

Examiners' Report

June 2022

IAL Chemistry WCH15 01

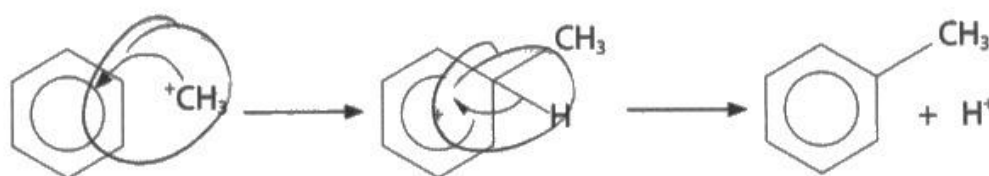
Introduction

It was evident that many candidates were extremely well prepared for this paper, and they showed themselves very adept at coping with questions based on factual recall. On the more extended questions involving explanations applied to unfamiliar phenomena there was perhaps predictably rather less success, and this particularly applied to question 12(e) where even basic terms such as 'nucleophile', 'electrophile' and 'free radical' were so easily confused. Calculations, on the other hand, were usually effectively and efficiently dealt with, and many good candidates scored full marks on most of them. However, examiners noticed a rather poor understanding of electrochemistry with a lack of ability in manipulating half-cell voltages to establish E_{cell} values, let alone applying these to predict the direction of a redox process. The ability to draw tidy, well-labelled diagrams was also found to be lacking in some cases.

Question 12 (a)

Circling the errors in the mechanism proved tricky for some candidates, particularly identifying the half arrow as a mistake in the intermediate. Some appeared to hedge their bets, circling the benzene ring as well as the methyl cation. In part (ii) the justification required was disappointingly answered with many restricting themselves to identifying what was wrong, without giving an explanation.

(a) A student proposed a mechanism for Step 1.



(i) Identify **two** errors in the mechanism by circling them.

The arrow must go from the benzene ring to the CH_3^+ (2)
The arrow from the H should be a full arrow, not curly

(ii) State how the errors identified in (a)(i) should be corrected.
Justify your answer in terms of the structures involved.

(2)

Arrow must go from benzene ring to the $\text{}^+\text{CH}_3$ and the arrow from the H to the horseshoe should be a full arrow

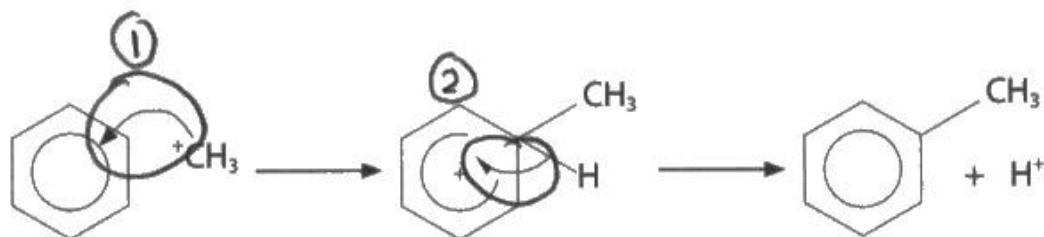


In this answer the candidate has correctly identified the two errors in part (i), but in part (ii) although these errors have been properly identified there is no attempt to explain these in further detail. Part (i) scored 2 marks and part (ii) was allowed a 'rescue mark' of 1.



'Justify' in a question implies more detail than simply stating the facts.

(a) A student proposed a mechanism for Step 1.



(i) Identify **two** errors in the mechanism by circling them.

(2)

(ii) State how the errors identified in (a)(i) should be corrected.
Justify your answer in terms of the structures involved.

(2)

① The arrow should point away from benzene ring towards electrophile as benzene provides the electrons (higher electron density).

② The arrow should be a full curly arrow and not half as 2 electrons donated towards benzene ring $\therefore$ half curly arrow shows 1 electron donated.



This answer gained all 4 marks. The candidate has identified the errors precisely in part (i) and has given excellent written answers with justification in part (ii).

Question 12 (b)

Many realised that the temperature needed to be kept below 30 °C to avoid further nitration/substitution, but a common misconception seen in several answers is that above this temperature the reagents would decompose.

Question 12 (c)

'Oxidation' was correctly given by most candidates. Common mistakes included 'substitution' and 'elimination'.

Question 12 (d)

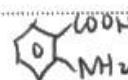
Most candidates knew that a combination of tin and (concentrated) hydrochloric acid are conventionally needed to reduce the nitro group, and several candidates mentioned that the mixture would need to be made alkaline after the process to liberate the free amine.

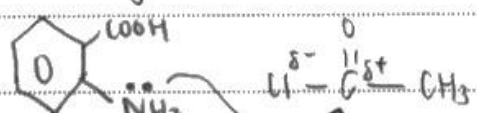
Question 12 (e)

This question was answered rather badly. There are several misconceptions including the one in which nucleophiles always need to attack carbocations, and so many candidates wrote about the lone pair on the nitrogen atom of the amine 'attacking the carbocation', whereas they simply had to recognise that the carbonyl carbon atom – attached to highly electronegative chlorine and oxygen atoms – would be highly electron deficient and serve as an electrophile. The fact that as this nucleophilic attack occurs, the carbon-chlorine bond would break was rarely mentioned. If this question had asked for a diagrammatic representation of the mechanism it might have been answered rather more successfully. Some candidates did helpfully sketch a mechanism below their written answer.

(e) Explain how the structures of ethanoyl chloride, CH_3COCl , and compound A enable them to react forming 2-ethanoylamino benzoic acid in Step 5.

(3)

In compound A, there is a pair of lone pair electrons on the nitrogen atom, making it a nucleophile. There is a slightly positive charge on the carbon atom bonded to Cl in CH_3COCl , making it susceptible to nucleophilic attack. The 2-ethanoylamino benzoic acid and CH_3COCl will undergo nucleophilic substitution reaction. The C atom is slightly positive in CH_3COCl because the Cl atom is ~~also~~ electronegative and will attract electrons and pull electrons away from carbon atom. The lone pair on nitrogen of  will attack the $\text{C}^\delta+$ atom.



This answer is clearly written and scores the first three marks in the mark scheme. A diagram is included to make things clearer. There is a failure to mention the breaking of the carbon-chlorine bond, but full marks were given here since only three marking points were required.



Carbocations are not the only electrophiles found in organic chemistry. In the context of a reaction like this they are of no relevance.

Question 12 (f)

Generally, this calculation was carried out extremely well, with many scoring full marks. Some candidates found it hard to deal with a 'reverse percentage calculation', so multiplied, rather than divided the moles/mass of benzene by 0.282. As in all multi-stage calculations, it is important not to round intermediate values but to use the raw values in the calculator until the end is reached. Some candidates lost marks through expressing a final answer to more significant figures than were justified. Here, with data given to 3 significant figures, a final answer to 2 or 3 would have been appropriate.

- (f) Calculate the volume of benzene required to form 5.92 g of 2-ethanoylamino benzoic acid, assuming the overall yield for the synthesis is 28.2%.

Give your answer to an appropriate number of significant figures.

[Density of benzene = 0.879 g cm^{-3}]

~~$$5.92 \div 0.879 = 6.73 \text{ cm}^3 = 6.73 \times 10^{-3} \text{ dm}^3 \quad (4)$$~~

~~Volume of 2-ethanoylamino benzoic acid~~

mol of 2-ethanoylamino benzoic acid = $5.92 \div (9 \times 12 + 16 \times 3 + 14 + 15)$
 $= 0.032 \text{ mol}$

mol of benzene = $\frac{0.032}{28.2\%} = 0.113 \text{ mol}$

mass: $0.113 \text{ mol} \times (12 \times 6 + 12)$
 $= 9.53 \text{ g}$

Volume = $9.53 \div 0.879$
 $= 10.8 \text{ cm}^3$



In this answer the calculation has been carried out correctly, but here the molar mass of 2-ethanoylaminobenzoic acid works out as 185, whereas it should have been 179. Further down the calculation the molar mass of benzene is also incorrect. It should have been 78, instead of 84. These two errors cost 2 marks, so the total achieved was 2 out of 4.



When you are asked to give your answer to an appropriate number of significant figures look at the question again and see how many significant figures have been given in the data. Do not express your answer to any more than this.

Question 13

There were some excellent answers from those who had thoroughly revised their nickel chemistry. It was easy for some candidates to get full marks in half a page. Most knew that a green precipitate of nickel(II) hydroxide would be formed in both cases and also that these were deprotonation reactions (not ligand exchange). Several knew that excess ammonia would cause the green precipitate to dissolve and turn into a blue solution but failed to mention the comparison with the addition of sodium hydroxide where there is no further reaction. Virtually all candidates knew that the formation of the ammine was an example of ligand exchange. The equations were often fully correct, but a careless placement of brackets lost marks for some, e.g. $[\text{Ni}(\text{H}_2\text{O})_4(\text{OH}_2)]$ instead of $[\text{Ni}(\text{H}_2\text{O})_4(\text{OH})_2]$. In questions like these where the candidate is asked to 'compare and contrast' it is hoped that similarities and differences will be described rather than listing the reactions of one reagent and then, further down the answer, the other.

*13 Compare and contrast the reactions in aqueous solution of nickel(II) sulfate with sodium hydroxide and with ammonia.

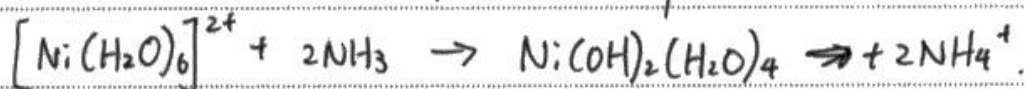
For each reaction include

- what would be seen
- the equation (state symbols are not required)
- the type of reaction.

(6)

Deprotonation will occur when nickel(II) sulfate react with both NaOH and NH_3 is added to nickel(II) sulfate dropwise. When NaOH is added, the equation is $\text{Ni}^{2+} + 2\text{OH}^- \rightarrow \text{Ni}(\text{OH})_2$.

When NH_3 is added, the equation is

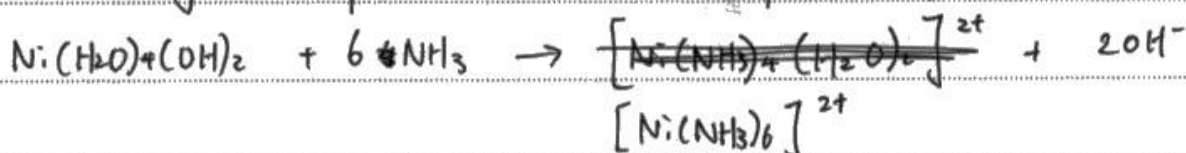


For both reactions, green precipitate will form in the green solution.

When excess NaOH is added, the green precipitate will not dissolve.

However, when excess NH_3 is added, green precipitate dissolves to form a blue solution, because ligand exchange reaction occurs.

The NH_3 ligand displace the H_2O . The equation is





This is an almost perfect answer. Notice that the reactions have been written in pairs, so that the similarities and differences of the reactions with aqueous sodium hydroxide and ammonia are highlighted. In this case the only fault is a missing ' $4\text{H}_2\text{O}$ ' as a product in the final equation.

Thus, the indicative marking points scored were IP1, IP2, IP3, IP4 and IP6. These 5 points gave rise to 3 marks plus 2 for structure and reasoning, so 5 marks overall.



Check that you have placed rounded brackets in the correct place when giving the formulae for complex molecules and ions. For example, $[\text{Ni}(\text{H}_2\text{O})_4(\text{OH})_2]$ is correct, whereas $[\text{Ni}(\text{H}_2\text{O})_4(\text{OH}_2)]$ isn't.

Make sure that you understand the difference between 'ligand exchange' and 'deprotonation'. These terms are often confused.

Question 14 (a)

The commonest mistake here was to work out the number of moles of carbon dioxide and water, and then to assume that the number of moles of water equals the number of moles of hydrogen atoms, so their answer was one half of what it should have been, leading to subsequent difficulties in the calculations. Generally, candidates need to realise that in this type of calculation it is vital to keep several significant figures for the intermediate values, so that an obvious whole number ratio is evident at the end. As it was, however, many candidates were completely successful and deduced the correct empirical formula for Q.

- 14** A compound, **Q**, is a pale yellow liquid that is the main constituent of cinnamon oil. **Q** contains the elements carbon, hydrogen and oxygen only.

- (a) Complete combustion of 6.02 g of **Q** produces 18.07 g of carbon dioxide and 3.30 g of water.

Determine the empirical formula of **Q**.

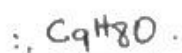
(4)

$$\underline{\text{CO}_2} : \frac{12}{44} \times 18.07 = 4.928$$

$$\underline{\text{H}_2\text{O}} : \frac{2}{18} \times 3.30 = 0.367$$

$$\text{O} : 6.02 - (4.928 + 0.367) = 0.725\text{g}$$

	C	H	O
mass	4.928	0.367	0.725
RAM	12	1	16
moles	$\frac{0.411}{0.0453}$	$\frac{0.367}{0.0453}$	$\frac{0.0453}{0.0453}$
Ratio	9	8	1





This answer uses the traditional approach of calculating directly the mass of carbon and hydrogen in the carbon dioxide formed, and is the most straightforward method of arriving at the mass of oxygen in the original sample of Q. It is very well set out and scored full marks.



In empirical formula calculations like this one it is much better to calculate the mass of carbon and hydrogen directly by realising that $\frac{12}{44}$ of the mass of carbon dioxide is due to carbon and that $\frac{2}{18}$ of the mass of water is due to hydrogen.

Question 14 (b)

Examiners were generally very pleased with the quality of answers to this question. A good number of candidates were aware of the implications of positive results to Brady's reagent, Tollens' reagent and bromine water, and many knew the implications of Q existing as a pair of geometric isomers. Consequently, many were able to deduce its structure, especially if they had been successful in determining its empirical formula in the previous question.

(b) Tests on samples of **Q** show that it

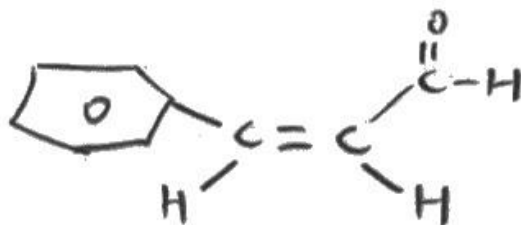
- burns in air with a very sooty flame
- forms an orange precipitate with Brady's reagent (2,4-dinitrophenylhydrazine solution)
- forms a silver precipitate with Tollens' reagent
- decolourises bromine water
- exists as a pair of geometric isomers.



Deduce a structure for **Q**, explaining how each piece of information supports your answer.

(6)

Q:



Q burns in air with a very sooty flame means **Q** should have a benzene ring (have a phenyl group) $\bigcirc$, which means **Q** is aromatic. **Q** form an orange precipitate with Brady's reagent means **Q** ~~has a~~ has a carbonyl group, which means **Q** has either a ketone group or aldehyde group. **Q** forms a silver precipitate with Tollens' reagent means **Q** is an aldehyde, not a ketone. **Q** decolourize bromine water means **Q** have a $\text{C}=\text{C}$ bond ~~and~~ (has an ~~alkene~~ alkene group). **Q** exist as a pair of geometric isomer (confirm **Q** has $\text{C}=\text{C}$ bond, and show that each C in the $\text{C}=\text{C}$ should have 2 different groups of atoms attached to it. The structure **Q** above have molecular formula of $\text{C}_9\text{H}_8\text{O}$, which fits the empirical formula of $\text{C}_9\text{H}_8\text{O}$.

(Total for Question 14 = 10 marks)



This answer contains all the salient points required for full marks. Notice too that this candidate has even mentioned that the displayed formula conforms with the empirical formula already determined in part (a).

Question 15 (a)(i)

A surprising number of candidates did not know the colours of the dichromate(VI) and chromium(III) ions. There were several references to blue or blue green for the colour of Cr^{3+} , but these did not score.

Question 15 (a)(ii)

This question was rather disappointingly answered. So many answers referred to pH change and other irrelevant information without once mentioning 'colour'. Only a minority focused on the need to make the colour change at the end point clear.

(ii) Suggest a reason why an indicator is needed in this titration.

(1)

to ensure it was very clear when the end point was reached



This answer is a little too vague to score the mark. It was decided that a mention of 'colour', or preferably 'colour change' would be needed in any answer.

Question 15 (a)(iii)

This calculation, like many of the other calculations in this paper, was tackled very successfully by many candidates. Surprisingly the commonest error was to use an incorrect value for the molar mass of potassium dichromate(VI) – the molar mass of the dichromate(VI) ion being used instead – but as this was only one error, the overall answer could still score 4 out of the 5 marks available. Examiners still comment that in so many cases the work is set out in a bit of a jumble, with little structure, and it is often these answers which score low marks.

(iii) Calculate the percentage by mass of potassium dichromate(VI) in the cement sample.

(5)

$$n(\text{Fe}^{2+}) = \text{CV} = 3.24 \times 10^{-4} \times \frac{10.90}{1000} = 3.5316 \times 10^{-6} \text{ mol}$$

$$n(\text{Cr}_2\text{O}_7^{2-}) = \frac{3.5316 \times 10^{-6}}{6} = 5.886 \times 10^{-7} \text{ mol}$$

• in 50 cm^3

$$n(\text{Cr}_2\text{O}_7^{2-}) = 5.886 \times 10^{-7} \times 2 = 1.1772 \times 10^{-6} \text{ mol}$$

in 100 cm^3

$$m(\text{K}_2\text{Cr}_2\text{O}_7) = n \times M_r = 1.1772 \times 10^{-6} \times 294.2$$
$$= 3.4633224 \times 10^{-4} \text{ g}$$

$$\% \text{ mass} = \frac{3.4633224 \times 10^{-4}}{50} \times 100 = 6.9266448 \times 10^{-4}$$
$$= 6.93 \times 10^{-4} \%$$



This answer is extremely well set out, and it is evident immediately that this candidate knows what to do. The answer gives the intermediate values to many significant figures, which is the correct thing to do, but at the end the final answer is rounded off appropriately. It scored the full 5 marks.



In a calculation like this, with several stages, make sure that you keep the accurate calculated values in the calculator until the end is reached when the final answer should be expressed to an appropriate number of significant figures.

Question 15 (b)

Examiners were surprised with how badly this question was answered. It would be expected that addition of sodium hydroxide probably has something to do with neutralisation, and that in this case, with a carboxyl group present, candidates should have realised that this type of reaction was taking place. So very few mentioned that a salt was going to be formed, let alone an ionic salt, and that such compounds tend to be much more soluble in water than the parent acid.

Question 15 (c)(i)

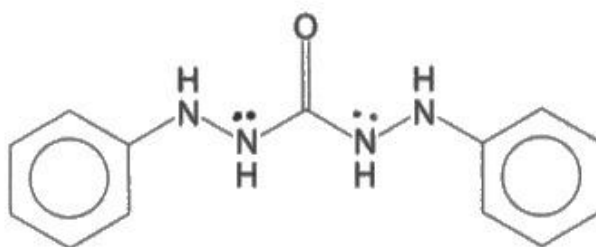
Answers to this question were often spoilt by poor written expression. However, if the candidate helpfully placed two lone pairs on DPC, one on each side of the central carbonyl group, 2 marks were immediately awarded. The further mark was available for those who went on to say that these lone pairs could form two dative covalent (coordinate) bonds with the central chromium(VI) ion.

This answer shows the two relevant lone pairs of electrons. Alternatively, they could have been placed on the nitrogen atoms closest to the two benzene rings. In the explanation below the candidate has referred to the fact that these lone pairs contribute to why DPC can act as a bidentate ligand, but there is no mention of the new type of bond – dative covalent – which will be formed, so there were only 2 marks awarded here.

- (c) The concentration of chromium(VI) in aqueous solution may also be determined using a colorimeter.

On adding 1,5-diphenylcarbazide, DPC, to a solution of chromium(VI) ions, an intensely coloured octahedral complex forms.
The formula of the complex is $\text{Cr}(\text{DPC})_3^{6+}$.

- (i) The structure of DPC is shown.



Describe how DPC is able to act as a bidentate ligand, using your diagram to show the atoms involved.

(3)

the Nitrogen atoms have ^a lone pair of electrons each that
they can donate to ~~form~~ act like a bidentate ligand.



ResultsPlus
Examiner Comments

If you are writing about lone pairs, there is no harm in adding these to any formula given in the question. You are illustrating your description.

Question 15 (c)(ii)

The creation of the chromium(VI) ion must surely involve removing, rather than adding electrons, so examiners were surprised to see answers which described the presence of a full set of d orbitals. This type of question has been asked before, yet candidates still refer to an empty d orbital, rather than empty d orbitals.

- (ii) The intense colour of this complex is due to the transfer of electrons from the ligand to the chromium(VI) ion.

Suggest a possible reason why the colour is **not** due to the transfer of electrons between split d-orbitals in the ion.

Refer to the electronic configuration of the chromium(VI) ion.

(1)

Chromium (VI) = 18 $1s^2 2s^2 2p^6 3s^2 3p^6$

There are no electrons occupying any d orbitals so d-d transitions will not take place.



ResultsPlus
Examiner Comments

It is not clear whether this candidate has written d orbital or d orbitals, but the electronic structure of chromium(VI) has been included in the answer, to make it clear that the d subshell is empty, so this answer was awarded the mark.



ResultsPlus
Examiner Tip

Remember that there are five d orbitals, so when electrons are lost from these, they are all empty. That is why your answer must make it clear that you are writing about all of them and not just one.

Question 15 (d)

Marks were lost in this question through a careless use of the term 'molecule'. In this reaction there are molecules and ions, and in any case the question is best answered by using the term 'particle' or, alternatively, moles of reactants/products. Most knew that the increase in this number was responsible for the reaction being favourable and were able to write about increasing 'disorder' or a positive change in entropy of the system. Many answers went on to explain that ΔS_{total} was likely to be positive as a result.

- (d) The concentration of nickel(II) ions, $\text{Ni}^{2+}(\text{aq})$, can be determined by forming a complex with the ligand dimethylglyoxime, $\text{C}_4\text{H}_8\text{N}_2\text{O}_2$.



Explain why the formation of the dimethylglyoxime complex is favoured, in terms of entropy.

(2)

The reaction causes the ~~for~~ number of product molecules to increase ^{from 5 molecules to 7 molecules}, so the entropy increases.



ResultsPlus
Examiner Comments

This answer did not score the first mark, as the term 'molecule' has been used too loosely, but the second mark was awarded for the prediction that the entropy would increase as a result.



ResultsPlus
Examiner Tip

The words 'atom', 'molecule' and 'ion' are very important terms in chemistry. Make sure that you really understand what they mean and use them properly in your answers.

Question 16

There was a very wide range of marks to the answers in this question. Those who had a good knowledge of their organic chemistry and had practised this type of synthetic exercise before seemed to find it very straightforward, and many candidates scored all six marks.

Candidates faced with this type of question need to think first how such an ester, ethyl 2-methylbenzoate, can be prepared. If they come to the correct conclusion that it's from the acid, 2-methylbenzoic acid, they should then realise that this compound has an extra carbon atom in it compared with the starting material, but-2-ene. Hopefully they will know that the conventional way of increasing the carbon chain is via the 'cyanide' route, or by using a Grignard reaction.

In practice about half the candidates who had some success with this question used the reaction via ethanolic potassium cyanide. Surprisingly, for candidates who knew what to do, the commonest mistake was to omit the acid catalyst in the final esterification stage.

16 The ester ethyl 2-methylbutanoate is found in wild berries such as bilberries.

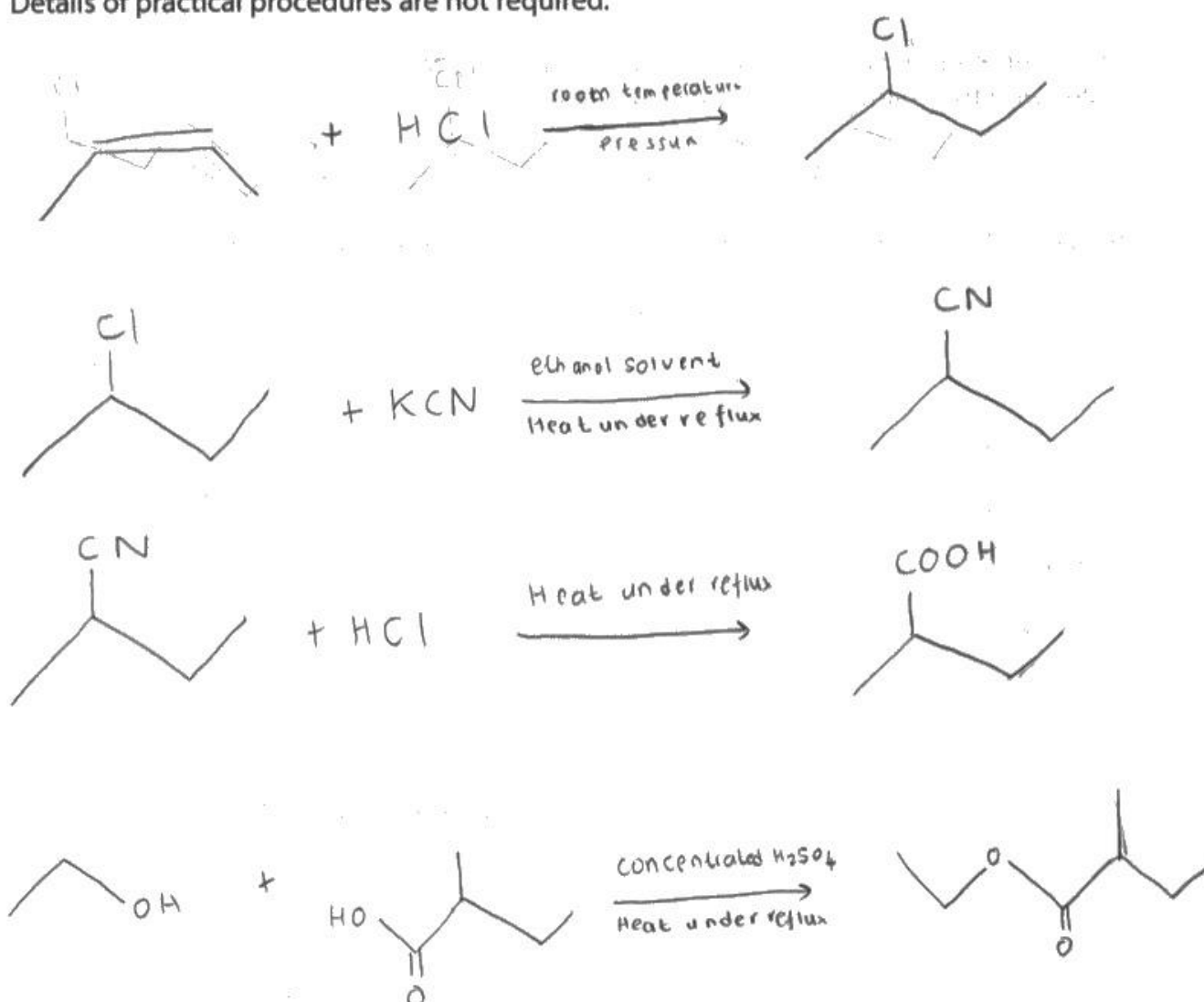
Devise a synthesis to convert but-2-ene into ethyl 2-methylbutanoate in **four** steps.

but-2-ene

ethyl 2-methylbutanoate

Include the reagents and essential conditions for each step and the name or structure of each of the intermediate compounds.

Details of practical procedures are not required.





This answer shows how the synthesis of ethyl 2-methylbutanoate can be carried out via the use of ethanolic potassium cyanide. This answer was adjudged to be worth all 6 marks. The mention of 'reflux' for step 3 implies that the reaction is being carried out in a liquid and so was allowed the M4 mark.



If you are not sure where to start in a question like this, always think about the final step first. In this case, how do we make an ester? The answer is: 'from an acid'. How do we make an acid with more carbon atoms than the original but-2-ene molecule? Answer: 'using a Grignard reagent OR using ethanolic potassium cyanide'. And what do we need to carry out either of these reactions? We need a halogenoalkane, and one way of generating this type of compound is by the addition of a hydrogen halide to an alkene.

In practice, it is understood that it's not as easy to work this out for yourself under exam conditions, so make sure you have a good knowledge of the reactions and, just as important, make sure that you have plenty of practice in this type of exercise.

Question 17 (a)(i)

As with all the other calculations on this paper this calculation was handled well by the majority, once again the commonest mistake being the use of an incorrect molar mass for copper(I) thiocyanate. In the final stage it was sometimes forgotten that the percentage calculated was that of copper in brass, not of zinc, so it was necessary to carry out a subtraction to arrive at 10.0%, the percentage of zinc. Full marks were only given if the answer confirmed that this type of brass was a gilding metal.

Gilding Metal

Gilding metal is a type of brass alloy that consists of copper and a small amount of zinc, ranging from 5 % to 11 % by mass. Copper is very malleable and is hardened by the addition of zinc.

Gilding metal is much less susceptible to cracking due to corrosion than brasses with a higher percentage of zinc.

It has a warm, golden colour and can be used to coat materials using electrolysis. It is also used to make test pieces in jewellery manufacture because it has similar properties to silver but is less expensive.

The proportions of copper and zinc determine the exact properties of the gilding metal and can be determined by chemical analysis.

- (a) 2.72 g of a type of brass is dissolved in excess concentrated nitric acid, forming a solution containing both Cu^{2+} and Zn^{2+} ions.

A solution containing hydrogensulfate(IV) ions, HSO_3^- , is then added.



The addition of ammonium thiocyanate, NH_4SCN , gives a precipitate of copper(I) thiocyanate, CuSCN .



The precipitate of copper(I) thiocyanate is collected, dried and found to have a mass of 4.69 g.

- (i) Determine whether or not this type of brass is a gilding metal, by calculating its percentage by mass of copper.

(4)

$$M_r = 32.1 + 63.5 + 12 + 14 = 121.6$$

$$\therefore \text{mols of CuSCN} = \frac{4.69}{121.6} = 0.0386 \text{ mol}$$

$$\text{mols of Cu}^+ = 0.0386 \text{ mol}$$

$$\text{mols of Cu}^{2+} = 0.0386 \text{ mol}$$

$$\therefore m \text{ of Cu} = 2.45 \text{ g}$$

$$\therefore \frac{2.45}{2.72} \times 100 = 90.1 \% \text{ for copper}$$

$$\therefore \text{zinc percentage} = 9.9 \%$$

$\therefore$ gilding metal



This answer scored full marks and included the statement that this brass was a gilding metal.



Do be careful when calculating molar masses. These are often incorrectly worked out. On the copy of the periodic table supplied on the last page of the exam paper, the atomic masses are at the top of each box above the symbol for the element. Do not use atomic numbers instead – this is a frequent mistake.

Question 17 (a)(ii)

Candidates found this question difficult. They need to ensure that they can work out correctly the E_{cell} for a particular redox process.

Most candidates worked out the relevant E_{cell} values wrongly as being +0.02 V and – 0.35 V which meant that they were unable to predict that the reduction of Cu^{2+} was in fact not possible under standard conditions, whereas that of Cu^+ to Cu would work on a thermodynamic basis. A few did get the signs the correct way round and it was generally these who went on to suggest why in practice the first reaction might work, whereas the second one might not.

This question was an excellent discriminator.

- (ii) Explain, by considering both thermodynamic and kinetic factors, why HSO_3^- reduces Cu^{2+} to Cu^+ but does **not** then reduce Cu^+ to Cu. Use the data in the table.

(3)

	Right-hand electrode system	E°/V
1	$\text{Cu}^{2+} + \text{e}^- \rightleftharpoons \text{Cu}^+$	+0.15
2	$\text{HSO}_4^- + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{HSO}_3^- + \text{H}_2\text{O}$	+0.17
3	$\text{Cu}^+ + \text{e}^- \rightleftharpoons \text{Cu}$	+0.52

Reduction of Cu^{2+} to Cu^+ $E^\circ_{\text{cell}} = 0.15 - 0.17 = -0.02 \text{ V} < 0$
 the reaction still may be thermodynamically feasible
 Even though E°_{cell} is negative, it is only slightly negative, and since the
 conditions are not standard, as an excess of, concentrated HNO_3 is used, so
 position of equilibrium 2
 position $[\text{H}^+]$ increases, so the E°_{cell} shifts to the right and becomes less positive, be positive
 Reduction of Cu^+ to Cu^{2+} : $E^\circ_{\text{cell}} = 0.52 - 0.17 = +0.35 \text{ V} > 0$
 Even though E°_{cell} is positive, the reaction has a high activation
 energy and thus does not occur.



This is an example of an answer that gained full credit. The only error is to predict that as the nitric acid is in excess and therefore probably has a concentration in excess of 1 mol dm^{-3} , then the standard half-cell voltage for the reduction of hydrogen sulfate(IV) ions in acid would become less positive, whereas in fact it would become more positive. However, the point had been made that the discrepancy between theory and practice could be due to the conditions not being standard and that is what the second mark was for. This candidate had simply gone an unnecessary – and wrong – step further.



Make sure that you can calculate E_{cell} values for a redox reaction, so that you can correctly predict whether a reaction should 'work' or not.

Question 17 (b)

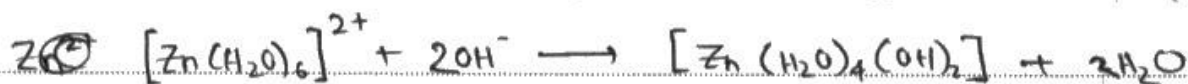
This question was handled successfully by the majority. Almost everybody knew that a white precipitate would be formed initially and that this would dissolve as an excess of hydroxide ions is added, and many gave a correctly balanced equation for the initial formation of zinc hydroxide. However, the formula of the complex ion present in the final solution was less widely known, with $[\text{Zn}(\text{OH})_6]^{4-}$, or even $[\text{Zn}(\text{OH})_6]^{2-}$ being given, instead of $[\text{Zn}(\text{OH})_4]^{2-}$.

(b) After the copper(I) thiocyanate is precipitated, Zn^{2+} ions remain in solution.

A student suggested that these Zn^{2+} ions can be precipitated by adding a large **excess** of aqueous sodium hydroxide.

Comment on this suggestion by describing the reactions that take place as a large **excess** of aqueous sodium hydroxide is **gradually** added.

(4)



this a deprotonation reaction where a white solid precipitate forms when sodium hydroxide is added

But when an excess sodium hydroxide is added



which is ligand exchange reaction. Here the

zinc precipitate turns to a colourless solution

So student is not correct as the precipitate won't be present

when excess sodium hydroxide is added but it can be

achieved if it is gradually added until precipitate forms



ResultsPlus
Examiner Comments

This answer contains information which merits the first three marking points, but has an incorrect formula for the zincate ion, so scored 3 marks overall.

Question 17 (c)

Most candidates were able to gain at least one of the two marks here. The term 'atoms' was allowed, though 'ions' was preferred. An alarming minority referred to 'intermolecular forces being disrupted'.

(c) Suggest why gilding metals are less malleable than pure copper, by considering their structure.

(2)

Gilding metal has zinc ions between the copper ion which holds the structure much more strongy. so the layer of ions doesn't slide as easily. So it is less malleable.



ResultsPlus
Examiner Comments

This answer neither referred to the structure being disrupted by the zinc ions, nor the difference in size between the two types of ions, so the first mark was not awarded. The second mark was given for the explanation that layers do not as easily slide over each other.



ResultsPlus
Examiner Tip

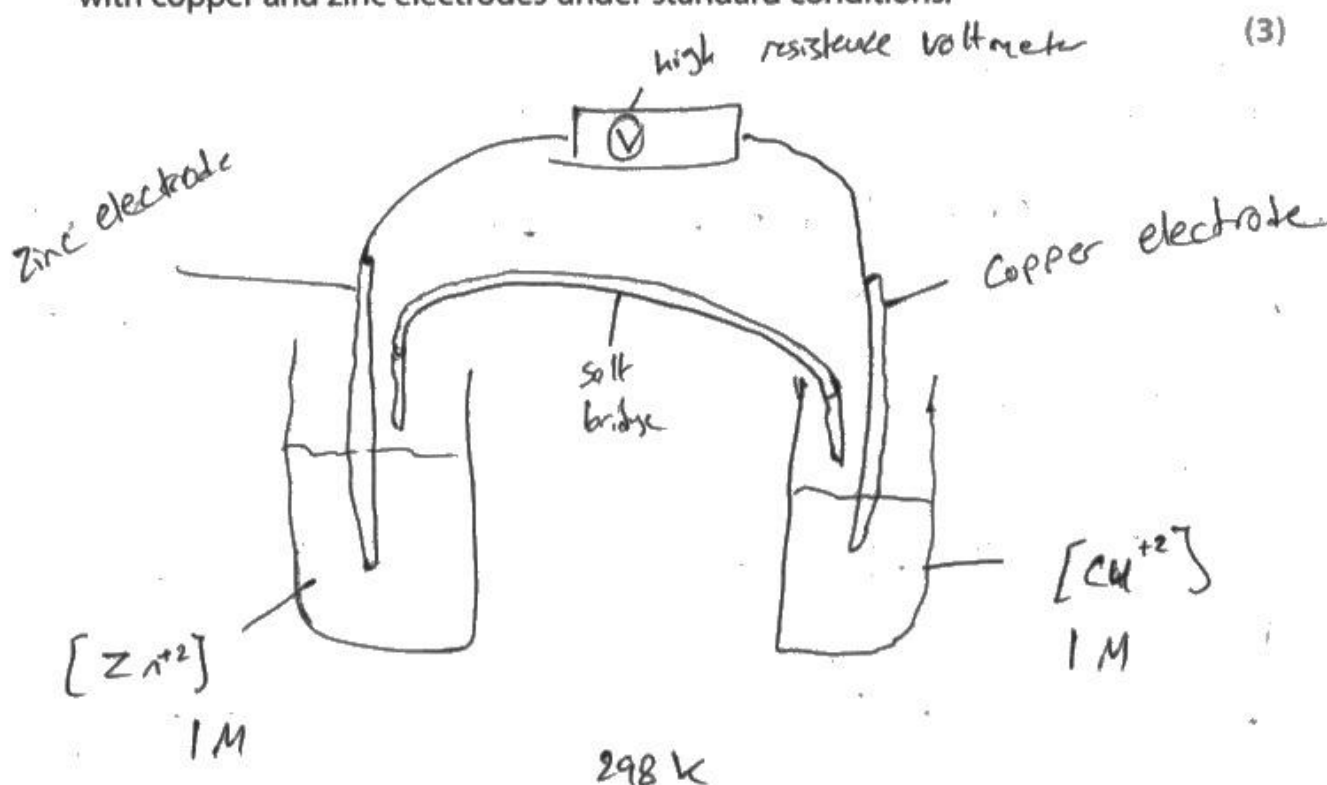
Remember that metallic structures involve positive ions from the metal, so it is much better to refer to 'ions' rather than 'atoms', but certainly NOT 'molecules'.

Question 17 (d)(i)

This question came near the end of the paper, which is possibly why some of the diagrams appeared very rushed. Many were certainly extremely untidy and carelessly drawn. The stem of the question clearly had not been studied carefully enough by some candidates because one of the electrodes often turned out to be of platinum. The solutions often had no information as to their concentrations. As for the (high resistance) voltmeter, this was often placed in position correctly, but the salt bridge was sometimes not dipping into the solutions at all. Consequently, many candidates scored only 1 mark in this question. Perhaps with more time for answering this question it might have performed better.

(d) Zinc and copper are also used in electrochemical cells.

- (i) Draw a labelled diagram of the apparatus used to measure the emf of a cell with copper and zinc electrodes under standard conditions.



ResultsPlus
Examiner Comments

This answer scored 2 marks. The electrodes were labelled correctly, as were the solutions, with their concentrations clearly indicated as being '1M'. However, the salt bridge is not dipping into either solution, so will be totally ineffective and the cell simply won't operate at all.



When drawing diagrams read the question carefully. Here it states clearly that the electrodes are of copper and zinc, so there is no excuse for using copper and platinum electrodes instead.

Question 17 (d)(ii)

Candidates were able to choose to use the Nernst equation on the cell itself or the zinc half-cell. Most chose the former method if they got anywhere with this question, but many gave up, not really knowing what to do. Transferred error marks were freely available for those unable to calculate E for the half cell, so that providing the rearrangement of the Nernst equation was correctly carried out candidates could score 2 marks from any two voltages, and for those who could not do this the third mark was available for candidates who were able to use a calculator to determine $[\text{Zn}^{2+}]$ from $\ln[\text{Zn}^{2+}]$.

- (ii) The Nernst equation describes the relationship between the concentration of metal ions in a half-cell and its electrode potential.

$$E = E^\ominus + \frac{0.0260}{z} \times \ln[\text{ion}]$$

E = electrode potential under non-standard concentrations

z = the number of positive charges on the metal ion

A cell is set up with Cu^{2+} ions of concentration 1.00 mol dm^{-3} and Zn^{2+} ions of unknown concentration. The emf of the cell is $+1.09 \text{ V}$.

Calculate the concentration of the zinc ions.

Use the data on page 10 of the Data Booklet.

(3)

$$E_{\text{cell}} = 0.34 + \frac{0.0260}{2} \times \ln[1] = 0.34$$

$$E_{\text{cell}} = E^\ominus_{\text{cathode}} - E^\ominus_{\text{anode}} \Rightarrow 0.34 - E^\ominus_{\text{Zn}} = -0.75$$

$$-0.75 = -0.76 + \left(\frac{0.0260}{2} \times \ln[x] \right)$$

$$\frac{10}{13} = \ln[x]$$

$$e^{\frac{10}{13}} = [x]$$

$$[x] = 2.16 \text{ mol dm}^{-3}$$



This answer scored all three marks. E for the zinc half-cell has been worked out and the relevant values have been substituted into the Nernst equation to arrive at the correct value for $[\text{Zn}^{2+}]$.



Nernst equation calculations can be a bit tricky. Try to get plenty of practice at them.

Paper Summary

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

- read the question fully and carefully and make sure you follow the instructions carefully (eg on this paper Q17di).
- practise doing 4-step organic syntheses; first make sure you have a good knowledge of the organic reactions in your specification; second, ask your teacher to give you simple examples, starting with a two-step synthesis, then a three-step one and finally a four-step process, such as the one here in question 16.
- show all your working in calculations and try to explain with a symbol or word what you are trying to do at each stage so that you can be credited for intermediate stages in your work if your final answer is wrong.
- when giving your final answer in a calculation, remember to give this answer to an appropriate number of significant figures even if you have not been asked to do so. Remember also to give the units and any relevant plus or minus sign in front of the value.
- practise E_{cell} calculations, learning how these enable you predict the direction of a redox process.
- practise calculations involving the Nernst equation.