Examiners' Report
June 2015

GCE Chemistry 5 6CH05 01

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June 2015

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Introduction

The paper included questions that assessed candidates across the ability range and generated some excellent responses.

Questions involving recall were generally answered well. Knowledge of organic reactions was good and the organic mechanism was very well known. However questions involving application showed that some concepts were poorly understood.

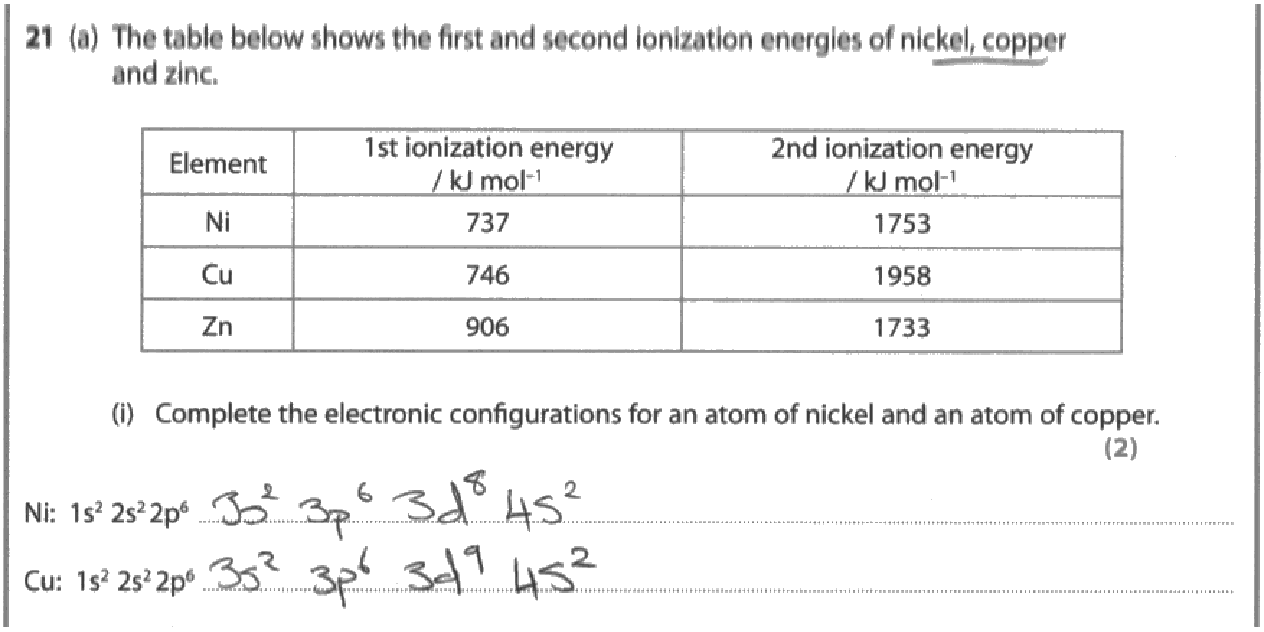
A few candidates seemed short of time towards the end of the paper, sometimes because they did unnecessary time consuming work in some of the earlier questions.

The work shown in some of the numerical questions was disappointing. Despite being asked to give an answer to three significant figures in one question, many candidates were rounding intermediate values down to two significant figures. In a calculation to find the percentage composition of a compound, some candidates completely ignored one of the elements present. In some cases calculations were difficult to follow as candidates gave no written explanation with the numbers.

Many candidates have difficulty writing ionic equations and half equations and this is a skill they should practice.

Question 21 (a) (i)

Most candidates answered this question correctly. They could show the 4s electrons before or after the 3d electrons. A few candidates forgot to include the 3s and 3p electrons, but only a very small number made more major errors.



21 (a) The table below shows the first and second ionization energies of nickel, copper and zinc.

Element	1st ionization energy / kJ mol^{-1}	2nd ionization energy / kJ mol^{-1}
Ni	737	1753
Cu	746	1958
Zn	906	1733

(i) Complete the electronic configurations for an atom of nickel and an atom of copper.
(2)

Ni: $1s^2\,2s^2\,2p^6$ $3s^2\,3p^6\,3d^8\,4s^2$

Cu: $1s^2\,2s^2\,2p^6$ $3s^2\,3p^6\,3d^9\,4s^2$

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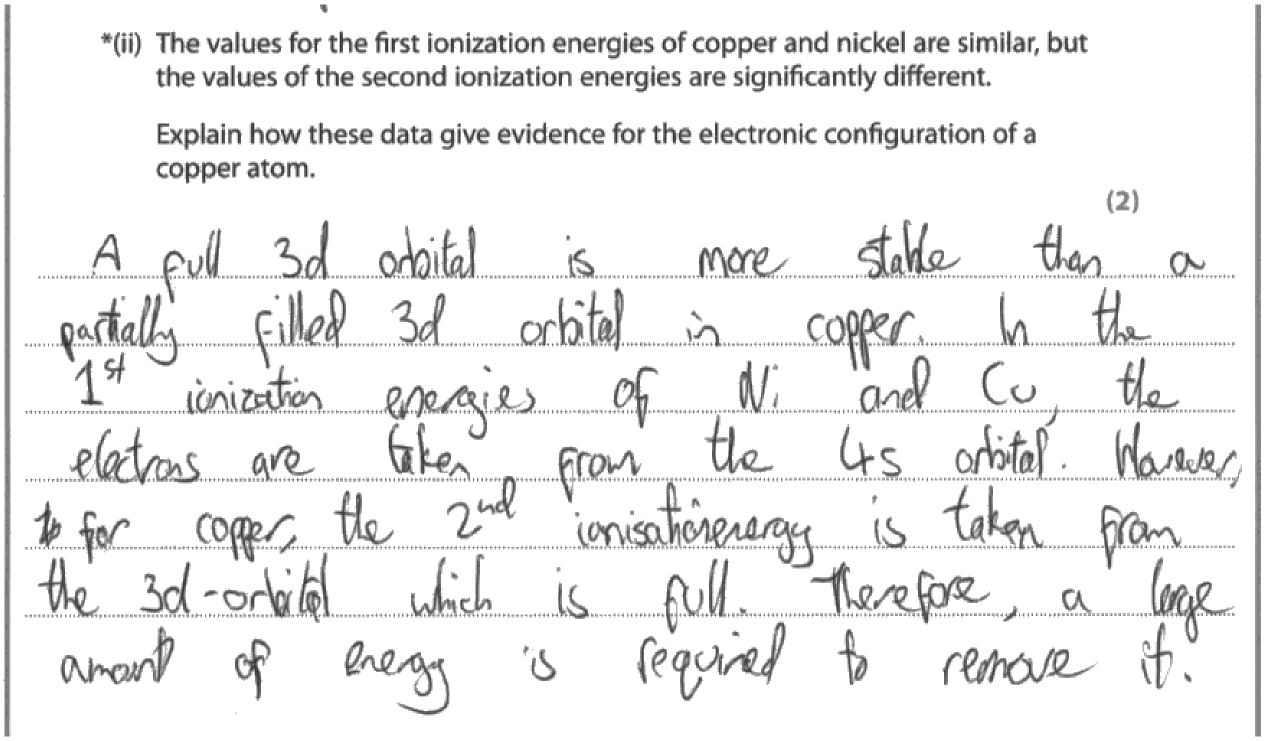
Examiner Comments

This candidate did not appreciate the fact that in copper the 3d sub-shell was full. Only 1 mark was awarded.

Question 21 (a) (ii)-(iii)

Most candidates scored the first mark in (a)(ii) as they realised that in both copper and nickel the first electron removed in ionization would come from 4s. However the second mark was often missed. Candidates thought that copper had a higher second ionization energy because it was hard to break into a full 3d sub-shell in copper, but did not give the reason that the 3d electrons were closer to the nucleus or less shielded than the second 4s electron in nickel.

In (a)(iii) many candidates did not think about the trend in the third ionization values from nickel to zinc, and simply discussed the electron configuration of zinc, or compared the second and third ionization energies. With a little thought candidates should have realised that the third electron in all three metals was being removed from the same shell. Some answers referred to the charge on the ions compared to the charge of the nucleus, but in each case an electron would have to be removed from an ion with two positive charges, and the change which occurred across the three elements was the proton number.



*(ii) The values for the first ionization energies of copper and nickel are similar, but the values of the second ionization energies are significantly different.

Explain how these data give evidence for the electronic configuration of a copper atom.

(2)

A full 3d orbital is more stable than a partially filled 3d orbital in copper. In the 1st ionization energies of Ni and Cu, the electrons are taken from the 4s orbital. However, ~~to~~ for copper, the 2nd ionisationenergy is taken from the 3d-orbital which is full. Therefore, a large amount of energy is required to remove it.

(iii) Suggest why you might expect the **third** ionization energies of the three elements to increase from nickel to zinc.

(1)

Because zinc has a full 4s orbital and a full 3d orbital.

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Examiner Comments

In (a)(ii) the candidate used the idea that a full orbital was hard to break into, and did not consider the attraction of the nucleus for the 3d electrons. This scored the first mark only.

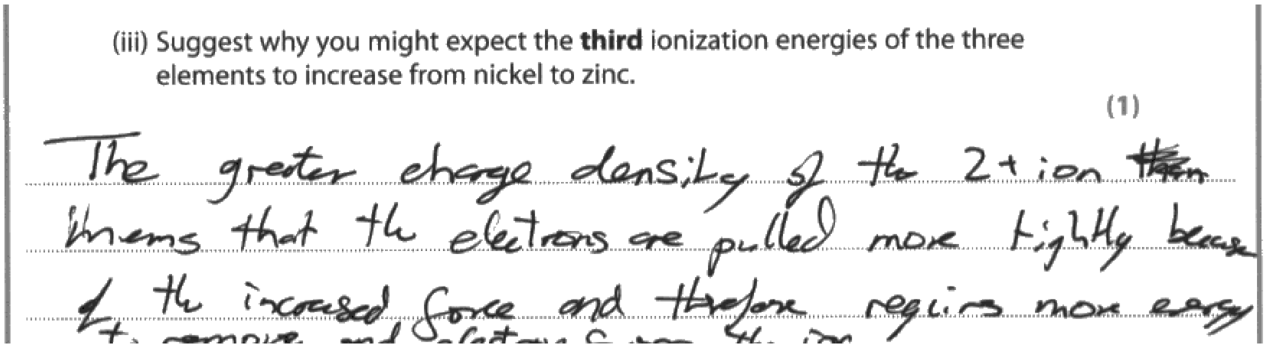
In (a)(iii) the answer did not consider the trend in third ionization energies from nickel to zinc, so scored 0.

*(ii) The values for the first ionization energies of copper and nickel are similar, but the values of the second ionization energies are significantly different.

Explain how these data give evidence for the electronic configuration of a copper atom.

(2)

The first ionization energy is similar as both Ni and Cu are losing an electron in the 4s substell. The second is different as Cu 2nd ionization energy is higher than Ni's because an electron is being removed from a new sub shell in Cu ($3d^{10}$) and so requires more energy to remove than the second electron in the 4s substell for Ni because of the increased pull on the electron from the nucleus because the $3d^{10}$ shell is closer than the 4s shell to the nucleus.



(iii) Suggest why you might expect the **third** ionization energies of the three elements to increase from nickel to zinc.

(1)

The greater charge density of the 2+ ion ~~then~~ means that the electrons are pulled more tightly because of the increased force and therefore requires more energy

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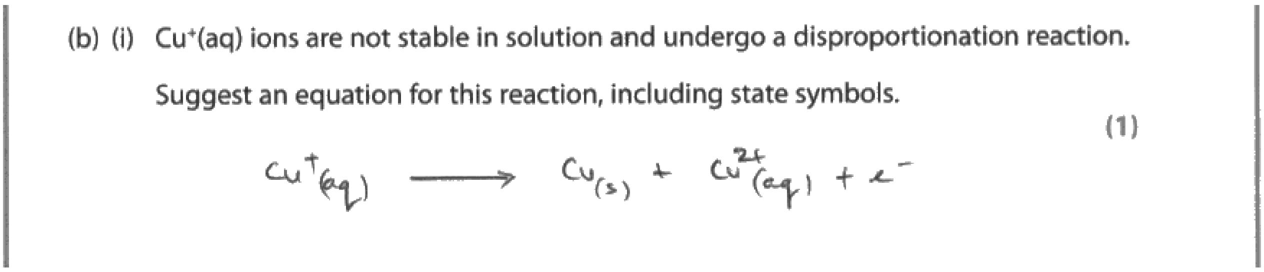
Examiner Comments

The answer to (a)(ii) was an example of one which scored both marks. In (a)(iii) the charge density of the 2+ ion was not the relevant factor affecting the third ionization energy. The charge density depended on the radius of the ion. The increasing number of protons in the nucleus was the point which had to be considered so this part scored 0.

Question 21 (b) (i)

Some candidates wrote ion-electron half equations showing the oxidation of the copper(I) ion but these did not show disproportionation. A common mistake was to forget to include the state symbols.



(b) (i) $Cu^+(aq)$ ions are not stable in solution and undergo a disproportionation reaction.

Suggest an equation for this reaction, including state symbols.

(1)

$Cu^+_{(aq)} \longrightarrow Cu_{(s)} + Cu^{2+}_{(aq)} + e^-$

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Examiner Comments

This candidate tried to balance the charge in the equation by adding an electron, but did not balance the copper. This scored 0.

ResultsPlus

Examiner Tip

Equations which include electrons are called half equations. This question required an equation for disproportionation so electrons should not have been included.

(b) (i) $Cu^{+}(aq)$ ions are not stable in solution and undergo a disproportionation reaction.

Suggest an equation for this reaction, including state symbols.

(1)

$$2Cu^{+}_{(aq)} \rightarrow Cu^{2+}_{(s)} + Cu_{(aq)}$$

ResultsPlus

Examiner Comments

This candidate wrote the equation correctly but made an error in the state symbols.

ResultsPlus

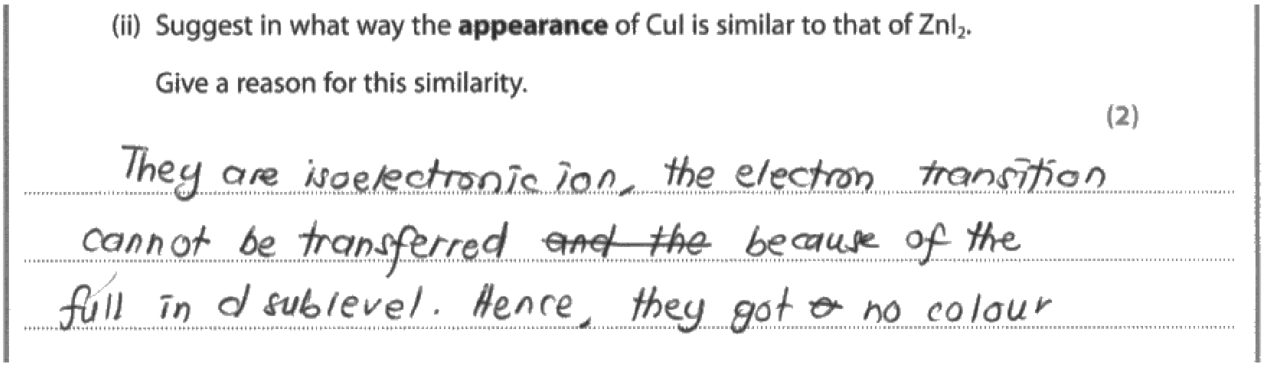
Examiner Tip

Check your work carefully so that you avoid mistakes like this one.

Question 21 (b) (ii)

Many answers correctly predicted that solid CuI and ZnI_2 would be white.

Answers stating that solutions would be colourless were allowed because of the reference to Cu^+ ions in solution in (b)(i). However the second mark was sometimes lost because candidates did not take enough care when they referred to 3d orbitals. It was not enough to say that the compounds had a full d orbital. The answer had to make clear that **all** the 3d orbitals would be full, or the 3d sub-shell would be full.



(ii) Suggest in what way the **appearance** of CuI is similar to that of ZnI_2.

Give a reason for this similarity.

(2)

They are isoelectronic ion, the electron transition cannot be transferred ~~and the~~ because of the full in d sublevel. Hence, they got ~~o~~ no colour

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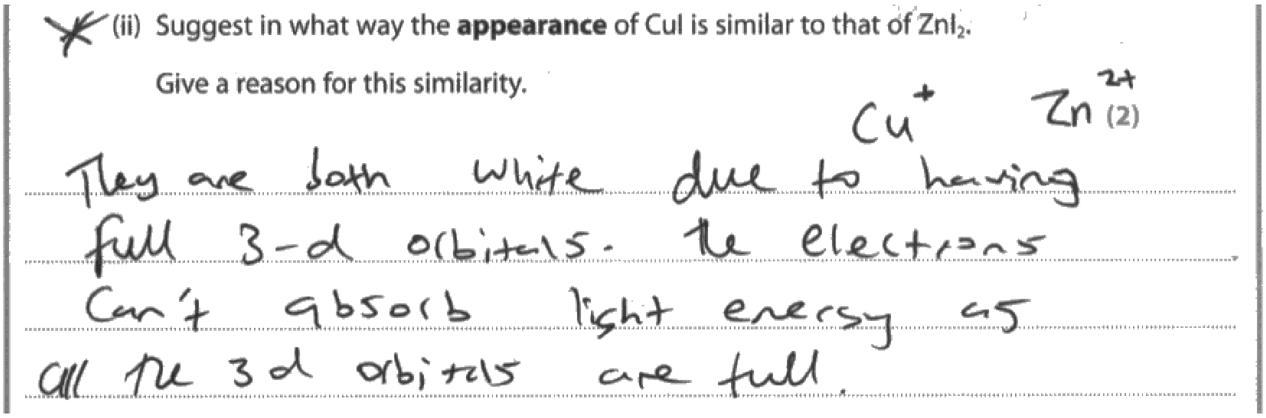
Examiner Comments

This candidate gained 1 mark for saying that the compounds had no colour.



(ii) Suggest in what way the **appearance** of CuI is similar to that of ZnI_2.

Give a reason for this similarity.

Cu^+ Zn^{2+} (2)

They are both white due to having full 3-d orbitals. The electrons can't absorb light energy as all the 3d orbitals are full.

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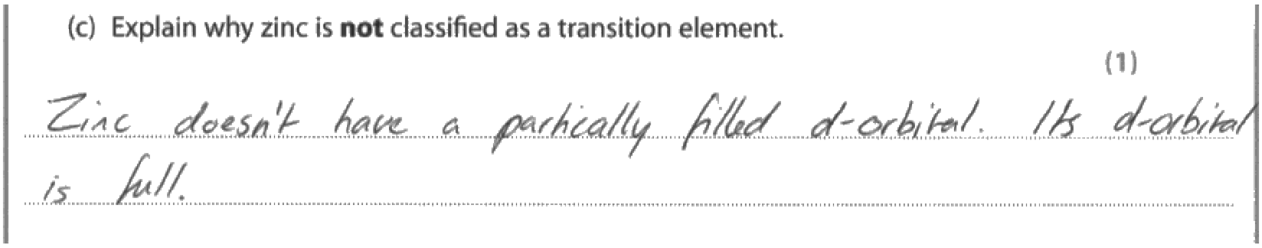
Examiner Comments

This response scored both marks. It stated that all 3d orbitals are full.

Question 21 (c)

Many candidates had learnt the text book definition of a transition element. Those who lost the mark usually forgot to refer to the element having an **ion** with an incomplete d orbital or d sub-shell.



(c) Explain why zinc is **not** classified as a transition element.

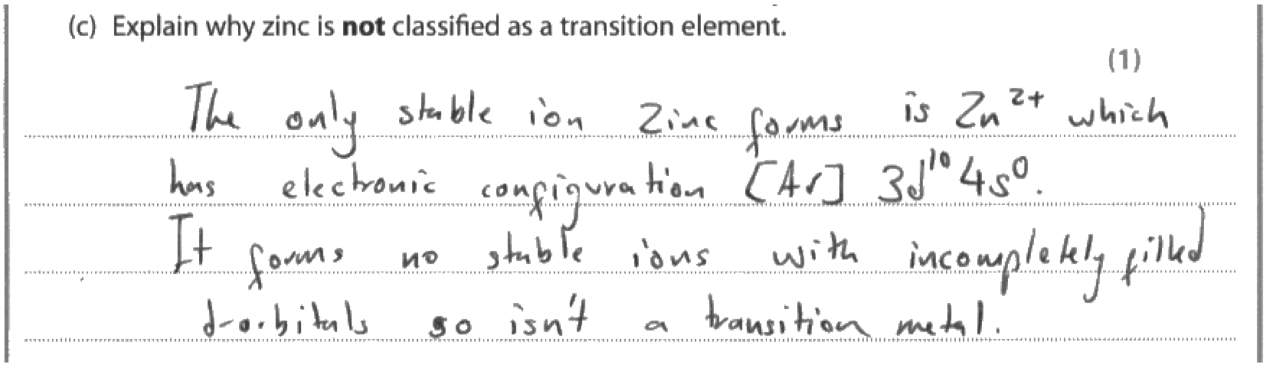
(1)

Zinc doesn't have a partially filled d-orbital. Its d-orbital is full.

ResultsPlus

Examiner Comments

This answer did not refer to either atoms or ions. Stating that in the ion the d orbital was full would still not have got the mark, as it would have to make clear that all the d orbitals in the ion were full or the d sub-shell was full. It scored 0.



(c) Explain why zinc is **not** classified as a transition element.

(1)

The only stable ion Zinc forms is Zn^{2+} which has electronic configuration [Ar] $3d^{10}4s^0$. It forms no stable ions with incompletely filled d-orbitals so isn't a transition metal.

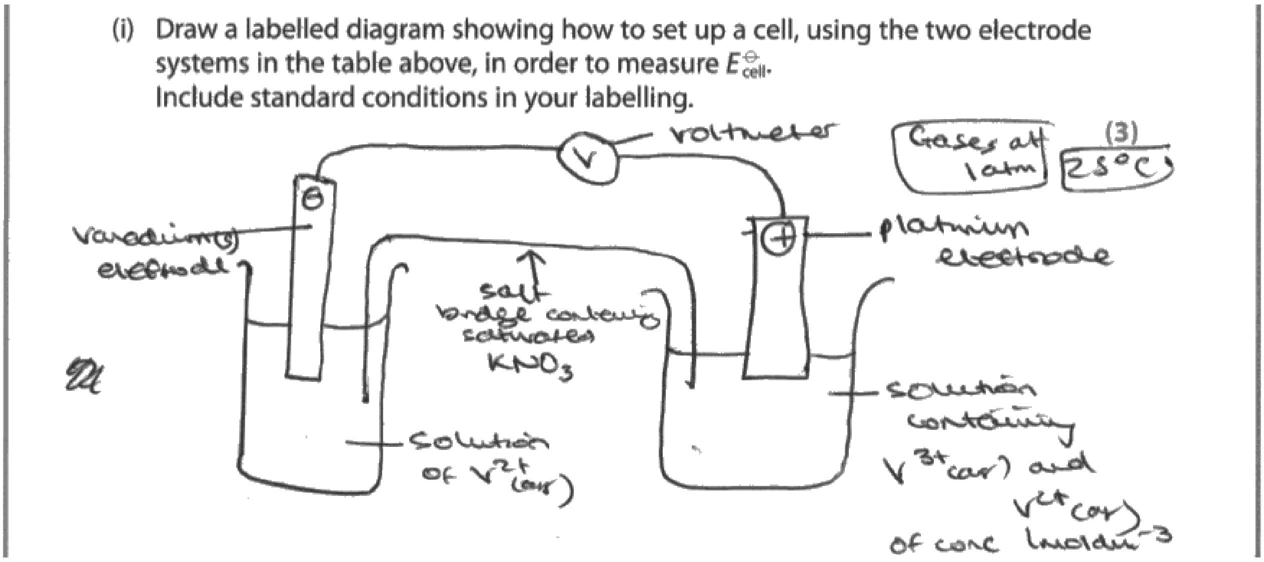
ResultsPlus

Examiner Comments

This was an example of a good answer.

Question 22 (a) (i)

The drawing of the cell should have shown two beakers with one of the two electrode systems in each and with the correct electrodes. Some candidates drew a hydrogen electrode on one side which lost the first mark. Solution levels were required with a representation of the salt bridge dipping into the solution. However some salt bridges were shown in mid-air above the beakers and were not given the second mark. The circuit should have been completed with connections from the electrodes to a voltmeter and a recurring mistake was to forget to show the voltmeter or, less frequently, to show a circuit with an ammeter or battery. The concentration of the solutions in at least one beaker should have been shown, but the concentration of the solution in the salt bridge was not relevant.



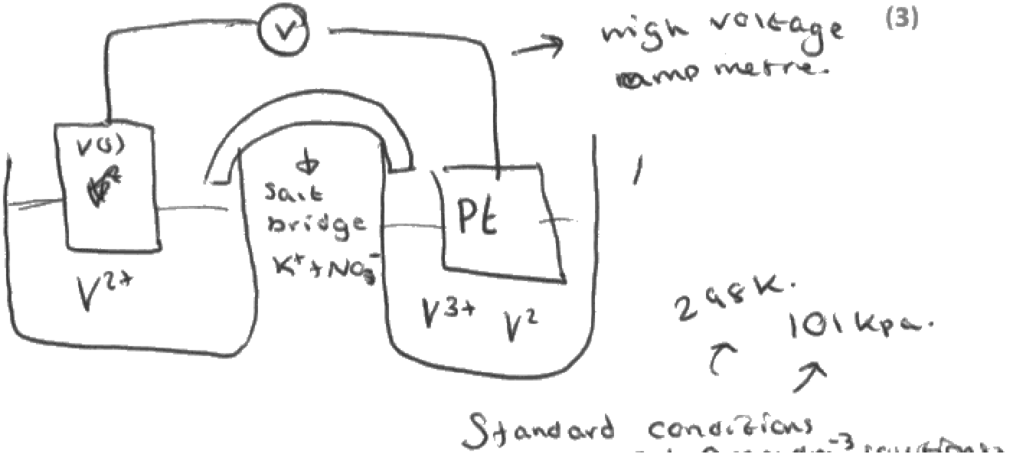
(i) Draw a labelled diagram showing how to set up a cell, using the two electrode systems in the table above, in order to measure $E^{\ominus}_{cell}$.
Include standard conditions in your labelling.
(3)

ResultsPlus
Examiner Comments

This was an example of a good answer which scored all 3 marks.

(i) Draw a labelled diagram showing how to set up a cell, using the two electrode systems in the table above, in order to measure $E^{\ominus}_{cell}$.
Include standard conditions in your labelling.

(3)



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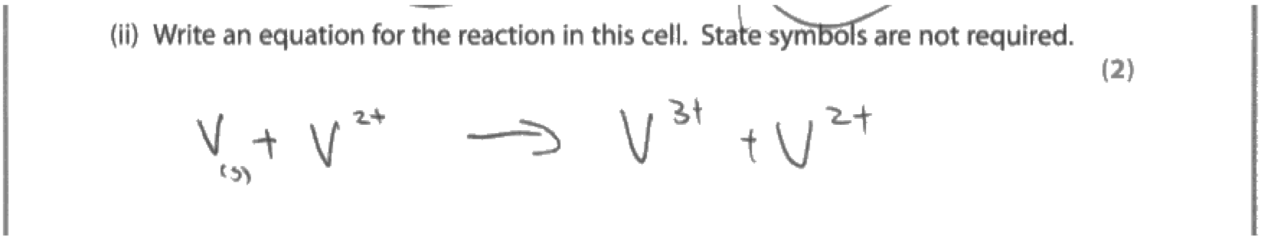
Examiner Comments

This answer lost the second marking point as the salt bridge was not in the solution. The concentrations are included at the very bottom of the clip so this scored 2 marks.

Question 22 (a) (ii)

Candidates could score 1 mark here for showing the correct direction of the cell reaction, which had to be deduced from the values of the standard electrode potentials. Another mark could be scored for a fully balanced equation. Many candidates found it difficult to balance the charge in ionic equations, and the final equation should not have had electrons in it.

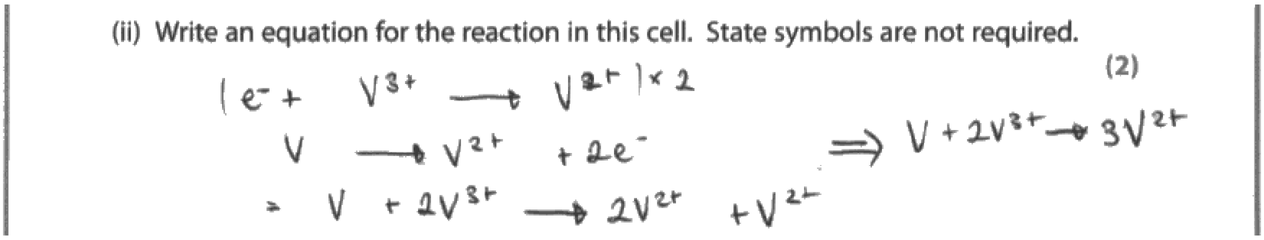


(ii) Write an equation for the reaction in this cell. State symbols are not required. (2)

$V_{(s)} + V^{2+} \longrightarrow V^{3+} + V^{2+}$

ResultsPlus
Examiner Comments

This answer did not score the mark for the direction of the reaction as the V^{2+} ions, which are the product, are shown on both sides. The rest of the equation was also incorrect so the mark was 0.



(ii) Write an equation for the reaction in this cell. State symbols are not required. (2)

$(e^- + V^{3+} \longrightarrow V^{2+}) \times 2$

$V \longrightarrow V^{2+} + 2e^-$

$\Rightarrow V + 2V^{3+} \longrightarrow 2V^{2+} + V^{2+}$

$\Rightarrow V + 2V^{3+} \longrightarrow 3V^{2+}$

ResultsPlus
Examiner Comments

This candidate correctly used the half equations to work out the final equation and this scored 2 marks.

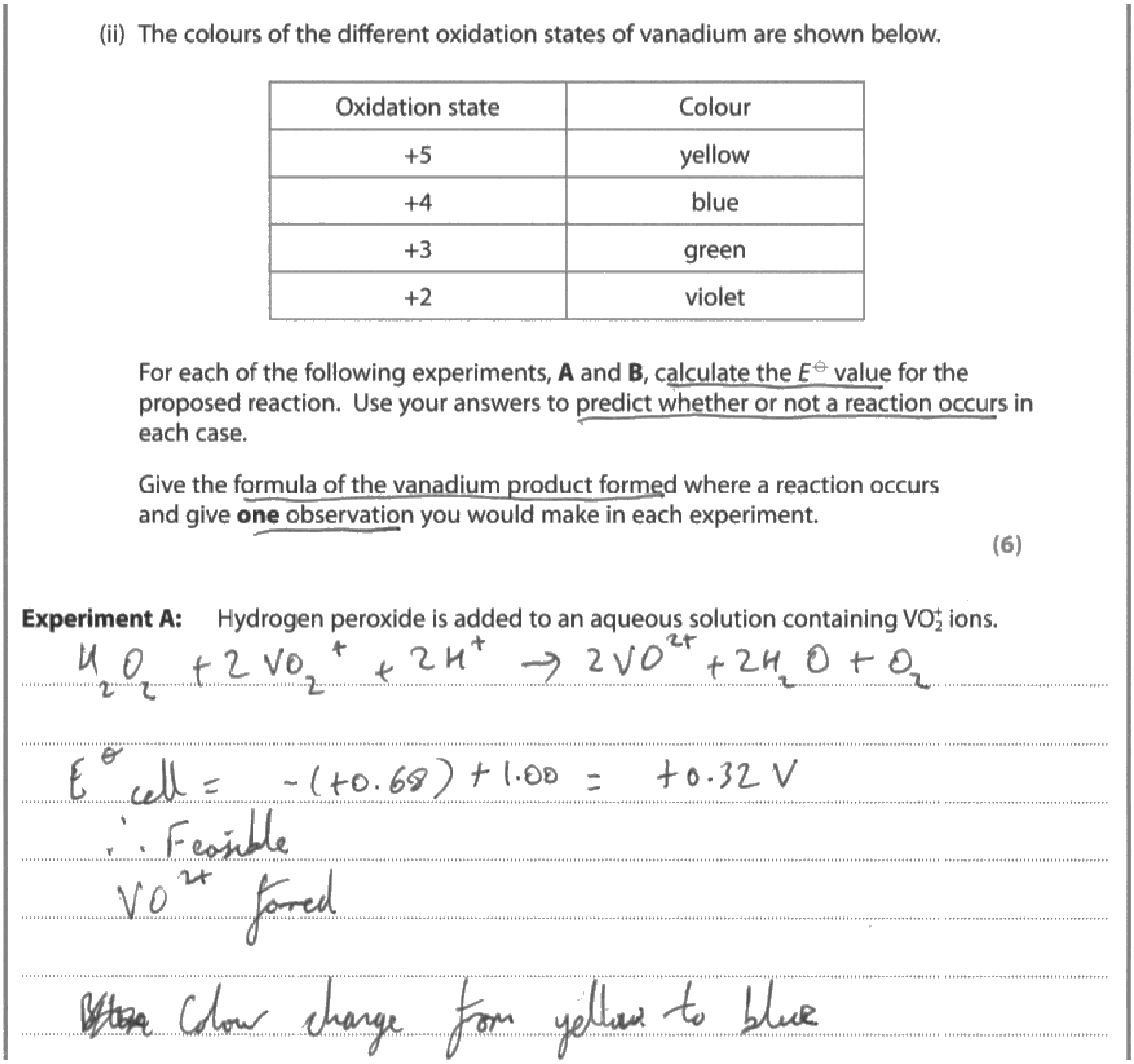
Question 22 (b) (i)

Nearly all candidates succeeded in finding the correct pieces of data and quoting them with their signs.

Question 22 (b) (ii)

In this question, candidates had to use the data on standard electrode potential to deduce whether a reaction occurred, and if so what was produced. It produced a full range of marks with many excellent answers, although some contained contradicting statements.

The sign and value for the electrode potential in experiment **A** was correct more often than for experiment **B**. Some candidates deduced the vanadium product in experiment **A** with apparent ease while others included many lines of equations. The observation here could have been the colour of the vanadium product or the bubbles which would be seen from the decomposition of hydrogen peroxide. The electrode potential for experiment **B** had a negative value so no reaction would be expected. Some answers said this, but then went on to name a vanadium product and give a colour change. Having said the reaction was not feasible, they did not seem to understand the term. If answers were consistent in their interpretation of the calculated electrode potentials they gained the final mark.



(ii) The colours of the different oxidation states of vanadium are shown below.

Oxidation state	Colour
+5	yellow
+4	blue
+3	green
+2	violet

For each of the following experiments, **A** and **B**, calculate the $E^\ominus$ value for the proposed reaction. Use your answers to predict whether or not a reaction occurs in each case.

Give the formula of the vanadium product formed where a reaction occurs and give **one** observation you would make in each experiment.

(6)

Experiment A: Hydrogen peroxide is added to an aqueous solution containing VO_2^+ ions.

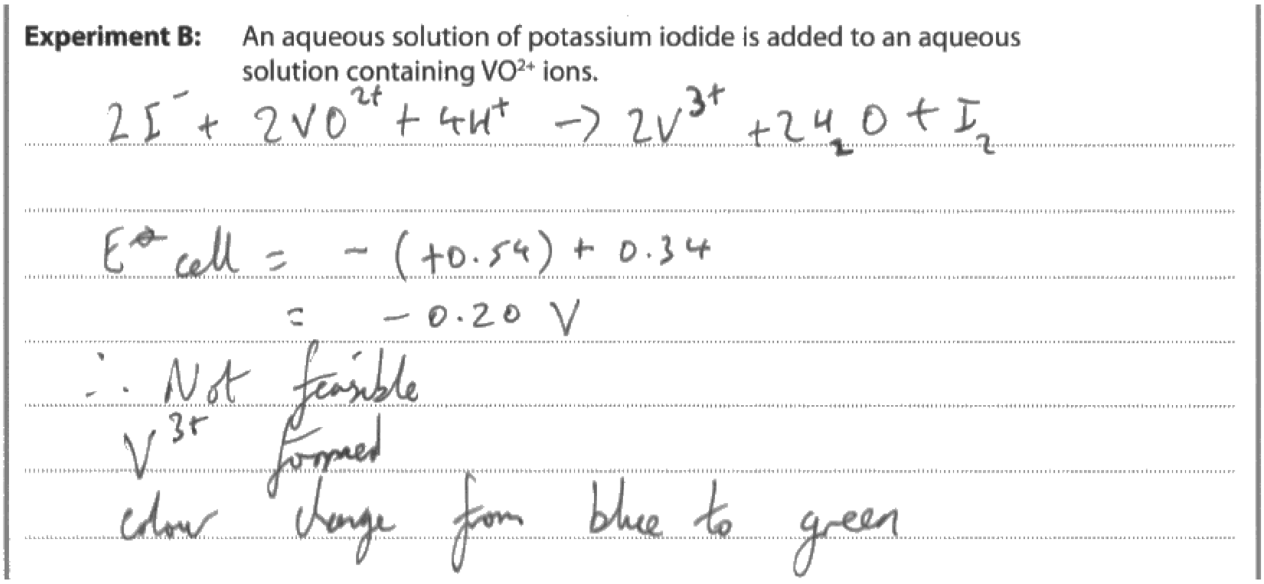
$H_2O_2 + 2VO_2^+ + 2H^+ \rightarrow 2VO^{2+} + 2H_2O + O_2$

$E^\theta_{cell} = -(+0.68) + 1.00 = +0.32\ V$

∴ Feasible

VO^{2+} formed

~~Obse~~ Colour change from yellow to blue



Experiment B: An aqueous solution of potassium iodide is added to an aqueous solution containing VO^{2+} ions.

$2I^- + 2VO^{2+} + 4H^+ \rightarrow 2V^{3+} + 2H_2O + I_2$

$E^\ominus cell = -(+0.54) + 0.34$

$= -0.20\ V$

∴ Not feasible

V^{3+} formed

colour change from blue to green

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Examiner Comments

This candidate calculated both electrode potentials correctly. In experiment **B** a reaction was described even though the reaction was said not to be feasible so the mark for consistent application of electrode potential data could not be given and so 4 marks were given.

ResultsPlus

Examiner Tip

In a question like this where there are several things to do it is worth ticking them off so that you don't leave something out.

(ii) The colours of the different oxidation states of vanadium are shown below.

Oxidation state	Colour
+5	yellow
+4	blue
+3	green
+2	violet

For each of the following experiments, **A** and **B**, calculate the $E^\ominus$ value for the proposed reaction. Use your answers to predict whether or not a reaction occurs in each case.

Give the formula of the vanadium product formed where a reaction occurs and give **one** observation you would make in each experiment.

(6)

Experiment A: Hydrogen peroxide is added to an aqueous solution containing VO_2^+ ions.

$E^\circ = +0.34$, a reaction occurs.

yellow solution. (VO_2^+)

Experiment B: An aqueous solution of potassium iodide is added to an aqueous solution containing VO^{2+} ions.

+0.20, a reaction occurs

(VO^{2+}) ∴ blue solution forms.

ResultsPlus
Examiner Comments

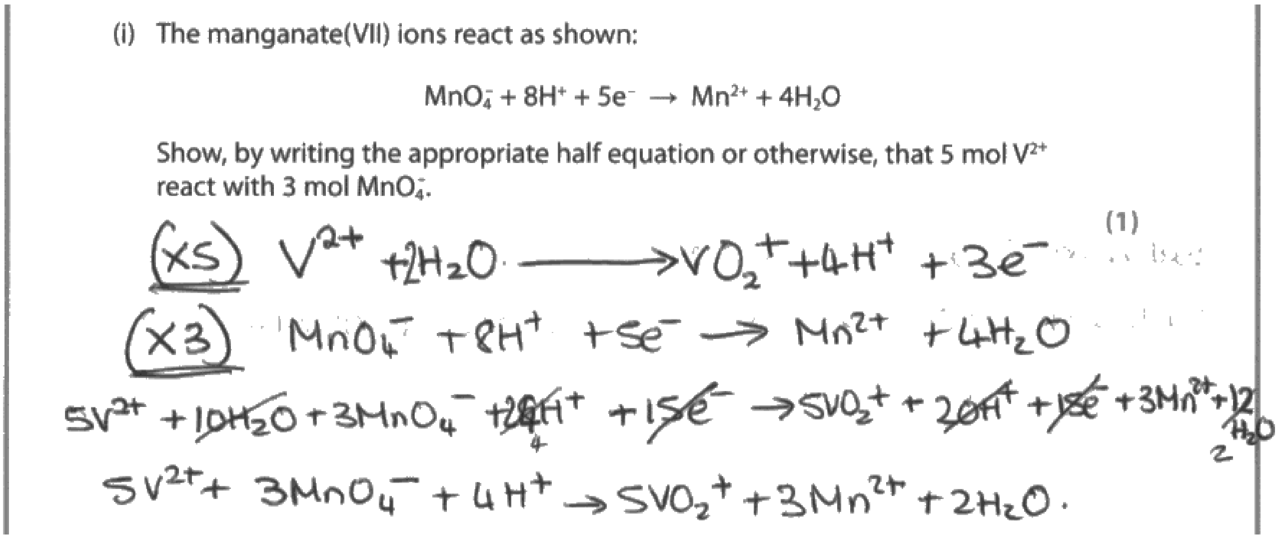
This answer showed consistency in thinking that a positive electrode potential means that a reaction will occur. However the solution in experiment **B** starts off blue, and if a reaction did occur it would end up green or brown. There was also an error in the calculated electrode potential in experiment **A** and the formula of the ion produced. Only the 1 mark for consistency was given.

Question 22 (c) (i)

The reacting ratio could be shown here in several ways. The mark was awarded for a balanced half equation in which V^{2+} ions were oxidized to VO_2^+ with the production of three electrons.

Alternatively the full equation for the reaction of $5V^{2+}$ ions with $3MnO_4^-$ ions could be shown.

Very few candidates chose to explain that the ratio arises because the oxidation number of vanadium increases by 3 while the oxidation number of manganese decreases by 5.



(i) The manganate(VII) ions react as shown:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

Show, by writing the appropriate half equation or otherwise, that 5 mol V^{2+} react with 3 mol MnO_4^-.

(1)

$(x5)\ V^{2+} + 2H_2O \longrightarrow VO_2^+ + 4H^+ + 3e^-$

$(x3)\ MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$5V^{2+} + \cancel{10H_2O} + 3MnO_4^- + \underset{4}{\cancel{24}}H^+ + \cancel{15e^-} \rightarrow 5VO_2^+ + \cancel{20H^+} + \cancel{15e^-} + 3Mn^{2+} + \underset{2}{\cancel{12}}H_2O$

$5V^{2+} + 3MnO_4^- + 4H^+ \rightarrow 5VO_2^+ + 3Mn^{2+} + 2H_2O.$

ResultsPlus

Examiner Comments

This candidate did what was asked and wrote the appropriate half equation. The full equation was also correct and it scored 1 mark.

(i) The manganate(VII) ions react as shown:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

Show, by writing the appropriate half equation or otherwise, that 5 mol V^{2+} react with 3 mol MnO_4^-.

(1)

$$\boxed{V^{2+} \rightarrow V^{5+}O_2 + 3e^-}$$

$V^{5+} + O_2 \rightarrow VO_2^+$

To balance the e^- being used by MnO_4^- and lost by V^{2+}, you must use a 5:3 ratio of V^{2+} : MnO_4^-.

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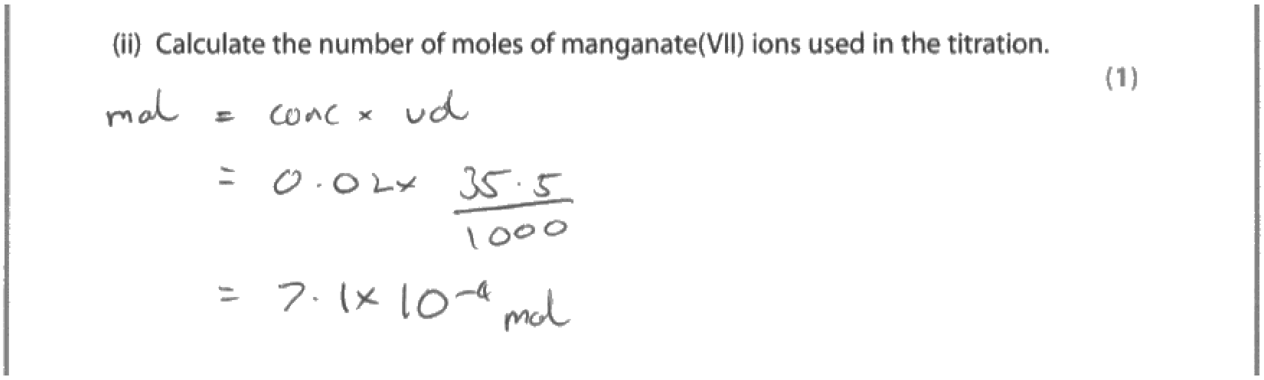
Examiner Comments

The half equation which was given was not the one which occurred in the reaction with MnO_4^- ions so this scored 0.

Question 22 (c) (ii)-(iii)

This question was well done. Most candidates calculated (c)(ii) correctly and there were also many correct answers in (c)(iii). Errors occurred in using the 5:3 ratio incorrectly, and in calculating the molar mass of ammonium vanadate.

The question asked for the percentage purity to three significant figures, so candidates should have kept answers to the intermediate stages to four or more figures, and rounded to three in the final answer. In this particular question, earlier rounding was not penalised as long as the principles of the method were correct, but candidates should be aware that if data is given to four significant figures it should not be rounded to two in calculations.



(ii) Calculate the number of moles of manganate(VII) ions used in the titration.

(1)

mol = conc × vol

$= 0.02 \times \frac{35.5}{1000}$

$= 7.1 \times 10^{-4}$ mol

(iii) Calculate the number of moles of VO_2^+ in the original solution, and hence the percentage purity of the sample of NH_4VO_3. Give your answer to **three** significant figures.

Molar mass of $NH_4VO_3 = 116.9\ g\ mol^{-1}$.

(3)

$$\text{mol } V^{2+} = \frac{3}{5} \times \text{mol } MnO_4^-$$

$$= \frac{3}{5} \times 7.1 \times 10^{-4}$$

$$= 4.26 \times 10^{-4} \text{ mol}$$

$$\text{mol } V^{4+} = \text{mol } VO_2^+ = \text{mol } NH_4VO_3$$

$$= 4.26 \times 10^{-4}$$

$$\text{mass } NH_4VO_3 = 4.26 \times 10^{-4} \times 116.9$$

$$= 0.0498 g \quad (3s.f)$$

$$\% \text{ purity} = \frac{0.0498}{0.150} \times 100\% = 33.2\%$$

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Examiner Comments

This candidate used the 5:3 ratio wrongly, a common fault, so only scored 2 in the second part. The first part was correct.

ResultsPlus

Examiner Tip

The question states that 5 mol V react with 3 mol MnO_4.

This means the number of vanadium ions must be greater than the number of manganate ions which gives you a quick way to check the answer to the first stage.

(ii) Calculate the number of moles of manganate(VII) ions used in the titration.

(1)

$$\text{Moles } (MnO_4^-) = 0.02 \times \frac{35.50}{1000} = 7.1 \times 10^{-4} \text{ moles.}$$

(iii) Calculate the number of moles of VO_2^+ in the original solution, and hence the percentage purity of the sample of NH_4VO_3. Give your answer to **three** significant figures.

Molar mass of NH_4VO_3 = 116.9 g mol^{-1}.

(3)

$$\text{Moles } (VO_2^+) = \frac{5}{3} \times 7.1 \times 10^{-4}$$

$$= 1.18 \times 10^{-3} \text{ mol} \quad (0.00118\dot{3})$$

$$\text{Mass } (VO_2^+) = 1.18 \times 10^{-3} \times \frac{\cancel{82.9}}{116.9}$$

~~(Molar mass 50.9 + 32 = 82.9 g)~~

~~= 0.098 g~~

$$= 0.138$$

$$\% \text{ } \cancel{VO_2^+} \text{ } (NH_4VO_3) = \cancel{\left(\frac{0.098}{\text{Mass } 0.15}\right) \times 100} \quad \frac{0.138}{0.15} \times 100$$

~~= 6.54 %~~ = 92.2 %.

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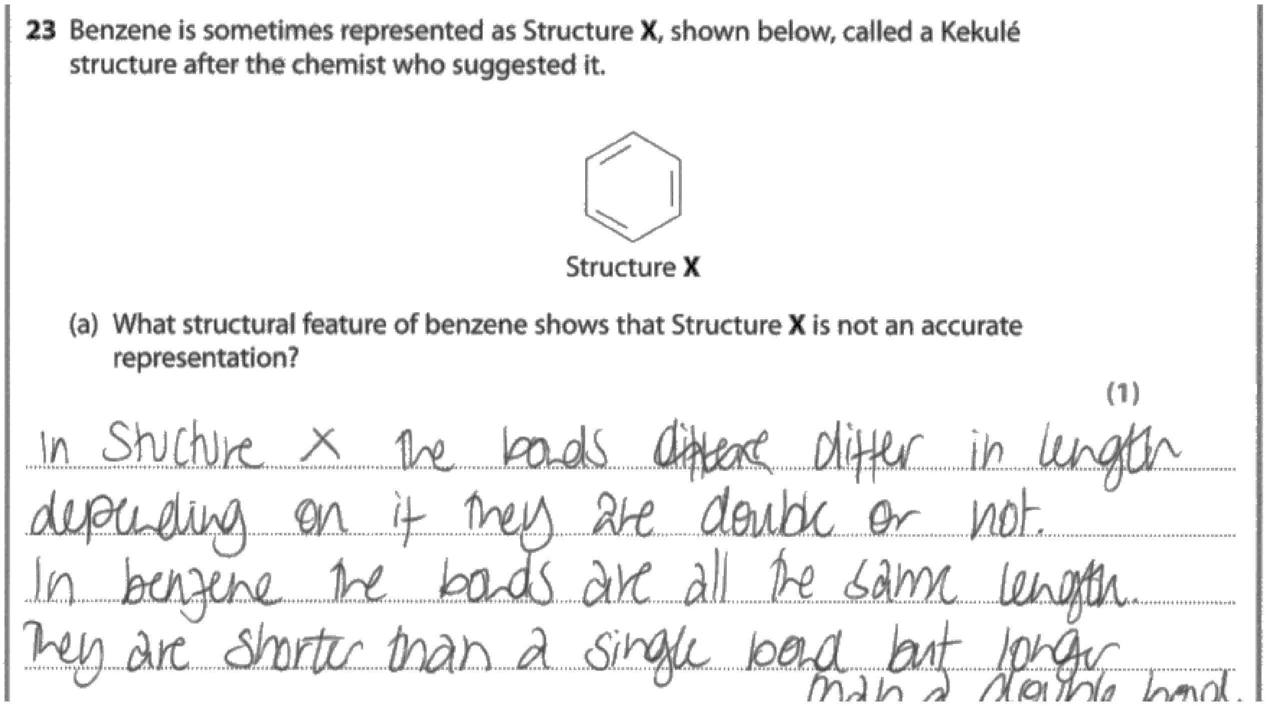
Examiner Comments

This was an example of a fully correct answer.

Question 23 (a)

The structure of benzene, deduced from X-ray diffraction, showed that the carbon-carbon bonds are all the same length.



23 Benzene is sometimes represented as Structure **X**, shown below, called a Kekulé structure after the chemist who suggested it.

Structure **X**

(a) What structural feature of benzene shows that Structure **X** is not an accurate representation?

(1)

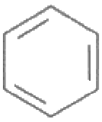
In Structure X the bonds ~~differe~~ differ in length depending on if they are double or not. In benzene the bonds are all the same length. They are shorter than a single bond but longer than a double bond.

ResultsPlus

Examiner Comments

This candidate clearly stated how the structure of bezene differs from X and scored the mark.

23 Benzene is sometimes represented as Structure **X**, shown below, called a Kekulé structure after the chemist who suggested it.



Structure **X**

(a) What structural feature of benzene shows that Structure **X** is not an accurate representation?

(1)

~~Benzene doesn't react with bromine~~

There is no C=C bond in benzene.

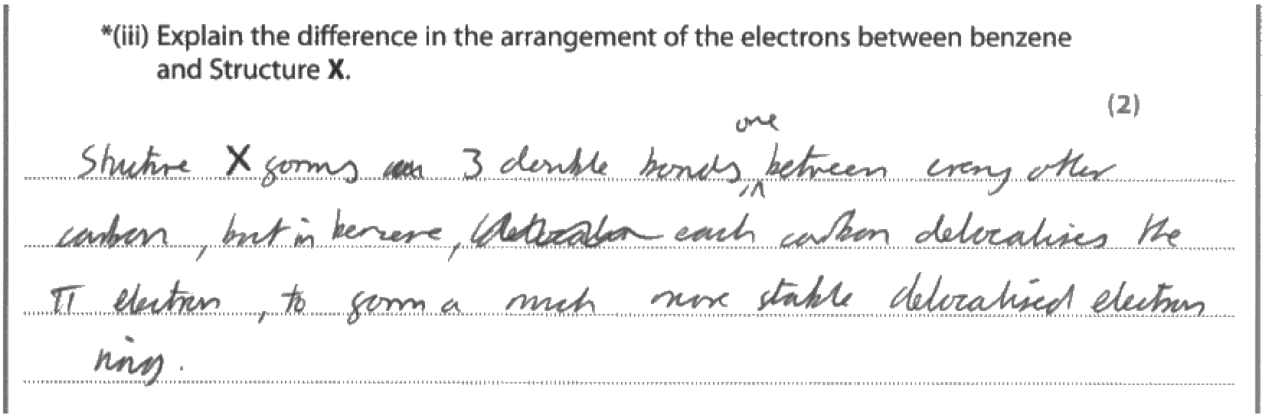
ResultsPlus

Examiner Comments

The statement made was true but it did not state what is present in benzene, only what is absent from the structure so was not awarded the mark.

Question 23 (b) (iii)

Most candidates referred to the delocalisation of electrons in benzene but many did not explain how the arrangement of electrons in **X** was different.



*(iii) Explain the difference in the arrangement of the electrons between benzene and Structure **X**.

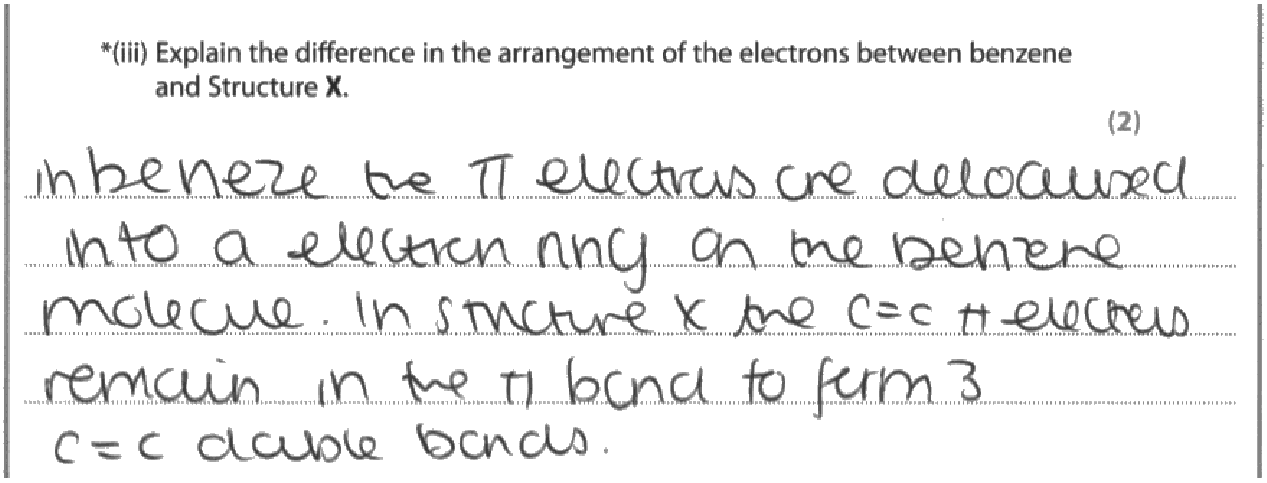
(2)

Structure X forms 3 double bonds, one between every other carbon, but in benzene, each carbon delocalises the π electron, to form a much more stable delocalised electron ring.

ResultsPlus

Examiner Comments

This answer was given 2 marks, though the comment on the electrons in X would have been better if it had referred to the pi component of the double bond.



*(iii) Explain the difference in the arrangement of the electrons between benzene and Structure **X**.

(2)

in beneze the π electrons are delocalised into a electron ring on the benzene molecule. In structure X the C=C π electrons remain in the π bond to form 3 C=C double bonds.

ResultsPlus

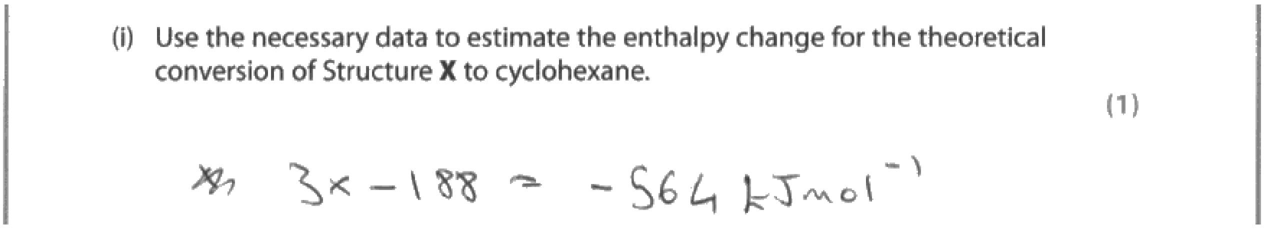
Examiner Comments

This answer referred to electrons in both X and benzene and gave the difference in arrangement so both marks were awarded.

Question 23 (b) (i)-(ii)

The first part of this question was usually correct, but candidates seemed to have little idea of the relative enthalpy levels of X, benzene and cyclohexane despite writing about the stability of delocalised systems in other parts of the question.

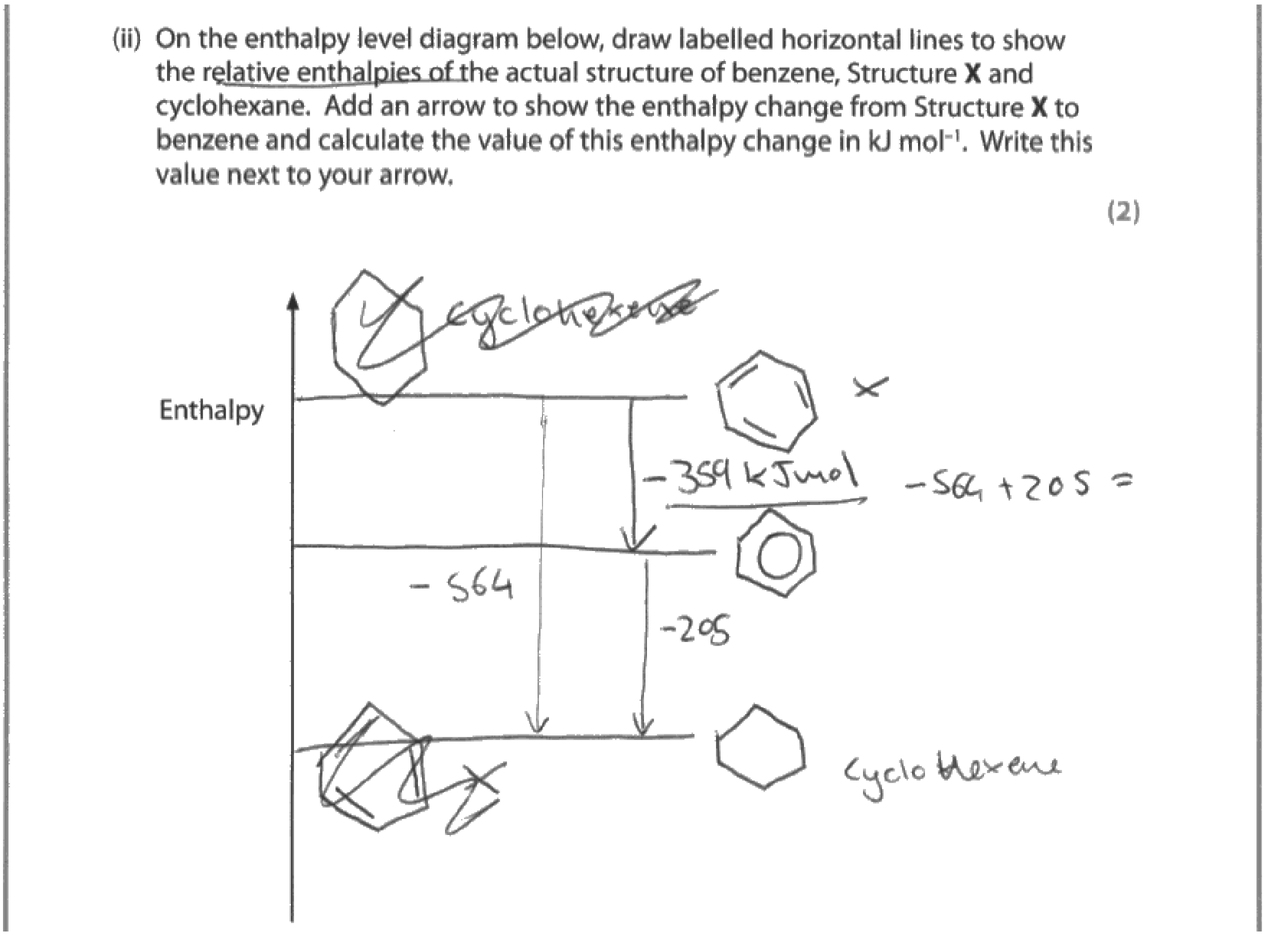
X was frequently shown at the lowest enthalpy level, and the enthalpy change going from X to benzene labelled as positive. Many diagrams omitted cyclohexane altogether, though they could still score the second mark for the enthalpy change. Some diagrams showed cyclohexene, and this was ignored as long as cyclohexane was there too.



(i) Use the necessary data to estimate the enthalpy change for the theoretical conversion of Structure **X** to cyclohexane.

(1)

3 × −188 = −564 kJmol^{-1}



(ii) On the enthalpy level diagram below, draw labelled horizontal lines to show the relative enthalpies of the actual structure of benzene, Structure **X** and cyclohexane. Add an arrow to show the enthalpy change from Structure **X** to benzene and calculate the value of this enthalpy change in kJ mol^{-1}. Write this value next to your arrow.

(2)

ResultsPlus

Examiner Comments

This answer was not awarded the first mark, but the energy levels in (ii) were in the correct positions relative to each other and the value in (i) was used correctly so it scored both marks in (ii).

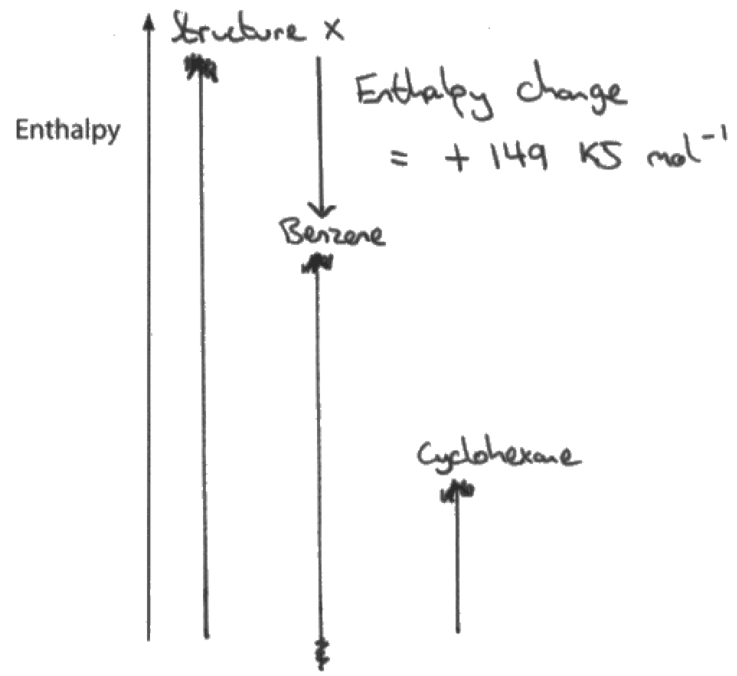
(i) Use the necessary data to estimate the enthalpy change for the theoretical conversion of Structure **X** to cyclohexane.

(1)

$-118 \times 3 = -354$ KJ mol^{-1}

(ii) On the enthalpy level diagram below, draw labelled horizontal lines to show the relative enthalpies of the actual structure of benzene, Structure **X** and cyclohexane. Add an arrow to show the enthalpy change from Structure **X** to benzene and calculate the value of this enthalpy change in kJ mol^{-1}. Write this value next to your arrow.

(2)



ResultsPlus

Examiner Comments

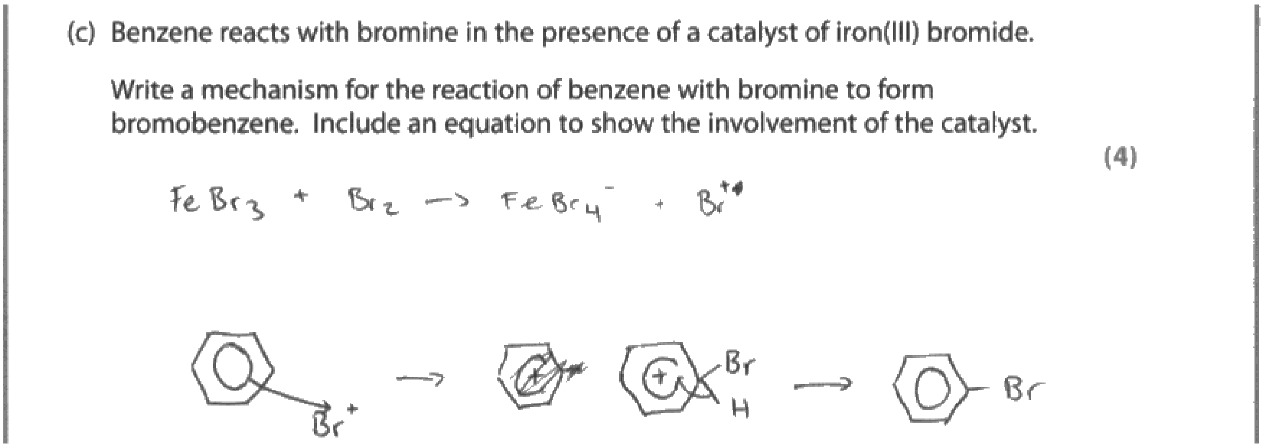
The first part of the question was correct.

The second part did not show the energy level of cyclohexane. The enthalpy change of conversion of X to benzene had an incorrect sign so it scored 0.

Question 23 (c)

Many candidates knew this mechanism well and scored all 4 marks. Most showed the production of Br^+ rather than the polarised bromine attached to the catalyst. A few answers showed Br^- forming and also lost the second mark as the electrons from the benzene ring would not move to a negatively charged species. The intermediate was often well drawn; however candidates should take care where they place the + charge, and in drawing the "horseshoe" of delocalised electrons.

Drawings in which the Br was bonded to a carbon atom at the top of the hexagon often showed these points more clearly than when the Br was on the side of the hexagon. There was not always enough care in drawing the arrow from the C-H bond to the + charge. It was not good enough to show it going from a space between the end of the bond and the H atom.



(c) Benzene reacts with bromine in the presence of a catalyst of iron(III) bromide.

Write a mechanism for the reaction of benzene with bromine to form bromobenzene. Include an equation to show the involvement of the catalyst.

(4)

$FeBr_3 + Br_2 \rightarrow FeBr_4^- + Br^+$

ResultsPlus

Examiner Comments

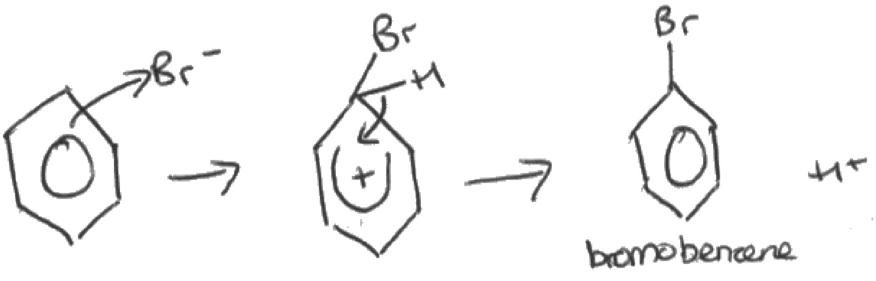
This answer omitted to show the H^+ produced at the end, but was otherwise correct so was given 3 marks.

(c) Benzene reacts with bromine in the presence of a catalyst of iron(III) bromide.

Write a mechanism for the reaction of benzene with bromine to form bromobenzene. Include an equation to show the involvement of the catalyst.

(4)

Br_2 + ~~Fe3~~ $FeBr_3 \rightarrow FeBr_4^{-} + Br^-$



$H^+ + FeBr_4^- \rightarrow HBr + FeBr_3$

(catalyst is regenerated)

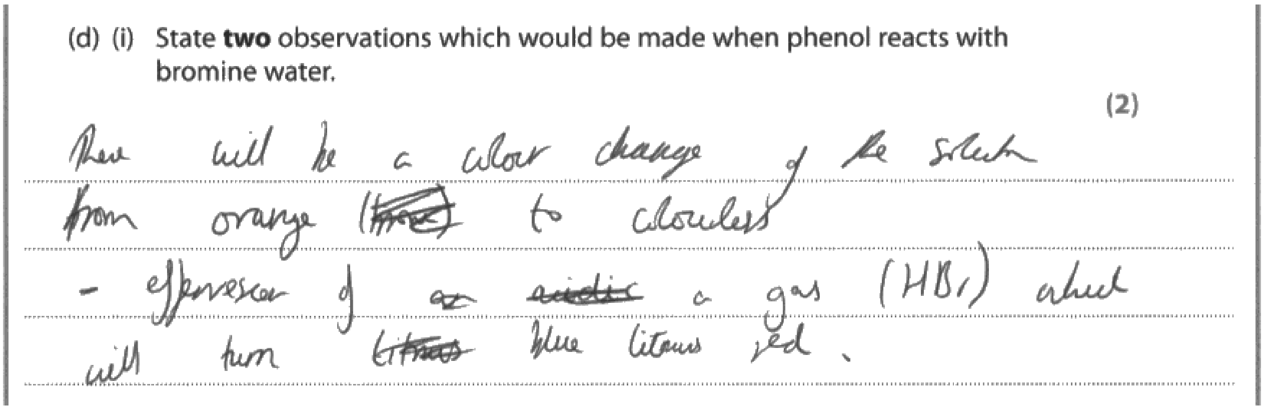
ResultsPlus

Examiner Comments

After a slow start in which a Br ion of the wrong charge was shown, this candidate scored the last 2 marks.

Question 23 (d) (i)

Candidates sometimes assumed that if a gas is produced in a reaction there will be fizzing. The hydrogen bromide which forms in the reaction of phenol with bromine water is soluble in water so it would be seen as steamy or misty fumes, not as effervescence. A white precipitate of tribromophenol also forms but the most obvious change is the decolourisation of the bromine water.



(d) (i) State **two** observations which would be made when phenol reacts with bromine water.

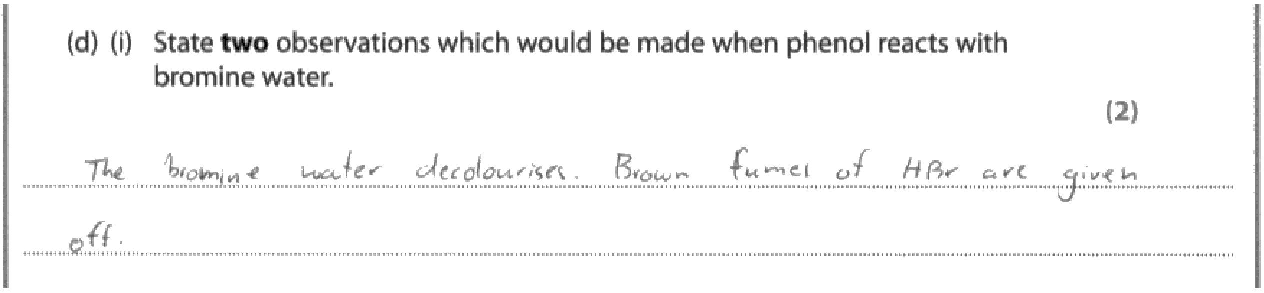
(2)

There will be a colour change of the solution from orange (~~[illegible]~~) to colourless

- effervescence of ~~an~~ ~~acidic~~ a gas (HBr) which will turn ~~litmus~~ blue litmus red.

Examiner Comments

This response just scored the first mark.



(d) (i) State **two** observations which would be made when phenol reacts with bromine water.

(2)

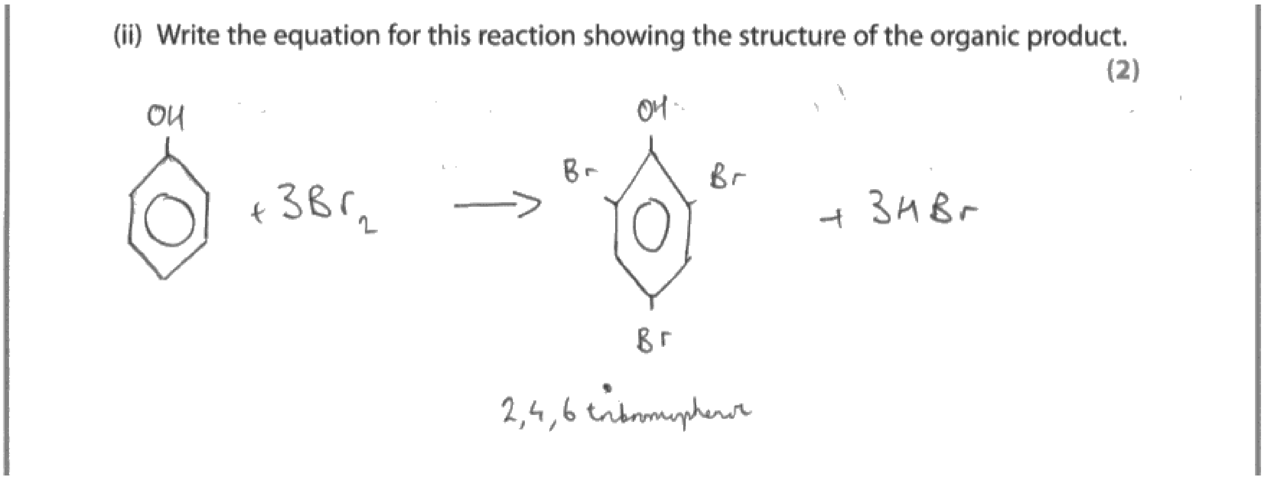
The bromine water decolourises. Brown fumes of HBr are given off.

Examiner Comments

It was not enough to say that fumes would be given off. They had to be described as misty or steamy but are definitely not brown so this also scored 1 mark.

Question 23 (d) (ii)

The structure of tribromophenol was needed in this question for one of the marks and a correct balanced equation was needed for the other. Some candidates forgot to include HBr in the equation; others thought hydrogen was produced. If the production of monobromophenol was shown, 1 mark was allowed for a balanced equation with the Br in one of the correct positions.



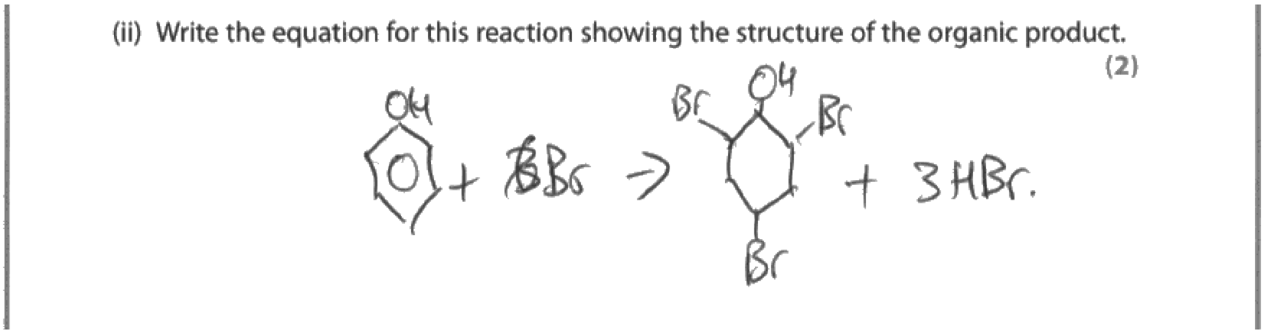
(ii) Write the equation for this reaction showing the structure of the organic product.

(2)

ResultsPlus

Examiner Comments

This was an example of a fully correct answer which scored 2 marks.



(ii) Write the equation for this reaction showing the structure of the organic product.

(2)

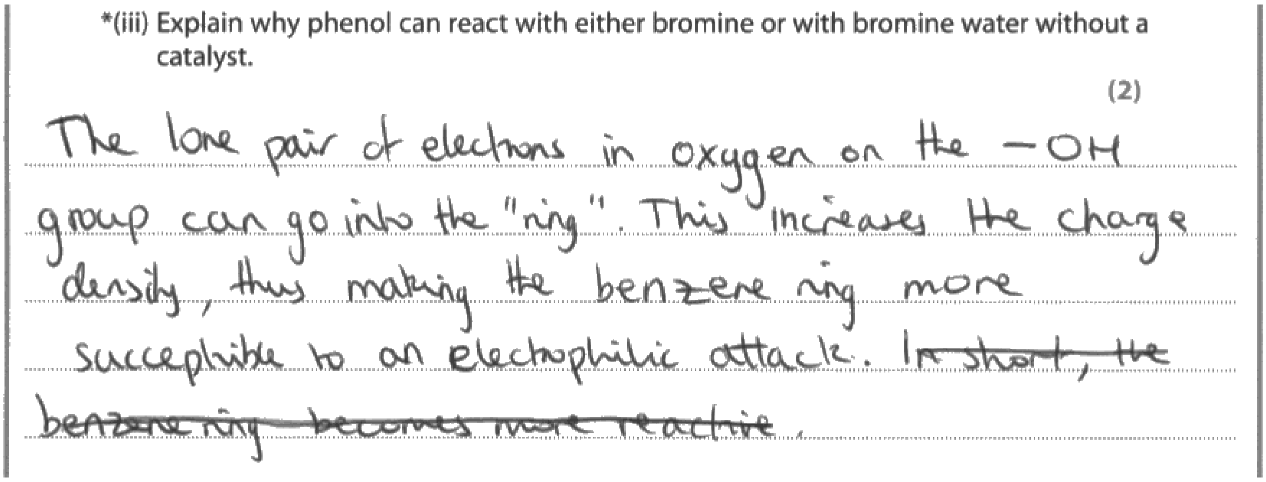
ResultsPlus

Examiner Comments

This answer omitted the delocalised ring in phenol and showed bromine atoms instead of Br_2 molecules so no marks were given.

Question 23 (d) (iii)

The explanation required seemed well rehearsed and many answers were clearly expressed.



*(iii) Explain why phenol can react with either bromine or with bromine water without a catalyst.

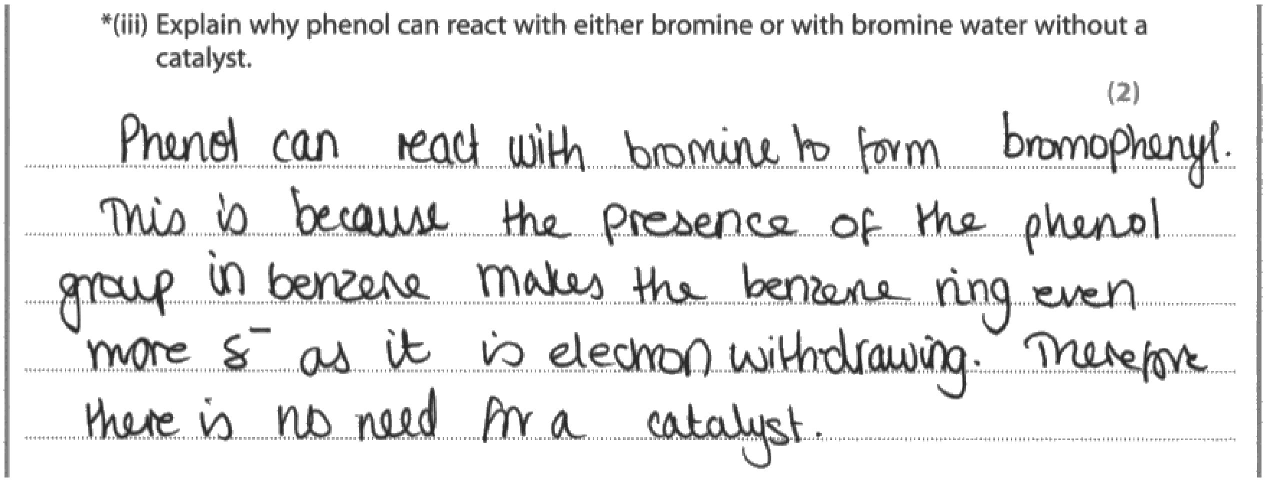
(2)

The lone pair of electrons in oxygen on the $-OH$ group can go into the "ring". This increases the charge density, thus making the benzene ring more succeptible to an electrophilic attack. ~~In short, the benzene ring becomes more reactive~~.

ResultsPlus

Examiner Comments

This was an example of a good answer which scored both marks.



*(iii) Explain why phenol can react with either bromine or with bromine water without a catalyst.

(2)

Phenol can react with bromine to form bromophenyl. This is because the presence of the phenol group in benzene makes the benzene ring even more δ^- as it is electron withdrawing. Therefore there is no need for a catalyst.

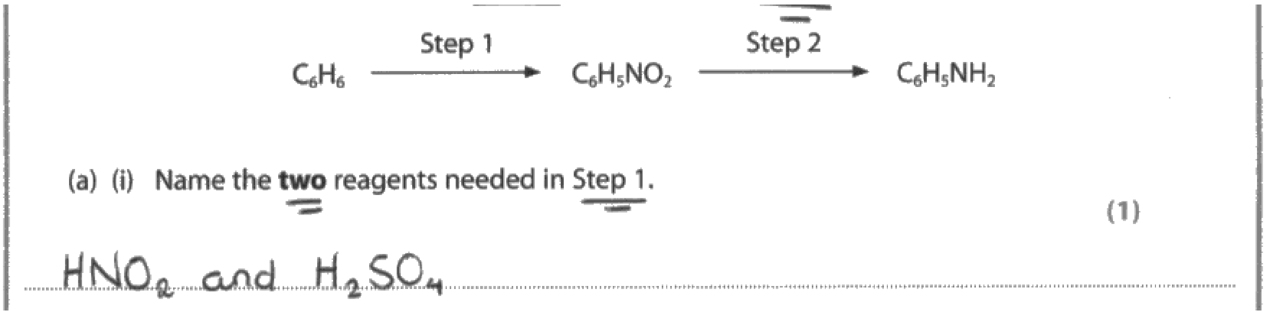
ResultsPlus

Examiner Comments

This candidate showed some understanding of the situation but the answer was not adequately expressed so it did not score. Candidates had to refer to the lone pair of electrons on the oxygen atom, not to the "phenol group" as here. The phrase "it is electron withdrawing" presumably refers to the benzene ring, but there was no explanation as to why increasing the electron density reduced the need for a catalyst.

Question 24 (a) (i)

The answer had to state that concentrated nitric and concentrated sulfuric acid were needed, and omitting the word concentrated was the most common error.



$C_6H_6 \xrightarrow{\text{Step 1}} C_6H_5NO_2 \xrightarrow{\text{Step 2}} C_6H_5NH_2$

(a) (i) Name the **two** reagents needed in Step 1.

(1)

HNO_2 and H_2SO_4

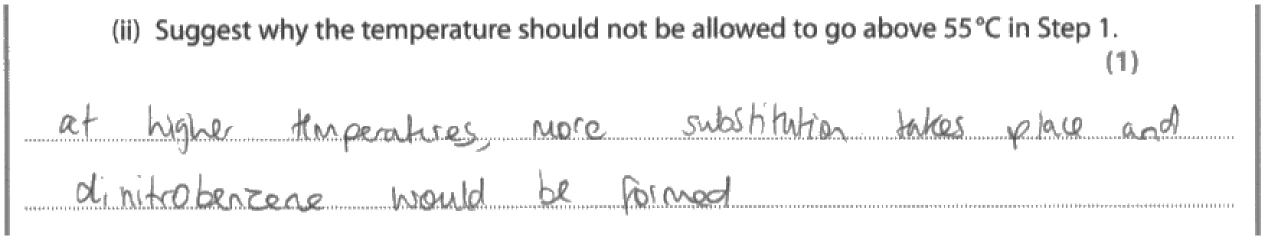
ResultsPlus

Examiner Comments

Names or formulae were accepted for the acids. In this case nitrous acid had been given wrongly, and the word concentrated was also missing so the mark was not given.

Question 24 (a) (ii)

There were many different ways of saying that more nitro groups might be substituted at a temperature above 55°C. Some candidates thought that decomposition would occur, or gave a safety reason such as saying that an explosive mixture would form, and these answers were not allowed.



(ii) Suggest why the temperature should not be allowed to go above 55 °C in Step 1.

(1)

at higher temperatures, more substitution takes place and dinitrobenzene would be formed

ResultsPlus

Examiner Comments

This was a correct response and scored the mark.

Question 24 (a) (iii)

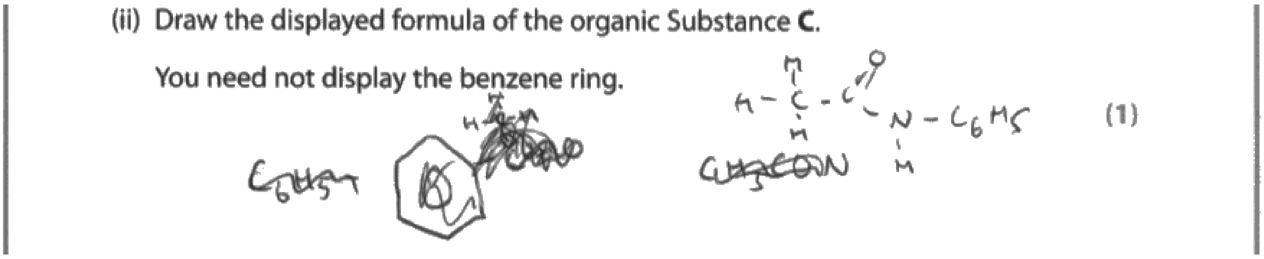
The specification refers to tin and concentrated hydrochloric acid for this reaction, though some other metals were allowed.

Question 24 (b) (i)

The formula of the diazonium compound could be given with or without charges on the ions. However if they were given both charges had to be correct.

Question 24 (b) (ii)

Some candidates did not appear to know that in a displayed formula the bonds should be shown. The essential bonds for the mark were in the CONH group; a hexagon with a circle or C_6H_5 was allowed for benzene and CH_3 for the methyl group.



(ii) Draw the displayed formula of the organic Substance **C**.

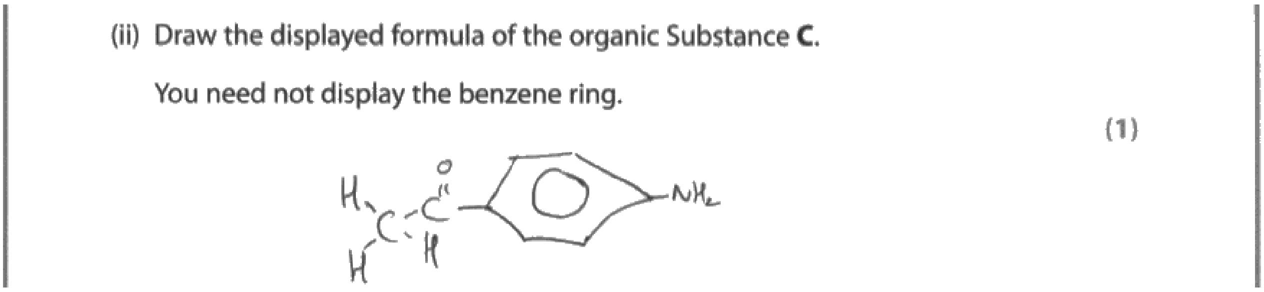
You need not display the benzene ring.

(1)

ResultsPlus

Examiner Comments

As the CONH was correctly displayed this was awarded the mark.



(ii) Draw the displayed formula of the organic Substance **C**.

You need not display the benzene ring.

(1)

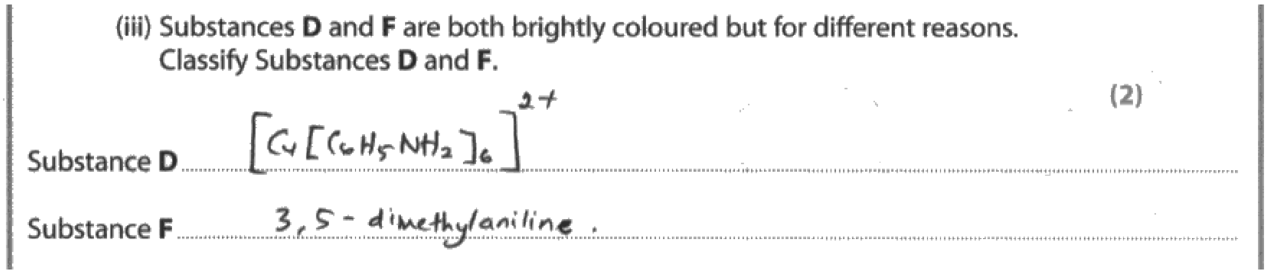
ResultsPlus

Examiner Comments

This formula had the group containing nitrogen in the wrong position so did not score any marks.

Question 24 (b) (iii)

The question made the point that **D** and **F** were coloured, and the expected answers were that **D** is a complex ion or transition metal complex and **F** is a dye. Some candidates suggested a formula for D without further comment, so there was no attempt to classify it. Answers saying that **F** was a diazo or azo compound were allowed without reference to the dye.



(iii) Substances **D** and **F** are both brightly coloured but for different reasons.
Classify Substances **D** and **F**.

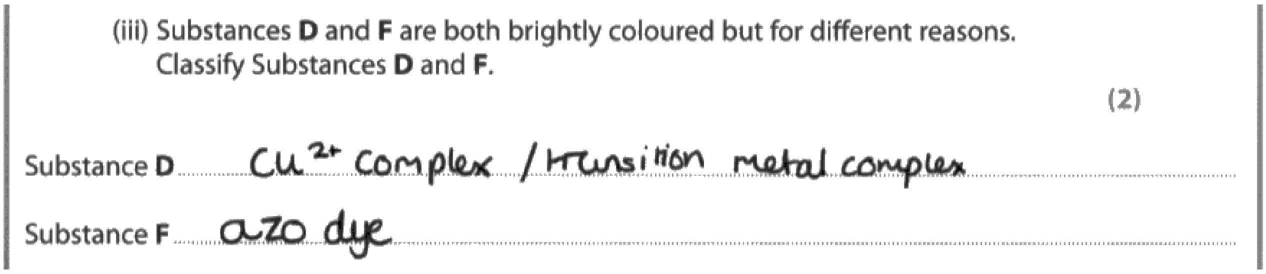
(2)

Substance **D** $[Cu[C_6H_5NH_2]_6]^{2+}$

Substance **F** 3,5 - dimethylaniline .

ResultsPlus
Examiner Comments

This candidate had suggested formulae, but the question asked for the compounds to be classified in some way so no marks were awarded.



(iii) Substances **D** and **F** are both brightly coloured but for different reasons.
Classify Substances **D** and **F**.

(2)

Substance **D** Cu^{2+} complex / transition metal complex

Substance **F** azo dye

ResultsPlus
Examiner Comments

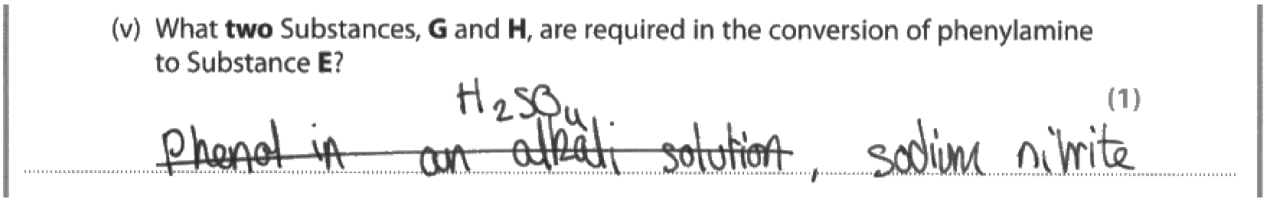
This was one way of answering the question which scored both marks.

Question 24 (b) (iv)

Many candidates just referred to a diazonium compound in this question without giving the full name.

Question 24 (b) (v)

As nitrous acid was not stable the two substances which were needed were hydrochloric acid and a nitrite, such as sodium nitrite.



(v) What **two** Substances, **G** and **H**, are required in the conversion of phenylamine to Substance **E**?

(1)

H_2SO_4

~~Phenol in an alkali solution~~, sodium nitrite

ResultsPlus

Examiner Comments

Sulfuric acid was not accepted in place of hydrochloric acid as E is a chloride so no marks were awarded.

Question 24 (b) (vi)

Candidates who drew a benzene ring and worked out what groups were bonded to it were often correct, though some formulae mistakenly showed an OH group on the ring. When a condensed formula was written there were often mistakes in the number of H atoms, as with three substituents on the benzene ring, three H atoms are still present.

(vi) Suggest the structural formula of the substance which reacts with Substance **E** to form Substance **F**.

(1)

~~$C_6H_2($~~[illegible]

$C_6H_2(CH_3)_2NH_2$.

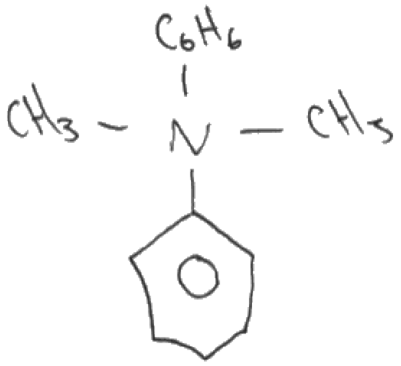
ResultsPlus

Examiner Comments

This formula had three substituents on the benzene ring so there should also be three H atoms.

(vi) Suggest the structural formula of the substance which reacts with Substance **E** to form Substance **F**. $NC_6H_4\ 2CH_3$

(1)



ResultsPlus

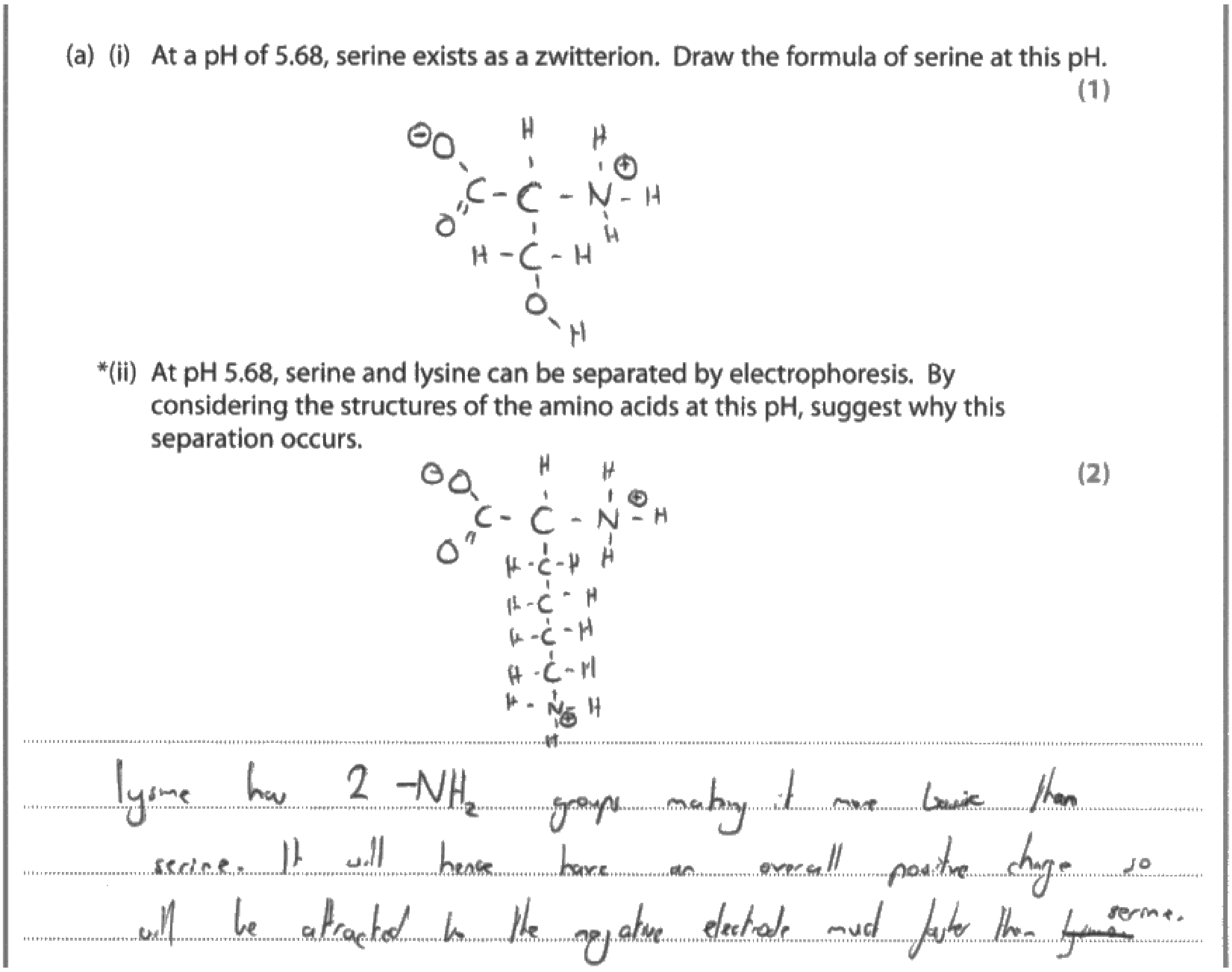
Examiner Comments

This candidate did not realise that a compound with NH_2 would be needed to form the diazo group in **F**.

Question 25 (a)

In (a)(i) many candidates did not appear to know what a zwitterion was, and when a charge was shown on serine it was often only protonation of the NH_2 group and sometimes ionization of CH_2OH.

A significant number of answers to (a)(ii) drew lysine with both NH_2 groups protonated. However the candidates were not necessarily able to suggest why lysine and serine could be separated in an electric field. The migration of ions studied in Unit 1 seemed to be forgotten, and there were suggestions that the positively charged end of the amino acid would move in a different direction to the negative end. Many answers stated that serine would move, even though it had no overall charge.



(a) (i) At a pH of 5.68, serine exists as a zwitterion. Draw the formula of serine at this pH.
(1)

*(ii) At pH 5.68, serine and lysine can be separated by electrophoresis. By considering the structures of the amino acids at this pH, suggest why this separation occurs.
(2)

lysine has 2 $-NH_2$ groups making it more basic than serine. It will hence have an overall positive charge so will be attracted to the negative electrode much faster than ~~lysine~~ serine.

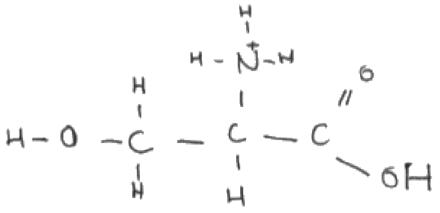
ResultsPlus
Examiner Comments

This was an example of a good answer scoring full marks.

The correct charges were shown on serine. Lysine did not have to be drawn out though the space was available for those who wished to do so, and the candidate understood the principles behind the separation method.

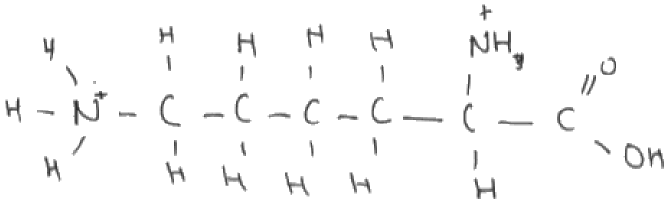
(a) (i) At a pH of 5.68, serine exists as a zwitterion. Draw the formula of serine at this pH.

(1)



*(ii) At pH 5.68, serine and lysine can be separated by electrophoresis. By considering the structures of the amino acids at this pH, suggest why this separation occurs.

(2)



lysine contain 2 NH_3^+ therefore one will bond more with the gel and serine will more more through the gel to form separation.

ResultsPlus

Examiner Comments

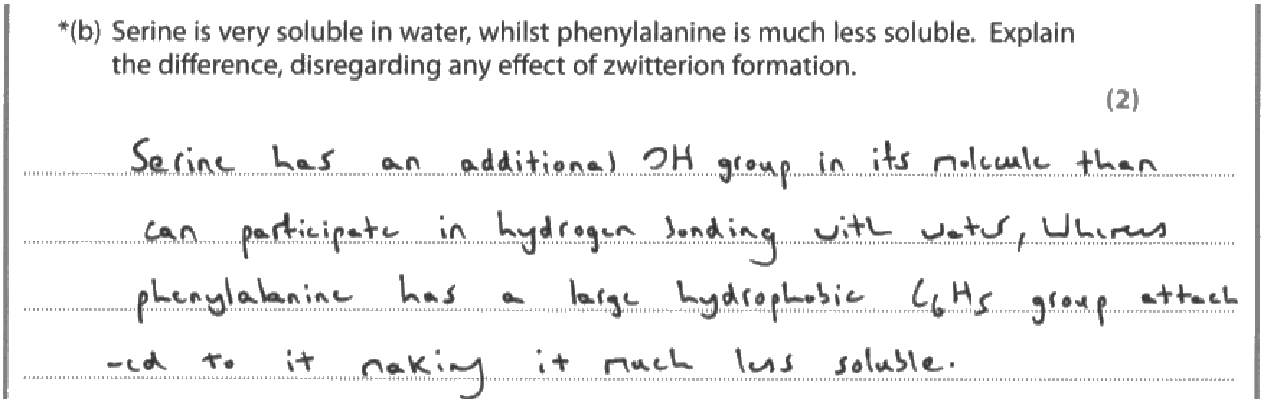
This candidate did not show the negative charge on the carboxyl group of the zwitterion.

The answer scored 1 mark for showing the two NH_3^+ groups in lysine, but the candidate missed the point that ions migrate in an electric field and was perhaps thinking about chromatography in the references about bonding to the gel.

Question 25 (b)

Candidates often wrote about only one of the amino acids. The most popular answer was to explain that the solubility of serine was due to the ability of the OH in the R group to form hydrogen bonds with water. When a question asks about a difference between two acids there has to be a reference to both of them.

Many answers scored a mark by saying that the benzene ring is hydrophobic. An alternative answer was that phenylalanine has significant London forces between its molecules which will reduce solubility, or even that London forces with water are likely to be weaker than hydrogen bonds. It can still form hydrogen bonds from its amino and acid groups but it was assumed in this question that candidates were discussing the effect of the different R groups unless they said otherwise.



*(b) Serine is very soluble in water, whilst phenylalanine is much less soluble. Explain the difference, disregarding any effect of zwitterion formation.

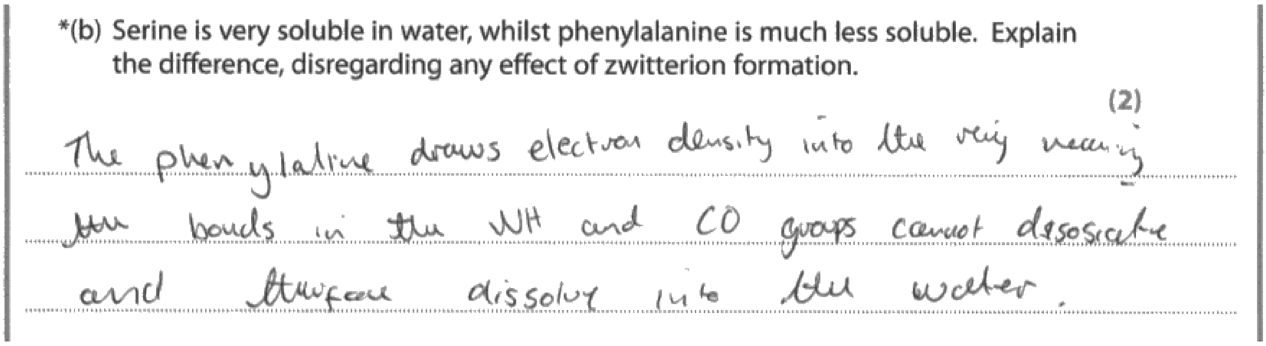
(2)

Serine has an additional OH group in its molecule than can participate in hydrogen bonding with water, whereas phenylalanine has a large hydrophobic C_6H_5 group attached to it making it much less soluble.

ResultsPlus

Examiner Comments

This was an example of an answer which scored both marks.



*(b) Serine is very soluble in water, whilst phenylalanine is much less soluble. Explain the difference, disregarding any effect of zwitterion formation.

(2)

The phenylaline draws electron density into the ring meaning the bonds in the NH and CO groups cannot dissociate and therefore dissolve into the water.

ResultsPlus

Examiner Comments

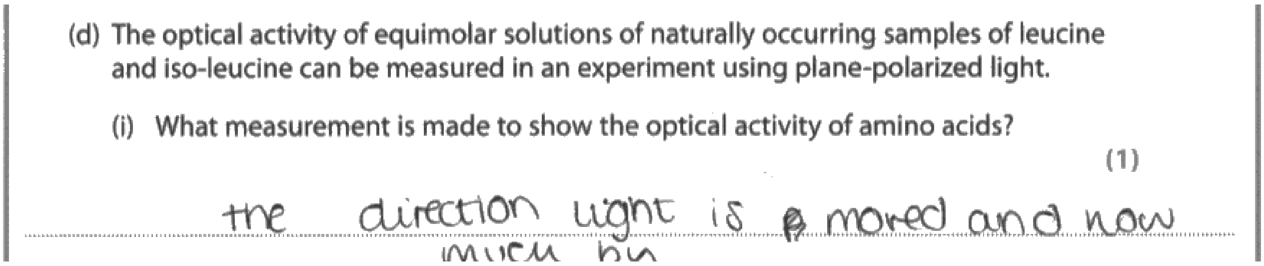
This response was not awarded any marks, as the benzene ring was separated from the NH_2 and COOH groups, and its main effect would be due to the intermolecular forces it forms.

Question 25 (c)

The R group in the amino acid which does not show optical activity is a hydrogen atom. Some candidates drew the formula of glycine which was allowed.

Question 25 (d) (i)

The question asked what measurement is made, so answers saying that amino acids rotate the plane of plane-polarized light were not enough. They had to say that the degree or extent of rotation would be measured.



(d) The optical activity of equimolar solutions of naturally occurring samples of leucine and iso-leucine can be measured in an experiment using plane-polarized light.

(i) What measurement is made to show the optical activity of amino acids?

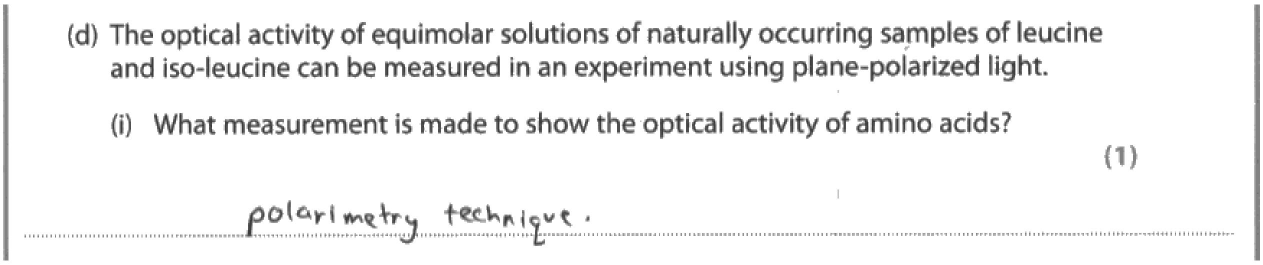
(1)

the direction light is moved and how much by

ResultsPlus

Examiner Comments

This answer would have been awarded a mark for saying "how much by" if it had referred to rotation, but saying that light was "moved" was not allowed.



(d) The optical activity of equimolar solutions of naturally occurring samples of leucine and iso-leucine can be measured in an experiment using plane-polarized light.

(i) What measurement is made to show the optical activity of amino acids?

(1)

polarimetry technique.

ResultsPlus

Examiner Comments

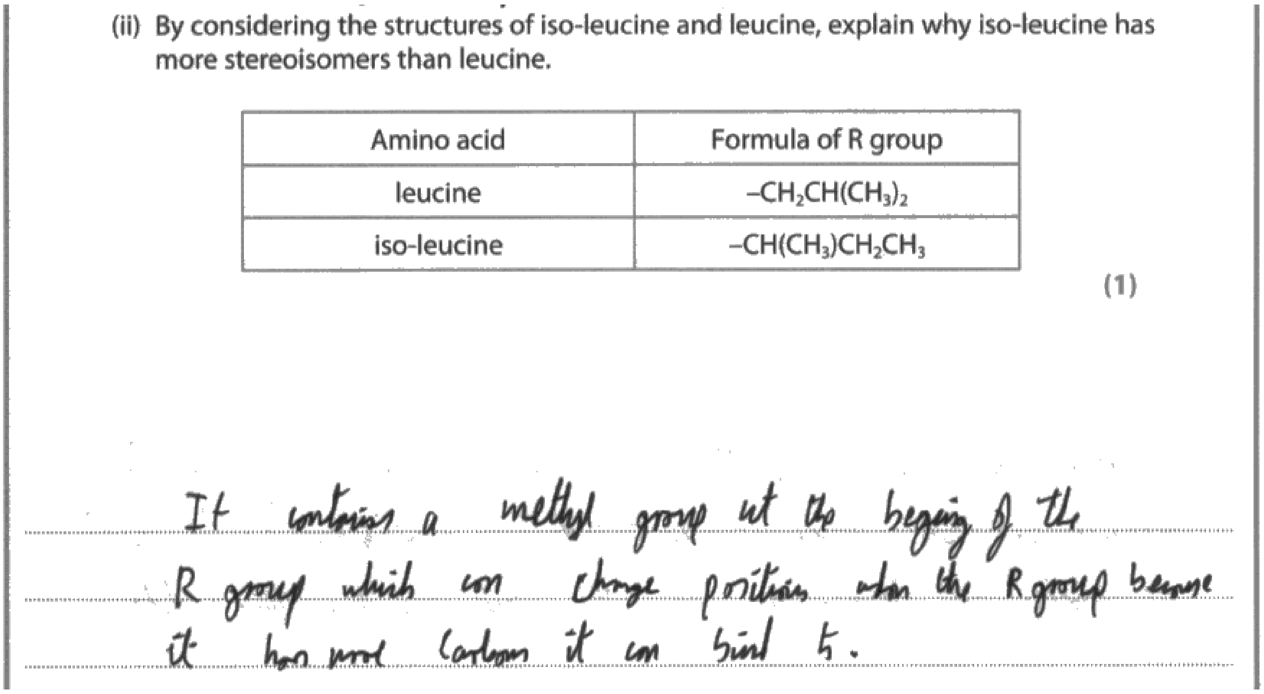
A polarimeter was used to measure the rotation of the plane of polarisation, but did not say what was measured so was not awarded a mark.

Question 25 (d) (ii)

Space was provided for candidates to draw the structure of iso-leucine, though this was optional. If the formula was drawn out it may have been more obvious that iso-leucine had a chiral carbon atom in its R group. Some answers said that leucine did not have any chiral carbon atoms, despite the information which had been given earlier in (c).

Correct answers could be that iso-leucine has more chiral carbon atoms than leucine or that iso-leucine had a chiral atom in its R group.

A few candidates confused geometric isomers and optical isomers and tried to find an explanation based on carbon-carbon double bonds.



(ii) By considering the structures of iso-leucine and leucine, explain why iso-leucine has more stereoisomers than leucine.

Amino acid	Formula of R group
leucine	$-CH_2CH(CH_3)_2$
iso-leucine	$-CH(CH_3)CH_2CH_3$

(1)

It contains a methyl group at the begaing of the R group which can change position when the R group because it has more carbons it can bind 5.

ResultsPlus

Examiner Comments

This was a common incorrect response. Candidates thought that there were more ways of arranging atoms in the larger R group, but did not explain why there were more stereoisomers. It was not given a mark.

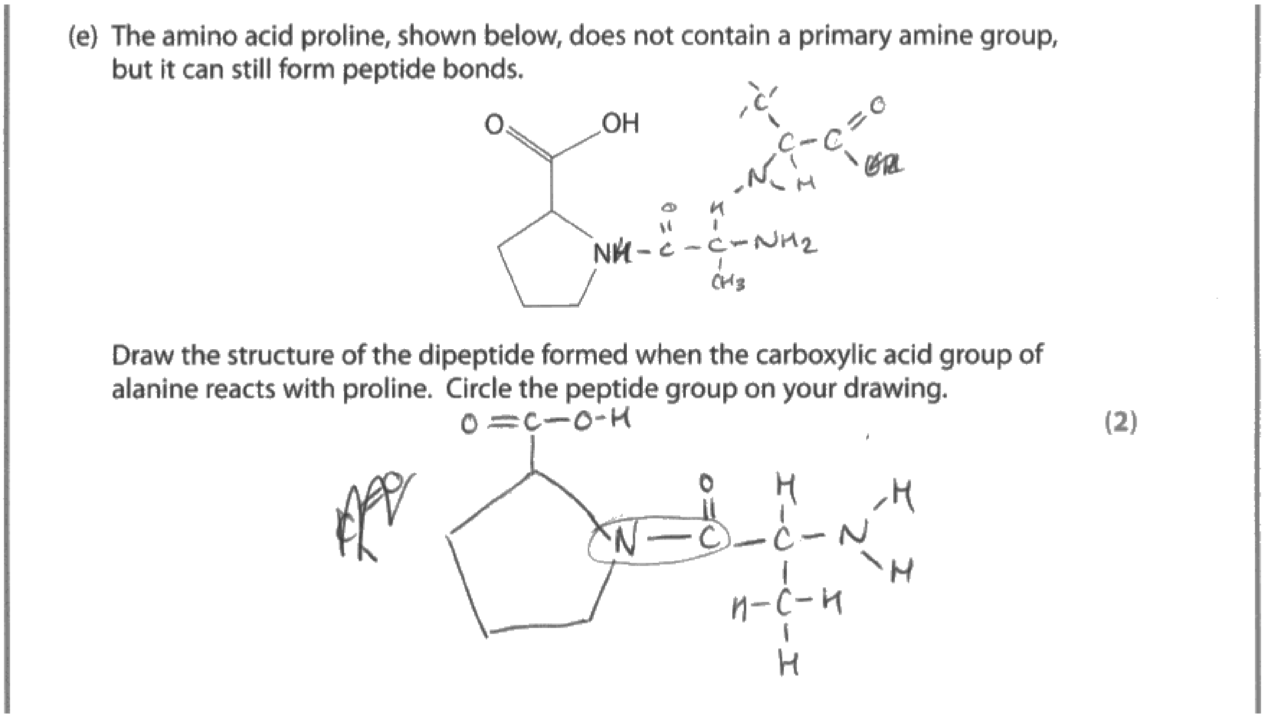
Question 25 (e)

The first step in this question was to select the N in proline and the COOH in alanine to construct the bond. Formulae based on the amino group of alanine and the COOH in proline scored 1 mark if fully correct.

Since the nitrogen atom in proline is in a ring, the peptide group does not contain the hydrogen atom found in other dipeptides. Some candidates thought the N atom was attached to the ring rather than being part of it.

Some candidates who successfully drew the dipeptide then forgot to circle the peptide group.

An answer which occurred very rarely was to show a dimer containing two peptide groups made from each functional group of the two acids, and this was allowed.



(e) The amino acid proline, shown below, does not contain a primary amine group, but it can still form peptide bonds.

Draw the structure of the dipeptide formed when the carboxylic acid group of alanine reacts with proline. Circle the peptide group on your drawing.

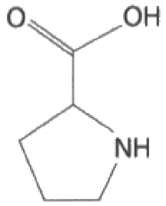
(2)

ResultsPlus

Examiner Comments

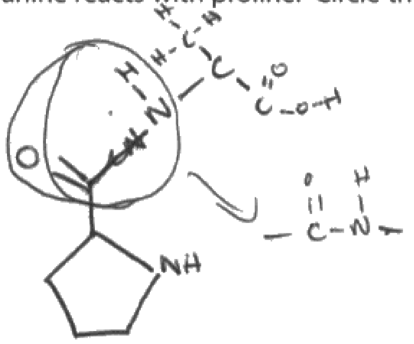
The dipeptide formula was correct, but the ring around the peptide group should have included the O atom so this response only scored 1 mark.

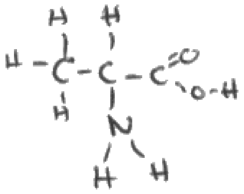
(e) The amino acid proline, shown below, does not contain a primary amine group, but it can still form peptide bonds.



Draw the structure of the dipeptide formed when the carboxylic acid group of alanine reacts with proline. Circle the peptide group on your drawing.

(2)





ResultsPlus
Examiner Comments

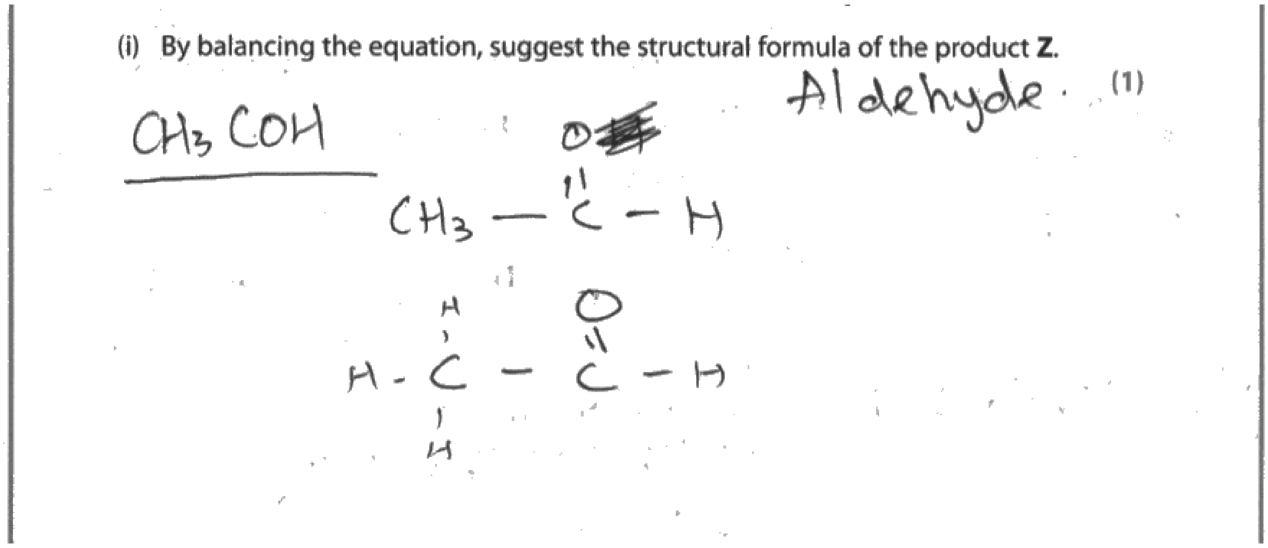
This candidate drew alanine on the left for reference, but then drew the dipeptide between the acid group in proline and the amino group in alanine. A hydrogen atom was also missing from alanine so was not awarded any marks.

ResultsPlus
Examiner Tip

It is very important to read questions carefully. In this question two different dipeptides can form between the two amino acids and you need to choose the right one.

Question 25 (f) (i)

The molecular formula was allowed in this question.



(i) By balancing the equation, suggest the structural formula of the product **Z**. (1)

CH_3COH

Aldehyde.

$CH_3-\overset{O}{\overset{\|}{C}}-H$

$H-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-H$

ResultsPlus

Examiner Comments

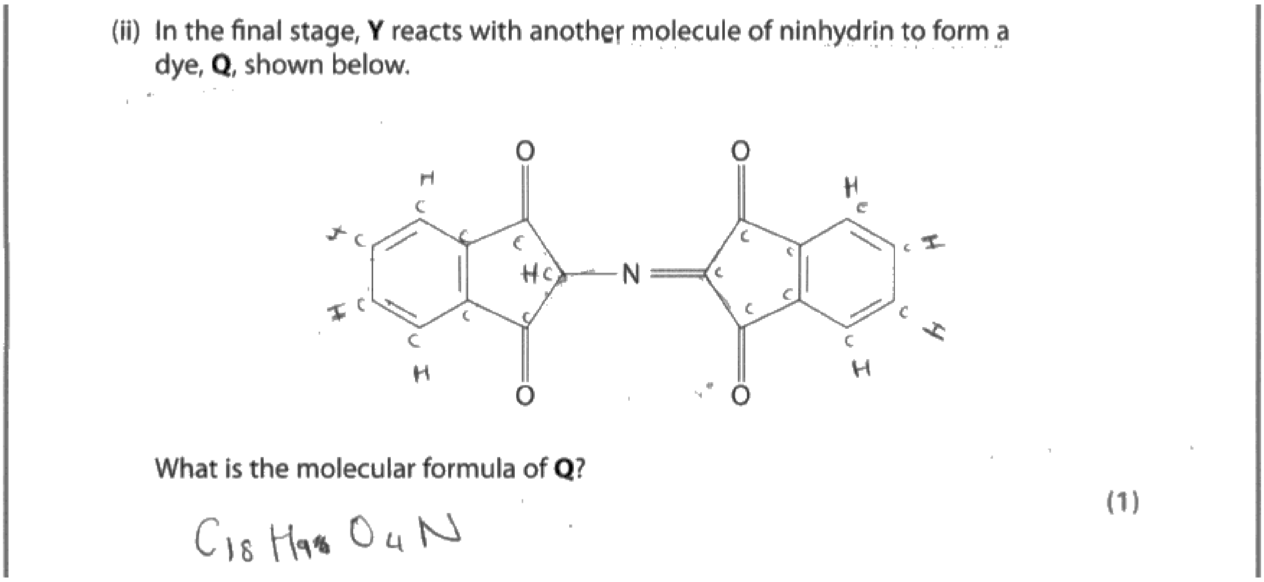
This was one correct alternative. Another possible structure was ethenol, $CH_2=CH_2OH$.

Question 25 (f) (ii)-(iii)

There were two issues noted by examiners when marking this question. One was that answers were often very disorganised; numbers were scattered around the page without any indication of what they referred to. The second was that few candidates seemed to realise that they could not calculate the percentage composition of **Q** unless they worked out how much oxygen was present. The mass of oxygen in 1.000 g of **Q** or the percentage were frequently ignored, though it was sometimes calculated (wrongly) from the amount in the carbon dioxide and/ or the water.

Candidates were asked to use the combustion data, and most started by calculating the number of moles of carbon dioxide and water formed. However many ran into trouble by stating that the mass of hydrogen was numerically equal to the number of moles of water, as they were thinking in terms of H_2. There were also problems calculating the number of moles of nitrogen as the mass given in the question (0.04620 g) was often divided by 28 which does not give moles of N atoms. Those who calculated the number of moles of each element then regularly stated that the ratio was what they had predicted in (f)(i) even when it was not. Some candidates lost track of whether they were working in masses or in moles and used the ratio of each element by mass to calculate the formula.

However there were many well organised calculations which were completed correctly in about 8 or 9 lines.

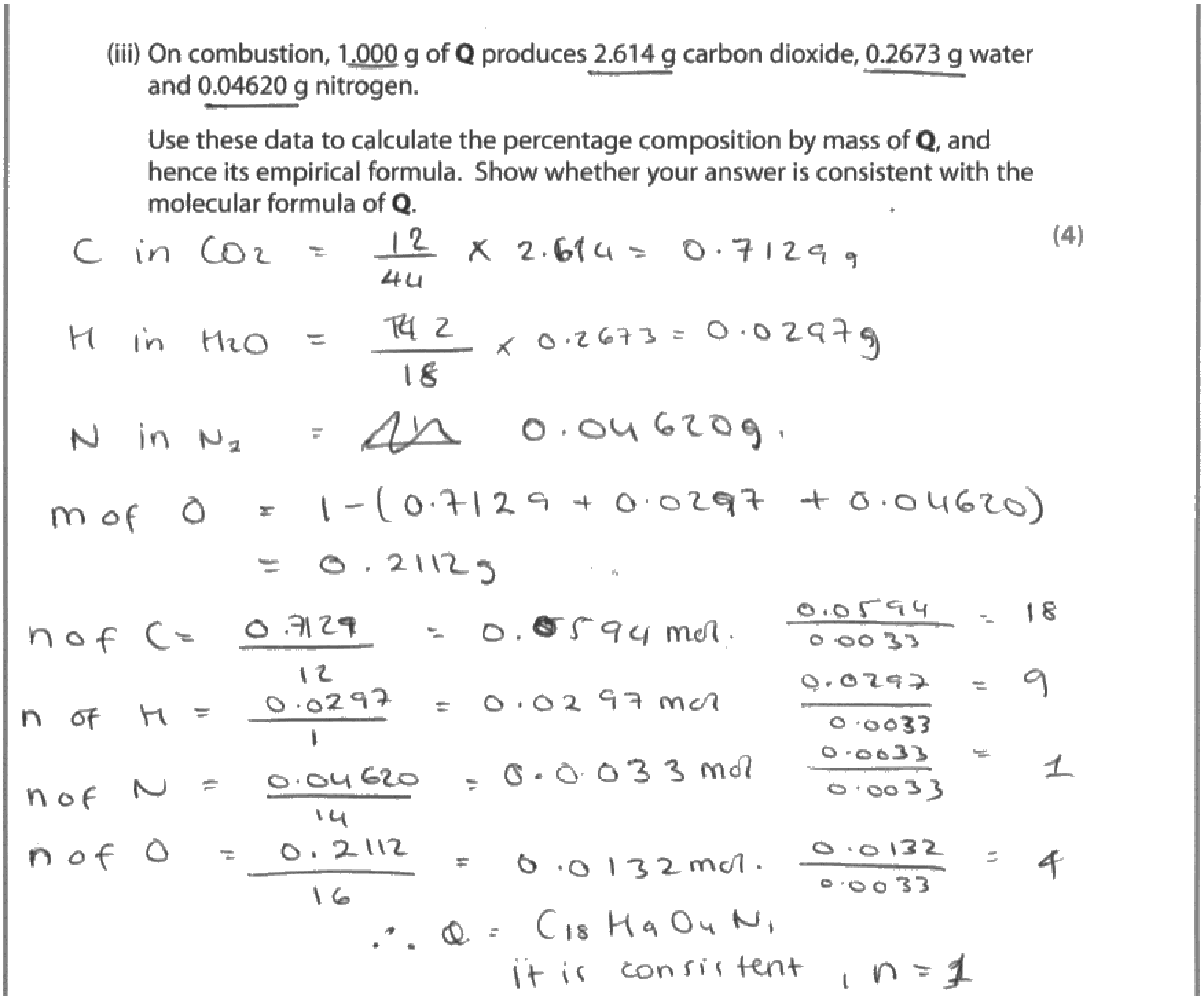


(ii) In the final stage, **Y** reacts with another molecule of ninhydrin to form a dye, **Q**, shown below.

What is the molecular formula of **Q**?

(1)

$C_{18}H_{9}O_4N$



(iii) On combustion, 1.000 g of **Q** produces 2.614 g carbon dioxide, 0.2673 g water and 0.04620 g nitrogen.

Use these data to calculate the percentage composition by mass of **Q**, and hence its empirical formula. Show whether your answer is consistent with the molecular formula of **Q**.

(4)

C in CO_2 = $\frac{12}{44} \times 2.614 = 0.7129$ g

H in H_2O = $\frac{2}{18} \times 0.2673 = 0.0297$g

N in N_2 = 0.04620g.

m of O = $1-(0.7129 + 0.0297 + 0.04620)$

= 0.2112g

n of C = $\frac{0.7129}{12}$ = 0.0594 mol. $\frac{0.0594}{0.0033} = 18$

n of H = $\frac{0.0297}{1}$ = 0.0297 mol $\frac{0.0297}{0.0033} = 9$

n of N = $\frac{0.04620}{14}$ = 0.0033 mol $\frac{0.0033}{0.0033} = 1$

n of O = $\frac{0.2112}{16}$ = 0.0132 mol. $\frac{0.0132}{0.0033} = 4$

∴ Q = $C_{18}H_9O_4N_1$

it is consistent, n = 1

ResultsPlus

Examiner Comments

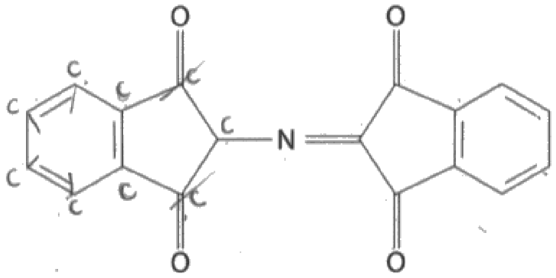
This response was clearly set out and showed that the candidate proceeded logically and could check each stage if needed. It was awarded full marks (4).

ResultsPlus

Examiner Tip

In a calculation always say what each number refers to. Then you can check it and think about your method easily.

(ii) In the final stage, **Y** reacts with another molecule of ninhydrin to form a dye, **Q**, shown below.



What is the molecular formula of **Q**?

(1)

C_6H_4 $(CO)_2$ $CN(CO)_2$ C_6H_4

$C_{18}H_8O_4N$

(iii) On combustion, 1.000 g of **Q** produces 2.614 g carbon dioxide, 0.2673 g water and 0.04620 g nitrogen.

Use these data to calculate the percentage composition by mass of **Q**, and hence its empirical formula. Show whether your answer is consistent with the molecular formula of **Q**.

(4)

	CO_2	H_2O	N_2
Mass in g	2.614	0.2673	0.04620
$n = \frac{m}{M_r}$	$\frac{2.614}{44}$	$\frac{0.2673}{18}$	$\frac{0.04620}{28}$
	$= 0.0594$	0.0149	1.65×10^{-3} $= 0.00165$

Dividing all by 0.00165

36	9	1

$C_{36}(H_2O)_9N_2$

$C_{36}H_{18}O_9N_2$

ResultsPlus

Examiner Comments

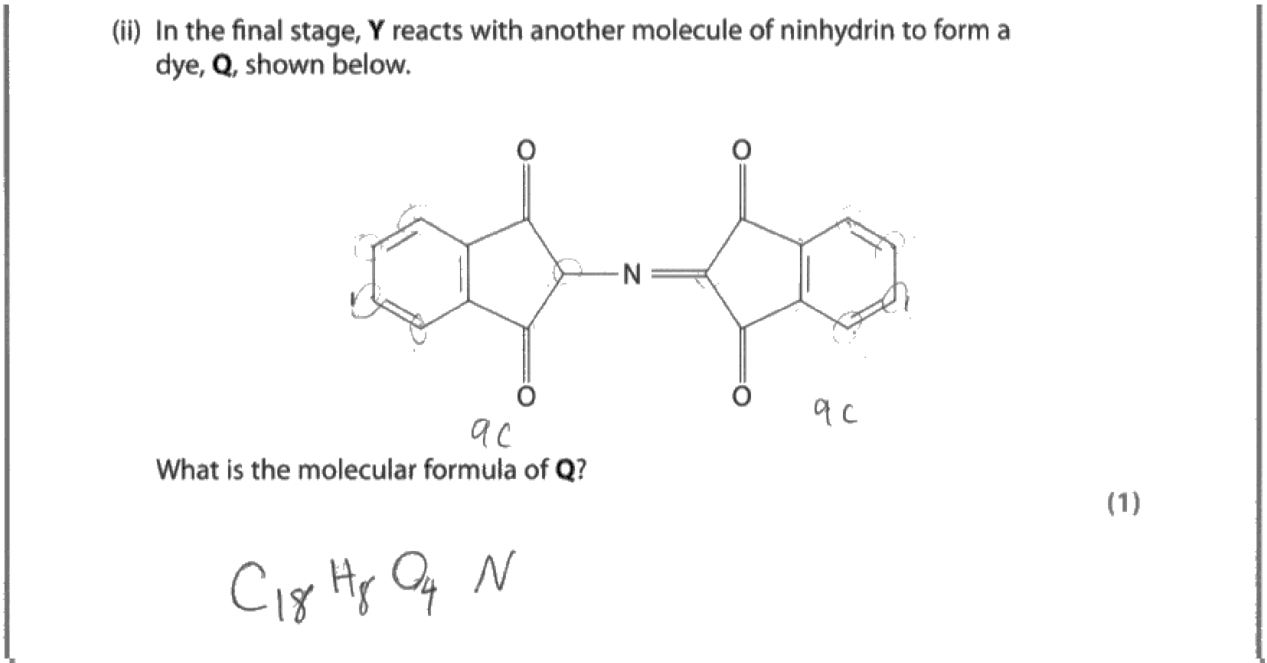
This candidate calculated the number of moles of carbon dioxide, water and nitrogen molecules. The oxygen was completely ignored. The ratios were calculated by comparison with N_2, not N atoms. It scored 1 mark.

Question 25 (f) (iv)

The question asked for evidence from mass spectra or nmr spectra, but quite a few suggestions were about infrared spectra.

Candidates who suggested the value of the mass/charge ratio of the parent ion in the mass spectrum could base their answer on the formula they had given in (f)(ii), or could suggest the mass of another fragment.

A variety of answers was allowed for the number of peaks in the low resolution nmr spectrum, as candidates did not have enough experience to know whether the hydrogen atoms on the benzene rings would show at different positions at low resolution.

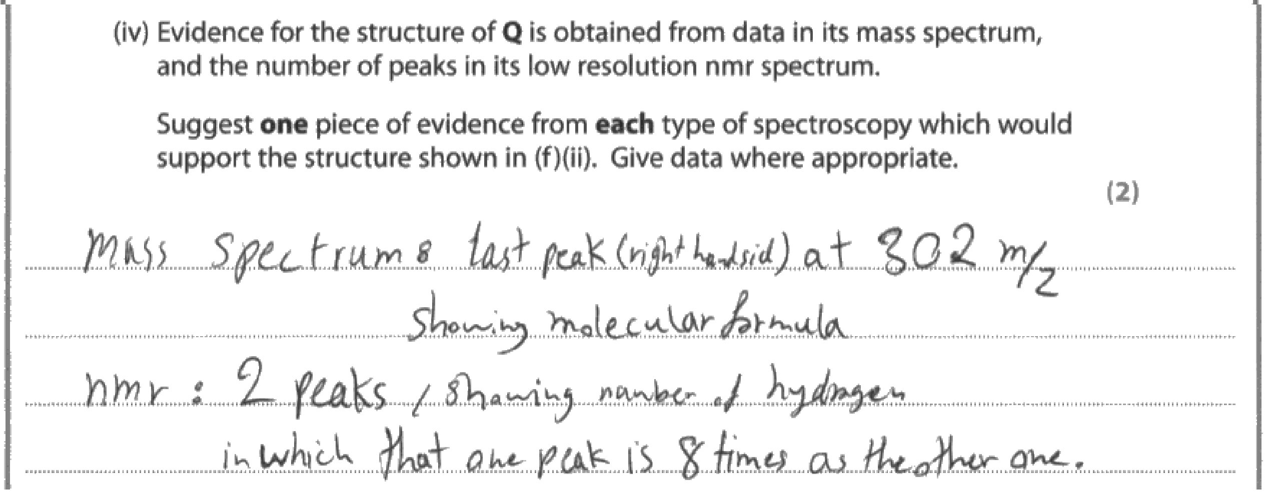


(ii) In the final stage, **Y** reacts with another molecule of ninhydrin to form a dye, **Q**, shown below.

What is the molecular formula of **Q**?

(1)

$C_{18}H_8O_4N$



(iv) Evidence for the structure of **Q** is obtained from data in its mass spectrum, and the number of peaks in its low resolution nmr spectrum.

Suggest **one** piece of evidence from **each** type of spectroscopy which would support the structure shown in (f)(ii). Give data where appropriate.

(2)

Mass Spectrum: last peak (right hand side) at 302 m/z showing molecular formula

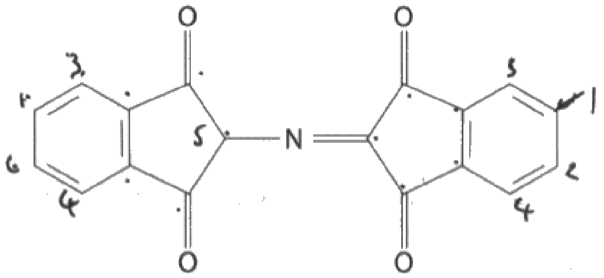
nmr: 2 peaks, showing number of hydrogen in which that one peak is 8 times as the other one.

ResultsPlus

Examiner Comments

The mass of the parent ion agrees with the formula suggested earlier. The number of peaks in nmr was one of the values allowed and suggests that the candidate was thinking of the 8 H atoms on the benzene ring and the one H atom next to the nitrogen, so this answer scored 2 marks.

(ii) In the final stage, **Y** reacts with another molecule of ninhydrin to form a dye, **Q**, shown below.



What is the molecular formula of **Q**?

(1)

$C_{18} H_{9} O_4 N$

(iv) Evidence for the structure of **Q** is obtained from data in its mass spectrum, and the number of peaks in its low resolution nmr spectrum.

Suggest **one** piece of evidence from **each** type of spectroscopy which would support the structure shown in (f)(ii). Give data where appropriate.

(2)

There would be five peaks in the low resolution nmr

The parent ion peak would be the same mass as $C_{18} H_9 O_4 N$

ResultsPlus

Examiner Comments

This answer did not give any data about the mass spectrum as required in the question.

Five peaks would occur in the nmr spectrum if each benzene ring had two different hydrogen environments and the hydrogen next to the N atom was another environment. It scored 1 mark.

Paper Summary

As usual, marks were lost by candidates who did not read the questions carefully. This is said every year, but remains true.

There was limited understanding of the evidence for the electron configuration of transition metals in question 21, and confusion between use of the terms orbital and sub-shell in explanations.

There were many good cell diagrams in 22(a)(i) and good answers to 22(b)(ii), which indicated understanding of electrode potentials and redox, but the equations involving ions or electrons in 21(b)(i), 22(a)(ii) and 22(c)(i) often caused difficulties, and more practice would help here.

A lot of the organic chemistry in questions 23 and 24 had been learnt well.

Question 25 proved difficult for some candidates who did not always manage to apply principles from earlier in the course in their answers.

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

- Read the question carefully
- Show your method in calculations
- Do not round numbers early
- Practice writing equations involving ions
- Make sure you write clearly and think before you write.

Grade Boundaries

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

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