

Examiners' Report

June 2019

IAL Chemistry WCH05 01

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June 2019

Publications Code WCH05_01_1906_ER

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Introduction

The overall standard of the responses on this paper was good and showed that candidates had been prepared well for this exam. Section A (the multiple choice) was the highest scoring; Q1 and Q10 were answered correctly by more than 90% of candidates. In contrast, the mean score on Section C was just 31.8%.

The standard of numerical work on the paper was very high. It was encouraging that most candidates set out their responses in a clear and logical way, and avoided premature rounding of calculated values. The shaping of the answers to the open response questions was much more varied; the best candidates structured their answers logically but many answers seemed poorly thought through and included far too much irrelevant material. Candidates should be aware that responses that include correct and incorrect material are unlikely to score full marks.

Candidates scored well in standard questions on areas of the specification that have been tested a number of times in earlier series but most were much less secure when required to apply their knowledge to unfamiliar situations. In these 'stretch and challenge' questions, marks were frequently lost by candidates seeming to rush to write their answer without ensuring that it matched the question. As has been stated before, the importance of reading each question carefully cannot be overstated.

Question 17 (a)

For part (a)(i) most candidates were able to select the appropriate pair of half-equations, although oxidation of chromium(II) to chromium(III) or of chromium(III) to chromium(VI) were not uncommon. The overall equation was then usually correct with the common error being failure to scale the hydroxide ions while some candidates gave the reaction in the reverse direction. Here and elsewhere in the paper, candidates would have benefited from an appreciation that charges must balance in ionic equations. The calculation of the E_{cell} value was usually correct although there were quite a number of E_{cell} values of -1.14 V and -0.34 V from correct overall equations.

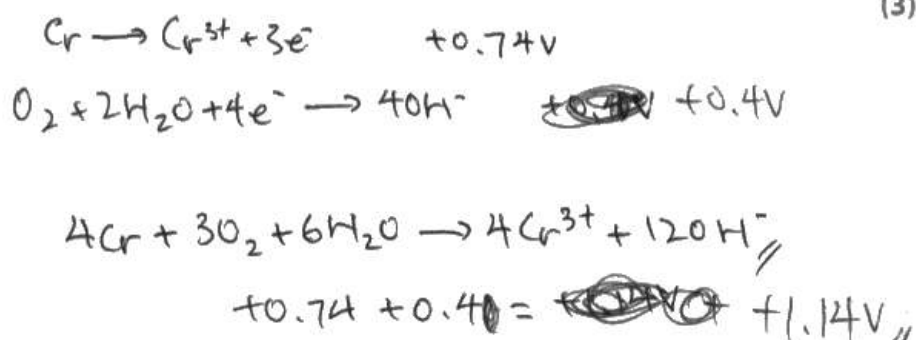
For part (a)(ii) candidates almost always appreciated that a positive E_{cell} value indicates that a reaction is thermodynamically feasible and stated this at the start. However, most answers then focused on the corrosion of the coated metal rather than corrosion resistance of the chromium coating specified in the question. This led to answers that ignored the information given in the stem of the question and assumed that chromium offered sacrificial protection.

(a) One of the most important uses of chromium is in plating other metals such as steel and brass. This gives them a hard shiny coating which is very resistant to corrosion.

(i) Calculate $E_{\text{cell}}^{\ominus}$ for the reaction of chromium with oxygen in the presence of water.

Write the equation for this reaction. State symbols are not required.

(3)



(ii) By considering the $E_{\text{cell}}^{\ominus}$ value calculated in (a)(i), suggest why a chromium coating is corrosion resistant.

(2)

The $E_{\text{cell}}^{\ominus}$ value is positive, therefore, the reaction is thermodynamically feasible. However, the activation energy for the reaction may be very high, preventing the corrosion reaction from occurring.



This was a fully correct answer which benefited from clear presentation.

Question 17 (b) (i)

The E_{cell} value for the reduction of chromium(III) to chromium(II) by zinc was correctly calculated by most candidates. However, quite a number failed to specify the reducing agent, just writing the Zn/Zn^{2+} half-equation, which was insufficient to merit the mark. A small number of candidates selected chromium as the reducing agent, which was accepted.

Question 17 (b) (ii)

This was generally very well answered. The common errors were failure to specify the oxidant and identification of an incorrect oxidation product. There were some complex responses involving the oxidation of zinc or chromium(III) which gained no credit.

(ii) When chromium(III) is converted to chromium(II) in aqueous solution, air has to be kept out of the apparatus.

Explain why this is necessary.

(2)

Chromium (iii) ion gets oxidized to Cr^{6+} ion when in air. presence of air. The color changes from green to yellow.



This candidate appreciated that aerial oxidation would occur but suggested a change in oxidation state that is ruled out by the information on the stability of chromium(III) given in the stem of part (b) as well as, less obviously, by the E° data at the start of Q17.



Read each question carefully; there is often helpful information given.

Question 17 (b) (iii)

These colours were well known.

Question 17 (b) (iv)

It was encouraging that the majority of candidates appreciated that this question was about the **differences** in the colours of transition metal ions. Thus, there were many good answers which scored the first and third marking points but clear explanations for the different energy gaps were relatively rare. Candidates who understood the general principles involved often lost marks through a lack of precision. Referring to the splitting of a d orbital rather than d orbitals was quite common as was absorbing light or colour rather than specific frequencies or wavelengths of radiation or photons of specific energy.

*(iv) Explain why solutions of chromium(II) and chromium(III) have **different** colours. (3)

Cr^{2+} and Cr^{3+}

(3)

~~The different~~ ions have different oxidation numbers, therefore different number of electrons in the 3d-subshells. Therefore, the 3d-subshells are split to different extents. Hence, the amount of energy/wavelengths absorbed by electrons are different. ~~The~~ The wavelengths that are not absorbed are reflected.



The causes of the different colours are well understood in general terms but the way in which energy is absorbed is not expressed with sufficient clarity. There needs to be a reference either to different frequencies or wavelengths of radiation being absorbed and reflected, or different photons of energy being absorbed and reflected.

Question 17 (c)

It was rare for candidates to score both marks on this item. Although the formulae of both complexes appear in the specification, these were often given with incorrect numbers of ligands or incorrect charges. The octahedral shape of the ammine complex was more likely to be known than the tetrahedral shape of the chloro complex.

Question 17 (d) (i)

The formulae of the chromate(VI) and dichromate(VI) were usually quoted correctly but fully correct equations were much less common and, even where the species were correct, the equation often did not balance.

Question 17 (d) (ii)

While there were a number of excellent answers to this question, most candidates were uncertain how to approach it and relied on vague generalisations about the stability of the complex. Among the better answers, Route 1 was more common with the final mark being the least likely to be scored.

*(ii) Suggest why the $[\text{Cr}(\text{H}_2\text{O})_6]^{6+}(\text{aq})$ ion does **not** exist.

(3)

Cr^{6+} is highly charged and highly polarising.

Cr^{6+} deforms O-H bonds in water and breaks them.



An impressively concise response, which scores all three marks.

Question 17 (d) (iii)

Most candidates suggested the colours usually associated with chromium(VI): yellow or orange. Those that did realise that it would be colourless, often did not score the mark because their justification was insufficient (e.g. d-d transitions do not occur) or incorrect (e.g. full d subshell).

Colourless, as no d-d transition occur, no splitting of d-subshell. So, no light is absorbed & reflected back.



The candidate realises that the complex would be colourless but misses the key point that d-d transitions cannot occur because there are no d electrons.

Colourless, because it won't be a transition metal due to no electrons in d-subshell for excitation (not incomplete).



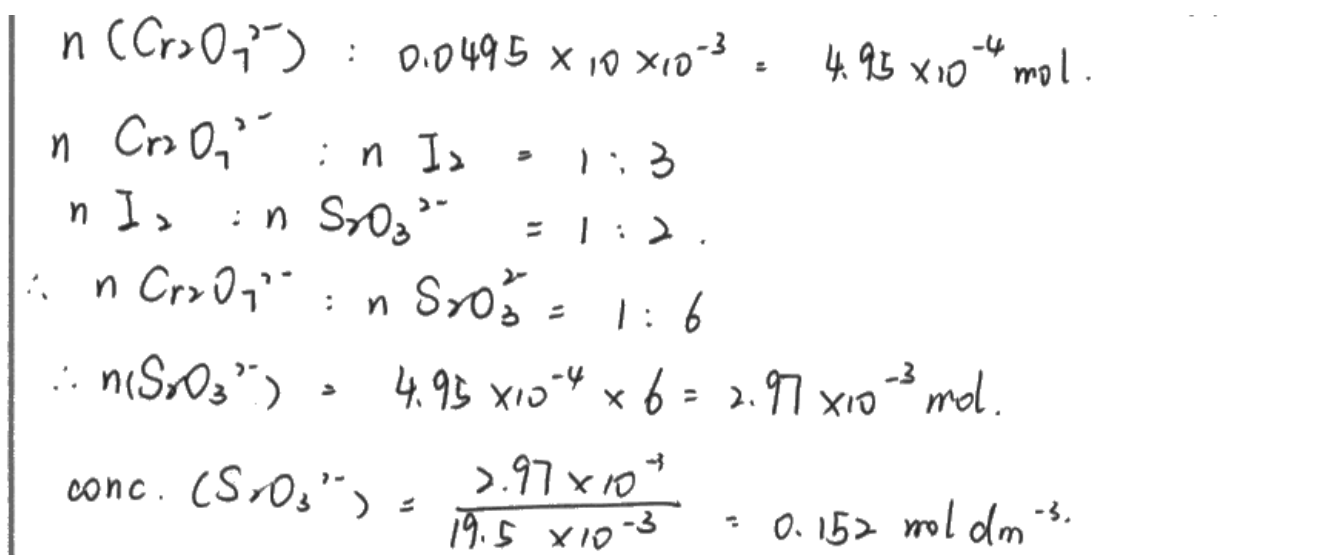
The idea that chromium ceases to be a transition metal if it loses all its d electrons was quite common. Here it has been ignored and there is enough correct chemistry to allow the mark to be awarded.

Question 17 (e) (i)

Almost all candidates correctly identified starch as the indicator with just a few of these reversing the colour change or omitting 'colourless' from their response.

Question 17 (e) (ii)

This item was very well answered in terms of both content and presentation. The most likely errors were the omission or inversion of one or more of the multiplying factors for the second and third marking points, while some candidates used the wrong volumes at the first and fourth stage of the calculation. Candidates almost invariably gave their final answer to an appropriate number of significant figures.



This calculation is not only correct but the stages are extremely easy to follow.

$$\text{Cr}_2\text{O}_7^{2-} \text{ mol} = 0.0495 \times \frac{10}{1000} = 4.95 \times 10^{-4}$$

$$\text{Mol of } 3\text{I}_2 = 4.95 \times 10^{-4} \times 3 = 1.485 \times 10^{-3}$$

$$\begin{aligned} \text{Mol of I}_2 \text{ in second equ} &= \frac{1.485 \times 10^{-3}}{3} \\ &= 4.95 \times 10^{-4} \end{aligned}$$

$$\begin{aligned} \text{mol of } 2\text{S}_2\text{O}_3^{2-} &\rightarrow 4.95 \times 10^{-4} \times 2 \\ &= 9.9 \times 10^{-4} \end{aligned}$$

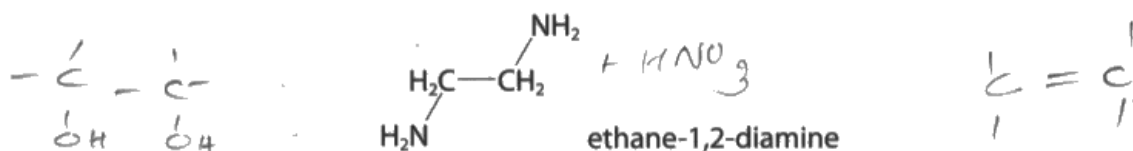
$$\text{conc. of } 2\text{S}_2\text{O}_3^{2-} = \frac{9.9 \times 10^{-4}}{19.50/1000} = 0.05 \text{ mol dm}^{-3}$$



In this response, the first two steps are correct but the second step is then reversed by dividing by three. This error in dealing with the pair of equations was quite common. The final answer (0.0508) has incorrectly been rounded to one significant figure.

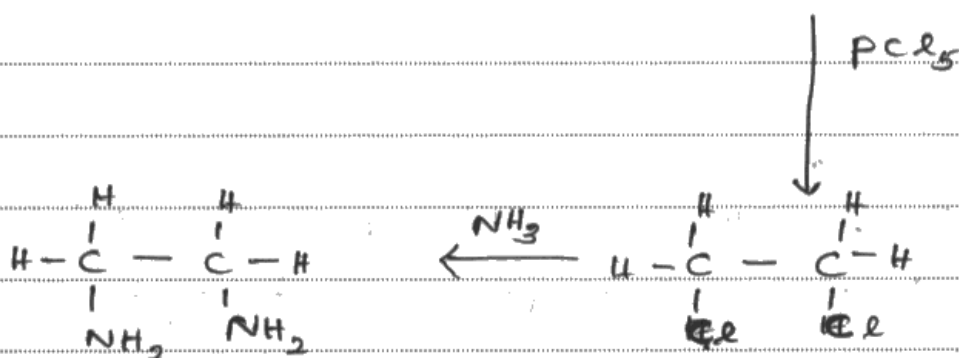
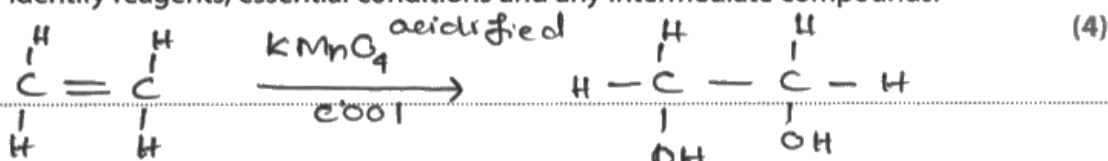
Question 18 (a)

This synthesis proved challenging and even when the correct route was identified, the conditions used were often incorrect (e.g. the use of bromine water or bromine and UV light in step 1) or omitted. A significant number of candidates began their synthesis by converting ethene to ethane despite the general inertness of alkanes, while others sought to draw on their knowledge of aromatic amines by proceeding via nitroalkanes.



(a) Outline a laboratory synthesis of ethane-1,2-diamine from ethene.

Identify reagents, essential conditions and any intermediate compounds.



Although this route is far from ideal from a practical perspective, it was allowed as chemically correct. No conditions were suggested for the final step so this mark was not awarded.

Ethene is heated with nickel and hydrogen to form an ethane.

Then, add HBr_2 ~~HBr~~ to ethane in which ~~CH_3~~ $\text{CH}_2\text{BrCH}_2\text{Br}$, 1,2-dibromoethane will form.

Lastly add ^{in ethanolic solution} excess ammonia ~~1~~ to ~~$\text{CH}_2\text{BrCH}_2\text{Br}$~~ 1,2-dibromoethane in a sealed ~~test~~ tube at 180°C to form ethane-1,2-diamine



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Examiner Comments

The route to 1,2-dibromoethane is incorrect but the remainder of the sequence scored full marks.

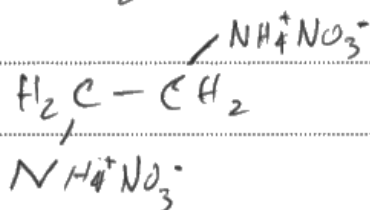
Question 18 (b)

Many candidates recognised the reaction as a neutralisation although some, relying on a general definition, gave water as a co-product. Correct salt structures were likely to be associated with a good understanding of the chemistry involved. The mark for explaining the basic character of ethane-1,2-diamine was the least likely to be scored.

- (b) When nitric acid was added to ethane-1,2-diamine and the resulting solution allowed to evaporate to dryness at room temperature, white crystals remained. Explain the chemical reaction that occurred and give the structure of the white crystals.

(3)

The amine groups are basic and react with the acid in a neutralization reaction to produce a crystalline salt.



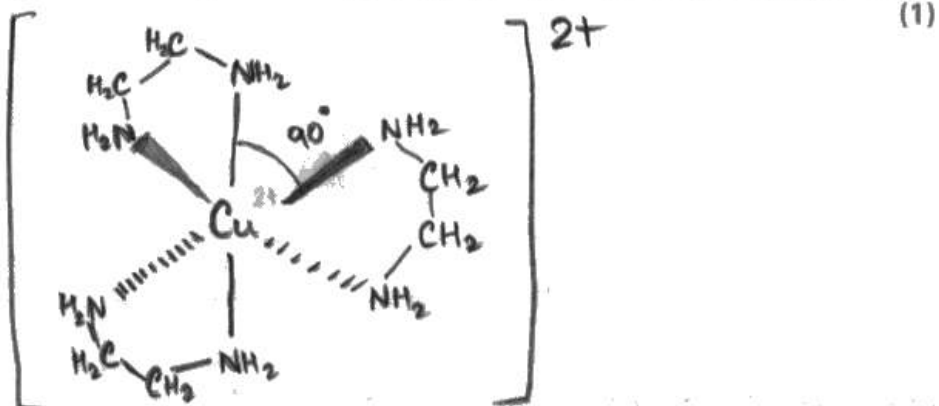
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Examiner Comments

The first two marks have been scored but the formula of the salt is incorrect. The amine groups have been protonated but to NH_4^+ instead of NH_3^+ .

Question 18 (c) (i)

There were many good responses showing the key points required: the bonding of nitrogen atoms to the central copper ion and a correct bidentate ligand. Although not a requirement, surprisingly few candidates drew diagrams showing the three-dimensional shape of the complex.

(i) Draw a diagram of a complex that copper(II) ions form with ethane-1,2-diamine.



This is an excellent response which covers both marking points and also shows the three-dimensional shape of the complex.



Practise drawing the basic shapes of molecules and complexes.

Question 18 (c) (ii)

Most candidates appreciated that the reaction was entropy driven. However, the first marking point proved much more difficult to score, with candidates using imprecise or incorrect terms, e.g. 'more products than reactants' or more 'product atoms'. Some of the clearest and best answers were given by those who wrote the equation for the reaction and then referred to it in their answer. Some candidates confused entropy and entropy change, giving answers which compared the molar entropies of the two complexes.

*(ii) When ethane-1,2-diamine is added to an aqueous solution of tetraamminecopper(II) ions, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, the formation of the ethane-1,2-diamine complex is favoured. Explain why this is so.

(2)

The formation of ethane-1,2-diamine complex results in more ~~particles~~ molecules been produced. This reaction will have a greater ^{positive} entropy of system so ΔS_{total} is more positive so reaction is more feasible.



This covers all the salient points very concisely.

The formation of ethane-1,2-diamine complex has a more positive ΔS_{system} as the number of moles increases. ΔS_{system} increases thus ΔS_{total} increases and reaction therefore more feasible and more favourable as it has a higher K value.



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Examiner Comments

This response is correct and comprehensive but note that both marks are scored in the first sentence. The reference to ΔS_{total} is useful but the last two lines are redundant.



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Examiner Tip

Aim for concise responses; the space provided will be ample for a fully correct answer and does not have to be filled.

Question 18 (d) (i)

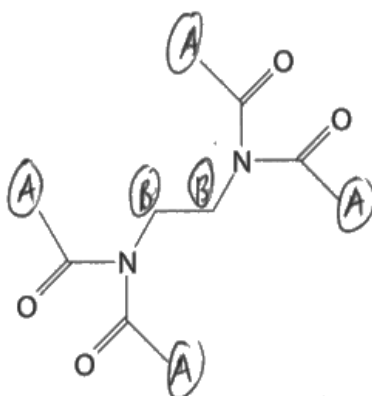
Ethanoyl chloride was identified as the reagent by most candidates while a few gave ethanoic anhydride. The most likely incorrect answer was ethanoic acid.

Question 18 (d) (ii)

There were many excellent answers to this item, with candidates appreciating the significance of molecular symmetry and using it to identify equivalent proton environments. Some candidates clearly knew the proton environments but failed to identify them or to link them together. The use of the diagram was the best way to do this, an approach that was clearly indicated in the question. The use of the skeletal formulae led to the $\text{CH}_3\text{CO}-$ groups being identified as $\text{HCO}-$ and some candidates elected to give splitting patterns despite being told not to do so.

- (ii) State the number of peaks and relative peak areas present in the **low resolution proton nmr spectrum of TAED**.
Justify your answer by referring to the diagram of the compound.

(3)



There would be two peaks ~~see~~ as there are only two unique proton environments in TAED as seen in the diagram above with (A) and (B). They would have a relative peak areas of 3:1, as there are twelve ~~hydrogen~~ protons in environment (A) and four protons in environment (B).



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Examiner Comments

A fully correct answer which uses the diagram to identify the proton environments and group them together.

Question 19

In part (a), most candidates determined the empirical formula correctly with the most common error being rounding the initial values obtained for the moles of the elements to the nearest whole number. A few gave the non-integer ratio ($C_{4.5}H_4O$) as the empirical formula. The final mark in Q19(a) required that the link with the molecular ion peak or the molar mass to be made and the identity of M or its molecular formula to be clearly stated.

In part(b)(i), the significance of the reaction with sodium hydrogencarbonate was generally known but the reaction with acidified potassium manganate(VII) was often attributed to the presence of an alcohol or an aldehyde, with the requirement for an extra oxygen atom being ignored. The deduction of a phenyl group from the mass spectrum peak at $m/e = 77$ was the least likely to be made. Some candidates gave the three correct groups without stating any justification, thereby forgoing two of the marks available.

In part(b)(ii), relatively few candidates gave all three structures; most who had correctly identified the groups present failed to spot the geometric isomers. Many responses showed di-substituted benzene rings even though this contradicted the peak at $m/e = 77$.

19 A white solid **M** has the following percentage composition by mass: carbon 72.97%; hydrogen 5.41%; oxygen 21.62%.

The mass spectrum of **M** has a molecular ion peak at $m/e = 148$.

- (a) Calculate the empirical formula of **M** and hence deduce its molecular formula.
You **must** show your working.

(4)

$$C : \frac{72.97}{12} = 6.081 \times \frac{2}{1.351} \approx 9$$

$$H : \frac{5.41}{1} = 5.41 \times \frac{2}{1.351} \approx 8$$

$$O : \frac{21.62}{16} = 1.351 \times \frac{2}{1.351} \approx 2$$

\therefore Empirical: $C_9H_8O_2$

$$\therefore \text{Empirical mass} = (9 \times 12) + (8 \times 1) + (2 \times 16) = 148$$

\therefore Molecular formula is $C_9H_8O_2$

(b) The mass spectrum of **M** had a significant peak at $m/e = 77$.

When **M** was added to a solution of sodium hydrogencarbonate, vigorous effervescence occurred.

M decolourised a cold dilute solution of acidified potassium manganate(VII).

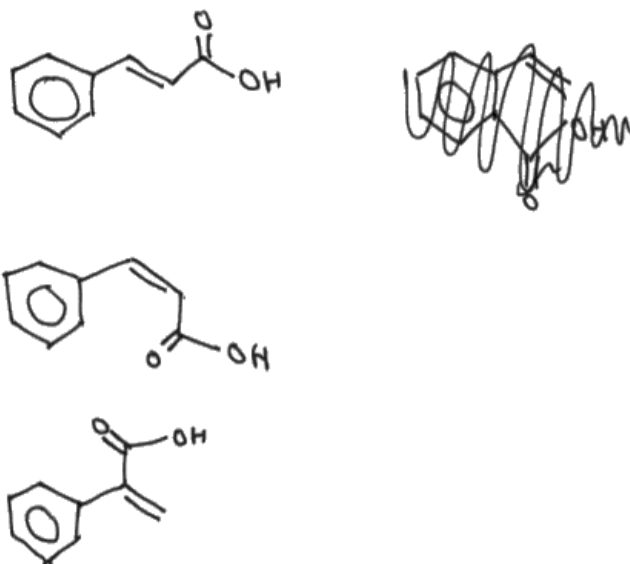
(i) Use this information to identify the three functional groups present in **M**.
Justify your answers.

(3)

A peak at m/e 77 could imply a $C_6H_5^+$ fragment, hence a benzene group. Effervescence with sodium hydrogencarbonate indicates an OH group in a carboxylic acid. Decolourising of acidified potassium manganate(VII) indicates an alkene group.

(ii) Draw **three** possible structures of **M**.

(3)



A crisp but comprehensive response that makes the question seem very straightforward.

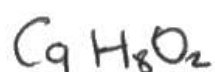
19 A white solid **M** has the following percentage composition by mass: carbon 72.97%; hydrogen 5.41%; oxygen 21.62%.

The mass spectrum of **M** has a molecular ion peak at $m/e = 148$.

- (a) Calculate the empirical formula of **M** and hence deduce its molecular formula. You **must** show your working.

(4)

	Carbon	hydrogen	oxygen
percentage mass	72.97	5.41	21.62
divided by RAM	$\frac{72.97}{12}$	$\frac{5.41}{1}$	$\frac{21.62}{16}$
	6.08	5.41	1.35
	$\frac{6.08}{1.35}$	$\frac{5.41}{1.35}$	$\frac{1.35}{1.35}$
	4.5	4	1
	x2	x2	x2
	9	8	2



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The calculation of the empirical formula is correct but this is not linked to the molecular formula.

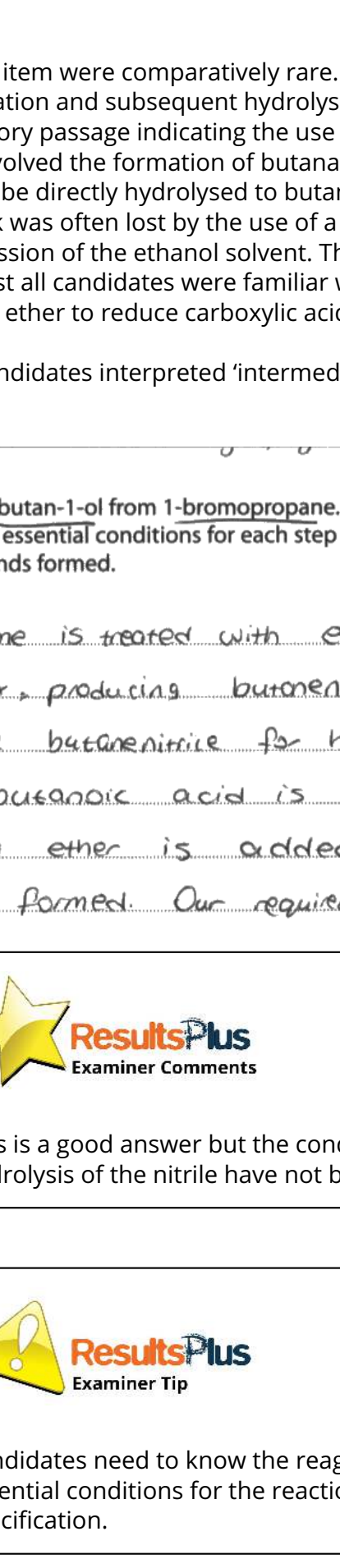
Question 20 (a)

Fully correct answers to this item were comparatively rare. Many candidates appreciated that the synthesis involved the formation and subsequent hydrolysis of a nitrile but failed to utilise the information in the introductory passage indicating the use of a simple nucleophilic substitution. Instead, many responses involved the formation of butanal based on the assumption that the resulting cyanohydrin could be directly hydrolysed to butanoic acid. Even when the correct route was identified, the first mark was often lost by the use of a mixture of potassium cyanide and hydrogen cyanide or by omission of the ethanol solvent. The need to heat the hydrolysis mixture was often omitted but almost all candidates were familiar with the use of lithium tetrahydroaluminate(III) in ether to reduce carboxylic acids.

Here and in Q20(b) some candidates interpreted 'intermediate compounds' as mechanism intermediates.

(a) Outline a synthesis of butan-1-ol from 1-bromopropane. Give the reagents and essential conditions for each step and identify the intermediate compounds formed.

The 1-bromopropane is treated with ethanolic KCN and heated under reflux, producing butanenitrile. Sulfuric acid is added to the butanenitrile for hydrolysis of nitrile group. As a result butanoic acid is formed. Then LiAlH_4 in dry ether is added distilling off the product as it is formed. Our required butan-1-ol form.



This is a good answer but the conditions for the hydrolysis of the nitrile have not been given.



Candidates need to know the reagents and essential conditions for the reactions in the specification.

Question 20 (b)

Most candidates realised that this synthesis involved the conversion of but-1-ene to 2-bromobutane but often did not know the reagent or conditions for the elimination of HBr. The intermediate compound was sometimes given as but-2-ene or even butane.

Question 20 (c) (i)

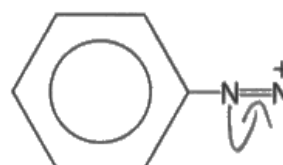
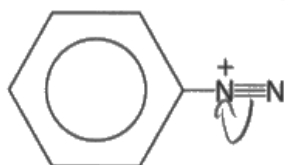
The reagents and conditions for the conversion of phenylamine to the diazonium ion were well known. The most usual error was the use of a nitrate instead of a nitrite. Candidates often gave maximum temperatures (e.g. $<5^{\circ}\text{C}$ or $<10^{\circ}\text{C}$); this was not penalised but a temperature range should be specified.

Question 20 (c) (ii)

Candidates found this application of the use of curly arrows in an unfamiliar context difficult. The arrows were often placed without regard to the fundamental characteristic that an arrow represents the movement of an electron pair either from a covalent bond to an atom or from a lone pair to form a bond.

- (ii) Two possible structures of the benzenediazonium ion are given. Use curly arrows and relevant lone pairs to show how **each** of these structures is converted into the other.

(2)



The mark for the curly arrow on the left-hand structure was the more likely to be awarded. Here the second mark has not been given because of the omission of the lone-pair of electrons.

Question 20 (c) (iii)

The azo dye structure was well known, with the most common error being a triple bond between the nitrogen atoms. Most candidates appreciated that the type and mechanism of the reaction were required but the combinations of electrophilic and nucleophilic with addition and substitution occurred in roughly equal numbers. Some answers just gave 'coupling'.

Question 20 (d) (i)

Some candidates realised that the high electron density of the benzene ring would repel nucleophiles but many gave a prepared response on the effect of a substituent on the rate of electrophilic attack. Few responses scored the second mark.

Question 20 (d) (ii)

There were a number of ways for candidates to access this mark and those who did not score usually made general references to the properties of transition metals or d-block elements, partially filled d orbitals or surface catalysis.

Question 20 (d) (iii)

Candidates were much more likely to give the first equation than the second, where molecular iodine often appeared as a reactant. In both equations, the mark would more likely have been scored if candidates had ensured that the charges balanced.

Paper Summary

Based on their performance on this paper, candidates should:

- be aware that in this examination they will be tested on their ability to apply scientific knowledge and processes to unfamiliar situations;
- remember to read questions carefully - be familiar with the meanings of command words and be alert for information that might be helpful in formulating their responses;
- remember that the appropriate use of diagrams will clarify and simplify their answers;
- always check that ionic equations and half-equations have balanced charges;
- make sure that they understand the exact significance of curly arrows and practise their use with unfamiliar mechanisms;
- practise examples of organic synthesis, including the selection of appropriate reagents and knowledge of the essential conditions.

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