0.25 mol dm^{-3} propanoic acid.

(i) Write an equation for the reaction which occurs. State symbols are **not** required.

(1)

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

7H 7H

(ii) At this point the titration mixture contains 1.5×10^{-3} moles of propanoic acid and 1.0×10^{-3} moles of propanoate ion.

Use your expression for K_a for propanoic acid to calculate the pH of the mixture.

(2)

$$(1.3 \times 10)\,K_a = \frac{(1.0 \times 10^{-3})\,[H^+]}{(1.5 \times 10^{-3})}$$

$$\frac{(1.5 \times 10^{-3})(1.3 \times 10^{-5})}{(1 \times 10^{-3})} = [H^+]$$

$$-\log(1.95 \times 10^{-5}) = 4.71$$

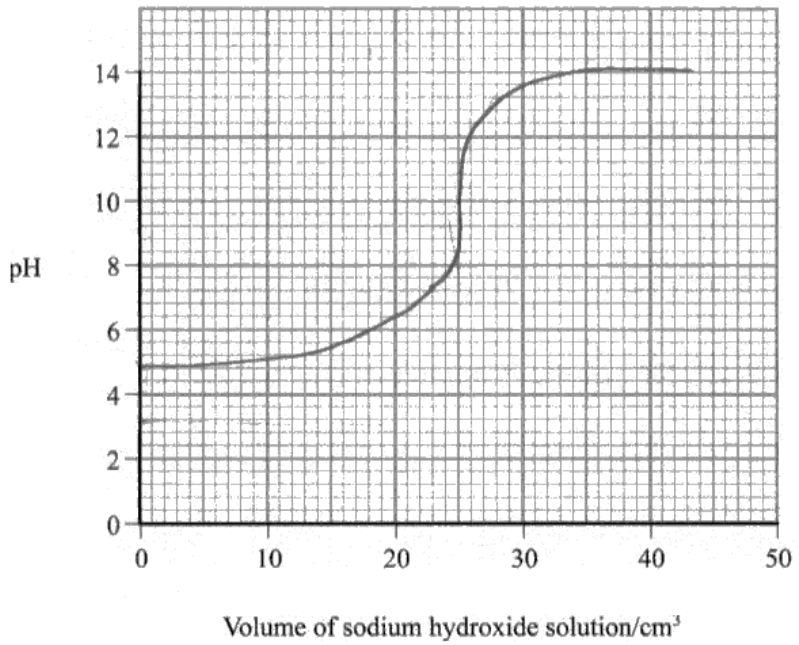
*(iii) When a further small amount of 0.10 mol dm^{-3} sodium hydroxide is added in the titration, the pH changes very little. Explain why the pH change is small.

(3)

The solution formed is a weak acid and one of its salts, so the solution acts as a buffer solution, and will resist changes in pH due to large pools of the acid, and its salt. adding more OH^- ions simply would cause the salt to dissociate to form more H^+ ions.

(iv) Draw the titration curve showing the change in pH when 0.10 mol dm^{-3} sodium hydroxide is added to 10 cm^3 of 0.25 mol dm^{-3} propanoic acid until present in excess. The equivalence point is 25 cm^3.

(3)



(v) Explain, referring to your data booklet, whether bromocresol green would be a suitable indicator for this titration.

(2)

because the indicator covers a wide change on the curve, which includes equivalence point on the curve, this will show a clear change when the titration is complete

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Examiner Comments

(b)(ii) is incorrect as the concentration of propanoate does not equal the concentration of propanoic acid. The equation in (c)(i) has errors in the formulae due to missing C atoms. (c)(ii) is correct. In (c)(iii) the hydroxide ions are said to cause the salt to ionize more which is incorrect though the other two marks were scored. The finishing point on the pH curve is too high, though the starting point follows on from the earlier error. The range of bromocresol green is not given, and it would change colour before the vertical section of the curve which was drawn.

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Examiner Tip

It is useful to learn where the pH changes sharply in titrations of acids and bases of different strengths.

(b) Propanoic acid, CH_3CH_2COOH, is a weak acid with $K_a = 1.3 \times 10^{-5}$ mol dm^{-3} at 25 °C.

(i) Write the expression for K_a for propanoic acid.

(1)

$$K_a = \frac{[CH_3CH_2COO^-][H^+]}{[CH_3CH_2COOH]}$$

(ii) Calculate the pH of 0.25 mol dm^{-3} propanoic acid at 25 °C.

(2)

$$1.3 \times 10^{-5} = \frac{[H^+]^2}{0.25}$$

$$[H^+] = 1.8 \times 10^{-3}$$

$$\rightarrow pH = 2.7$$

(c) During a titration, 10 cm^3 0.10 mol dm^{-3} sodium hydroxide was added to 10 cm^3 of 0.25 mol dm^{-3} propanoic acid.

(i) Write an equation for the reaction which occurs. State symbols are **not** required.

(1)

$$CH_3CH_2COOH + NaOH \longrightarrow CH_3CH_2COO^-Na^+ + H_2O$$

(ii) At this point the titration mixture contains 1.5×10^{-3} moles of propanoic acid and 1.0×10^{-3} moles of propanoate ion.

Use your expression for K_a for propanoic acid to calculate the pH of the mixture.

(2)

$$[H^+] = \frac{K_a \times [CH_3CH_2COOH]}{[CH_3CH_2COO^-]}$$

$$= \frac{1.3 \times 10^{-5} \times 1.5 \times 10^{-3}}{1.0 \times 10^{-3}} = 1.95 \times 10^{-5}$$

$$pH = 4.7$$

*(iii) When a further small amount of 0.10 mol dm^{-3} sodium hydroxide is added in the titration, the pH changes very little. Explain why the pH change is small.

(3)

- Because, there is a buffer solution formed of propanoic acid and its conjugate base.
- adding NaOH is adding OH^-, the OH^- reacts.

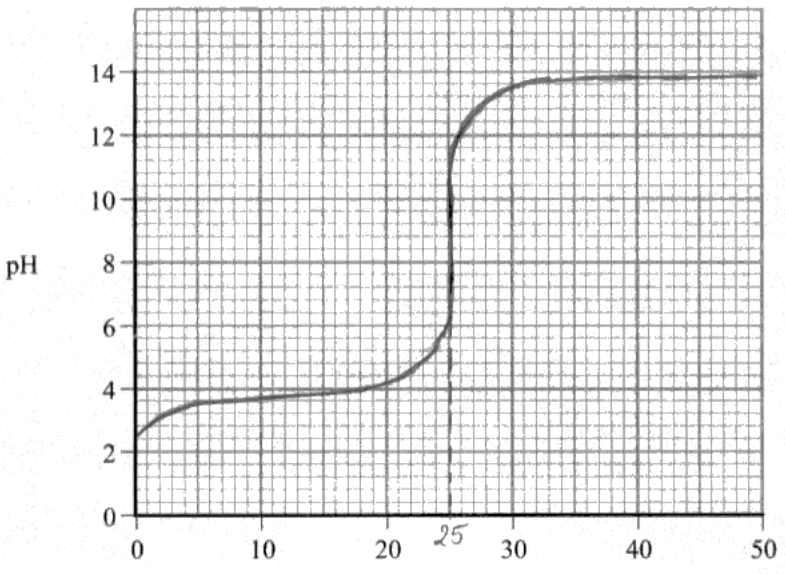
$$CH_3CH_2COOH + OH^- \longrightarrow CH_3CH_2COO^- + H_2O$$

resist the pH change, the ratio $\frac{[CH_3CH_2COOH]}{[CH_3CH_2COO^-]}$ does not change much.

- there are large ~~ns~~ amount of both propanoic acid and ~~propano~~ sodium propanoate.

(iv) Draw the titration curve showing the change in pH when 0.10 mol dm^{-3} sodium hydroxide is added to 10 cm^3 of 0.25 mol dm^{-3} propanoic acid until present in excess. The equivalence point is 25 cm^3.

(3)



(v) Explain, referring to your data booklet, whether bromocresol green would be a suitable indicator for this titration.

(2)

• Bromocresol green is not a suitable indicator for this titration.
• Because the pH range of it (3.8 - 5.4) is not perfectly in the vertical section of the titration curve.

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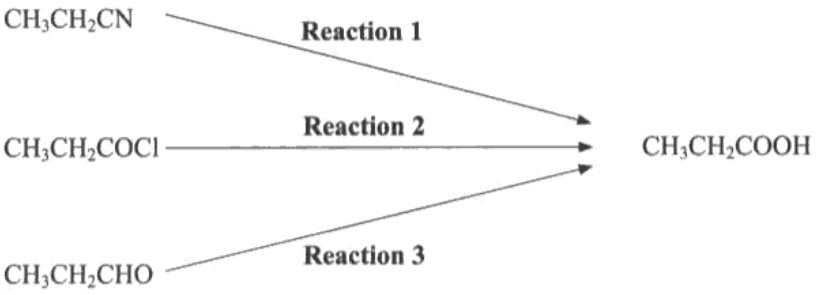
Examiner Comments

This is an example of a good answer, the only error being that the finishing point of the titration curve is too high.

Question 18(d)

The knowledge of these organic reactions was limited in many cases.

In (i) water alone would not be a suitable reagent, and a dilute strong acid is needed. Some candidates suggested using a mixture of KCN and HCN, probably thinking of the reagents used to make a nitrile. Sodium hydroxide would produce the salt of propanoic acid, not the free acid so would not be suitable in either (i) or (ii). The colour change in (iii) was usually known, though a few got it the wrong way round.



(i) Suggest a reagent which could be used to carry out **reaction 1**.

(1)

HCN

(ii) Write an equation for **reaction 2**. State symbols are **not** required.

$CH_3CH_2COCl + H_2O \rightleftharpoons CH_3CH_2COOH + HCl$ (1)

(iii) What would be observed if **reaction 3** was carried out using potassium dichromate(VI) and sulfuric acid?

(1)

Orange to yellow colour change.

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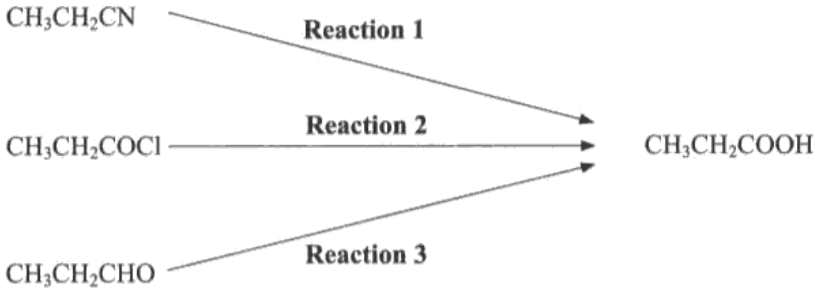
Examiner Comments

These are typical errors.



(i) Suggest a reagent which could be used to carry out **reaction 1**.

(1)

HCl and H_2O

(ii) Write an equation for **reaction 2**. State symbols are **not** required.

(1)

$CH_3CH_2COCl + H_2O \longrightarrow CH_3CH_2COOH + HCl$

(iii) What would be observed if **reaction 3** was carried out using potassium dichromate(VI) and sulfuric acid?

(1)

the colour change of $K_2Cr_2O_7$ ~~it's~~

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Examiner Comments

(i) was accepted. The colour change should be stated in (iii).

Question 18(e)

This question was well answered. The formula $LiAlH_4$ is probably an easier option than the name lithium tetrahydridoaluminate.

(e) What type of reagent would be used to convert propanoic acid to propan-1-ol? Identify a suitable reagent for this reaction.

(2)

Lithium tetrahydrido Aluminate ($LiAlH_4$) in dry ether will reduce the carboxylic acid to a primary alcohol

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Examiner Comments

The solvent for the reducing agent was not required. The mark was given if the reaction was described as a reduction.

Question 19(a)

Despite the reaction in this question being one of the specified core practicals, some candidates were unaware of the purpose of adding the reaction mixture to sodium hydrogen carbonate. Many answers stated that quenching occurs, but did not explain the use of sodium carbonate to neutralise the acid. Some candidates used the word quenching, but did not appear to understand it, as they said that the sodium carbonate was quenched. Stating that the reaction was stopped was equally good for the first mark.

(a) Explain the purpose of adding the reaction mixture to the sodium hydrogencarbonate.

(2)

It would ~~ed~~ neutralise the hydrogen ions that are acting as a catalyst. Therefore Stopping the reaction at that moment in time so it can be analysed.

(b) What indicator should be used in the titration?

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Examiner Comments

This is a good answer.

(a) Explain the purpose of adding the reaction mixture to the sodium hydrogencarbonate.

(2)

~~The~~ acted as the rate determining step To test if the reaction mixture was Acidic. Addition of Sodium hydrogencarbonate is the test for an acid - bubbles of CO_2 produced.

(b) What indicator should be used in the titration?

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Examiner Comments

The candidate knows that sodium hydrogen carbonate reacts with acid, but does not make the point that it stops the reaction by removing the acid, so doesn't score the mark.

(a) Explain the purpose of adding the reaction mixture to the sodium hydrogencarbonate.

(2)

This ends the reaction ~~quickly~~ instantly by reacting with any unreacted iodine.

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Examiner Comments

This candidate does not understand the purpose of using sodium hydrogen carbonate to stop the reaction.

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Examiner Tip

When you follow an experimental procedure, make sure you understand why things are done in a certain way.

Question 19(b)

Acid-base indicators were often suggested instead of starch.

Question 19(c)

The reason for choosing these concentrations was poorly understood, and the most common answers were that propanone and sulfuric acid had to be present in excess, or to be sure that all the iodine reacted. Few candidates stated that the change in propanone or sulfuric acid concentrations would be insignificant, or that any rate change would only depend on the iodine concentration. Some potentially good answers lost the mark because they did not refer clearly to the concentration of iodine.

*(c) In this experiment the concentration of the iodine was 0.020 mol dm^{-3} and the concentrations of propanone and sulfuric acid were both 1.00 mol dm^{-3}. Why was the iodine solution used much less concentrated than the propanone and sulfuric acid?

(2)

the iodine is not involved in the rate determining step as it is zero order so you don't need excess of it.

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Examiner Comments

This assumes the order with respect to iodine, rather than explaining how to design the experiment to find the order with respect to iodine, so did not score any marks.

*(c) In this experiment the concentration of the iodine was 0.020 mol dm^{-3} and the concentrations of propanone and sulfuric acid were both 1.00 mol dm^{-3}. Why was the iodine solution used much less concentrated than the propanone and sulfuric acid?

(2)

So that the reaction did not occur so rapidly so ~~result could~~ accurate results could be obtained and longer time periods could be taken as the concentration was lower.

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Examiner Comments

This was a common misunderstanding.

*(c) In this experiment the concentration of the iodine was 0.020 mol dm^{-3} and the concentrations of propanone and sulfuric acid were both 1.00 mol dm^{-3}. Why was the iodine solution used much less concentrated than the propanone and sulfuric acid?

(2)

So that its conc remained approximately constant while the concs of the Propanone + H_2SO_4 were observed. I_2 is not involved in the rate determining step whereas H^+ and CH_3COCH_3 are.
It is negligible – conc remains constant and negligible to the reaction.

ResultsPlus
Examiner Comments

This confuses the reagents which should change in concentration when the order is being investigated.

*(c) In this experiment the concentration of the iodine was 0.020 mol dm^{-3} and the concentrations of propanone and sulfuric acid were both 1.00 mol dm^{-3}. Why was the iodine solution used much less concentrated than the propanone and sulfuric acid?

(2)

To show that any change in rate was due to no change in iodine concentration. Propanone and sulphuric acid in excess so concentration is kept constant.

ResultsPlus
Examiner Comments

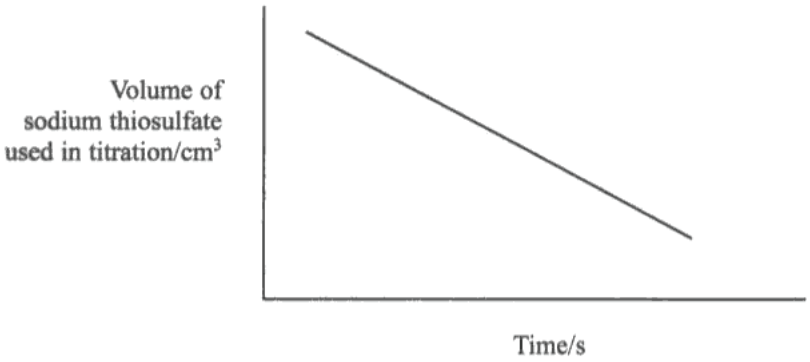
This is an example of an answer which scored both marks. The final word was assumed to mean constant.

Question 19(d)

There were many correct answers for the order with respect to iodine. The comments that followed suggested that this was a fact which candidates remembered as their comments about the graph were often not relevant, and commonly just said that a straight line graph meant zero order.

For credit, candidates had to link the order with the fact that the rate of reaction was not changing. Many thought the thiosulfate was involved in the reaction rather than being used to determine the amount of iodine remaining.

(d) The shape of the graph obtained from the results of the experiment is shown below.



Use the graph to deduce the order of reaction with respect to iodine, explaining your reasoning.

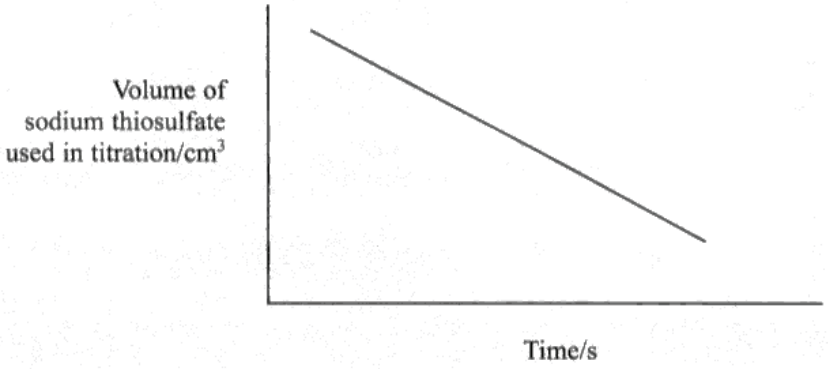
(2)

The order of reaction with respect to iodine is zero because the rate of the reaction isn't changing

ResultsPlus
Examiner Comments

This scored both marks. The constant gradient shows that the rate of the reaction is not changing.

(d) The shape of the graph obtained from the results of the experiment is shown below.



Use the graph to deduce the order of reaction with respect to iodine, explaining your reasoning.

(2)

1st order, as the graph is a straight line it shows for every [redacted] so after is a change in half the volume of sodium thiosulfate.

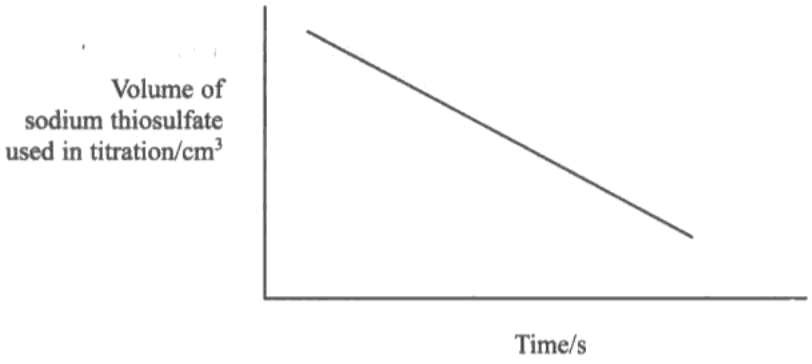
ResultsPlus
Examiner Comments

Many candidates did not look carefully at what was being plotted when interpreting the graph.

ResultsPlus
Examiner Tip

The graph of rate against concentration is a straight line when reaction is first order, but this graph is of volume of thiosulfate (which is proportional to the concentration of iodine) against time. it is important to check which variables are being plotted.

(d) The shape of the graph obtained from the results of the experiment is shown below.



Use the graph to deduce the order of reaction with respect to iodine, explaining your reasoning.

(2)

The order of reaction is zero as ~~there~~ rate is not $\propto [I_2]$ and is not $\propto [I_2]^2$. Therefore there is no change in concentration of iodine as the rate increases.

ResultsPlus
Examiner Comments

This scores the first mark only. The iodine concentration does change during the reaction. It is the rate of change of concentration which is constant.

Question 19(e)

In this experiment, samples for titration are normally removed by pipette, as an accurately known volume is required for the titration calculation. Solutions present in excess are normally measured by measuring cylinders for speed. Candidates often said that measuring cylinders were "easier", presumably thinking of the technique needed to use a pipette filler, but this was not allowed. Other answers appeared to be referring to the use of dropping pipettes. Candidates trying to give a reason for the use of the measuring cylinder often failed to appreciate the context of the experiment, giving reasons such as the use of measuring cylinders for larger volumes.

Candidates are not necessarily familiar with different types and sizes of pipette, but the idea of choosing the instrument for accuracy or for speed still applies.

(e) The solutions used in this experiment could be measured using either measuring cylinders or pipettes.

Give **one** advantage of using a measuring cylinder and **one** advantage of using a pipette.

i.e. requires less laboratory skill (2)

Measuring cylinder easier to use, and does not matter for propanone and sulfuric acid as in excess

Pipette is more precise ∴ more accurate measure of volume of I_2 being used - results more accurate.

ResultsPlus

Examiner Comments

This is making the same point twice i.e. that a pipette is used when accurate measurements are needed.

(e) The solutions used in this experiment could be measured using either measuring cylinders or pipettes.

Give **one** advantage of using a measuring cylinder and **one** advantage of using a pipette.

(2)

A measuring cylinder is easier for measuring large volumes.
The use of a pipette would be more accurate as it is a more precise measuring apparatus than a measuring cylinder.

ResultsPlus
Examiner Comments

This was a typical response scoring one mark.

Question 19(f)(i)

A substantial percentage of candidates did not understand that volumes of reagents are only proportional to their concentrations if they are in the same total volume of reaction mixture, and this is why water is added. Many thought that water was a reagent, or that it provided hydrogen ions, or that it was needed to dilute the solution because the colour of iodine is dark.

(i) Explain why water is added in experiments 2 and 3.

(1)

~~[illegible]~~ So that all the solutions has the same total volume of $32cm^3$ so the results were accurate as equal total volumes were used in each experiment.

(ii) Show how you would use the data in the table to deduce the order of reaction

ResultsPlus
Examiner Comments

This scored the mark.

(i) Explain why water is added in experiments 2 and 3.

(1)

To check if it affected the rate

ResultsPlus
Examiner Comments

This was a typical misunderstanding.

Question 19(f)(ii)

The orders of reaction were usually deduced correctly. It was surprising that, after a successful explanation and derivation of the orders of reaction the rate equation was sometimes missing, thus losing the third mark. Some candidates gave their explanation in terms of volumes and experiment numbers but failed to quote the orders. Some candidates thought that the propanone was zero order by incorrect use of data for experiments 2 and 3.

An error in writing the rate equation was to omit the rate constant. If an incorrect order with respect to iodine was included it was ignored, as the order with respect to iodine had been marked earlier in the question.

(ii) Show how you would use the data in the table to deduce the order of reaction with respect to propanone and hydrogen ions. Write the rate equation for the reaction.

(3)

experiment 2 and 1 are 1st order with respect to hydrogen ions as when concentration of H^+ ions is halved, the rate halves proportionally.

experiment 1 and 3 are 1st order with respect to propanone as when the concentration of propanone is halved the rate halves proportionally.

~~Rate = K [CH$_3$COCH$_3$]~~, rate = $K[CH_3COCH_3]^1[H^+]^1$

overall reaction = 2nd order

(Total for Question 19 = 13 marks)

ResultsPlus
Examiner Comments

This scored full marks.

(ii) Show how you would use the data in the table to deduce the order of reaction with respect to propanone and hydrogen ions. Write the rate equation for the reaction.

(3)

both are ~~first~~ second order as doubling the amount double the rate, using 1 and 2 we can see that doubling H_2SO_4, and hence hydrogen ion content, doubles the rate from 4×10^{-5} to 8×10^{-5}. From 2nd 3 we can see that halving the propanone, whilst doubling the H_2SO_4 makes no change, and so this shows that both have equal effect.

ResultsPlus Examiner Comments

This candidate has selected the correct data but made errors in deducing the orders. If a rate equation had been written based on these orders, the final mark could have been scored.

ResultsPlus Examiner Tip

Read the question carefully so that if there is more than one task to be completed you do not miss one out!

(ii) Show how you would use the data in the table to deduce the order of reaction with respect to propanone and hydrogen ions. Write the rate equation for the reaction.

(3)

The order with respect to Hydrogen ions can be deduced from the change in rate when $[H^+]$ is doubled but concentration of propanone is kept constant. Here, the rate also doubles so it is 1st order with respect to H^+

The order with respect to propanone can be deduced from change in rate when $[H^+]$ is kept constant but concentration of propanone is altered. From this table the order with respect to propanone is 1st

(Total for Question 19 = 13 marks)

ResultsPlus Examiner Comments

The two orders are deduced correctly, but the answer does not state the factor by which the propanone concentration was changed which caused the change in rate. The rate equation is missing.

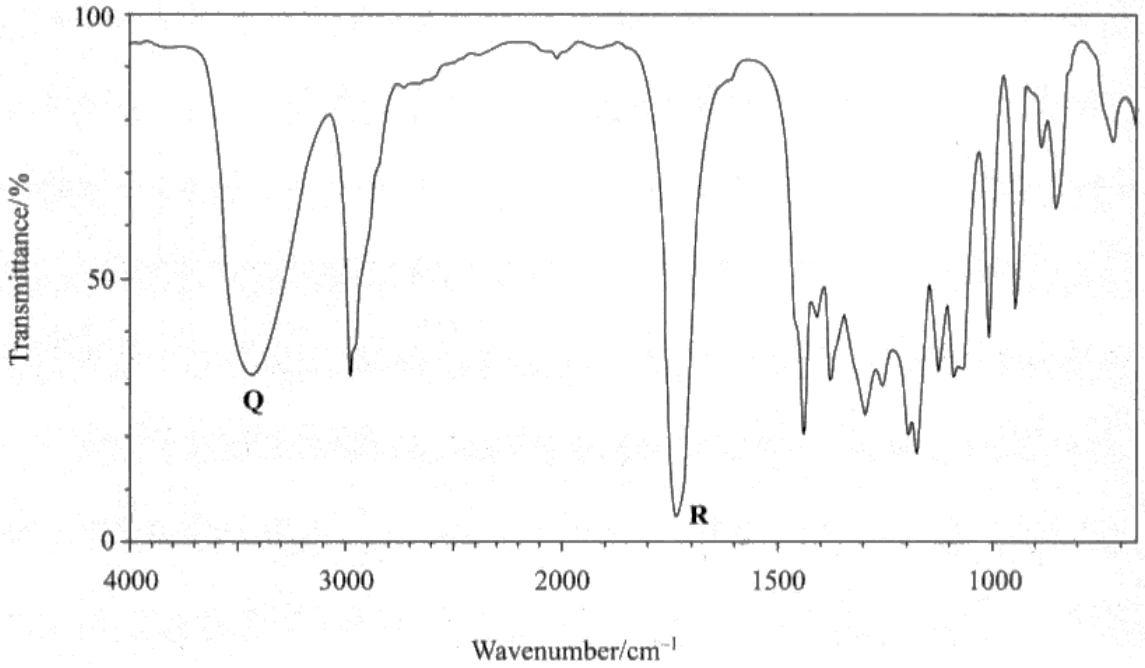
Question 20(a)

Marks were lost here by not specifying bonds clearly. Sometimes names were given, sometimes more than one bond was give e.g. by drawing out a full ester link with both a C-O and a C=O bond.

20 An organic compound **X** is an ester found in orange peel and has the molecular formula $C_5H_{10}O_3$.

(a) Identify the bonds responsible for the peaks labelled **Q** and **R** in the infrared spectrum of **X** shown below, referring to your data booklet.

(2)



Q O–H group

R C=O group

ResultsPlus
Examiner Comments

This way of writing the O-H bond is recommended as it is clear and unambiguous.

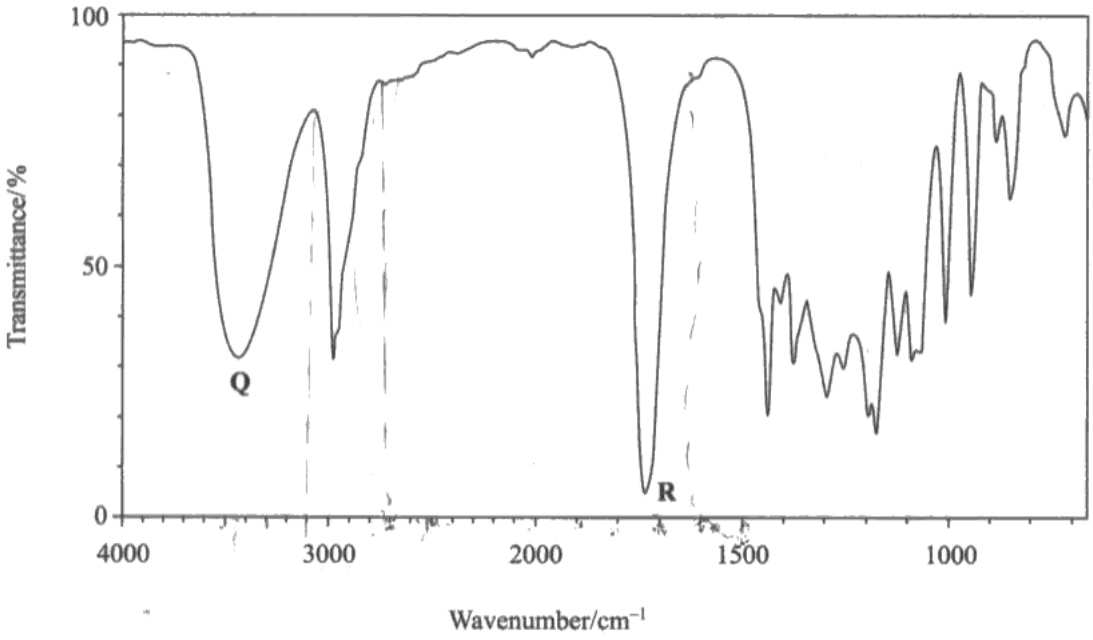
ResultsPlus
Examiner Tip

If you write the bond as -OH it means the bond to the OH group, not the bond between O and H.

20 An organic compound **X** is an ester found in orange peel and has the molecular formula $C_5H_{10}O_3$.

(a) Identify the bonds responsible for the peaks labelled **Q** and **R** in the infrared spectrum of **X** shown below, referring to your data booklet.

(2)



Q AZ Alcohol

R Carboxilic Acid

ResultsPlus
Examiner Comments

The bonds are not identified here.

ResultsPlus
Examiner Tip

The carboxylic acid functional group contains more than one type of bond. Each peak in the spectrum is for one type of bond only, so you have to select the bond which produces the peak.

Question 20(b)

X was produced during hydrolysis of the ester. This gave a clue that it was an alcohol or an acid, but this clue was sometimes missed. This led to answers containing elements other than C,H and O. Many candidates seemed to think that the tallest peak, at mass/ charge ratio of 31, was due to the parent ion rather than the peak at 32. The absence of a peak at 17 for OH worried some candidates. When the parent ion fragments to produce the methyl ion, the other product is a hydroxyl radical which is uncharged and so does not appear in the mass spectrum.

Methanol produces two peaks in an nmr spectrum, though some candidates thought each hydrogen would produce a peak. Interpretation of the chemical shift data in the data booklet requires care and some practice. Many correctly predicted the shift value due to the H in OH, but thought that the H in the methyl group would produce a peak at the value for an alkane. As the methyl hydrogen is on a carbon connected to an oxygen atom the shift corresponds to the H-C-O data. Alternatively, the specific value for this shift for methanol is in the booklet and could have been given.

(i) Identify **Y**, by name or formula, using the information available. Use **two** pieces of data from the mass spectrum to support your answer.

(2)

Y is methanol because it has an M+ peak at 32 so the relative molecular mass is 32. It also has a peak at 15 which is the methyl fragment CH_3 being broken off. It also has a peak at 30 which represents $+CO+H$ when this has broken off.

(ii) The identity of **Y** could be confirmed using nmr spectroscopy. Predict the number of peaks in the low resolution proton nmr spectrum of **Y**. Give the chemical shift range for each peak, referring to your data booklet.

(2)

there would be 2 peaks
one peak at 3.0 representing the alcohol hydrogen
one peak at 3.5 representing the methyl hydrogens.

ResultsPlus
Examiner Comments

This scored full marks.

(i) Identify **Y**, by name or formula, using the information available. Use **two** pieces of data from the mass spectrum to support your answer.

(2)

End peak = 32

peak 15 = CH_3 CH_3OH

32 − 15 = 17 - OH

(ii) The identity of **Y** could be confirmed using nmr spectroscopy. Predict the number of peaks in the low resolution proton nmr spectrum of **Y**. Give the chemical shift range for each peak, referring to your data booklet.

(2)

2 peaks : CH_3 = 0.05-1.95 δ/ppm

OH = 2-4 δ/ppm

ResultsPlus

Examiner Comments

The methanol was identified, but the peak at 32 was not, and there was no peak at 17 so one mark was scored in (i).

The nmr shift at 0.05-1.95 is for H atoms in alkyl groups in alkanes.

Question 20(c-d)

The level of chemical knowledge shown in this question was sometimes disappointing. Many candidates missed the reference to two moles of phosphorus(V) chloride and simply said that an OH group was present. Surprisingly few realised that the reaction with sodium carbonate shows that Z is an acid.

In (iii), most assumed that Z is a ketone, rather than realising that Z reacts to make a ketone. The iodoform test in (iv) gives a positive test with both a methyl ketone or a methyl secondary alcohol, the second alternative being less well known.

In (d) candidates who made errors would have had to base their answers on conflicting evidence, and allowance was made for this in the marking. Candidates who used all the information in the question realised that hydrolysis of an ester produced an acid and an alcohol, and this was helpful in deducing the structure of Z.

(c) A second product from the reaction of **X** with hydrochloric acid is **Z**, which has the molecular formula $C_4H_8O_3$.

What can you deduce about **Z** from the results of the following tests?

(i) One mole of **Z** reacts with two moles of phosphorus(V) chloride, PCl_5.

(1)

it is a carboxylic acid

(ii) When sodium carbonate solution is added to **Z**, effervescence is seen.

(1)

an O-H group is present

(iii) **Z** is warmed gently with potassium dichromate(VI) and sulfuric acid. The organic product of the reaction gives a yellow precipitate with 2,4-dinitrophenylhydrazine (Brady's reagent) but does not react with Tollens' reagent.

(1)

there is a carbonyl group present which is not an aldehyde so must be a ketone

(iv) **Z** reacts with a solution of iodine in sodium hydroxide to produce a yellow precipitate with an antiseptic smell.

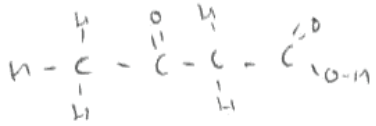
(1)

there is a carbonyl group next to a methyl group.

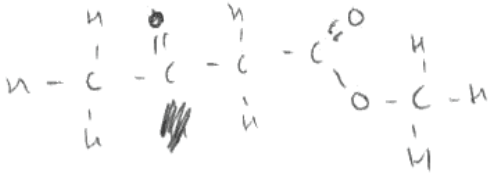
(d) Use the results of these tests to deduce the structural formula of **Z** and hence the structural formula of **X**.

(2)

Z: CH_3COCH_2COOH



X ~~$CH_3CH_2CH_2COOCH_3$~~ $CH_3COCH_2COOCH_3$



ResultsPlus

Examiner Comments

The reactions with phosphorus(V) chloride and sodium carbonate have been confused here. The candidate thinks that Z is a methyl ketone, rather than the ketone forming on oxidation, but goes on to make a sensible prediction on this basis. This scored three of the six available marks.

The iodoform test is positive with both ketones containing $CH_3C{=}O$ and $CH_3CH(OH)$ groups.

(c) A second product from the reaction of **X** with hydrochloric acid is **Z**, which has the molecular formula $C_4H_8O_3$.

What can you deduce about **Z** from the results of the following tests?

(i) One mole of **Z** reacts with two moles of phosphorus(V) chloride, PCl_5.

(1)

Two alcohol groups.

(ii) When sodium carbonate solution is added to **Z**, effervescence is seen.

(1)

Produces HCl

(iii) **Z** is warmed gently with potassium dichromate(VI) and sulfuric acid. The organic product of the reaction gives a yellow precipitate with 2,4-dinitrophenylhydrazine (Brady's reagent) but does not react with Tollens' reagent.

(1)

Forms a ketone.

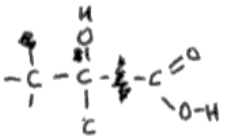
(iv) **Z** reacts with a solution of iodine in sodium hydroxide to produce a yellow precipitate with an antiseptic smell.

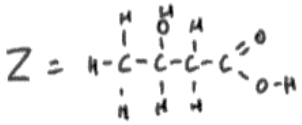
(1)

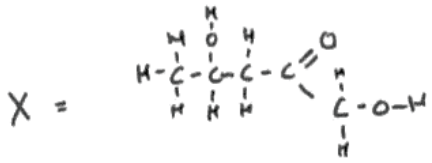
$CH_3-\overset{\overset{O}{\uparrow}}{C}$ present.

(d) Use the results of these tests to deduce the structural formula of **Z** and hence the structural formula of **X**.

(2)







ResultsPlus
Examiner Comments

This scored three marks. The OH groups which react with phoshporus(V) chloride can be in alcohols or acids, but the deduction in (i) was allowed. The candidate did not know that a methyl secondary alcohol gives a positive iodoform test in (iv) but used the molecular formulae to come up with the correct structure of Z. However X is not the methyl ester of Z.

Question 21(a)(i)

About half of the candidates recognised the reaction as transesterification. Esterification, saponification and most other organic mechanism names also appeared as answers.

Question 21(a)(ii)

Many answers said that water would react with ethanol, or that hydrogen bonding with ethanol would prevent the ethanol reacting.

(ii) Suggest why water must not be present when this reaction with ethanol is carried out.

(1)

because water would hydrolyse the esters and break ~~open~~ them apart into carboxylic acids and alcohols

ResultsPlus
Examiner Comments

This was one of the acceptable answers.

(ii) Suggest why water must not be present when this reaction with ethanol is carried out.

(1)

Because the water would replace the ethanol.

ResultsPlus
Examiner Comments

This was too vague to score the mark.

Question 21(b)

There were many good answers based on the idea that photosynthesis occurs when plants grow, and this helps to make use of biodiesel more carbon neutral. Assertions about the energy needed to produce biodiesel or the amount of carbon dioxide produced on burning being less than in burning diesel were not allowed, as they were not based on evidence. Indeed, a surprising number of responses suggested that biodiesel does not produce CO_2 when used as a fuel.

The answer that biodiesel is biodegradable is irrelevant even if true, as fuels are not produced with degradability in mind.

(b) Give **one** reason why biodiesel is considered a "greener" fuel than diesel produced from crude oil.

(1)

Biodiesel is produced from natural oils found in the environment. It emits less CO_2 upon combustion compared to diesel from crude oil.

ResultsPlus
Examiner Comments

Referring to "natural oils" is not good enough to indicate that biodiesel is made from renewable sources, so this did not score the mark.

(b) Give **one** reason why biodiesel is considered a "greener" fuel than diesel produced from crude oil.

(1)

because the crops used to make the biodiesel absorb CO_2 when grown and is released when burnt. no more extra CO_2 is released.

ResultsPlus
Examiner Comments

This was given the mark for explaining why use of biodiesel is close to being carbon neutral, even though there is room for improvement in the quality of language used.

Question 21(c)

There were some excellent succinct answers to (c). However the first mark was given least often, as the explanation of the principle involved in separating a mixture was often poorly expressed.

There is a misconception that substances are separated simply by difference in size or mass. Many discussed retention times at great length without giving any explanation of why they might vary for different substances. Answers which referred to intermolecular attractions sometimes implied that the mobile phase attracted the stationary phase, and did not refer to differing attractions of the substances being analysed to one or other of these phases. A significant number saw no incongruity in discussing the movement of the stationary phase.

Some candidates did not clearly specify the nature of the phases used in each type of chromatography. They described the tubes which are used, the substances which could be separated and other details without answering the question.

*(c) The products of the type of reaction shown with ethanol can be separated and identified using gas chromatography (GC).

In chromatography, compounds are separated because of the difference in distribution between a mobile phase and a stationary phase.

Explain why this difference in distribution occurs, and contrast the phases used in gas chromatography (GC) and high performance liquid chromatography (HPLC).

(5)

The difference occurs because the molecules moving through have different amounts of intermolecular forces. The more powerful its intermolecular forces then the slower it moves through the chromatography machine. In GC a gas is bubbled through a solvent. In liquid, a liquid is passed through a chamber with beads that are polar / non-polar depending on the liquid used.

ResultsPlus
Examiner Comments

This answer does not make the point that the relevant intermolecular forces are those between the components of the mixtrue and the substances making up the phases in the chromatography. When describing the phases the answer should have referred to the mobile and stationary phase in each type of chromatography.

*(c) The products of the type of reaction shown with ethanol can be separated and identified using gas chromatography (GC).

In chromatography, compounds are separated because of the difference in distribution between a mobile phase and a stationary phase.

Explain why this difference in distribution occurs, and contrast the phases used in gas chromatography (GC) and high performance liquid chromatography (HPLC).

(5)

Each compound in the sample adsorbs to the stationary phase by different amounts (strength of London Forces different), meaning it takes some compounds longer than others to pass through the stationary phase (different retention times). In gas chromatography, the stationary phase is an viscous liquid and the mobile phase is an unreactive carrier gas such as nitrogen. In HPLC the mobile phase is a solution forced through the stationary phase under high pressure. The stationary phase is small particles of solid (usually silica bonded to hydrocarbons) packed densely into a tube.

ResultsPlus
Examiner Comments

The first mark was given for the explanation that the components of the mixture being separated adsorbed differently to the stationary phase.

Full marks were given for contrasting the phases. The liquid mobile phase in HPLC becomes a solution when the mixture dissolves in it.

The paper allowed all the candidates to show what they knew. Question 20, on organic identification, was the most demanding and allowed the most able to demonstrate their understanding.

The recommendation to read the question carefully appears in nearly every examiners report. Unfortunately it is still needed, and writing irrelevant material is one of the causes of time pressure for the candidates.

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