Examiners' Report
June 2014

IAL Chemistry WCH05 01

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June 2014

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Introduction

There was some excellent work from well prepared candidates and no evidence of candidates having insufficient time to complete the paper. Most questions were answered very well by a good number of candidates, but some were challenging to all but a few. There were some issues associated with precise use of chemical terminology, notably orbital, subshell and shell.

Multiple Choice Section

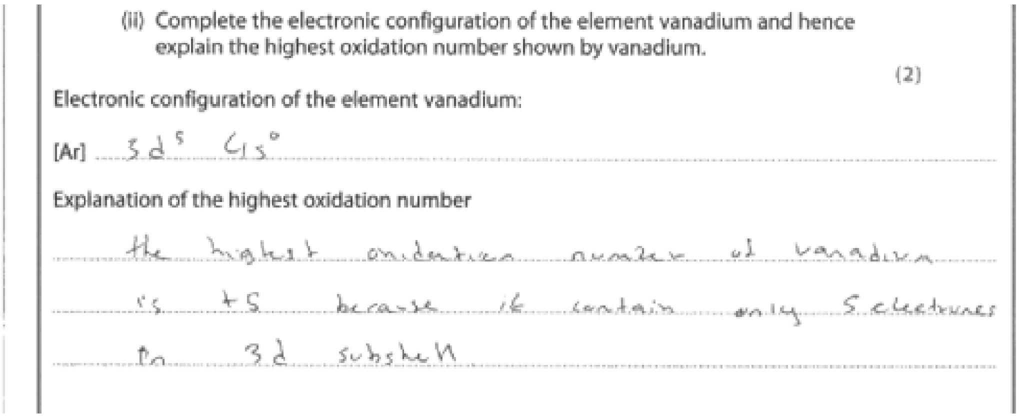
This was the highest scoring section of the paper with a mean score across all candidates of 60.1%. It discriminated significantly better at the higher than the lower end, with A grade candidates typically scoring over 84% while E grade candidates scored around 58%. There were no exceptionally easy or exceptionally difficult questions; there was one question to which 80% of candidates gave the correct response and 39% of candidates answered the two most difficult questions correctly.

Question 20 (a)(i)

The vast majority of candidates scored this mark.

Question 20 (a)(ii)

Candidates often scored the first mark, and where they did not they often gave $3d^5$ or $3d^5\ 4s^0$ as the incorrect electronic structure. The second mark was most often scored by candidates stating that 5 electrons were lost, which was an 'allow'.



(ii) Complete the electronic configuration of the element vanadium and hence explain the highest oxidation number shown by vanadium.

(2)

Electronic configuration of the element vanadium:

[Ar] $3d^5\ 4s^0$

Explanation of the highest oxidation number

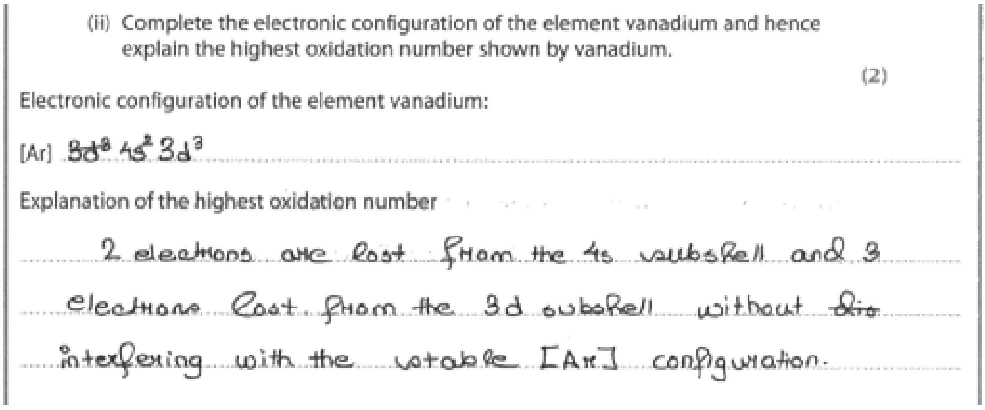
the highest oxidation number of vanadium is +5 because it contain only 5 electrones in 3d subshell

ResultsPlus
Examiner Comments

The candidate has not scored the mark for electronic structure but the second mark was allow although only on this incorrect structure where 5 electons were in the outer shell.

ResultsPlus
Examiner Tip

Remember that the Transition Metals will usually have electrons in the 4s orbital before starting to fill the 3d orbitals.



(ii) Complete the electronic configuration of the element vanadium and hence explain the highest oxidation number shown by vanadium.

(2)

Electronic configuration of the element vanadium:

[Ar] ~~3d~~ $4s^2\ 3d^3$

Explanation of the highest oxidation number

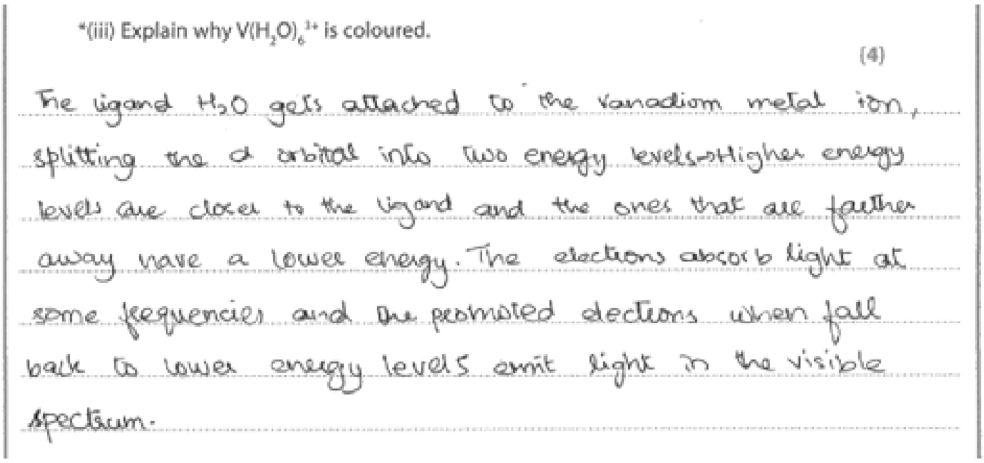
2 electrons are lost from the 4s subshell and 3 electrons lost from the 3d subshell without ~~the~~ interfering with the stable [Ar] configuration.

ResultsPlus
Examiner Comments

The candidate scores 2 marks for correctly stating the electronic structure and that this arises due to the loss of 5 electrons.

Question 20 (a)(iii)

Although many candidates could correctly describe the splitting of the orbitals in the 3d subshell, too many stated that 'the d-orbital was split'. While many recognised that absorption of energy in the visible region resulted in the promotion of electrons to higher energy orbitals. a minority of candidates then described the emission of light as the electron returned to the lower energy orbital.



*(iii) Explain why $V(H_2O)_6^{3+}$ is coloured.

(4)

The ligand H_2O gets attached to the vanadiom metal ion, splitting the d orbital into two energy levels→Higher energy levels are closer to the ligand and the ones that are farther away have a lower energy. The electrons absorb light at some frequencies and the promoted electrons when fall back to lower energy levels emit light in the visible spectrum.

ResultsPlus

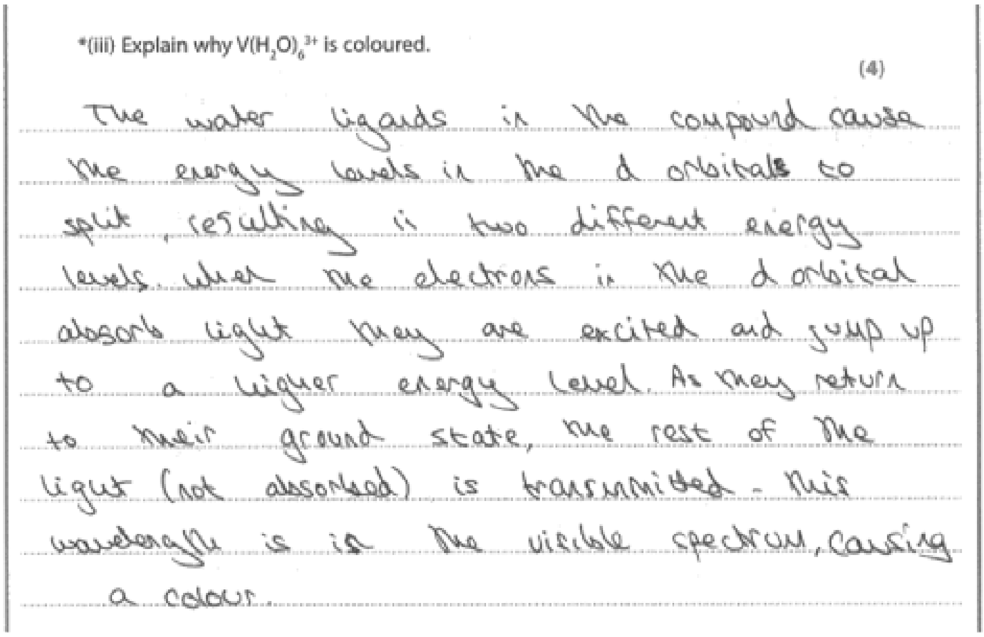
Examiner Comments

This example clearly demonstrated both of the errors described above, but scores 2 marks for the absorbing of light and the fact that electrons have been promoted to higher energy levels.

ResultsPlus

Examiner Tip

Practise answering questions of this type by carefully structuring answers to demonstrate understanding of chemical phenomena and with the number of marks available in mind.



*(iii) Explain why $V(H_2O)_6^{3+}$ is coloured.

(4)

The water ligands in the compound cause the energy levels in the d orbitals to split, resulting in two different energy levels. when the electrons in the d orbital absorb light they are excited and jump up to a higher energy level. As they return to their ground state, the rest of the light (not absorbed) is transmitted - this wavelength is in the visible spectrum, causing a colour.

ResultsPlus

Examiner Comments

This example would have scored all 4 marks but for the orbital (singular) in the second line.

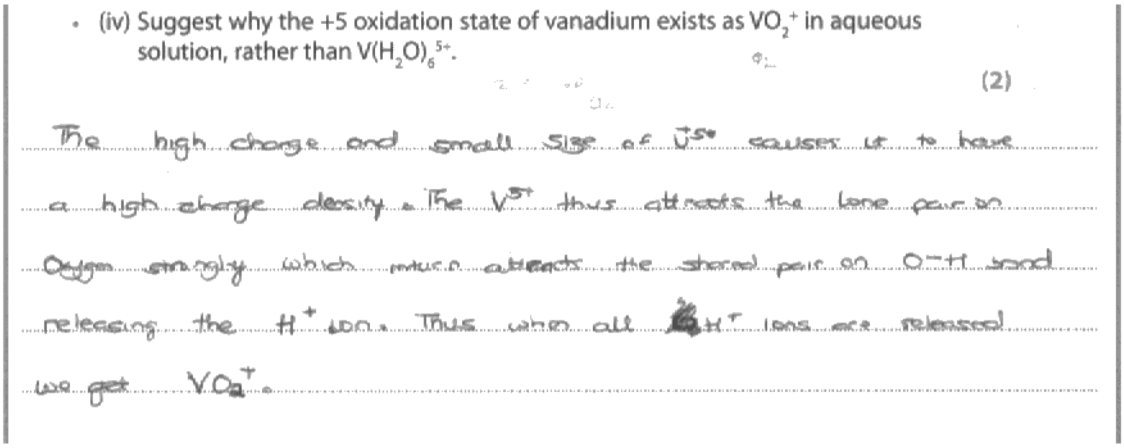
ResultsPlus

Examiner Tip

Think carefully about the precise use of chemical terminology like orbital, subshell and shell.

Question 20 (a)(iv)

The importance of the high charge on V^{5+} was not recognised by many candidates, and few of those who did were able to describe the resulting effect on the water molecules. Some candidates attempted to answer the question by comparing the stability of the two ions, although this had already been done in the question.



- (iv) Suggest why the +5 oxidation state of vanadium exists as VO_2^+ in aqueous solution, rather than $V(H_2O)_6^{5+}$.

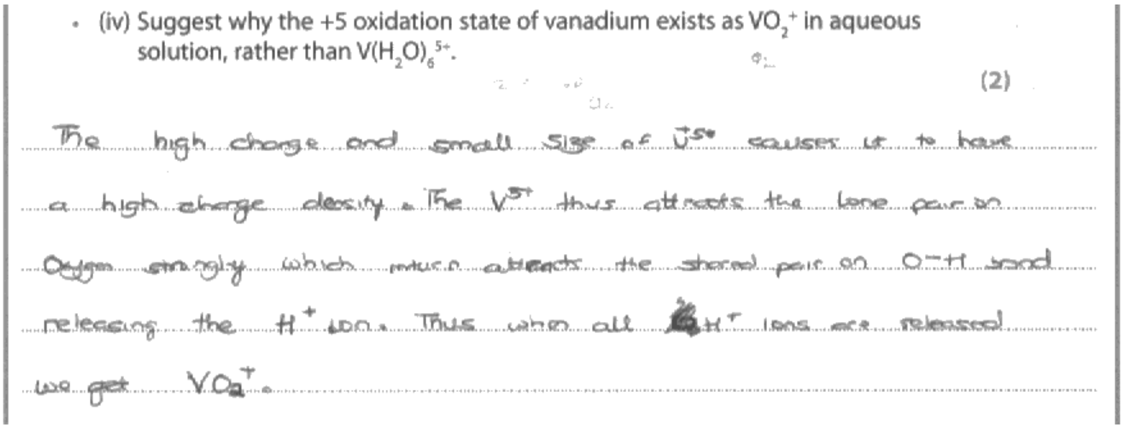
(2)

The high charge and small sige of V^{5+} causes it to have a high charge density. The V^{5+} thus attracts the lone pair on Oxygen strongly which much attracts the shared pair on O–H bond releasing the H^+ ion. Thus when all H^+ ions are released we get VO_2^+.

ResultsPlus

Examiner Comments

An extremely detailed answer which was awarded both marks.



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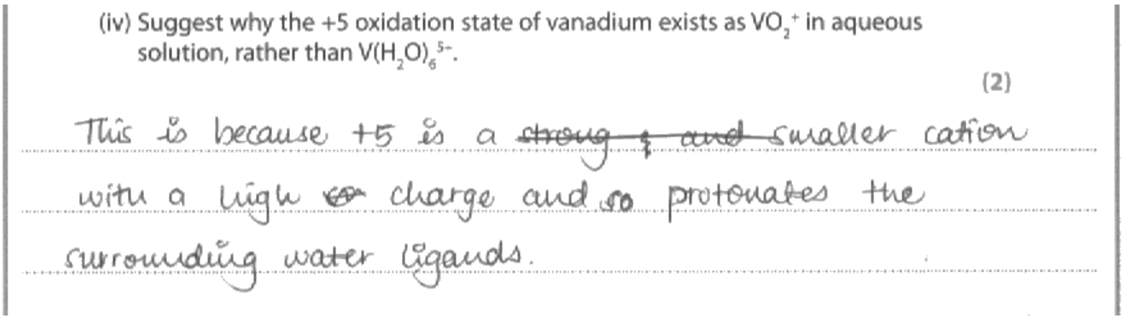
ResultsPlus

Examiner Comments

A fairly common incorrect response scoring no marks.



(iv) Suggest why the +5 oxidation state of vanadium exists as VO_2^+ in aqueous solution, rather than $V(H_2O)_6^{5+}$.

(2)

This is because +5 is a ~~strong & and~~ smaller cation with a high charge and protonates the surrounding water ligands.

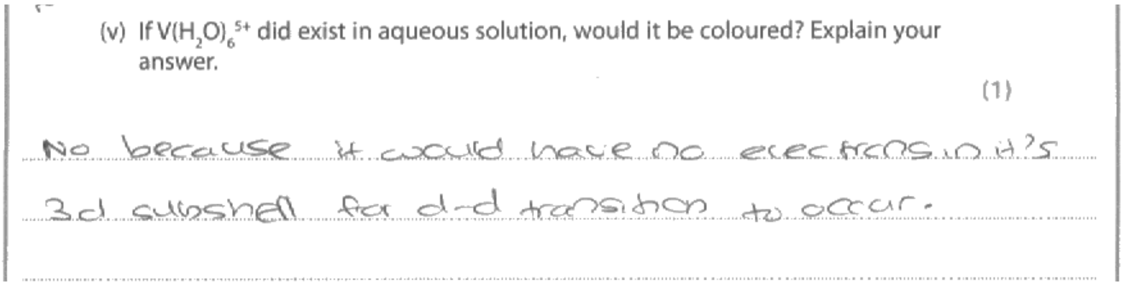
ResultsPlus

Examiner Comments

This candidate had the right idea, and scored the first mark, but unfortunately protonated rather than deprotonated the water.

Question 20 (a)(v)

Many candidates correctly recognised that V^{5+}(aq) would be colourless as it would contain no electrons in the d-subshell. However, some inaccurately stated that it had no electrons in the d-orbital (singular), and others that it had no partially filled d-orbitals. Whilst this statement is true, it does not demonstrate sufficient knowledge to be awarded the mark.



(v) If $V(H_2O)_6^{5+}$ did exist in aqueous solution, would it be coloured? Explain your answer.

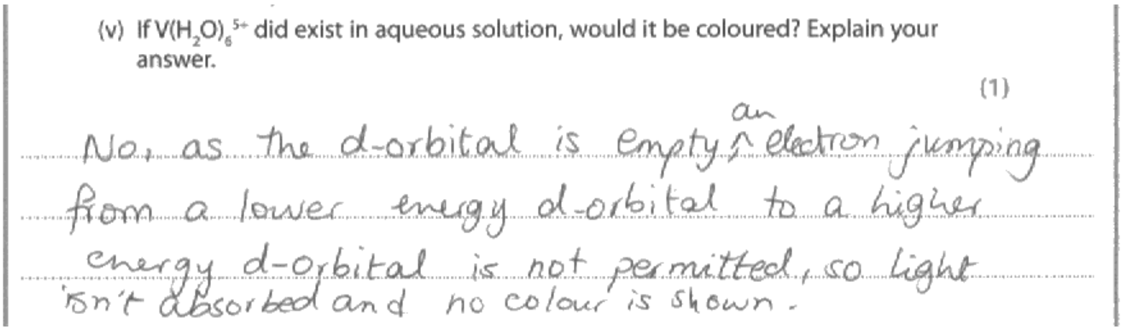
(1)

No because it would have no electrons in it's 3d subshell for d-d transition to occur.

ResultsPlus

Examiner Comments

This response is typical of a correct answer and was awarded the mark.



(v) If $V(H_2O)_6^{5+}$ did exist in aqueous solution, would it be coloured? Explain your answer.

(1)

No, as the d-orbital is Empty an electron jumping from a lower energy d-orbital to a higher energy d-orbital is not permitted, so light isn't absorbed and no colour is shown.

ResultsPlus

Examiner Comments

This response, though factually correct, was not deemed sufficient to explain why the ion would not be coloured as it does not use the term orbitals.

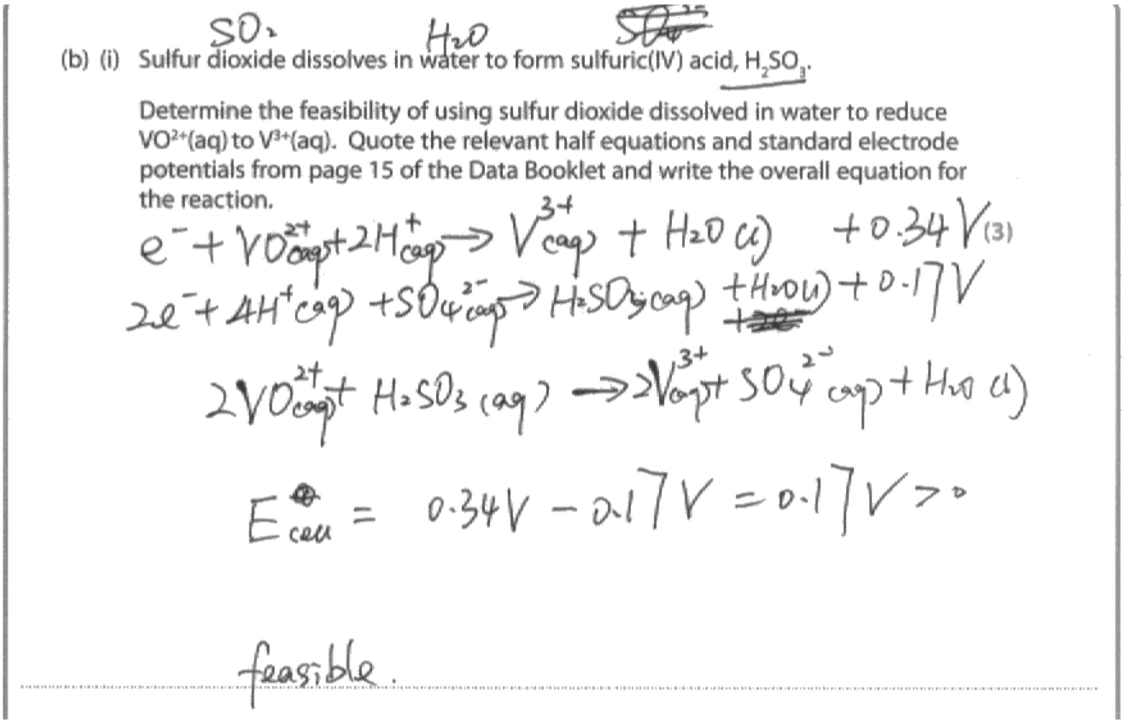
ResultsPlus

Examiner Tip

Once again, be careful that use of chemical terminology is accurate.

Question 20 (b)(i)

Many candidates were able to select the correct vanadium half equation to use, but fewer were able to identify the correct equations involving H_2SO_3. Irrespective of the half equations selected, a significant number of candidates wrote half equations without electrons, and therefore found combining the half equations in the correct ratio very difficult. A good number of candidates who were able to find the correct equations were able to calculate and comment accurately on the feasibility of the reaction.



SO_2 H_2O ~~SO~~

(b) (i) Sulfur dioxide dissolves in water to form sulfuric(IV) acid, H_2SO_3.

Determine the feasibility of using sulfur dioxide dissolved in water to reduce VO^{2+}(aq) to V^{3+}(aq). Quote the relevant half equations and standard electrode potentials from page 15 of the Data Booklet and write the overall equation for the reaction.

$e^- + VO^{2+}_{(aq)} + 2H^+_{(aq)} \rightarrow V^{3+}_{(aq)} + H_2O\,(l) \quad +0.34\,V$ (3)

$2e^- + 4H^+(aq) + SO_4^{2-}{}_{(aq)} \rightarrow H_2SO_3(aq) + H_2O(l) + 0.17\,V$ ~~$+2e^-$~~

$2VO^{2+}_{(aq)} + H_2SO_3\,(aq) \rightarrow 2V^{3+}_{(aq)} + SO_4^{2-}\,(aq) + H_2O\,(l)$

$E^{\ominus}_{cell} = 0.34\,V - 0.17\,V = 0.17\,V > 0$

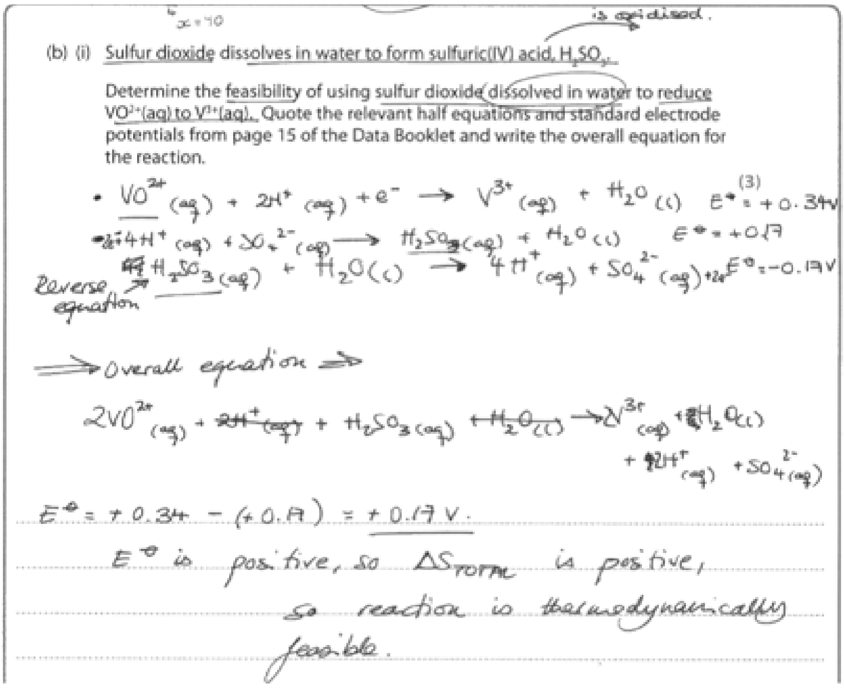
feasible.

ResultsPlus
Examiner Comments

This candidate managed to identify the correct equations, calculate the E_{cell} value and comment on feasibility, but unfortunately did not correctly cancel the H^+ ions in the final equation so scored 2 out of 3.

ResultsPlus
Examiner Tip

When multiplying a half equation prior to adding two half equations together, write it out in full to ensure you get the correct numbers of each species and can then cancel out ones that appear on both sides of the equation.



$x = 10$ is oxidised.

(b) (i) Sulfur dioxide dissolves in water to form sulfuric(IV) acid, H_2SO_3.

Determine the feasibility of using sulfur dioxide dissolved in water to reduce $VO^{2+}(aq)$ to $V^{3+}(aq)$. Quote the relevant half equations and standard electrode potentials from page 15 of the Data Booklet and write the overall equation for the reaction.

(3)

• $VO^{2+}(aq) + 2H^+(aq) + e^- \rightarrow V^{3+}(aq) + H_2O(l)$ $E^\ominus = +0.34V$

$4H^+(aq) + SO_4^{2-}(aq) \rightarrow H_2SO_3(aq) + H_2O(l)$ $E^\ominus = +0.17$

Reverse equation → $H_2SO_3(aq) + H_2O(l) \rightarrow 4H^+(aq) + SO_4^{2-}(aq) + 2e^-$ $E^\ominus = -0.17V$

⟹ Overall equation ⟹

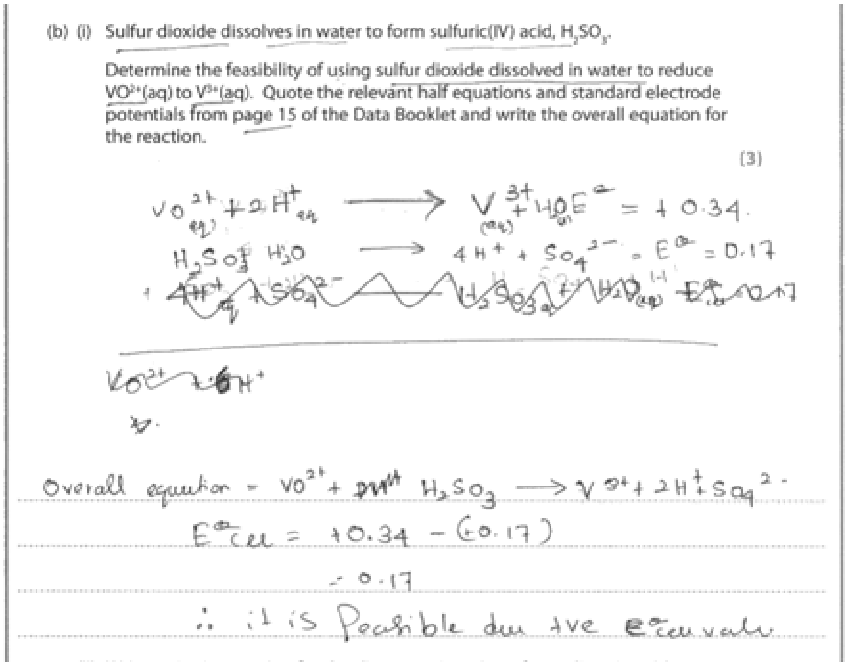
$2VO^{2+}(aq) + \cancel{2H^+(aq)} + H_2SO_3(aq) \cancel{+ H_2O(l)} \rightarrow V^{3+}(aq) + H_2O(l) + 2H^+(aq) + SO_4^{2-}(aq)$

$E^\ominus = +0.34 - (+0.17) = +0.17\ V.$

$E^\ominus$ is positive, so ΔS_{total} is positive, so reaction is thermodynamically feasible.

Examiner Comments

The omission of electrons in the half equations loses the first mark, and makes adding the two half equations very difficult. As a result the candidate has not multiplied the half equation with vanadium by 2 and therefore does not get the full equation correct. They have, however, completed the calculation correctly and commented on feasibility and therefore scored the final mark.



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Determine the feasibility of using sulfur dioxide dissolved in water to reduce $VO^{2+}(aq)$ to $V^{3+}(aq)$. Quote the relevant half equations and standard electrode potentials from page 15 of the Data Booklet and write the overall equation for the reaction.

(3)

$VO^{2+}(aq) + 2H^+(aq) \longrightarrow V^{3+}(aq) + H_2O(l)$ $E^\ominus = +0.34.$

$H_2SO_3 + H_2O \longrightarrow 4H^+ + SO_4^{2-}$ $E^\ominus = 0.17$

~~$4H^+(aq) + SO_4^{2-} \longrightarrow H_2SO_3(aq) + H_2O(aq)$ $E^\ominus = 0.17$~~

VO^{2+} $6H^+$

3v.

Overall equation = $VO^{2+} + \cancel{2H^+}\ H_2SO_3 \longrightarrow V^{3+} + 2H^+ + SO_4^{2-}$

$E^\ominus_{cell} = +0.34 - (+0.17)$

$= 0.17$

∴ it is feasible due +ve $E^\ominus_{cell}$ value

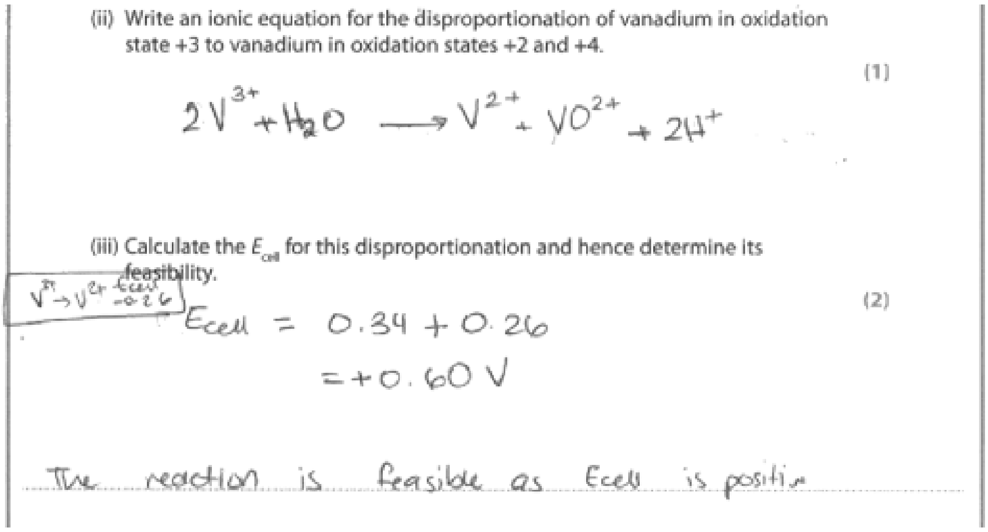
Examiner Comments

Although the candidate is rather economical with their final explanation of the feasibility of the reaction, all three marks were awarded.

Question 20 (b)(ii-iii)

Although the formula for the vanadium(IV) ion VO^{2+} is given clearly at the beginning of the question a minority of candidates used V^{4+} instead. Of those who selected the correct half equations to use, a number failed to balance the final equation and showed one V^{3+} producing a V^{2+} and a VO^{2+}.

This E_{cell} calculation was much more accessible to candidates than 20bi, and had the advantage of an error carried forward mark for the feasibility of the reaction which allowed some candidates to score.



(ii) Write an ionic equation for the disproportionation of vanadium in oxidation state +3 to vanadium in oxidation states +2 and +4.

(1)

$$2V^{3+} + H_2O \longrightarrow V^{2+} + VO^{2+} + 2H^+$$

(iii) Calculate the E_{cell} for this disproportionation and hence determine its feasibility.

(2)

$\boxed{V^{3+} \rightarrow V^{2+} \; E_{cell} \; -0.26}$

$$E_{cell} = 0.34 + 0.26$$
$$= +0.60 \text{ V}$$

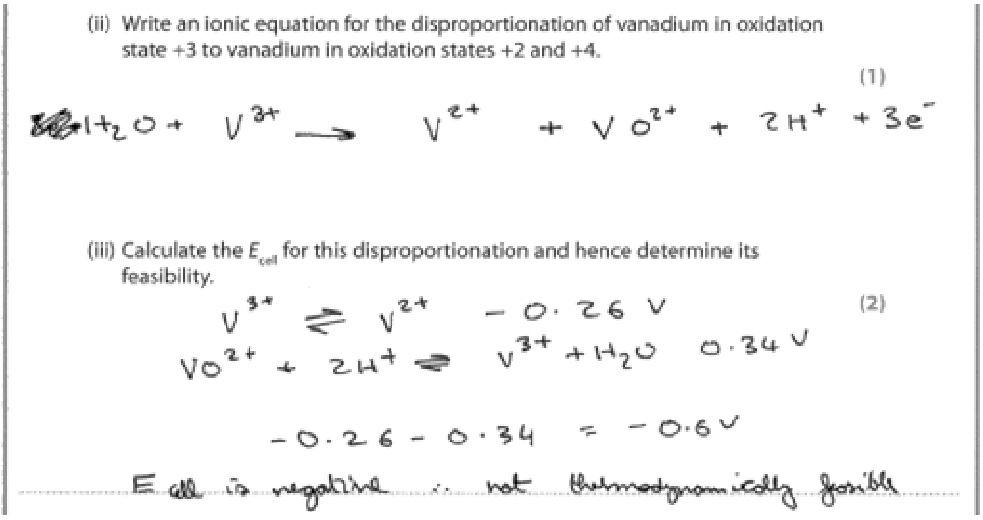
The reaction is feasible as Ecell is positive

ResultsPlus
Examiner Comments

The candidate correctly balanced the charge on each side of the equations by adding 3 electrons to the product side, but failed to recognise that the number of vanadium species is different.

ResultsPlus
Examiner Tip

Always check your equations balance both for charge and for atoms.



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(1)

$$H_2O + V^{3+} \longrightarrow V^{2+} + VO^{2+} + 2H^+ + 3e^-$$

(iii) Calculate the E_{cell} for this disproportionation and hence determine its feasibility.

(2)

$V^{3+} \rightleftharpoons V^{2+} \quad -0.26 \text{ V}$

$VO^{2+} + 2H^+ \rightleftharpoons V^{3+} + H_2O \quad 0.34 \text{ V}$

$-0.26 - 0.34 = -0.6\text{V}$

E cell is negative ∴ not thermodynamically feasible

ResultsPlus
Examiner Comments

Here the correct equation was recognised, but the half cell values were added incorrectly giving +0.60V instead of -0.06V. The final mark was, however, awarded for the suggestion that a +0.60V E_{cell} would be feasible.

Question 21 (a)(i)

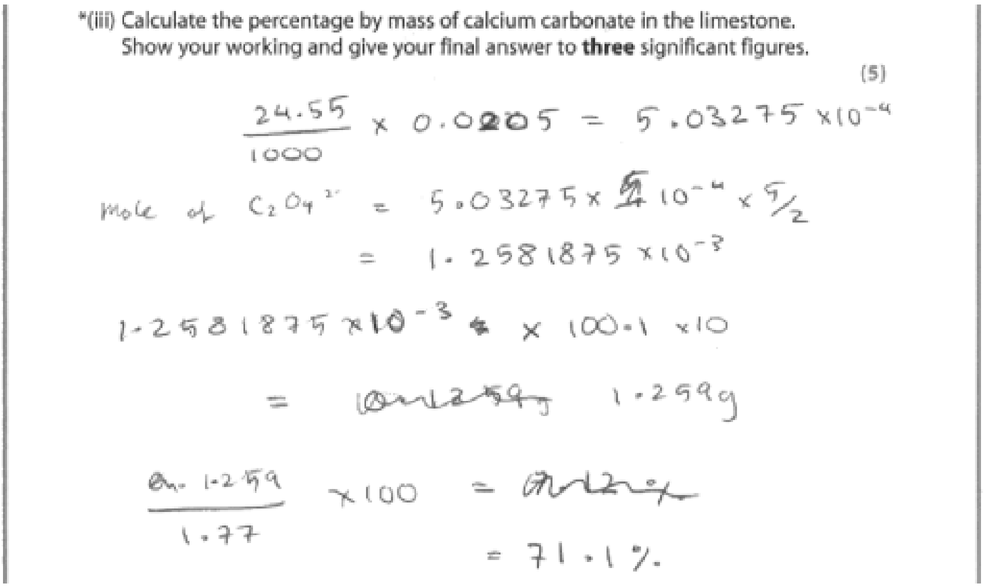
Somewhat surprisingly, this question proved highly discriminating at all grades. While some candidates gave the end-point for the titration with potassium manganate(VII) in the flask, there were quite a number of colours suggested that had no conection whatsoever with this titration.

Question 21 (a)(ii)

While the score on this question was better than on 20ai, many candidates were unable to complete this basic task; identification of the manganese product was the main difficulty here.

Question 21 (a)(iii)

This extended calculation was handled very well by an encouraging number of candidates. While the first two marks were often scored, a common error was the omission of the scaling factor of 10. Many candidates did not understand which substance was being measured and multiplied by molecular masses of calcium ethanedioate (128.1), ethanedioate ions (88) or just calcium ions (40.1). However, it was still possible to score 4 marks by correctly finding the percentage to 3 significant figures.



*(iii) Calculate the percentage by mass of calcium carbonate in the limestone.
Show your working and give your final answer to **three** significant figures.
(5)

$$\frac{24.55}{1000} \times 0.0205 = 5.03275 \times 10^{-4}$$

Mole of $C_2O_4^{2-}$ $= 5.03275 \times 10^{-4} \times 5/2$

$= 1.2581875 \times 10^{-3}$

$1.2581875 \times 10^{-3} \times 100.1 \times 10$

$= 1.259g$

$$\frac{1.259}{1.77} \times 100$$

$= 71.1\%$.

ResultsPlus
Examiner Comments

This fully correct example was awarded all five marks.

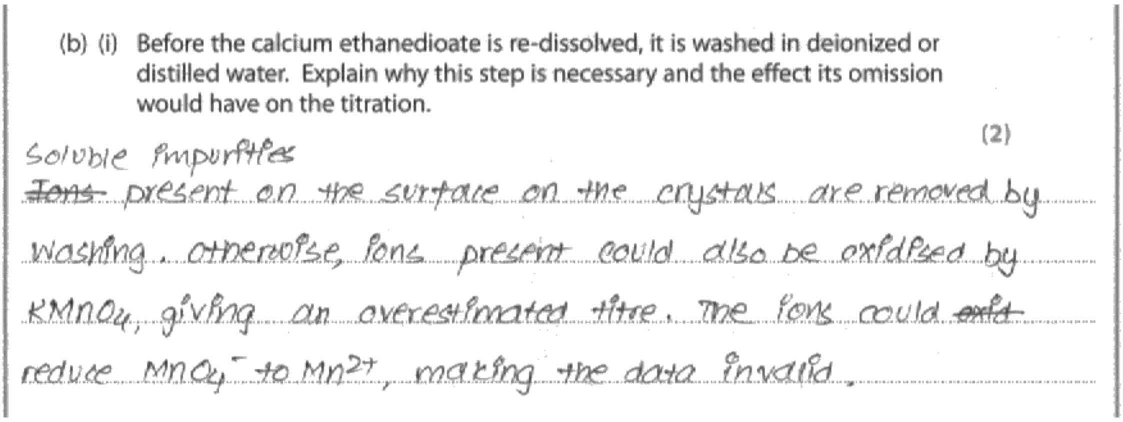
Although the reasoning has not been explained, all the steps are given and the required value is correctly calculated to 3 significant figures.

ResultsPlus
Examiner Tip

Don’t round your answers until you reach the final answer.

Question 21 (b)(i)

Relatively few marks were awarded on this question as the candidates' responses often lacked precision, too often giving general answers such as to wash off impurities or acid. When the correct answer was given, it was usually followed by a correct description of the effect on the titration volume.



(b) (i) Before the calcium ethanedioate is re-dissolved, it is washed in deionized or distilled water. Explain why this step is necessary and the effect its omission would have on the titration.

(2)

soluble impurities

~~Ions~~ present on the surface on the crystals are removed by washing. otherwise, ions present could also be oxidised by $KMnO_4$, giving an overestimated titre. The ions could ~~oxid~~ reduce MnO_4^- to Mn^{2+}, making the data invalid.

ResultsPlus

Examiner Comments

This answer has a nice description of a possible effect of the titration volume, but without the presence of the ethanedioate ions for the first mark, it does not score.

ResultsPlus

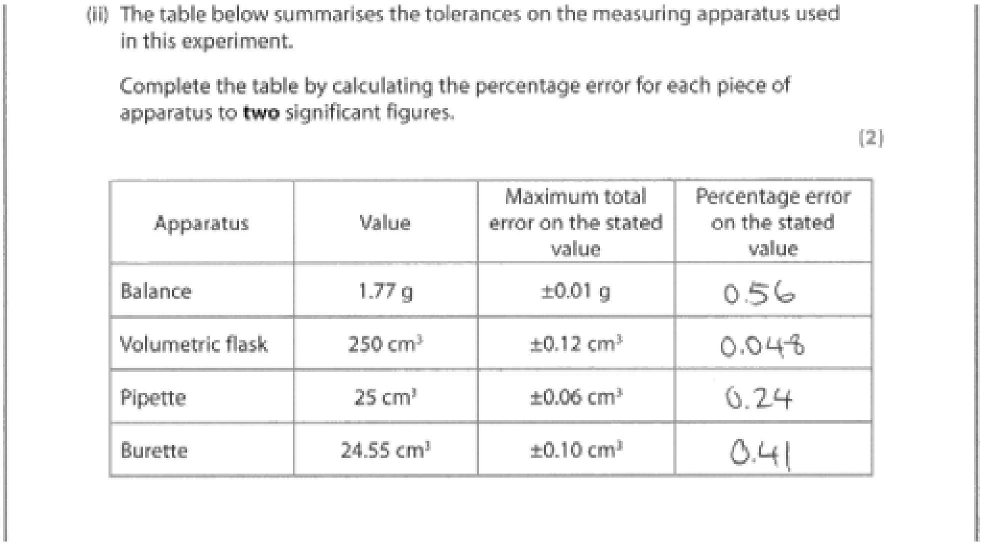
Examiner Tip

Try to be precise when answering questions about impurities present.

Question 21 (b)(ii-iii)

Many candidates were able to answer 21bii, but some tried to multiply some or all of the answers by 2, presumably because they believed that the apparatus was read twice and the the error therefore would double, despite the clear heading for the column in the table.

Few candidates scored well in 21biii. The only commonly scored mark was to find the mass of calcium ethanedioate remaining in solution.

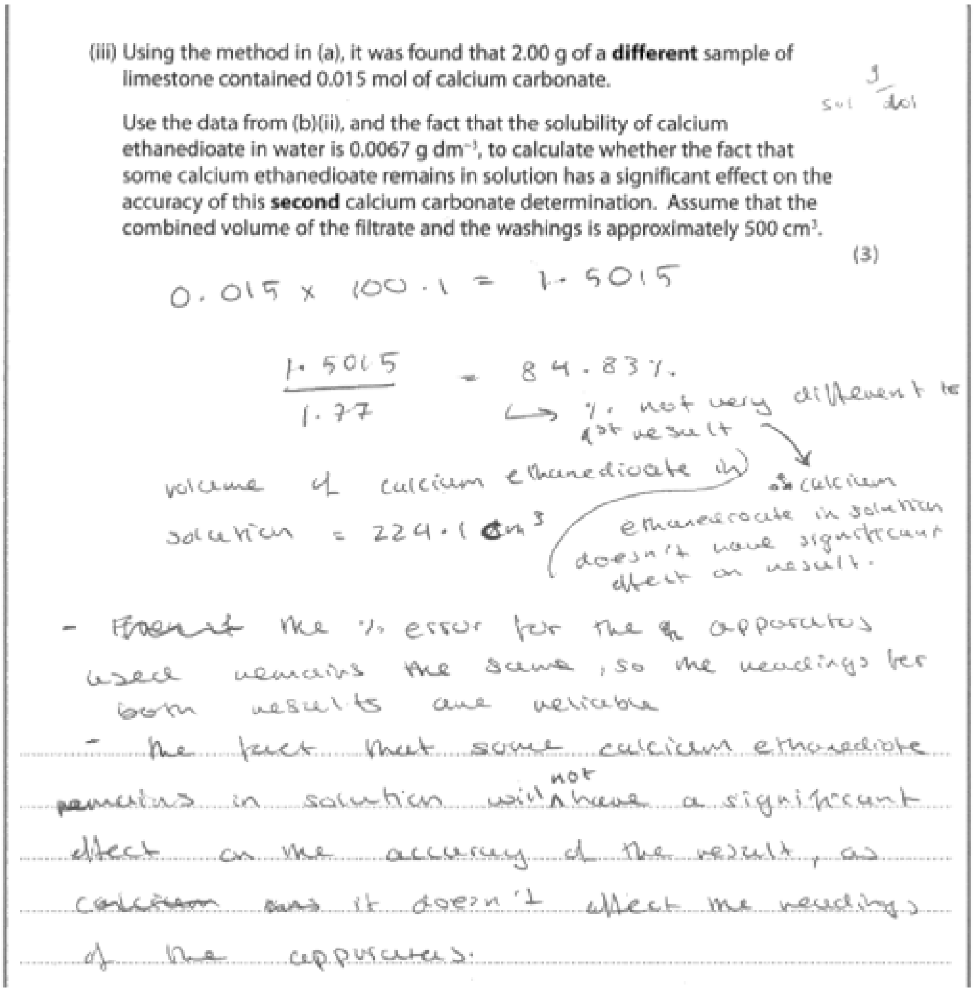


(ii) The table below summarises the tolerances on the measuring apparatus used in this experiment.

Complete the table by calculating the percentage error for each piece of apparatus to **two** significant figures.

(2)

Apparatus	Value	Maximum total error on the stated value	Percentage error on the stated value
Balance	1.77 g	±0.01 g	0.56
Volumetric flask	250 cm³	±0.12 cm³	0.048
Pipette	25 cm³	±0.06 cm³	0.24
Burette	24.55 cm³	±0.10 cm³	0.41



(iii) Using the method in (a), it was found that 2.00 g of a **different** sample of limestone contained 0.015 mol of calcium carbonate.

sol g/dm

Use the data from (b)(ii), and the fact that the solubility of calcium ethanedioate in water is 0.0067 g dm⁻³, to calculate whether the fact that some calcium ethanedioate remains in solution has a significant effect on the accuracy of this **second** calcium carbonate determination. Assume that the combined volume of the filtrate and the washings is approximately 500 cm³.

(3)

$0.015 \times 100.1 = 1.5015$

$\frac{1.5015}{1.77} = 84.83\%$

→ % not very different to 1st result

volume of calcium ethanedioate in solution = 224.1 cm³

∴ calcium ethanedioate in solution doesn't have significant effect on result.

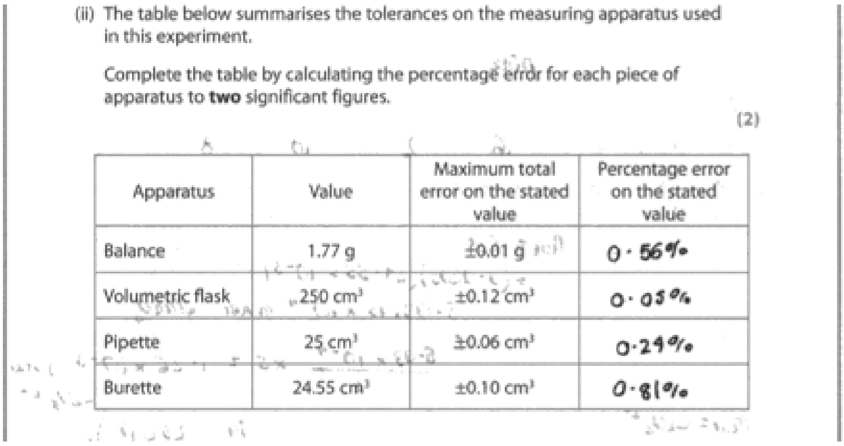
- ~~[illegible]~~ the % error for the ~~[illegible]~~ apparatus used remains the same, so the readings for both results are reliable
- the fact that some calcium ethanedioate remains in solution will not have a significant effect on the accuracy of the result, as ~~calcium~~ ~~was~~ it doesn't affect the readings of the apparatus.

ResultsPlus
Examiner Comments

This example scored two marks as, although only three answers were to 3 significant figures, all were correct and at least two needed to have the incorrect number of significant figures before a mark was lost.

ResultsPlus
Examiner Tip

Read the questions carefully to identify when an answer must be given to a stated number of significant figures.



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(2)

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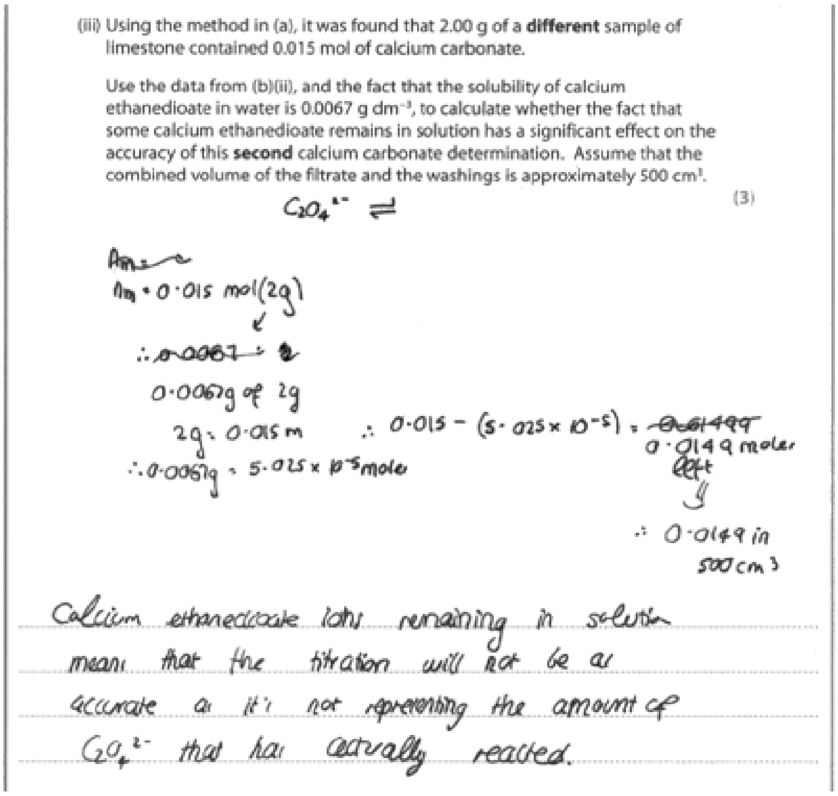
Balance	1.77 g	±0.01 g	0·56%
Volumetric flask	250 cm³	±0.12 cm³	0·05%
Pipette	25 cm³	±0.06 cm³	0·24%
Burette	24.55 cm³	±0.10 cm³	0·81%



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(3)

$C_2O_4^{2-} \rightleftharpoons$

~~Ans~~

$n_m = 0·015$ mol(2g)

∴ ~~0.0067~~ ÷ 2

0·0067g of 2g

2g = 0·015 m

∴ 0·0067g = $5·025 \times 10^{-5}$ moles

∴ $0·015 - (5·025 \times 10^{-5})$ = ~~0.01499~~ 0·0149 moles left

∴ 0·0149 in 500 cm³

Calcium ethanedioate ions remaining in solution means that the titration will not be as accurate as it's not representing the amount of $C_2O_4^{2-}$ that has actually reacted.

ResultsPlus
Examiner Comments

This scored 1 mark as three of the answers were correct. The fourth has been doubled.

(ii) The table below summarises the tolerances on the measuring apparatus used in this experiment.

Complete the table by calculating the percentage error for each piece of apparatus to **two** significant figures.

(2)

Apparatus	Value	Maximum total error on the stated value	Percentage error on the stated value
Balance	1.77 g	±0.01 g	0.56
Volumetric flask	250 cm³	±0.12 cm³	0.048
Pipette	25 cm³	±0.06 cm³	0.24
Burette	24.55 cm³	±0.10 cm³	0.41

(iii) Using the method in (a), it was found that 2.00 g of a **different** sample of limestone contained 0.015 mol of calcium carbonate.

Use the data from (b)(ii), and the fact that the solubility of calcium ethanedioate in water is 0.0067 g dm^{-3}, to calculate whether the fact that some calcium ethanedioate remains in solution has a significant effect on the accuracy of this **second** calcium carbonate determination. Assume that the combined volume of the filtrate and the washings is approximately 500 cm³.

(3)

solubility: 0.0067 g dm^{-3} = 0.00335 g per 500 cm^3

0.015 × ~~[illegible]~~ 128.1 = 1.9215 g of calcium carbonate

0.00335 g remains in solution

~~0.00335~~ $100\% \times \frac{0.00335}{1.9215}$ = 0.364 % error

total error from apparatus = 0.56 + 0.048 + 0.24 + 0.41

= 1.26%

1.26% > 0.364%

∴ error from apparatus > error due to solubility ∴

solubility has ~~little effect~~ an insignificant effect on the accuracy

(Total for Question 21 = 14 marks)

ResultsPlus

Examiner Comments

This candidate has the right idea, but unfortunately has miscalculated, getting 0.364% instead of 0.174%, consequently only scoring two marks.

(ii) The table below summarises the tolerances on the measuring apparatus used in this experiment.

Complete the table by calculating the percentage error for each piece of apparatus to **two** significant figures.

(2)

Apparatus	Value	Maximum total error on the stated value	Percentage error on the stated value
Balance	1.77 g	±0.01 g	~~1.13~~ 0.56
Volumetric flask	250 cm³	±0.12 cm³	~~0.096~~ 0.048
Pipette	25 cm³	±0.06 cm³	0.24
Burette	24.55 cm³	±0.10 cm³	0.41

(iii) Using the method in (a), it was found that 2.00 g of a **different** sample of limestone contained 0.015 mol of calcium carbonate.

Use the data from (b)(ii), and the fact that the solubility of calcium ethanedioate in water is 0.0067 g dm⁻³, to calculate whether the fact that some calcium ethanedioate remains in solution has a significant effect on the accuracy of this **second** calcium carbonate determination. Assume that the combined volume of the filtrate and the washings is approximately 500 cm³.

(3)

0.015 mol of CaC_2O_4 = 1.9215g of CaC_2O_4

0.0067 in 1000 cm3

∴ Solubility = 3.35×10^{-3} $g\,dm^{-3}$ in 500 cm³

$\frac{3.35 \times 10^{-3}}{1.9215}$ = 0.174% which is smaller than Percentage error due to balance (0.56%)

∴ There wouldn't be any significant effect.

ResultsPlus

Examiner Comments

A fully correct answer.

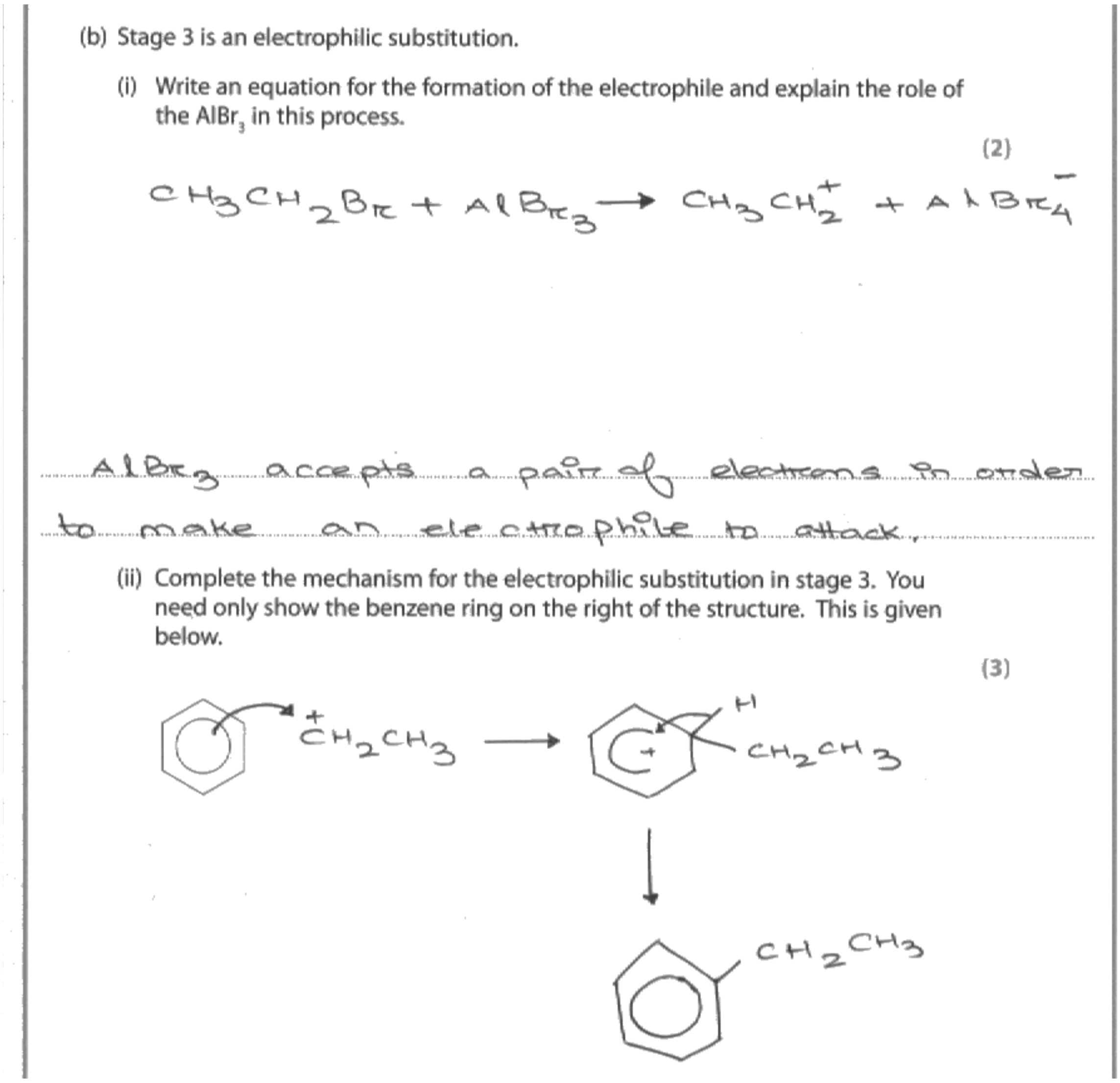
Question 22 (a)

Selecting appropriate reagents, along with identifying suitable practical procedures, should be core skills at this level but are often neglected by candidates.

Question 22 (b)(i-ii)

The equation forming the electrophile was well-known but the role of aluminium bromide was not clearly understood. The most common answer was 'acts as a halogen carrier' which applies to halogenation of a benzene ring but is not correct for a Friedel-Crafts alkylation.

While there were some extremely clear and accurate answers to this mechanism, drawing the intermediate proved a real challenge. Marks were also lost through inaccurate drawing of curly arrows.



(b) Stage 3 is an electrophilic substitution.

(i) Write an equation for the formation of the electrophile and explain the role of the $AlBr_3$ in this process.

(2)

$CH_3CH_2Br + AlBr_3 \rightarrow CH_3CH_2^+ + AlBr_4^-$

$AlBr_3$ accepts a pair of electrons in order to make an electrophile to attack.

(ii) Complete the mechanism for the electrophilic substitution in stage 3. You need only show the benzene ring on the right of the structure. This is given below.

(3)

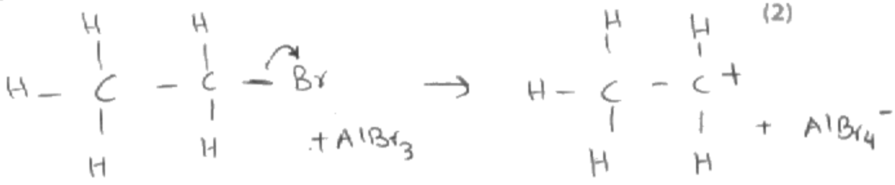
ResultsPlus
Examiner Comments

This is an example of the most commonly seen answer to b (i), worth 2 marks.

(b) Stage 3 is an electrophilic substitution.

(i) Write an equation for the formation of the electrophile and explain the role of the $AlBr_3$ in this process.

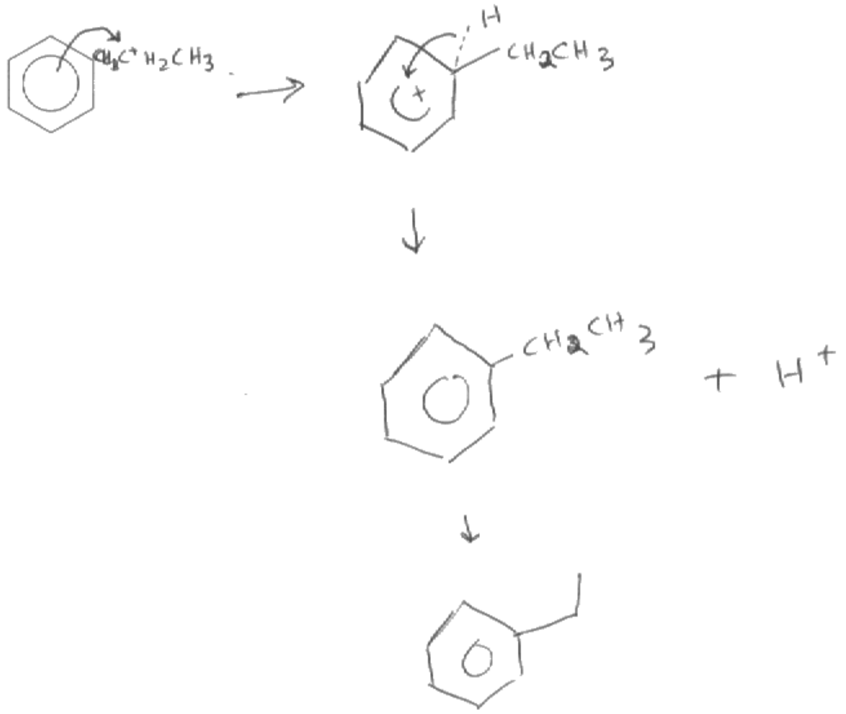
(2)



AlBr3 acts as a catalyst.

(ii) Complete the mechanism for the electrophilic substitution in stage 3. You need only show the benzene ring on the right of the structure. This is given below.

(3)



ResultsPlus

Examiner Comments

A typical answer to b (i), worth one mark. Catalyst is not enough for the second mark.

(b) Stage 3 is an electrophilic substitution.

(i) Write an equation for the formation of the electrophile and explain the role of the $AlBr_3$ in this process.

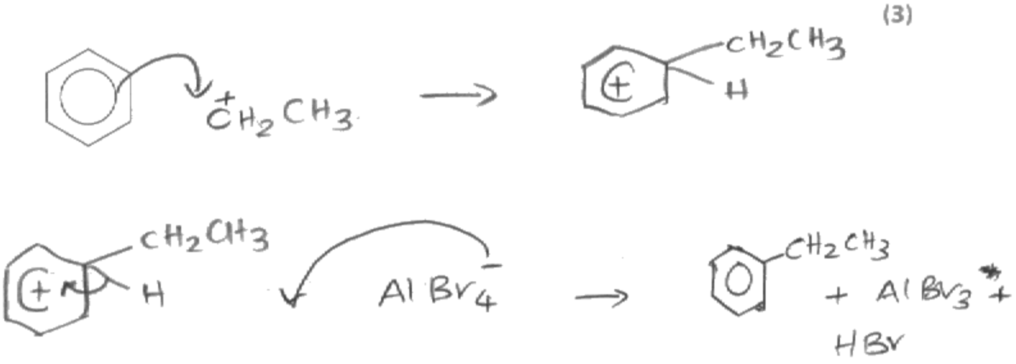
(2)

$CH_3CH_2Br + AlBr_3 \longrightarrow AlBr_4^{-} + CH_3\overset{+}{C}H_2$

catalyst.

(ii) Complete the mechanism for the electrophilic substitution in stage 3. You need only show the benzene ring on the right of the structure. This is given below.

(3)



ResultsPlus

Examiner Comments

2 marks were scored in this bii response as, although the arrows are both correct, the intermediate carbocation has a horseshoe of delocalised electrons which does not point towards the tetrahedral benzene carbon.

(b) Stage 3 is an electrophilic substitution.

(i) Write an equation for the formation of the electrophile and explain the role of the $AlBr_3$ in this process.

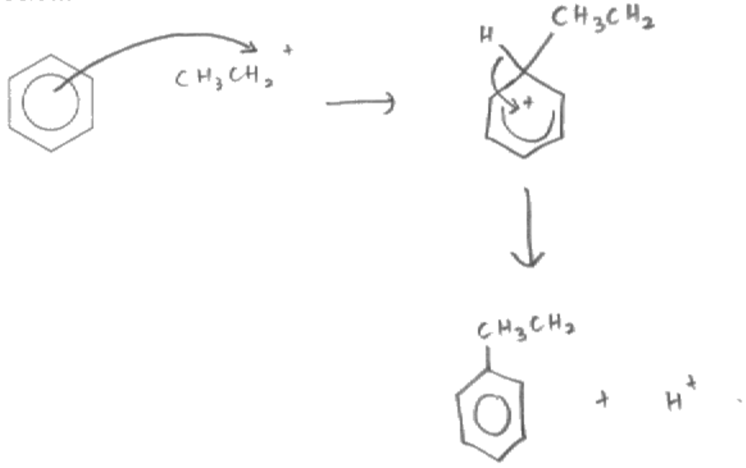
(2)

$CH_3CH_2Br + AlBr_3 \rightarrow CH_3CH_2^+ + AlBr_4^-$

$AlBr_3$ is the halogen carrier.

(ii) Complete the mechanism for the electrophilic substitution in stage 3. You need only show the benzene ring on the right of the structure. This is given below.

(3)



ResultsPlus

Examiner Comments

2 marks were again scored for this answer to b (ii). The intermediate here has a quite common error: the ethyl group is attached to the benzene ring by the wrong carbon.

Question 22 (c)(i)

Many candidates wanted to use HCN for this reaction, sometimes as a reagent, sometimes as solvent, often but not always coupled with KCN.

Question 22 (c)(ii)

There were a good number of correct responses here, although candidates who used a strong alkali often omitted the acidication step.

Question 22 (d)(i-ii)

This question produced a variety of responses including some which included absorptions for the O-H bonds of the acid groups. The question clearly required the C=O absorptions.

Question 23 (a)

Most correct answers here answered in terms of the total number of moles of gaseous reactants and products. A surprising number of answers did not include discussion of the number of moles or molecules and relied on the answer being linked to the formation of liquid water.

Question 23 (b)

There were many correct answers but, as with the previous question, some lacked sufficient detail usually failing to identify the gas absorbed by the potassium hydroxide.

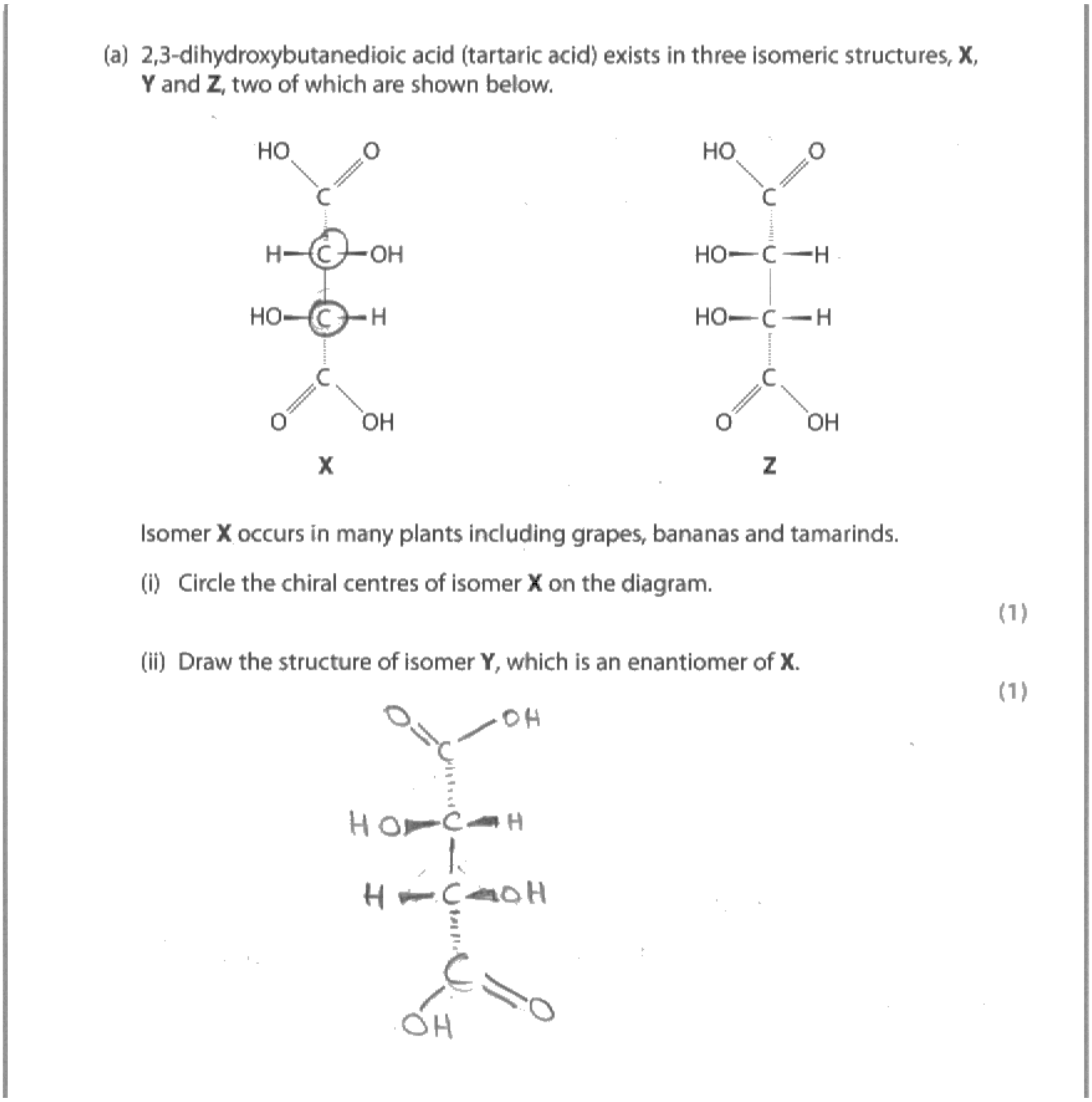
Question 23 (c)

This question had a number of correct responses, although, when the calculation broke down, it was often difficult to award marks for working as candidates did not explain their method clearly.

Question 24 (a)(i-ii)

This was well answered though combinations including any of the four carbons were seen.

There were a good number of correct answers here, although some candidates did not recognise the need for an indication of the three dimensional structure of the isomer.



(a) 2,3-dihydroxybutanedioic acid (tartaric acid) exists in three isomeric structures, **X**, **Y** and **Z**, two of which are shown below.

Isomer **X** occurs in many plants including grapes, bananas and tamarinds.

(i) Circle the chiral centres of isomer **X** on the diagram.

(1)

(ii) Draw the structure of isomer **Y**, which is an enantiomer of **X**.

(1)

ResultsPlus

Examiner Comments

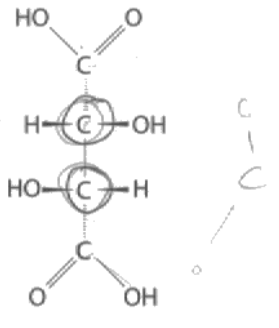
A nice example of the correct answer showing a good 3-D structure.

ResultsPlus

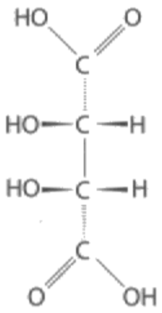
Examiner Tip

Practice drawing 3D structures, particularly of optical isomers

(a) 2,3-dihydroxybutanedioic acid (tartaric acid) exists in three isomeric structures, **X**, **Y** and **Z**, two of which are shown below.



X



Z

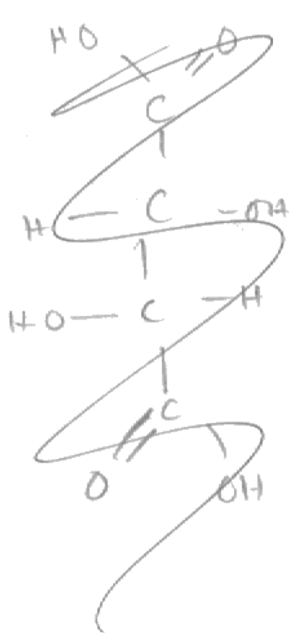
Isomer **X** occurs in many plants including grapes, bananas and tamarinds.

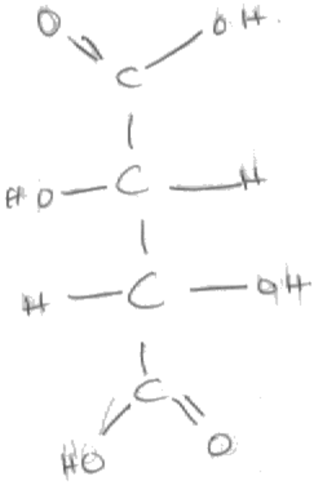
(i) Circle the chiral centres of isomer **X** on the diagram.

(1)

(ii) Draw the structure of isomer **Y**, which is an enantiomer of **X**.

(1)





ResultsPlus
Examiner Comments

This is typical of those who had drawn a 2 dimensional structure so did not score this mark.

Question 24 (a)iii

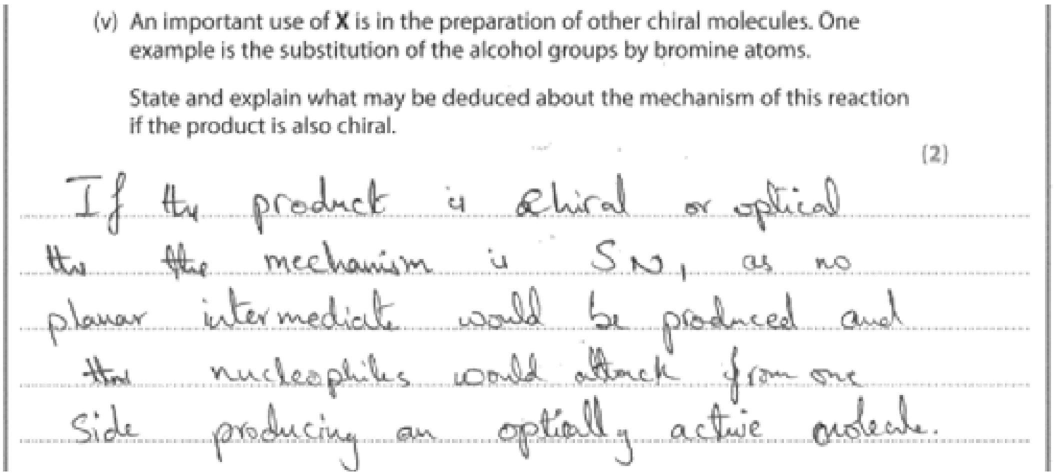
This familiar question was very well answered.

Question 24 (a)(iv)

This question was well answered with most candidates recognising that nmr could not be used to distinguish the two isomers. The best answers referred to the fact that hydrogen environments were the same although the most common explanation stated that the spectra or the peaks were the same and this was deemed sufficient for the mark.

Question 24 (a)(v)

A wide variety of different mechanisms were suggested, but most candidates recognised the reaction was a nucleophilic substitution. The type of substitution was also required, and S_N1 an S_N2 were seen in fairly equal numbers. Some candidates described the formation of intermediate carbocations or transition states, but did not recognise that it was the direction of attack by the incoming nucleophile which determined that a chiral product was formed.



(v) An important use of **X** is in the preparation of other chiral molecules. One example is the substitution of the alcohol groups by bromine atoms.

State and explain what may be deduced about the mechanism of this reaction if the product is also chiral.

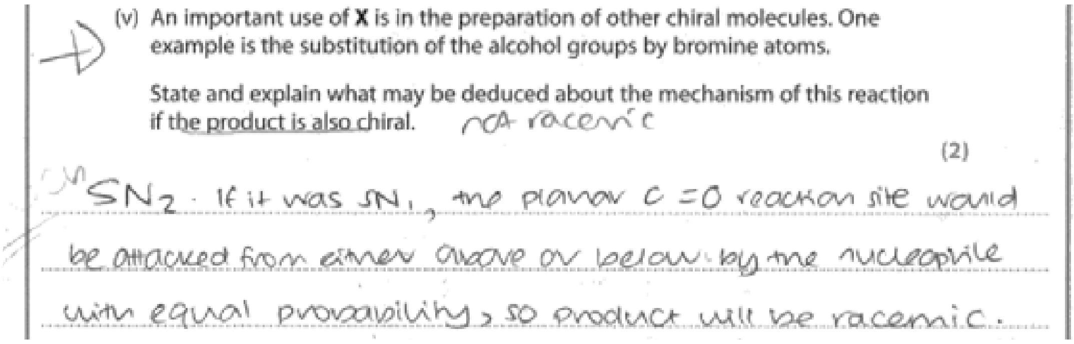
(2)

If the product is chiral or optical then the mechanism is S_N1, as no planar intermediate would be produced and then nucleophiles would attack from one side producing an optically active molecule.

ResultsPlus

Examiner Comments

This candidate correctly identifies the importance of the direction of attack, but does not remember the right mechanism.



(v) An important use of **X** is in the preparation of other chiral molecules. One example is the substitution of the alcohol groups by bromine atoms.

State and explain what may be deduced about the mechanism of this reaction if the product is also chiral. not racemic

(2)

S_N2. If it was S_N1, the planar C=O reaction site would be attacked from either above or below by the nucleophile with equal probability, so product will be racemic.

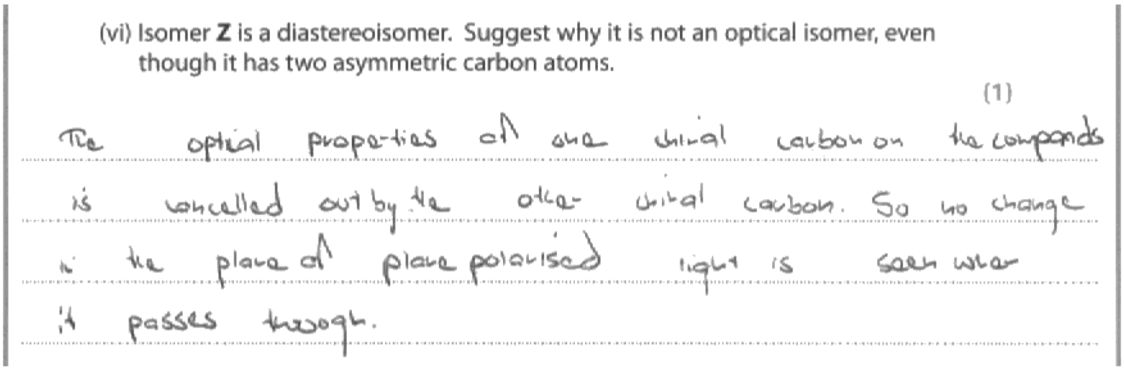
ResultsPlus

Examiner Comments

Two marks for S_N2 and then a nice description of how attack from both sides in S_N1 leads to a racemic mixture.

Question 24 (a)(vi)

Many candidates realised that the molecule would be superimposable on its mirror image and the mark was also scored by describing the effect on plane polarised light of having two chiral centres of the type shown by this molecule



(vi) Isomer **Z** is a diastereoisomer. Suggest why it is not an optical isomer, even though it has two asymmetric carbon atoms.

(1)

The optical properties of one chiral carbon on the compounds is cancelled out by the other chiral carbon. So no change in the plane of plane polarised light is seen when it passes through.

ResultsPlus

Examiner Comments

A good description of the equal and opposite rotation of plane polarised light.

Question 24 (b)(i)

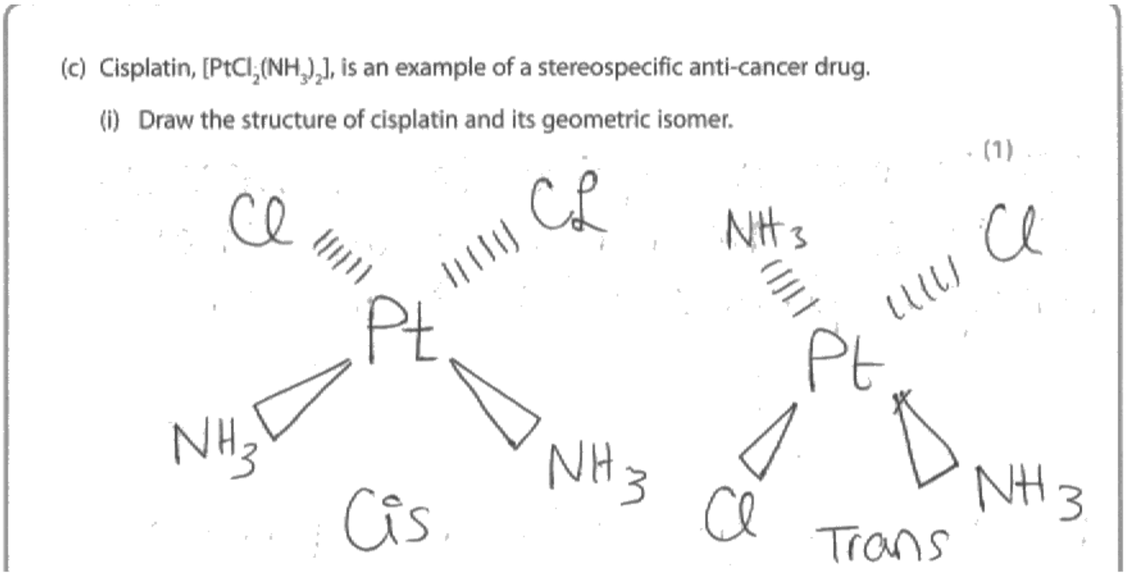
Few candidates appreciated the scope of this question and there were many answers that simply described the formation of the p bond.

Question 24 (b)(ii)

This was another challenging question. Many different types of isomerism were suggested, including positional isomerism and mirror images of flat hexagonal structures were drawn.

Question 24 (c)(i)

Most candidates tackled this question confidently although some failed to read the question with sufficient care and drew only one isomer, Many correct answers were seen including some drawn in the plane of the paper and others shown with dots and wedges.



(c) Cisplatin, $[PtCl_2(NH_3)_2]$, is an example of a stereospecific anti-cancer drug.

(i) Draw the structure of cisplatin and its geometric isomer.

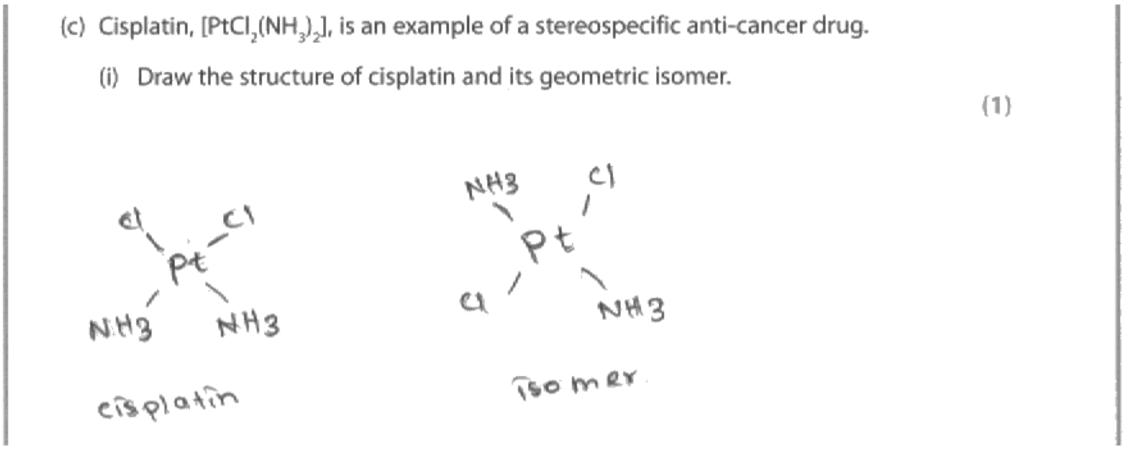
(1)

ResultsPlus
Examiner Comments

A 'dots and wedges' example which scored the mark.

ResultsPlus
Examiner Tip

Learn to draw and practice the shapes of complexes ions mentioned in the specification.



(c) Cisplatin, $[PtCl_2(NH_3)_2]$, is an example of a stereospecific anti-cancer drug.

(i) Draw the structure of cisplatin and its geometric isomer.

(1)

ResultsPlus
Examiner Comments

An excellent example of diagrams drawn in the plane of the paper.

Question 24 (c)(ii)

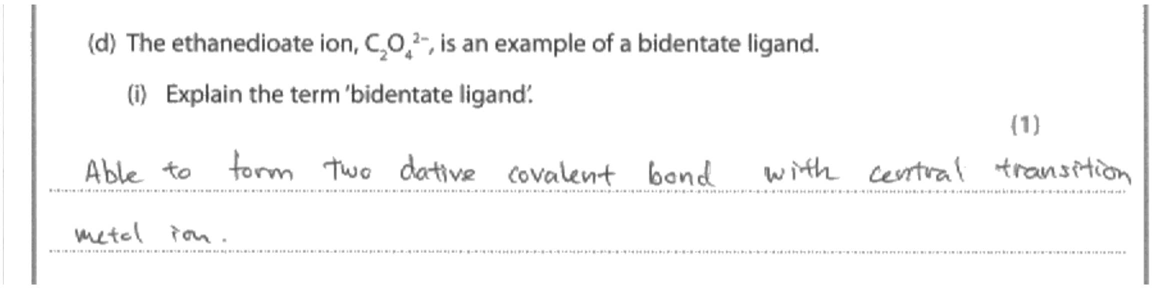
Few candidates provided a convincing explanation of this term with many focusing on the need for a single enantiomer without any attempt to explain why this was desirable.

Question 24 (c)(iii)

Questions on industrial chemical applications frequently attract generalised answers about yield, atom economy, fossil fuel use and greenhouse emissions which are insuffficently specific.

Question 24 (d)(i)

Most candidates were able to score this mark and there were a number who appear to understand the basic requirement without being able to explain it with sufficient precision.



(d) The ethanedioate ion, $C_2O_4^{2-}$, is an example of a bidentate ligand.

(i) Explain the term 'bidentate ligand'.

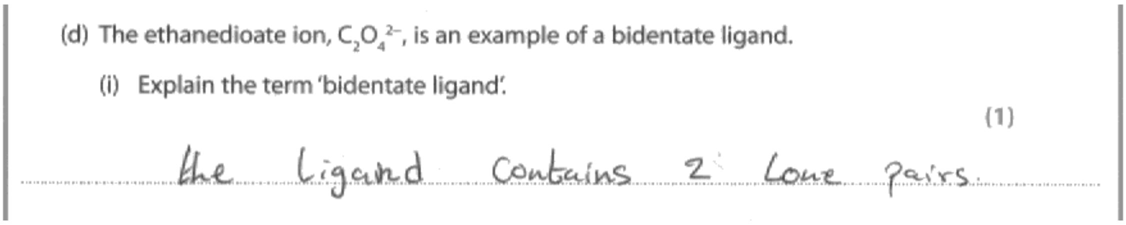
(1)

Able to form Two dative covalent bond with central transition metal ion.

ResultsPlus

Examiner Comments

A typical correct response.



(d) The ethanedioate ion, $C_2O_4^{2-}$, is an example of a bidentate ligand.

(i) Explain the term 'bidentate ligand'.

(1)

the Ligand Contains 2 Lone pairs.

ResultsPlus

Examiner Comments

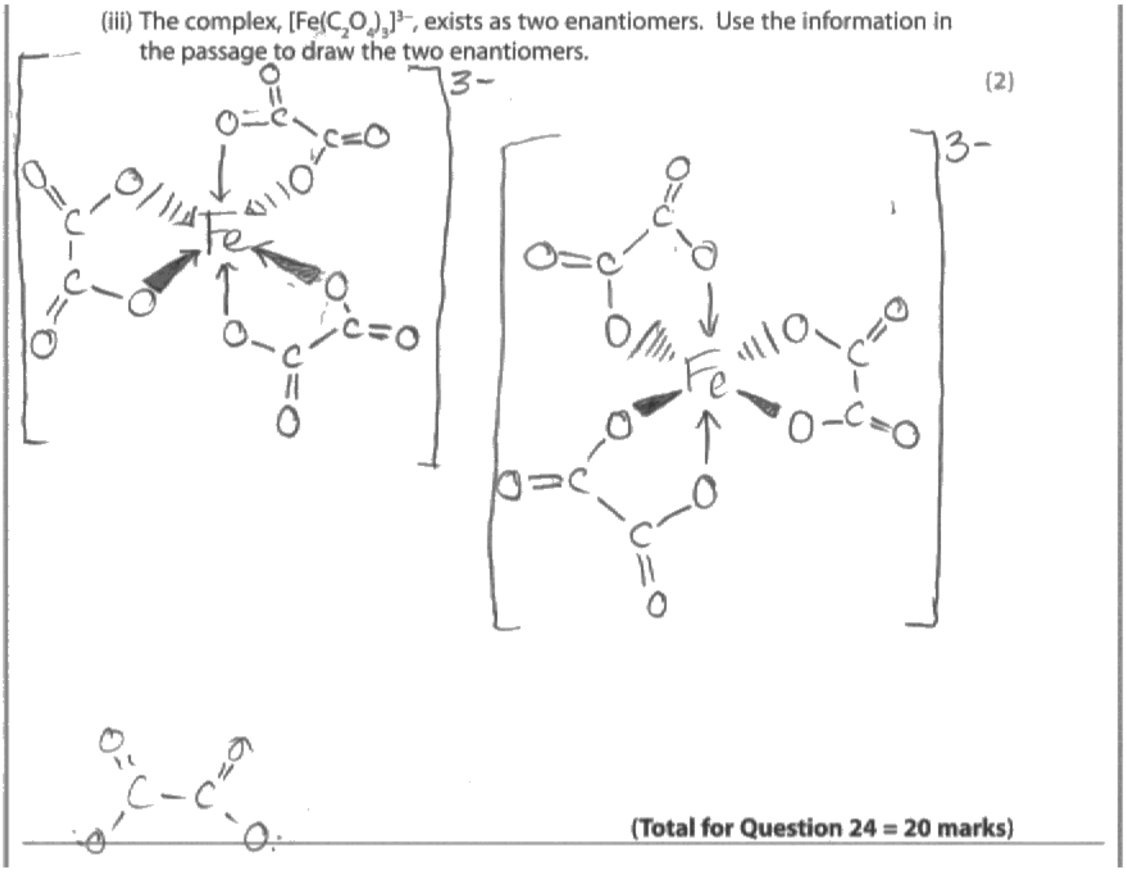
This is not sufficient for credit. Many species have more than one lone pair of electrons without being able to act as bidentate ligands.

Question 24dii

This proved to be a poorly understood concept, with many candidates guessing that stability was a function of bond strength.

Question 24diii

Most candidates attempted to answer this question using a shorthand type of diagram. This could score 1 mark if both isomers were given correctly, including the correct charge. Full marks were only scored for fully correct isomers showing clearly the structure and bonding involved.



(iii) The complex, $[Fe(C_2O_4)_3]^{3-}$, exists as two enantiomers. Use the information in the passage to draw the two enantiomers.

(2)

(Total for Question 24 = 20 marks)

ResultsPlus

Examiner Comments

A good example of a fully correct diagram.

Paper Summary

Questions that were familiar to candidates from previous years, for example colour in complex ions and Friedel-Crafts Alkylation were generally answered well. Drawing three dimensional diagrams showing the structure of molecules and complex ions was a weakness. For some candidates question 23 proved challenging and question 24 appeared to discriminate well at a number of levels. General advice would include:

- remember that AS content will be required when answering A2 question papers;
- practice drawing three dimensional diagrams showing all bonds clearly;
- organic mechanisms need to be accurately drawn. Try to ensure the correct part of the electrophile has been bonded to the benzene ring in electrophilic substitution;
- read questions carefully, especially those in Section C or questions set in an unfamiliar context. You may find highlighting or underlining helpful;
- learn how to balance half-equations and then how to add them together to produce the overall equation for a reaction. Remember to include the electrons in half-equations but that full equations never show electrons;
- label each step of a calculation to show clearly what you are attempting to work out.

Grade Boundaries

Grade boundaries for this, and all other papers, can be found on the website on this link:

http://www.edexcel.com/iwantto/Pages/grade-boundaries.aspx

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