

Examiners' Report
June 2018

IAL Chemistry 5 WCH05 01

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Introduction

The overall quality of candidates' responses on this paper was high: the performance on the three sections was quite uniform and the mean overall score was 60%. The multiple-choice section provided a good range of challenge to the candidates and the mean score was 12.5. Only question 1 was correctly answered by more than 90% of candidates, while the most difficult questions proved to be question 9 (correctly answered by 33.4%) and question 10 (correctly answered by 35.2%).

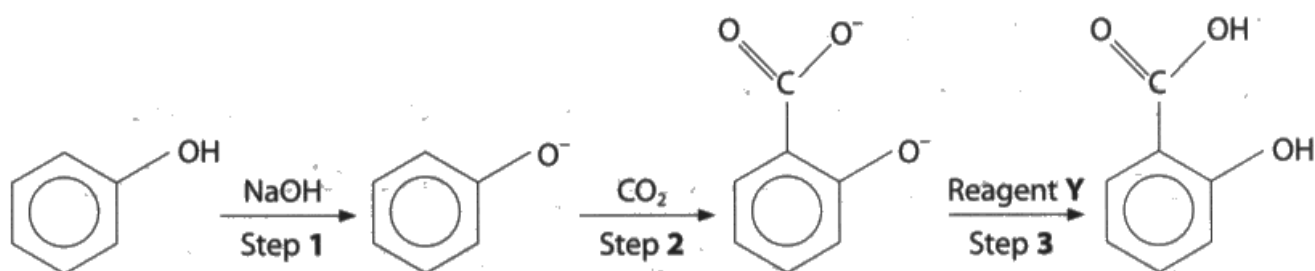
Most candidates proved competent in the numerical calculations and the great majority presented their solutions in a clear and well-structured format. However, unlikely answers did not seem to prompt candidates to review their working. Some candidates continue to round intermediate answers in calculations; best practice is to retain numbers in the calculator and only round the final answer. Areas of the specification that have been tested a number of times in earlier series produced some excellent answers, evidently informed by reports and mark schemes. However, some memorised responses were reproduced without adaptation to the current question or with important details omitted or incorrect.

Marks were frequently lost by candidates seeming to rush to write their answer without ensuring that it matches the question and provides all the necessary detail. The importance of reading each question carefully cannot be overstated.

Question 19 (a) (i)

Most candidates were familiar with the general features of the mechanism of electrophilic substitution to the benzene ring and the requirements of mark schemes from earlier series. Thus the mark awarded depended largely on the precision of the structures shown, the accuracy of the charges on the various ions and on the use of curly arrows. In addition the question required application of their knowledge of electrophiles to a novel example (carbon dioxide) which tested the understanding of curly arrows and the balancing of charge. This fourth mark proved beyond the reach of most candidates.

19 Salicylic acid (2-hydroxybenzoic acid) is a starting material in the manufacture of aspirin; it is synthesised from phenol in the Kolbe-Schmitt process outlined.

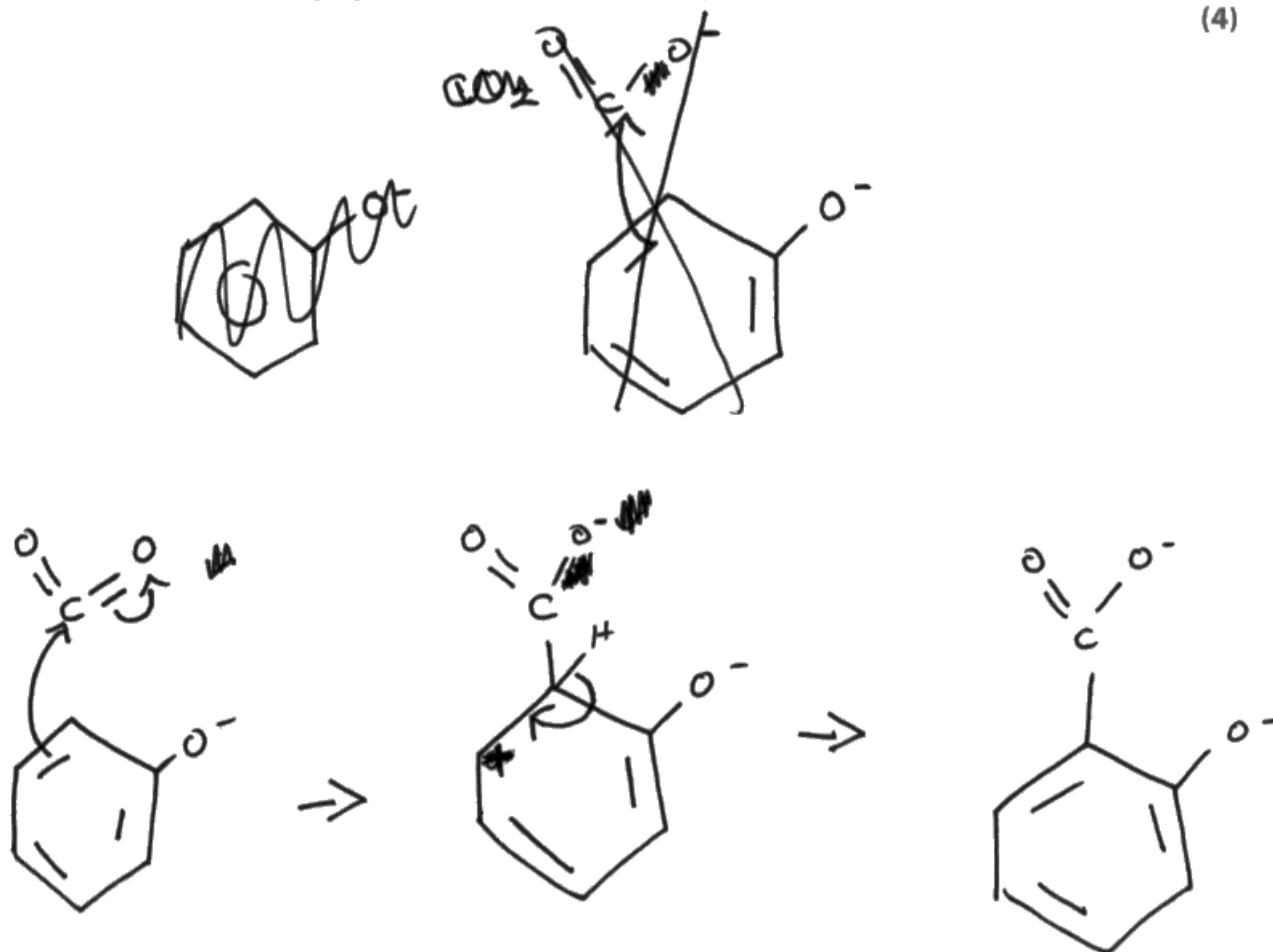


(a) Step 2 of the Kolbe-Schmitt process involves an electrophilic substitution.

(i) Using your knowledge of electrophilic substitutions, draw the mechanism for the reaction in Step 2.

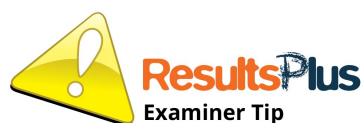
Show the displayed formula of the electrophile CO₂, and all relevant curly arrows.

(4)

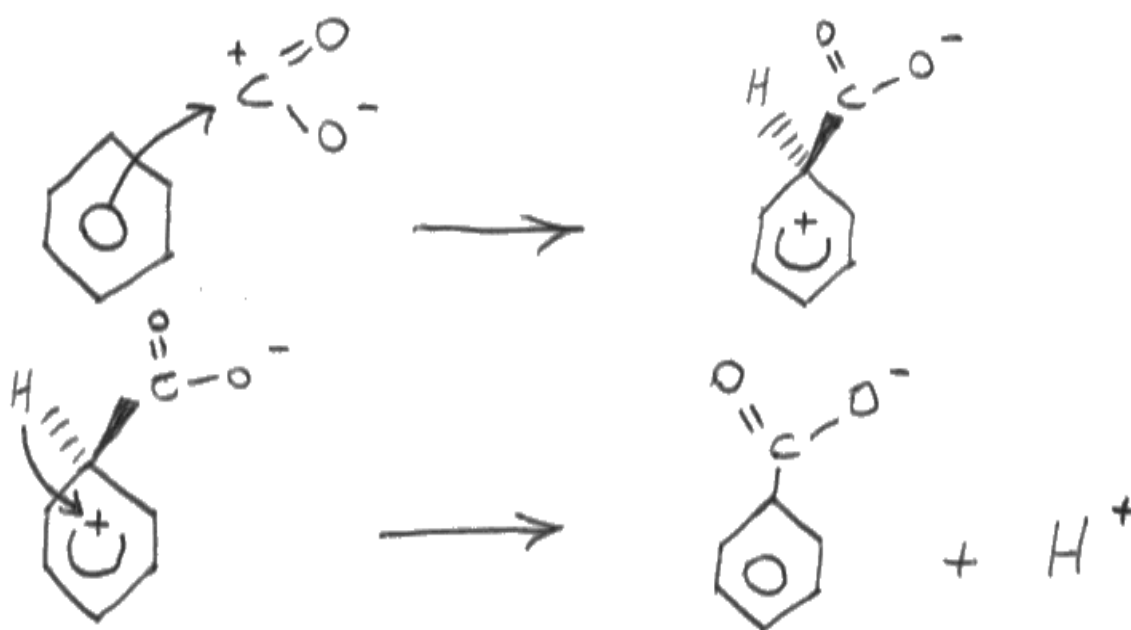




This is a fully correct response. Although the use of Kekulé structures is unusual, it is correct. Note the accurate placement of the curly arrows which should always start from a bond (pair of electrons) or a lone pair.



Curly arrows represent the movement of electrons: a single electron for a 'half-headed' arrow and an electron pair for a full arrow. Try to make sure that your diagrams show this.



This answer has omitted the curly arrow showing the conversion of a carbon dioxide molecule into the electrophile and shows the curly arrow in the intermediate coming from the H atom rather than the C—H bond. Note the use of dashes and a wedge to represent the 3-D structure of the tetrahedral carbon. This is accurate but dotted lines for bonds should be avoided. This response scored 1 mark.

Question 19 (a) (ii)

The need to protonate the anion with a strong acid was widely understood although quite a number of candidates did suggest water or hydrogen gas for this. Otherwise the most frequent error was to give hydrogen ions rather than a specific reagent.

Question 19 (b)

The core of this question has featured in a number of earlier series and there were some well-rehearsed responses explaining the relative reactivity of benzene and phenol. However, a number of good candidates overlooked the first marking point which related to the change in conditions required. Marks were also lost when candidates confused the two reactants and their associated conditions.

- *(b) The Kolbe-Schmitt process is carried out at 125 °C and high pressure. State how, if at all, these conditions for electrophilic substitution would have to change if the Kolbe-Schmitt process was carried out with benzene in place of phenol.

Fully justify your answer in terms of the relative reactivity of benzene and phenol.

(4)

phenol is more reactive than benzene because of the lone pair on one of the oxygens in the OH bond which overlaps with the delocalized ring system. This makes the ring more electron dense hence making it more vulnerable/receptable to electrophilic attack. The structure of benzene is very stable and therefore doesn't react as well as phenol.



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Examiner Comments

This response scores three clear marks but does not quite match the question as there is no mention of the change in conditions needed if benzene is used. The final sentence referring to the stability of benzene hints at a lack of understanding of the reactivity being considered here.



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Examiner Tip

Read the question carefully. Aspects of the specification may well be tested in ways that are slightly different to previous series.

*(b) The Kolbe-Schmitt process is carried out at 125 °C and high pressure. State how, if at all, these conditions for electrophilic substitution would have to change if the Kolbe-Schmitt process was carried out with benzene in place of phenol.

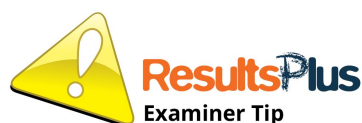
Fully justify your answer in terms of the relative reactivity of benzene and phenol.

(4)

The reaction would not have to be carried out at a high temperature and pressure (if at all), if phenol was used instead of benzene. This is because the oxygen of the OH on phenol has a lone pair of electrons ^{in its p-orbital} that it donates (overlaps with) the pi electron system of benzene ~~again~~ increasing the electron density of the benzene ring, making it much more susceptible to ~~multiple~~ attack by electrophiles so electrophilic substitution would occur very quickly and easily and multiple substitutions would occur with phenol if the temperature and pressure were this high so much milder conditions would be required.



This response involves a reverse argument, considering the conditions needed if phenol were used instead of benzene. This is a perfectly acceptable approach but great care is needed. Here the candidate ends by confusing the two reagents, implying that the conditions given in the question applied to benzene.



Do take care that your answer matches the question.

Question 19 (c) (i)

This mark was scored by 64% of candidates. The majority of these gave 'esterification', which was the preferred answer, with 'acylation' being much the most popular scoring alternative.

Question 19 (c) (ii)

There were many excellent answers to this question although some responses were excessively detailed and repetitive. In general, the relative merits of the two reactants in forming an ester were well understood.

- * (ii) One student suggested that ethanoic acid would be a suitable reagent for this final reaction. A second student suggested using ethanoyl chloride.
Compare the suitability of these two reagents, stating any advantages or disadvantages of each.

(3)

- * Ethanoic acid is a carboxylic acid, therefore it cannot be used as a reagent in the final reaction.
- * The ~~for~~ required functional groups in the products will not be formed. To produce 'aspirin'.
- * Ethanoyl chloride is an acyl chloride, so it can be used as a reagent.
- * The reaction would be faster and would not need extreme conditions for the reaction to start.



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Examiner Comments

The first statement in this response is correct but does not give sufficient explanation to match the first marking point. A mark has been awarded for the comment on the rate of reaction at the end.

Question 20 (a) (i)

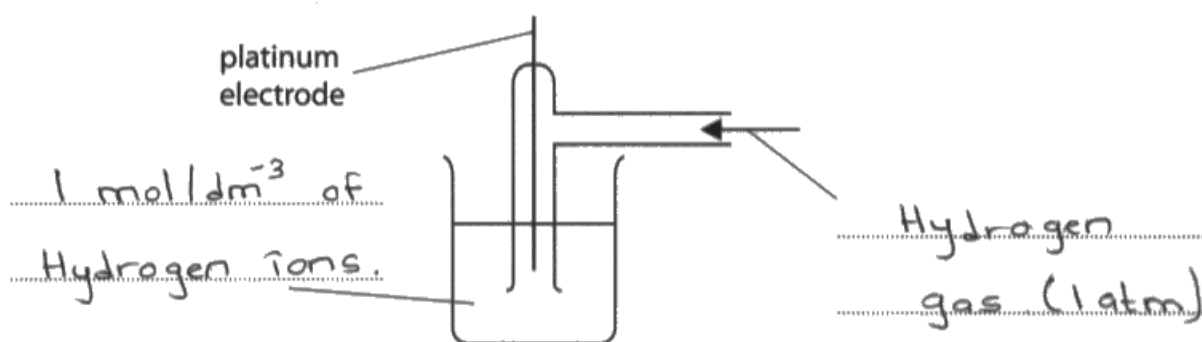
The reactants and conditions for the standard hydrogen electrode were well known although oxygen was suggested a number of times. The most common error was the omission of the standard pressure.

20 Standard electrode potentials are used to predict the thermodynamic feasibility of chemical reactions.

(a) Standard electrode potentials can be determined by using the standard hydrogen electrode as a reference standard.

(i) Label the diagram of the standard hydrogen electrode, indicating the essential conditions associated with each substance used.

(2)



This response scored 1 mark. The concentration units are incorrect: either mol dm⁻³ or mol / dm³. The first is the standard and preferred form.

Question 20 (a) (ii)

The first marking point was most commonly awarded for stating that platinum is inert; some candidates lost this mark by modifying their response with 'fairly inert', or similar. The role of the platinum in catalysing the electrode reaction was not widely known. Whether candidates gained the second mark seemed to depend on whether they picked up the clue in the stem that platinum black is a finely divided form of the metal.

Question 20 (a) (iii)

The value assigned to the electrode potential of the standard hydrogen electrode was known by 89% of candidates.

Question 20 (a) (iv)

This question tested a fundamental aspect of electrode potentials but just 23% of candidates scored the mark. A significant number of candidates ignored the word 'measure' and attempted to answer the question in terms of the application of standard electrode potentials in predicting thermodynamic feasibility. Candidates who did understand what the question required struggled to articulate their ideas. The main expected answer was rare and those working along the lines indicated by the 'allow' points in the mark scheme often confused potential and potential difference, or failed to appreciate the need for a complete circuit to allow current to flow.

(iv) Explain why a reference electrode is needed to measure the electrode potentials of chemical systems.

(1)

A potential difference needs to be set up to measure the electrode potential, so there must be a current flowing.



This was a reasonable response, combining features of the first and second 'allows' in a way that was sufficient to score the mark.

(iv) Explain why a reference electrode is needed to measure the electrode potentials of chemical systems.

(1)

So the electrode potentials of chemical systems are all compared to the same standards, to allow a valid comparison of the strengths of oxidising and reducing agents of different chemicals.



This answer focuses on the application of standard electrode potentials rather than their measurement.

Question 20 (a) (v)

There were many good responses to this question, with the kinetic stability mark being awarded rather more frequently than the standard conditions mark. Some candidates gave two kinetic reasons such as 'high activation energy' and 'slow rate'. Another fairly common error was to refer to the entropy of the reaction, not realising that E_{cell} and ΔS_{total} are related.

Question 20 (b) (i)

The method of combining half-equations was understood by the majority of candidates although marks were lost in the detail, particularly the successful elimination of hydrogen ions and the balancing of water.

Question 20 (b) (ii) - (iii)

The calculation of the two E_{cell} values was very well done with many candidates scoring full marks.

The common error in Q20(b)(iii) was to ignore the requirement to use the answer to (b)(ii). This resulted in very many responses which did not compare the ease of oxidising ethanal and ethanol.

(ii) Calculate E_{cell} for the oxidation by acidified potassium dichromate(VI) of

- ethanol to ethanal
- ethanal to ethanoic acid.

(2)

$$\begin{aligned} E_{\text{cell}} \text{ for ethanol to ethanal} \\ = 0.61 + 1.33 \\ = 1.94 \text{ V } \# \end{aligned}$$

$$\begin{aligned} E_{\text{cell}} \text{ for ethanal to ethanoic acid} \\ = 0.94 + 1.33 \\ = 2.27 \text{ V } \# \end{aligned}$$

(iii) Use your answer to (b)(ii) to suggest why it is necessary to distil ethanal directly out of the reaction mixture in the preparation of ethanal by the oxidation of ethanol.

(1)

The E_{cell} of both reactions is positive, which means the reactions are feasible. Ethanal will further oxidize to ethanoic acid.



This is a nice example of a response which scored full marks, using 'Route 2' in (b)(iii).

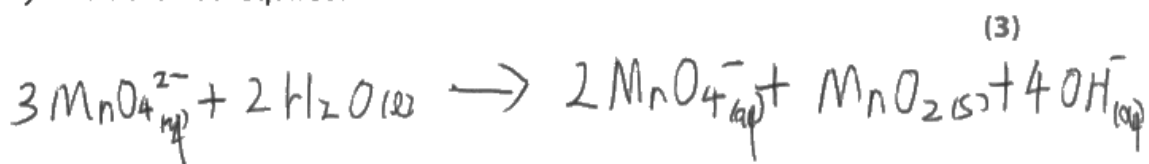


Note that the E_{cell} values have been given without signs. Because both values are positive, the omission has not been penalised but remember that including the sign of thermodynamic quantities is good practice.



Check that equations balance! All equations must balance in mass and ionic equations must balance in charge.

- (ii) Write the equation for the disproportionation of manganate(VI) ions, MnO_4^{2-} , and calculate whether or not the reaction is thermodynamically feasible. State symbols are not required.



$$\begin{aligned} \Delta E_{\text{cell}}^{\circ} &= +0.59 - (+0.56) \\ &= +0.03 \text{ (V)} \end{aligned}$$

As $\Delta E_{\text{cell}}^{\circ} > 0$, the reaction is thermodynamically feasible.



No working but a textbook example for clarity and chemical precision.

Question 21 (a)

There were many excellent responses to this question although, in general, the reagents were better known than the conditions. A variety of temperatures was suggested for the nitration of benzene but only temperatures in the range 50-60°C were accepted. Phrases such as 'below 55°C' should be avoided as they are open to the interpretation that this encompasses any temperature below the stated value. The role of tin in the reduction of nitrobenzene was often given as 'catalyst', an error which was not penalised. However, candidates who added sodium hydroxide to the reaction mixture before reduction was complete did lose the condition mark. The most common error in the final step was to include a halogen carrier, usually aluminium chloride.

Question 21 (b)

Very many candidates omitted the charge from one or more of their ion structures and the use of structural rather molecular formulae was also a common error, particularly in identifying the $m/e = 135$ ion. Candidates should pay particular attention to the parts of a question given in bold type.

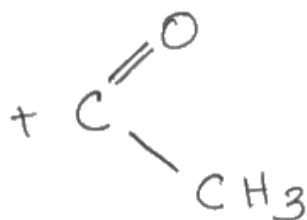
(b) The mass spectrum of acetanilide contains peaks at $m/e = 43$, $m/e = 77$ and $m/e = 135$.

(i) Give the **molecular formulae** of the species that produce the peaks at $m/e = 135$ and $m/e = 77$.

- $C_6H_5^+$ responsible for ($m/e = 77$) (2)
- $C_6H_5NHCOCH_3^+$ responsible for ($m/e = 135$)

(ii) Give the **structure** of the species responsible for the peak at $m/e = 43$.

(1)





A molecular formula only gives the numbers of each atom in a molecular. Here structural features of the $m/e = 135$ ion have been included so this mark was not awarded.

Question 21 (c)

Few candidates scored full marks on this question. A common error was to identify the N—H stretch of amides, overlooking the fact that it overlaps considerably with the N—H stretch of amines. Many candidates identified the wrong C=O stretch, usually opting for the aldehyde or ketone C=O stretch. Choosing the C—H bend, and giving the group rather than the bond, were errors which arose from a failure to read the question with sufficient care.

Question 22

There were many excellent responses to this question. Candidates at all levels calculated the empirical formula correctly with clearly presented solutions. A small number of candidates first calculated the mass of each element in the 0.105 g sample but most of these managed to successfully work their way through the additional complications. The calculation of the molar mass was less familiar and presented more of a challenge to weaker candidates but the most usual reason for withholding a mark on this item was the omission of any sort of working in the deduction of the molecular formula.

Candidates who completed the formula calculations were usually able to suggest two sensible amine structures, often but by no means always choosing primary amines. Responses to 22(c) generally scored two marks or zero, with a small number of candidates losing themselves in descriptions of splitting patterns.

22 A volatile organic compound X has the percentage by mass composition:

$$C = 61.0\%; H = 15.3\%; N = 23.7\%.$$

0.105 g of X was vaporised and the volume of dry air displaced measured. After adjustment to room temperature and pressure, the volume of air displaced was 42.7 cm³.

(a) Calculate the empirical formula of X. You **must** show your working.

(3)

	C	H	N
Mass / g	61.0	15.3	23.7
Moles / mol	$\frac{61.0}{12} = 5.08$	$\frac{15.3}{1} = 15.3$	$\frac{23.7}{14} = 1.69$
Ratio	$\frac{5.08}{1.69} = 3$	$\frac{15.3}{1.69} = 9$	$\frac{1.69}{1.69} = 1$

\therefore Empirical formula of X = C₃H₉N

(b) Calculate the molar mass of X and hence deduce its molecular formula. You **must** show your working.

Molar volume of gas at room temperature and pressure = 24.0 dm³ mol⁻¹

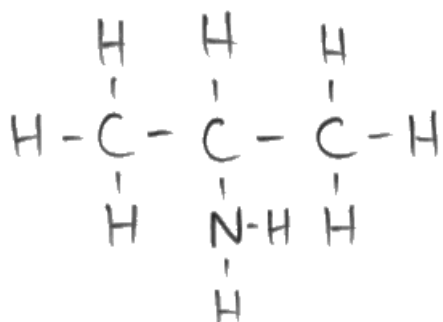
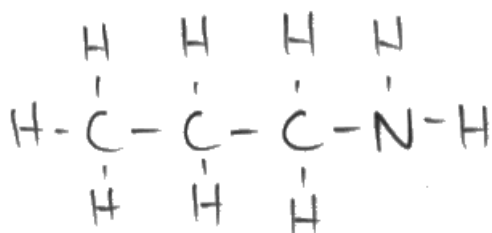
(2)

$$\begin{aligned} \text{Moles of gas} &= 42.7 \div 24000 \\ &= 1.779 \times 10^{-3} \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Mass} \div \text{Molar mass} &= \text{Moles} \\ 0.105 \div \text{Molar mass} &= 1.779 \times 10^{-3} \\ \text{Molar mass} &= 59.0 \text{ g mol}^{-1} \end{aligned}$$

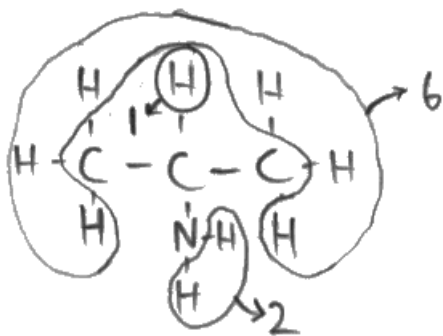
(c) Draw two of the possible structures for X.

(2)



(d) The low resolution proton nmr spectrum of X has three peaks of relative area 6:2:1. Identify the structure of X and explain how your structure is consistent with the nmr spectrum.

(2)



The structure shown has 3 different environments and hence, 3 peaks. ~~There are 2 doublets~~ The area is 6 because the hydrogens ^{circled} are in the same environment, ~~while~~ and they are doublets, while the other two areas are 2 and 1 with them being ~~is~~ doublet and heptet respectively.



This is an example of a very good response, scoring nearly full marks. However, in (b) although the calculation has been completed concisely and correctly the deduction of the molecular formula has not been attempted.



Read each question carefully.

22 A volatile organic compound **X** has the percentage by mass composition:

$$C = 61.0\%; H = 15.3\%; N = 23.7\%.$$

0.105 g of **X** was vaporised and the volume of dry air displaced measured. After adjustment to room temperature and pressure, the volume of air displaced was 42.7 cm³.

(a) Calculate the empirical formula of **X**. You **must** show your working.

(3)

C	H	N
$\frac{61}{12}$	$\frac{15.3}{1}$	$\frac{23.7}{14}$

number of moles = $\frac{5.1}{9.17} : \frac{15.3}{9.17} : \frac{1.7}{9.17}$

ratio = 3 : 9 : 1

no empirical formula of $C_3H_9N_1$

(b) Calculate the molar mass of **X** and hence deduce its molecular formula. You **must** show your working.

Molar volume of gas at room temperature and pressure = 24.0 dm³ mol⁻¹

(2)

$$\frac{1}{x} \sqrt{\frac{24}{42.7}} \times 1000$$

$$x = 1.78 \text{ moles}$$

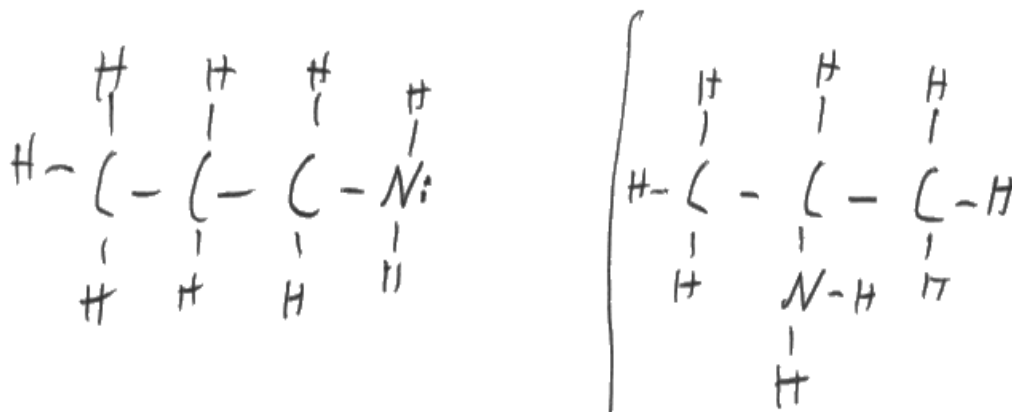
$$M_r = \frac{0.105}{1.78} = 59 \text{ g mol}^{-1}$$

no molecular formula = $59 \div (12 \times 3 + 9 + 14) = 1$

no molecular formula is $C_3H_9N_1$

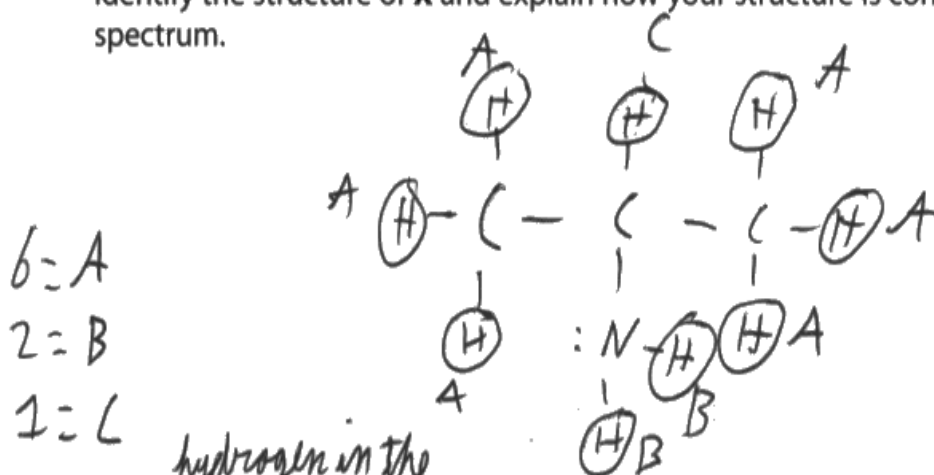
(c) Draw two of the possible structures for X.

(2)



(d) The low resolution proton nmr spectrum of X has three peaks of relative area 6:2:1. Identify the structure of X and explain how your structure is consistent with the nmr spectrum.

(2)



hydrogen in the
 the 2 (H₃ is for the 6 hydrogen atom (ratio 6)
 the NH₂ is for the ratio of 2 and the H on the
 (is for ratio of 1



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 Examiner Comments

This is an excellent response. In (a) and (b) clear working is given. In (c) a displayed formula with each of the proton environments clearly labelled illustrates an effective approach to NMR questions.

Question 23 (a) (i)

Nearly all candidates used the correct notation for the 'electrons-in-boxes' structures with many scoring full marks. The most common error was to give the copper atom with a full 4s orbital, sometimes removing 3d electrons in the formation of the ions but in some cases going on to give the correct configurations for the two ions.

Question 23 (a) (ii)

A good number of candidates were able to quote the mark scheme response from an earlier series, including mentioning the *aufbau* principle. The common non-scoring responses were to refer to the valence or outer electrons being in the d subshell and to give the definition of a transition element.

Question 23 (a) (iii)

Many candidates relied on the generic definition of a transition metal. This was an allowed response, but candidates should realise that the idea of 'Cu²⁺ forming ions' rather misses the point.

Question 23 (b)

23(b)(i) was another familiar question which produced many well-rehearsed and high scoring responses. However, some answers appeared to rely on memory rather than understanding, resulting in some crucial errors in detail, such as references to the splitting of the 'd orbital' and to the 'emission' of the observed radiation. Some candidates could only produce vague attempts at the unusual first marking point.

There were many correct responses to 23(b)(ii) but otherwise candidates relied on stock answers which did not match the chemical situation. Typical of these were the idea that the complementary radiation was outside the visible region, ignoring the fact that there were no ligands and therefore no splitting of the d subshell; and the suggestion that the d subshell was full, contradicting their answer to 23(b)(i).

(b) Anhydrous copper(II) sulfate is a white crystalline solid which dissolves in water to form a solution that has a pale blue colour.

(i) Explain fully why it becomes coloured when it is dissolved in water.

(5)

Water is a ligand, so when copper(II) sulfate reacts with water a hexaqua copper(II) ion is formed. The ligand will split the d-orbitals into two energy states. When light is present the ~~elec~~ electron with in copper (II) in low energy state is excited, as it absorbs the light photon, to a higher energy state. The ~~for~~ wavelength that is not absorbed from the light is the colour of the solution.

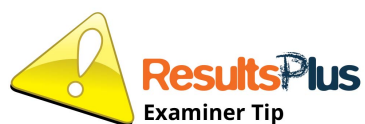
(ii) Explain why anhydrous copper(II) sulfate has no colour.

(1)

Sulfate ion is not a ligand, so no splitting in the d-orbitals energy occurs. Thus no electron transition occurs.



This a nice example of a response to (b)(i) which scores full marks.



The structure and precision of this response are well worth studying.

Question 23 (c) (i)

Most candidates scored this mark although a significant minority suggested the addition of a strong acid.

Question 23 (c) (ii)

For the most part, candidates tackled this calculation confidently giving well-structured, correct answers. Errors were most likely in marking-point 2 with the omission of the factor of ten or the use of 29 (atomic number of copper) or 171.5 (formula mass of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$) instead of 63.5. A result which gave less than 10% copper in copper tubing should really have prompted candidates to check their work.

Question 23 (c) (iii)

The idea that EDTA might also form a complex with nickel ions was generally understood.

Question 23 (d) (iii)

Some candidates appreciated that copper (I) complexes are linear but few made any attempt to analyse the difficulty in wrapping a bidentate ligand around a metal ion with 180-degree bond angles. Many candidates suggested that copper (I) would form octahedral complexes and that this would prevent a bidentate ligand attaching, an idea that clearly contradicts the information given in the stem that they have used in the previous question. A very common misconception was that copper (I) does not have enough space in its 3d orbitals to form more than one dative covalent bond with a ligand although candidates should be familiar with at least one copper (I) complex.

Question 23 (d) (i) - (ii)

Bidentate ligands were rather better understood in the generality than with the detail required by this question. Thus, marks were lost by failing to mention the dative covalent bonds or the central ion in the definition or by drawing covalent rather than dative covalent bonds in the diagram. The role of the lone pairs was not well understood. Some centres continue to use the older 'coordinate covalent' bond'. This is correct but the modern 'dative covalent bond' is preferred.

Paper Summary

On the basis of their performance on this paper, candidates are offered the following advice.

- Read each question carefully and identify what is required. When you have finished your answer re-read the question and check that you have covered all the required points.
- Use specific terminology such as shell, subshell and orbital accurately.
- In calculations use the full intermediate numbers in your calculator at each stage and only round the final number.
- In calculations consider whether your final answer is sensible.
- Make sure that you are fully conversant with the use of curly arrows in organic mechanisms; their accurate placement is essential to score full marks on these questions.
- Remember that all equations (full equations, ionic equations and half equations) must be balanced both in amounts of each element and in charge.

Grade Boundaries

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

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