

Examiners' Report
January 2013

GCE Chemistry 6CH05 01

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Introduction

The paper proved accessible to most candidates and appeared to provide reasonable opportunities for well-prepared candidates to demonstrate their knowledge and understanding of Unit 5 of the specification.

The mean score in the multiple choice section was 67%, significantly higher than in sections B and C, in both of which the mean score was 51%. Over 80% of candidates gave the correct response to (in order of increasing difficulty) 1b, 13c, 13a, 8, 6c, 1a while, at the other end of the scale, three questions caused particular difficulty: 2c, 5, and 11.

Most candidates attempted the volumetric calculation quite confidently but the numerical work on redox potentials and the associated discussion of reactions proved a real challenge to all but the best candidates. The arene electrophilic substitution was tackled extremely well by many candidates who showed an encouraging ability to apply their knowledge in a slightly unfamiliar situation. The quality of written English was a real issue, with many candidates unable to express their ideas clearly or synthesise a logical multi-step argument; even straightforward ideas or such as geometric isomerism and disproportionation were not well described.

Question 14 (a)

Candidates were most likely to correctly identify the species in which the oxidation state of copper was +2, although the formula of the ammine complex was frequently given as $\text{Cu}(\text{NH}_3)_6^{2+}$. Candidates were much less likely to be familiar with the +1 state, often failing to recognise that an ammine complex is formed in this case also. The copper metal was often identified as an iodine compound.

Question 14 (b)

Most candidates realised that sulfuric acid is needed to convert the copper(II) oxide to copper(II) sulfate although a number of alternative compounds were suggested, including some that did not even contain the sulfate ion. The use of *concentrated* sulfuric acid was not penalised although it would be ineffective in this type of acid-base reaction.

Question 14 (c) (i)

Most candidates correctly identified the appropriate species but some negated their answer by giving an additional, incorrect response. 'Ligand' was a common erroneous or additional answer.

(c) (i) C and F are the same type of chemical species. Name this type.

(1)

Transition metal ions.



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Examiner Comments

This answer is clearly not specific enough; the copper species fits this description in all these species.

Question 14 (c) (ii)

To score full marks on this item required a good understanding of why transition metal ions are coloured combined with a precise appreciation of chemical terms. Common misconceptions included the idea that the d subshell of a transition metal ion will not be split by the surrounding ligands if it is full and confusion between colours arising from emission and absorption of visible light. Many candidates used key terms without due regard to their meaning. Thus, 'orbital', 'orbitals', 'subshell' and 'shell' were often used interchangeably and 'complete' and 'incomplete' used as synonymous with 'filled' and 'partially filled'. Responses frequently omitted mention of electronic transitions.

(ii) Explain why **C** is coloured but **F** is colourless.

(3)

C is a ^{Cu²⁺} copper (II) salt but F is a ^{Cu⁺} copper (I) salt. For this reason, the ^{Cu²⁺} copper (II) has incompletely filled d-orbitals whereas ^{Cu⁺} copper (I) has completely filled d-orbitals. So ^{Cu²⁺} copper (II) is coloured and ^{Cu⁺} copper (I) is colourless and as the colour of solution depends on the metal C is coloured while F is colourless.



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Examiner Comments

'd-orbital' (singular) is used rather than the precise '3d-subshell' or even the acceptable 'd-orbitals'. There is no real attempt at the third marking point and electronic transition is not even mentioned.

(ii) Explain why **C** is coloured but **F** is colourless.

(3)

Ligands cation in F has no split d-orbitals as its d-orbital is full. So the ligands in F cannot cause the d-orbital of the cation to split. So there is no electron transition in the d-orbital. So no light is absorbed by the electrons by transition between split d-orbitals.



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Examiner Comments

This illustrates the frequently seen error that the lack of colour associated with a filled d-subshell is because a filled subshell cannot be (energetically) split.

Question 14 (c) (iii)

This item proved quite challenging and, even when candidates understood that oxidation of **F** was involved, the role of oxygen in the process was often not appreciated. A surprising number of candidates associated the shaking of the solution with an increase in the kinetic energy of the particles or even with the mechanical dislodging of the ligands from the complex.

*(iii) Explain why **F** changes into **C** on shaking.

(2)

Cu^+ is unstable and can easily be oxidised into Cu^{2+} and when shaken Cu^+ in **F** is given enough energy to change it to Cu^{2+} .



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Examiner Comments

This typical example demonstrates an awareness that oxidation occurs but associates the transformation with an increase in kinetic energy effected by the shaking.



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Examiner Tip

While shaking reagents promotes mixing, its effect on the energy of the particles is negligible.

*(iii) Explain why **F** changes into **C** on shaking.

(2)

Because upon shaking, the particles of **F** get's kinetic energy increases, allowing them to achieve activation energy for reaction, in this case ligand exchange to occur.



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Examiner Comments

Another common misconception, in which the idea of increased energy is extended by reference to rates of reaction.

*(iii) Explain why **F** changes into **C** on shaking.

(2)

the copper(I) is oxidised into copper(II) by reaction with O_2 in the air. this results in the blue colour displayed by the ~~reaction~~ $Cu(II)$.



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Examiner Comments

However, there were some excellent answers.

Question 14 (d) (i)

There were many excellent definitions of disproportionation but many candidates failed to realise that it must involve oxidation and reduction of atoms of the same element, using instead terms such as reactant or substance. A few candidates suggested a *reaction* involving simultaneous oxidation and reduction which, of course, applies to all redox reactions.

(d) The reaction of copper(I) iodide to form **D** and **E** is a disproportionation.

(i) Explain the term disproportionation.

(2)

When the reactant gets reduced and oxidised at the same time.



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Examiner Comments

This is a typical response that would gain one mark; the term 'reactant' is not precise enough.



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Examiner Tip

Definitions offer easy marks on an A2 paper if they are learned accurately.

(d) The reaction of copper(I) iodide to form **D** and **E** is a disproportionation.

(i) Explain the term disproportionation.

(2)

Copper of copper(I) iodide undergoes both oxidation and reduction
O.N: +1 → 0 and +2



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Examiner Comments

This is an alternative approach which focuses on the species specifically referred to in the question.

Question 14 (d) (ii)-(iv)

Overall this section proved one of the most challenging of the paper, requiring candidates to complete some routine tasks involving redox potentials and then to apply their knowledge in an unfamiliar context, retrieving the relevant data from the Data Booklet in the process. There were many errors in writing the disproportionation equation, including non-ionic equations and redox reactions involving iodine; even when the species were correctly identified, the ionic equations were often left unbalanced. Calculation of the E_{cell} value for the disproportionation was most likely to gain full marks but even here many candidates were inaccurate either in choosing the appropriate E^\ominus values, transferring them to the paper, applying the correct calculation or giving the E_{cell} value the appropriate sign.

Few candidates appeared to consider the role of the nitric acid in 14(d)(iv) which led to much fruitless analysis of the likelihood of nitric acid reducing copper(I) or copper(II) to copper or the possibility of sulfuric acid acting as an oxidizing agent. Even when candidates identified the correct approach, the technical quality of the answers was often very inaccurate, with equations or cell diagrams incomplete and E_{cell} values calculated incorrectly. There were some excellent answers but, sadly, these were very rare.

HNO₃ @

*(iv) If copper(I) iodide is treated with nitric acid, rather than sulfuric acid, a blue solution is still formed but no pink solid. Use the standard electrode potentials on page 15 of your data booklet to explain this. Quote any data that you use.

$E = \text{Cu}(\text{H}_2\text{O})_6^{2+} + e^- \rightarrow \text{Cu}^+ + 6\text{H}_2\text{O}$

$E = \text{Cu}^+ \rightarrow \text{Cu}^{2+} + e^- = -0.15$

$E = \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} = +0.15$ (4)

$\text{NO}_3^- + 3\text{H}^+ \rightarrow \text{HNO}_2 + \text{H}_2\text{O} = +0.94$

$E_{\text{cell}} = +0.94 - 0.15 = +0.79\text{V}$

$\text{D} = \text{Cu}^+ \rightarrow \text{Cu}(\text{s}) = +0.52$

$\text{NO}_3^- + 3\text{H}^+ \rightarrow \text{HNO}_2 + \text{H}_2\text{O} = +0.79$

$0.79 - (0.52)$
 $0.52 - 0.79$
 $= -0.29$

For D
 \downarrow
 E_{cell} is negative therefore reaction not feasible for pink solid reaction, so it does not occur and $E_{\text{cell}} = -0.29\text{V}$

For E
 \downarrow
 E_{cell} positive for production of blue solution so reaction does occur, $E_{\text{cell}} = +0.79\text{V}$



ResultsPlus Examiner Comments

The candidate correctly identifies the relevant equations and calculates the E_{cell} value. However, the half-equations are incomplete and the nature of the reaction involving the nitric acid is not identified. Also, the candidate has spent time with completely irrelevant discussion of the reduction of copper(I) to copper.

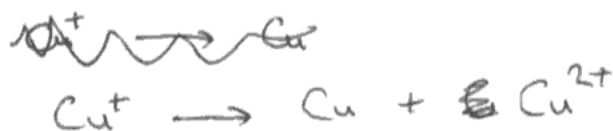


ResultsPlus Examiner Tip

This answer needed to be planned much more carefully. Data (and associated equations) need to be quoted in full.

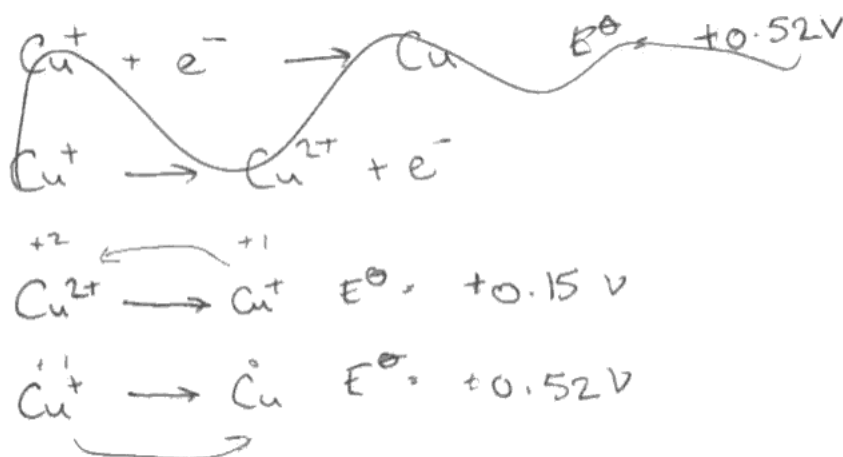
(ii) Write an ionic equation for this reaction. State symbols are **not** required.

(1)



(iii) Use the relevant standard reduction (electrode) potentials, from the table on page 17 of your data booklet, to calculate the $E_{\text{cell}}^{\ominus}$ value for this reaction, giving your answer with the appropriate sign.

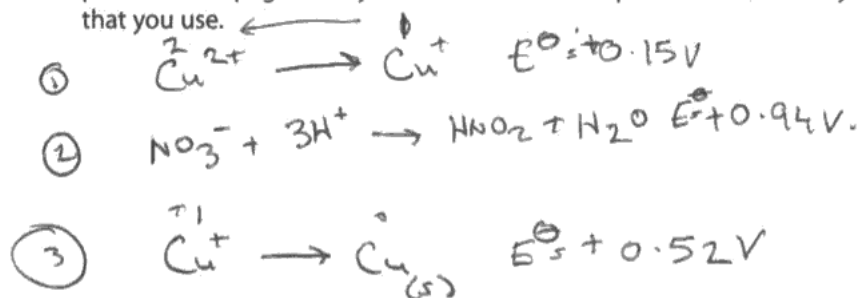
(2)



$$E_{\text{cell}}^{\ominus} = 0.52 - 0.15 = +0.37\text{V}$$

* (iv) If copper(I) iodide is treated with nitric acid, rather than sulfuric acid, a blue solution is still formed but no pink solid. Use the standard electrode potentials on page 15 of your data booklet to explain this. Quote any data that you use.

(4)



E^{\ominus} cell for 1 and 2 will be $0.94 - 0.15 = +0.79V$,
which is positive, so a blue solution will form.

E^{\ominus} cell for 2 and 3 will be $+0.52 - 0.94 = -0.42V$,
giving a negative value; this means that the reaction ^{between 2 and 3} is not
thermodynamically spontaneous, so no ^{solid} reaction will ~~take place~~ be
formed in standard conditions.

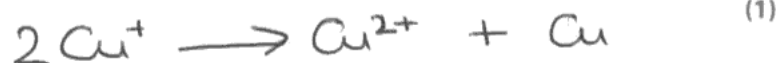


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Examiner Comments

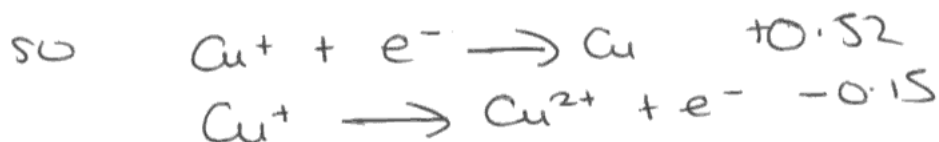
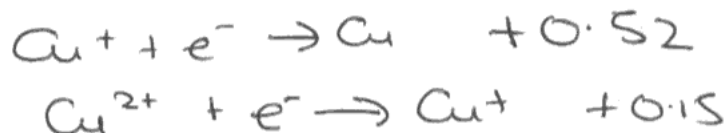
This answer had the potential to score full marks but, unfortunately, the candidate showed too little regard for basic precision. The disproportionation equation gives the correct species but is not balanced and throughout electrons are omitted from ionic half-equations. The nature of the reaction involving nitric acid is not specified.

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



(iii) Use the relevant standard reduction (electrode) potentials, from the table on page 17 of your data booklet, to calculate the $E_{\text{cell}}^{\ominus}$ value for this reaction, giving your answer with the appropriate sign.

(2)

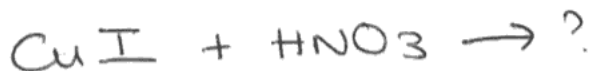


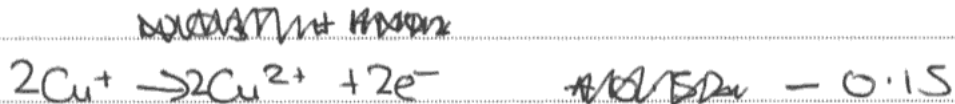
$$E_{\text{cell}}^{\ominus} = +0.52 - 0.15 = +0.37\text{V}$$

This reaction is thermodynamically feasible.

* (iv) If copper(I) iodide is treated with nitric acid, rather than sulfuric acid, a blue solution is still formed but no pink solid. Use the standard electrode potentials on page 15 of your data booklet to explain this. Quote any data that you use.

(4)





$$-0.15 + 0.94 = +0.79 \quad (\text{Reaction is feasible})$$

The equations shows us that only Cu^{2+} is formed and no $\text{Cu}(s)$ is formed.

(Total for Question 14 = 22 marks)

The Cu is the pink solid and the Cu^{2+} is the blue solution. The E^\ominus_{cell} value ~~is~~ shows us that this reaction is feasible. The equation shows us that no $\text{Cu}(s)$ is formed. Only Cu^{2+} (blue solution) is formed.



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Examiner Comments

Overall this is a good set of answers, missing only the relatively simple point that nitric acid is oxidizing in the reaction with copper(I) or copper.

Question 15 (a) (i)

While most candidates scored this mark there were a number of candidates who suggested reduction or redox rather than oxidation.

Question 15 (a) (ii)-(iii)

In 15(a)(ii) few candidates scored zero but many did lose one mark often due to a simple omission such as the word 'pale' or one of the colours at the final end-point. Some candidates ignored the starch addition altogether, others the point at which the starch is added.

Most candidates scored well on the calculation. The most common error was the omission of the subtraction in the third step of the sequence, an error which does give a plausible final answer.

(ii) State the colour of the solution in the flask just before the starch is added to the titration mixture and state the colour change at the end-point of the titration.

(2)

Pale yellow ^{before} starch is added
After starch addition, blue-black to colourless
at the end-point

(iii) Calculate the percentage by mass of ascorbic acid in the tablets. The molar mass of ascorbic acid is 176 g mol^{-1} .

(5)

$$\text{moles thiosulfate} = \frac{c \times v}{1000} = \frac{0.0631 \times 27.85}{1000} = 1.757335 \times 10^{-3}$$

$$\text{moles } I_2 = \frac{\text{thiosulfate}}{2} = 8.786675 \times 10^{-4} \text{ in } 25 \text{ cm}^3$$

$$\text{moles } I_2 \text{ in } 250 \text{ cm}^3 = \text{moles } I_2 \text{ in } 25 \text{ cm}^3 \times 10 = 8.786675 \times 10^{-3}$$

1:1 ratio \therefore moles ascorbic acid = $8.78 \dots \times 10^{-3}$

$$n = \frac{m}{M_r} \rightarrow m = n \times M_r \text{ mol} \times \frac{\text{g}}{\text{mol}}$$
$$= 8.78 \dots \times 10^{-3} \times 176 = 1.54 \text{ } 1.55 \text{ g (3 sf)}$$

$$4 \times 500 \text{ mg} = 2 \text{ g}$$

$$\frac{1.55}{2} \times 100\% = 77.37\%$$

(1 dp)



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Examiner Comments

The calculation fails to take into account that a back titration is involved. Apart from this rather important omission, the various steps of the calculation are carried out correctly. The description of the colour changes near to and at the end-point are excellent.

Question 15 (a) (iv)

The answer to this type of question must be specific to the experimental context. Thus the all too popular generalisation about percentage error scored no marks while those who suggested that the titre error would be reduced failed to realise or to take into account that this was a back titration.

(iv) Explain why using four tablets in 250 cm³ of solution gives a more accurate result than two tablets in 250 cm³.

(1)

Higher ~~the~~ reacting volume lowers percentage error.

An overall result.



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Examiner Comments

In the context of this question this answer is not only insufficiently specific but also incorrect.



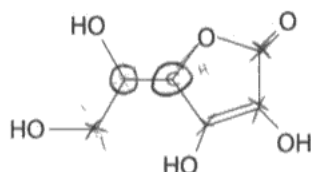
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Examiner Tip

Try to think through the impact of a change in quantity on the accuracy of an experiment.

Question 15 (b) (i)

Most candidates correctly identified the chiral centres in the molecule although most of the other atoms and even some bonds were also selected. The most popular means of identification was to circle the atoms although some candidates used asterisks; both were easy to mark. A few candidates crossed out non-chiral atoms, a procedure which had the potential to confuse examiners.

(b) The structure of ascorbic acid is shown again below. Vitamin C is one of the optical isomers of this structure.



(i) Mark on this diagram the two chiral centres of this molecule.

(2)



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Examiner Comments

Here the candidate has circled the chiral carbons but also put a cross against four other atoms. Without a key, there is some ambiguity in the answer.



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Examiner Tip

Do ensure that your intentions are clear to an examiner.

Question 15 (b) (ii)

While most candidates seemed to be aware that the answer involved the use of plane polarised light, expressing this knowledge in a clear, concise and accurate fashion proved to be a major hurdle for many.

Question 15 (b) (iii)

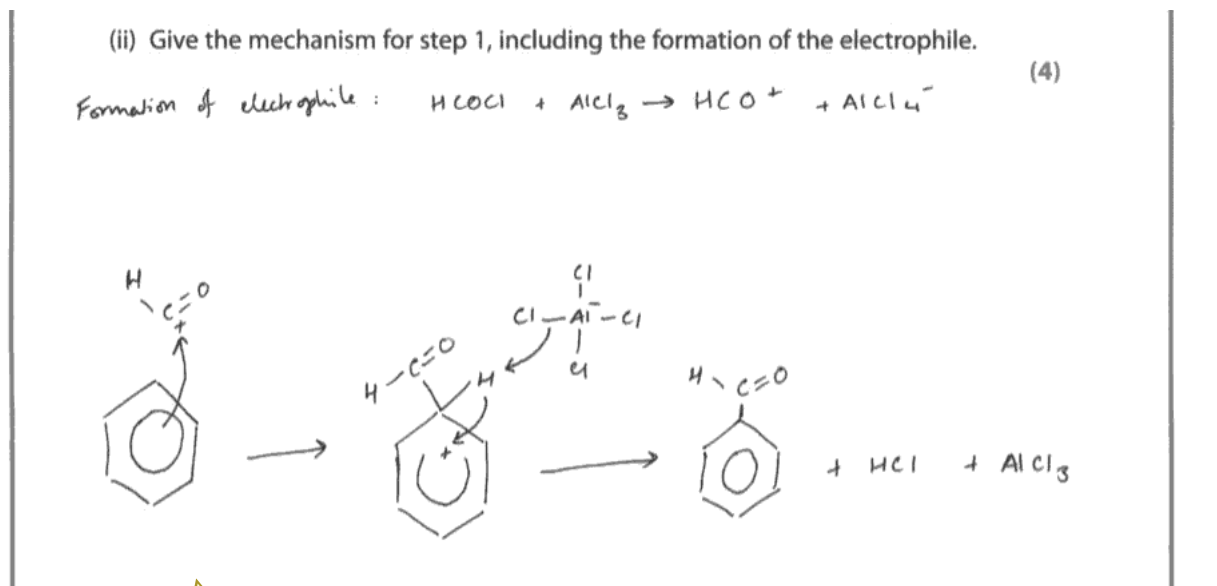
The question was framed to elicit a possible explanation that was specific to the ester group. Many responses simply suggested that the ester group might 'break down' and it should be clear to candidates that so simple an answer is unlikely to gain credit at this level. Another common idea was that the vitamin C might be denatured.

Question 16 (a) (i)

Candidates found it difficult to combine all the features needed to score full marks i.e. the delocalized π electrons of benzene, the consequent stabilisation of the structure and the retention of this structure with substitution. All too often candidates gave imprecise answers omitting key features of the required response.

Question 16 (a) (ii)

Candidates who knew the mechanism of benzene electrophilic substitution experienced no difficulties with the unfamiliar electrophile but often lost marks due to simple inaccuracies in the mechanism. Common errors were incorrect placing of the curly arrows, placing the positive charge outside the Wheland diagram 'horseshoe' (and often adjacent to the tetrahedral carbon), failing to extend the 'horseshoe' over enough carbon atoms (ideally this should be five atoms although fewer were allowed) and orienting the 'horseshoe' incorrectly (the gap must face the tetrahedral carbon).



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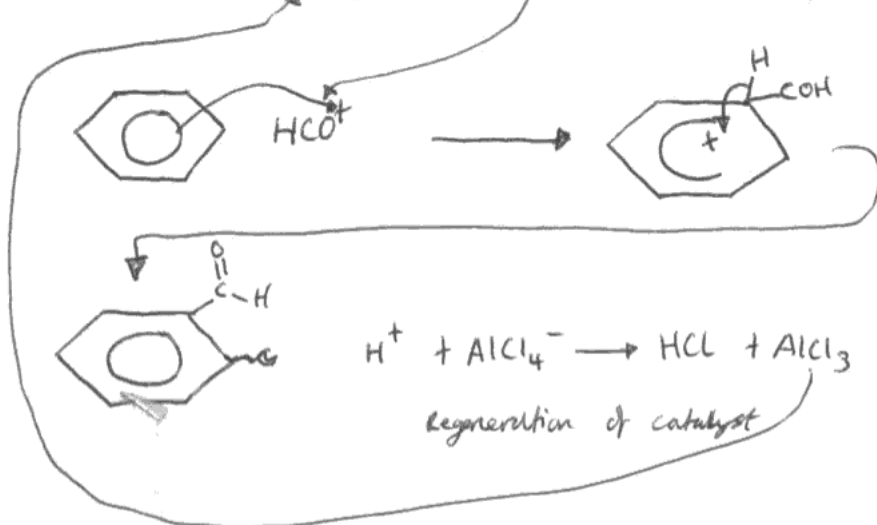
The second curly arrow originates from the hydrogen rather than the C-H bond. The positive charge on the Wheland diagram is borderline; ideally it should be in the centre of the horseshoe.



ResultsPlus Examiner Tip

Remember that curly arrows show the movement of *electrons*.

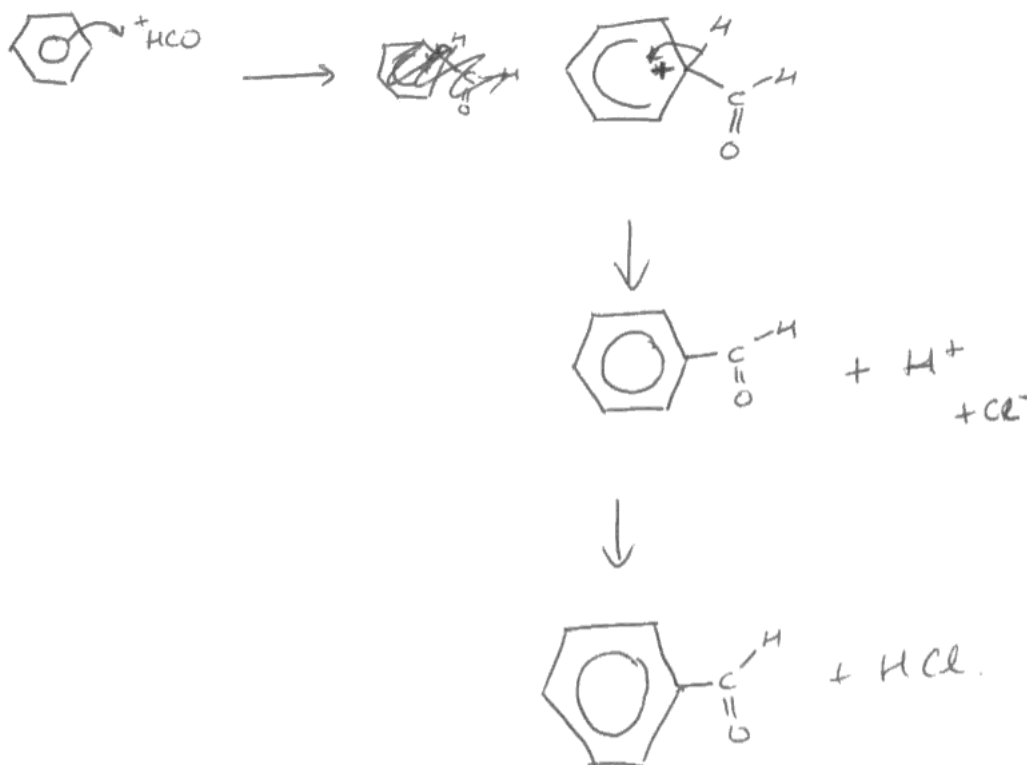
(ii) Give the mechanism for step 1, including the formation of the electrophile. (4)



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Examiner Comments

The horseshoe in the Wheland diagram is pointing towards the wrong carbon.

(ii) Give the mechanism for step 1, including the formation of the electrophile. (4)



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Examiner Comments

Two marks are lost in this example. The first is for the omission of the aluminium chloride from the equation for the production of the electrophile and the second is for the position of the positive charge on the tetrahedral carbon.

Question 16 (a) (iii)

Most candidates knew appropriate reagents for carrying out these reactions although some failed to identify the need for a suitable acid for the oxidation, or the need for ether for the reduction. Some candidates lost a mark by giving the formula of the dichromate(VI) ion rather than the name or formula of the compound, a requirement clearly indicated by the wording of the question.

Question 16 (b)

While many candidates had a reasonable general idea of the explanation for the difference in reactivity between phenol and phenylmethanol, all too often they were unable to present the argument logically and using scientific terminology precisely. Correct ideas were often mixed up with irrelevancies or significant misconceptions, particularly common were discussions about the increased negative charge or electronegativity of the benzene ring. Only the best candidates could explain clearly why the benzene ring is activated in phenol but not in phenylmethanol.

*(b) Phenol reacts faster than phenylmethanol in electrophilic substitution reactions. Suggest why this is so.

~~the oxygen~~ On the phenol the oxygen's ⁽⁴⁾ p orbital overlaps with the benzene ring increasing its electron density especially in 2 & 4 positions. While in phenylmethanol oxygen atom is far away from the benzene ring so there is no overlap between the benzene ring & the p-orbital of the oxygen atom. Therefore Phenol is more susceptible to electrophilic attacks.



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Examiner Comments

The omission of mention of the oxygen lone pair is the only problem with what is otherwise a very good answer.

*(b) Phenol reacts faster than phenylmethanol in electrophilic substitution reactions. Suggest why this is so.

(4)

phenol has a OH group directly attach to the benzene.
The lone pair of electrons on the oxygen atom of OH group donates the electron density into the ring. This makes the ring a stronger nucleophile. So it is more susceptible to attack by electrophile. ~~Whereas phenylmethanol~~ The OH group activates the ring. Whereas in phenylmethanol, the OH group is not directly attach to the benzene. The ring is not activated.



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Examiner Comments

This type of discussion in which the reactivity of phenol is discussed in terms of it acting as a nucleophile was by no means uncommon. While it might be argued that, because it reacts with electrophiles, phenol (or indeed benzene) could be regarded as a nucleophile, this is conventionally incorrect.

Question 17 (a) (iii)

This was an easy enough mark for most candidates with the omission of the amine CH_2 being the most common error. A surprising number of candidates failed to attempt the question.

Question 17 (a) (i)-(ii)

The explanation of geometric isomerism in alkenes proved unexpectedly difficult. Even the first mark eluded many, with candidates failing to specify that it is rotation *around* the double bond that is restricted while there were frequent references to the *molecule* being unable to rotate. The idea that different groups need to be bonded to each carbon was frequently forgotten and there was a good deal of irrelevant discussion of priority groups.

Where candidates had been unable to define geometric isomerism there was little prospect of gaining the mark in 17(a)(ii) but even those who scored the first mark in 17(a)(i) often did not make the connection between the two sections.

(a) (i) Explain why some molecules which contain a C=C double bond show geometric isomerism.

(2)
They can have different groups attached to each carbon. The double bond prevents free rotation, so they are locked in place. This means that there are different structures for the same molecule.

(ii) Suggest how tranexamic acid can form geometric isomers although it does not have a C=C double bond.

(1)
When it forms zwitter ions, its structure is locked in place. The cyclohexane ring does not allow free rotation around it.



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Examiner Comments

In this response the second mark for 17(a)(i) is scored well in the first clause but it is not entirely clear what rotation is being referred to in the remainder of the answer.

In 17(a)(ii) the candidate offers two contrasting answers and, although the second is fine, the first is incorrect so no credit can be given.



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Examiner Tip

If more than one answer is given to a question all must be correct to score full marks.

(a) (i) Explain why some molecules which contain a C=C double bond show geometric isomerism.

(2)

Restricted

• ~~Restricted~~ rotation about the C=C bond

• Only some molecules show geometric isomerism if they have C=C because you require 2 different groups attached to each carbon of the C=C to display geometric isomerism, some do not.

(ii) Suggest how tranexamic acid can form geometric isomers although it does not have a C=C double bond.

(1)

Ring structure restricts rotation of molecule.



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Examiner Comments

17(a)(i) is fine but in 17(a)(ii) the candidate refers to rotation of the molecule.

Question 17 (a) (iv)

The majority of candidates focused on the possibility of tranexamic acid forming hydrogen bonds, failing to realise that a zwitterion would form even though it is stated in the stem of the question that tranexamic acid is an amino acid. Another common error was failure to state the type of intermolecular force in undecane, often just observing that it would *not* form hydrogen bonds.

(iv) Explain why tranexamic acid melts at 300 °C while the alkane, undecane ($C_{11}H_{24}$) which has almost the same number of electrons, melts at -26 °C. A detailed description of the forces involved is **not** required.

(3)

The alkane would not be able to form H-bonds between it's molecules because it wouldn't have an -OH group. Also, the amino acid can form zwitterions, which have strong intermolecular forces due to the positive $-NH_3^+$ group of one molecule being strongly attracted to the negative $-COO^-$ group of another.



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The candidate realises that a zwitterions are formed and describes the nature of the resulting intermolecular forces. Unfortunately, there is no description of the intermolecular forces in the alkane, only the statement that hydrogen bonds are not formed.



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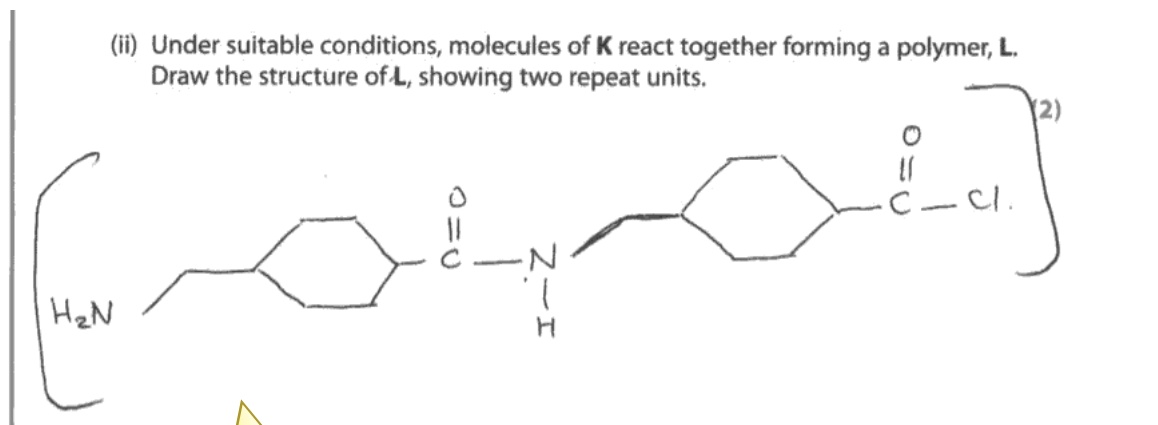
It should be clear that in this type of question the intermolecular forces in both molecules need to be identified.

Question 17 (b) (i)

While many candidates scored this mark a surprising number suggested hydrogen chloride or ethanoyl chloride.

Question 17 (b) (ii)

This question proved a significant challenge at all levels. Reasonably well-prepared candidates were able to draw the amide link correctly but only the better candidates could bring the necessary precision to the rest of the structure.



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Examiner Comments

The term polymer requires a continuous extension of the structure but here a dimer is given.

Question 17 (b) (iii)

Most candidates knew that the reaction involved condensation although a fair number suggested addition.

Question 17 (b) (iv)

Although most candidates scored this mark, a surprising number suggested materials like nylon and kevlar as examples of naturally occurring substances.

Question 17 (c) (i)

Many candidates were able to score three marks on this item, typically losing the final marking point by failure to correctly pair the proton environments.

Question 17 (c) (ii)

Clarity of expression was again at a premium here with many candidates attributing both absorptions to the amide group, and not appreciating that IR peaks are related to bonds rather than groups. A number of candidates lost a mark by referring to the C=O as the 'ketone' group.

(ii) Explain how the IR data are consistent with the structure of **M**.

(2)

The 1700-1660 cm⁻¹ peak indicated that there is an amide present.
This is consistent with **M**. The 3500-3140 cm⁻¹ peak also indicates an amide.
So this is also consistent.



ResultsPlus Examiner Comments

A typical one mark response. Both peaks are assigned to the 'amide' group despite the more detailed information available in the Data Booklet.



ResultsPlus Examiner Tip

Use the information that is provided and this should include the mark allocation for the question.

(ii) Explain how the IR data are consistent with the structure of **M**.

(2)

- 1700-1630 is a C=O stretching vibration - **M** has a C=O bond.
- 3500-3140 is an amide N-H stretching vibration **M** contains
N-H groups



ResultsPlus Examiner Comments

This candidate makes it all look very easy!

Question 17 (c) (iii)

For some candidates the concept of intramolecular and intermolecular reactions was unfamiliar despite the obvious clues in the question. Even where they had the right idea, as elsewhere on this paper, candidates seemed unable to express their ideas with sufficient clarity or appropriate use of technical language.

Paper Summary

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

- Remember that AS material will be required in A2 papers.
- Organic mechanisms need to be very precise: ensure that curly arrows are precisely located and structures are exact.
- In extended responses, make sure that the chain of an argument is maintained and that it matches the number of marks allocated.
- In comparison questions, both aspects need to be considered.

Grade Boundaries

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