

Examiners' Report June 2017

IAL Chemistry WCH05 01



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Introduction

This paper proved accessible to most candidates and provided them with the opportunity to demonstrate their knowledge and understanding of the key concepts in this A level course as a whole and attracted a wide range of marks. There was little evidence of candidates having insufficient time to complete the paper.

The majority of candidates attempted the calculations with confidence and many showed clear working which allowed them to be awarded marks for this. Many candidates were able to deduce the steps for the synthetic route by giving correct reagents and intermediates, though the need for heat in the final step was sometimes lacking. The electrophilic substitution mechanism scored well, with only a few marks being lost due to misunderstandings about the meaning of a curly arrow.

Candidates would have benefited from reading the question more thoroughly, ensuring their answers are complete, answering the question that has been asked. The use of correct terminology is important in the answers as there was evidence of marks lost due to the use of imprecise language, particularly centred around the questions on electronic structure of copper and its atomic radius. Candidates should make sure that they know how to write balanced equations, particularly those involving transition metals.

Question 20 (a)

Whilst the tetrahedral shape of this complex ion was familiar to the majority of the candidates relatively few could explain in sufficient detail the reasons for it adopting this configuration. A number of suggestions were offered including repulsion between the chlorine ions.

(a) State and explain the shape of the [CrCl₄]⁻ complex ion.

shape Tetrahedral

Explanation

There is equal repulsion between the electrons in the dative covalent bonds.

(2)



Whilst this candidate has the right idea, they have not explained the result of these repulsions, which is that the ions move to minimise the repulsion or maximise the separation.



Remember that much of this paper is building on earlier work and you will need to answer these questions in at least as much depth as you did before.

Question 20 (b)

There was a number of ways in which this question could be successfully answered, with several different ways to express the formula of the intermediate precipitate, and a few variations on the formula of the final product. Many candidates found this question challenging, with some not knowing how to approach the writing of these equations, while some who had the right idea lost marks through small mistakes, for example forgetting to use state symbols.

(b) When a small amount of aqueous sodium hydroxide is added to a solution of chromium(III) ions, [Cr(H₂O)₆]³⁺(aq), a green precipitate forms.

This precipitate dissolves in excess aqueous sodium hydroxide.

Write the ionic equations for these two reactions. Include state symbols.



This example is a correct response for both equations.



Practice these equations as they require careful thought and precision, particularly when state symbols are required.

(2)

(b) When a small amount of aqueous sodium hydroxide is added to a solution of chromium(III) ions, $[Cr(H_2O)_6]^{3+}(aq)$, a green precipitate forms.

This precipitate dissolves in excess aqueous sodium hydroxide.

Write the ionic equations for these two reactions. Include state symbols.

(2)



This gives one of the alternatives for the second equation involving redissolving of the precipitate. Again this answer scored both marks.

Question 20 (c)

This question was answered well with almost all candidates achieving at least one of the two marks. Many scored two marks with fully correct answers while some only scored one mark as they gave two isomers which were the same. The responses required were one trans- isomer with the two chlorines at 180° and one cis- isomer with them at 90° to each other. Some candidates were perhaps confused by the need for two diagrams which were isomers, and thought a mirror image was what was required.

This excellent answer scored both marks, with the trans- isomer on the left and the cisisomer on the right.

(c) The complex ion [Cr(NH₃)₄Cl₂]⁺ is octahedral and exists as two isomers.

Complete the diagrams to show these two isomers.

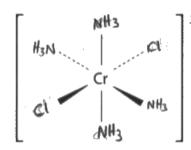
(2)

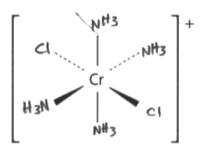


Notice that all the ammonia ligands are connected to the chromium by the nitrogen, which is the atom in ammonia capable of forming a dative covalent bond and thus making ammonia a good ligand. (c) The complex ion [Cr(NH₃)₄Cl₂]⁺ is octahedral and exists as two isomers.

Complete the diagrams to show these two isomers.

(2)





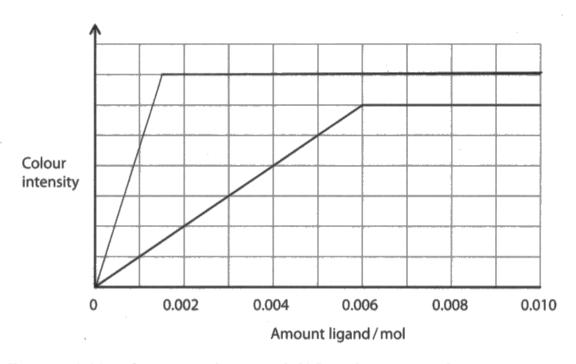


This diagram of two mirror images only scored one mark as both the complexes have the chlorines at 180° to each other in the trans- arrangement.

Question 20 (d)

This was also a question where although few candidates came away with no marks, two marks being scored was quite rare. Here candidates had to apply their knowledge of the reactivity of hexadentate ligands in what for many would be an unfamiliar context. Most were able to recognise that the line required would be a similar shape to the one given, but that it would go higher, and many realised it would peak sooner, though very few had the peak at the required value of 0.001 mol of ligand.

(d) The diagram shows how the colour intensity of an aqueous solution containing 0.001 mol of chromium(III) ions varies with increasing amounts of cyanide ions, CN⁻.



Chromium(III) ions form a complex ion with EDTA with a greater colour intensity than the complex ion formed with cyanide ions.

Sketch on the above axes the result you would expect to obtain if increasing amounts of EDTA were used instead of CN⁻.

(2)



This candidate scored 1 mark as the line is horizontal above the one which had been given showing a greater colour intensity, but the peak is just a little late, at around 0.0015 mol of ligand.

Question 20 (e)

This was again a slightly unusual style of question and context. Many candidates were able to draw the structure of the ligand, but relatively few were able to recognise it had a negative charge on the single bonded oxygen atom.

(e) Chromium(III) ions form a **neutral** complex with the bidentate ligand commonly known as 'acac'.

The structure of the chromium(III) complex Cr(acac)₃ is

Draw the structure of the bidentate ligand 'acac'.

(1)



This candidate gave two of the most typical incorrect answers, where both the oxygens are carrying a negative charge whereas only the single bonded one should be. The top one of these two diagrams was much more common.



Candidates would benefit from reading the question more thoroughly. If you give more answers than the number required they must all be correct.

(e) Chromium(III) ions form a **neutral** complex with the bidentate ligand commonly known as 'acac'.

The structure of the chromium(III) complex Cr(acac)₃ is

Draw the structure of the bidentate ligand 'acac'.

(1)





This very neat response was the expected answer, and scored the mark.

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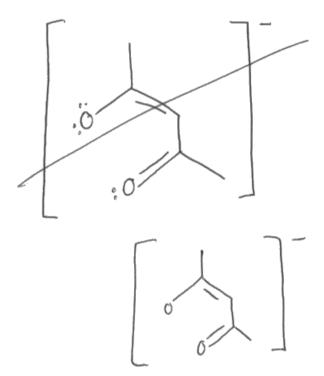
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(e) Chromium(III) ions form a **neutral** complex with the bidentate ligand commonly known as 'acac'.

The structure of the chromium(III) complex Cr(acac)₃ is

Draw the structure of the bidentate ligand 'acac'.

(1)





This example gives the charge outside a bracket which was a perfectly acceptable approach and scored the mark.



In organic structures, count the number of bonds. Carbon usually has four, nitrogen three and oxygen two. If they do not then something needs to be thought about! In this case a negative charge on the O.

Question 21 (a) (i)

Answers in this question usually fell into one of three groups. The first group described the formation of the white precipitate which was the answer which was being sought. The second group discussed the decolourisation of bromine water. While the addition of a few drops of bromine water might demonstrate decolourisation, the addition of an excess, as in the question, would result in a brown solution containing the bromine which had not reacted. The third group described both.

(i) State what is **seen** when phenol reacts with excess bromine water.

(1)

A white precipitate forms. Red brown woor of bromine water

disappears



This scores the mark for describing the formation of a white precipitate. The decolourising of the bromine water is ignored here.



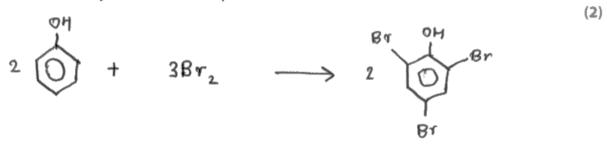
Carefully revise observations for practical activities. You need to be precise with these.

Question 21 (a) (ii)

This question has appeared many times before in past papers. The candidates are expected to know the structure of the product and the equation for its formation. Many candidates were able to write either a displayed or structural formula of the product, but fewer could write a fully correct equation, with the formation of HBr as a second product often missed or changed for H₂.

Here is a very common mistake which was to try to balance the equations using only the tribromophenol as the product of the reaction.

(ii) Write the equation for the reaction between phenol and excess bromine water. State symbols are not required.





This answer was quite a common one which scored 1 mark for the structure of the organic product.



For benzene reactions, don't forget there is a hydrogen on each carbon.

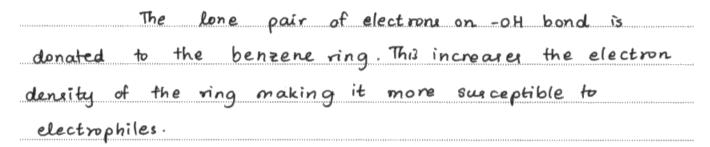
Question 21 (a) (iii)

This is also a question which has appeared many times in recent examination papers. Many candidates had clearly worked through this type of question before with answers closely matching the mark scheme. The most common mistakes here were to forget to explain exactly where the lone pair of electrons which is incorporated into the benzene ring in phenol originates, and to describe phenol as susceptible to attack by nucleophiles instead of electrophiles.

This example describes the origin of the lone pair as on the OH bond. To score this mark the answer needed to refer to the lone pair of electrons on oxygen.

*(iii) Benzene only reacts with bromine in the presence of a Friedel-Crafts catalyst. Explain why bromine reacts much more readily with phenol than with benzene.

(2)





This scores the second point for the increase in susceptibility to electrophiles.



Common questions which come up often, like this one, can be practised. Remember you may have to apply it to an unfamiliar situation.

Question 21 (a) (iv)

Misunderstandings around the numbering system of benzene rings were common on this question. Where the numbering system was understood it was quite common for candidates to miss out the 'di' from the dimethyl part of the name.

(iv) Compound P is a powerful antiseptic.

Give the systematic name of compound P.

(1)

4-chioro, 3,5-methyl phenol



One of the typical incorrect responses, this candidate has just missed the 'di' from the dimethyl in the name of the compound.

Question 21 (b)

Many candidates did well with this calculation, though some did not seem to know what the final aim was. An answer in grams was quite often given for a question asking for a percentage.

*(b) Phenol is more acidic than aliphatic alcohols, such as ethanol, but less acidic than carboxylic acids. It reacts with sodium hydroxide but not with sodium carbonate.

2.5 g of a mixture of phenol and benzoic acid, C_6H_5COOH , was added to excess sodium carbonate solution, Na_2CO_3 . 185 cm³ of carbon dioxide was produced.

$$2C_6H_5COOH + Na_2CO_3 \rightarrow 2C_6H_5COONa + H_2O + CO_2$$

Calculate the percentage by mass of phenol in the mixture.

(The volume of 1 mol of gas under the conditions of the experiment is 24000 cm³)

(4)



This candidate has done everything right, except for the calculation in line 3 where they have made a mistake. The numbers in the expression are correct so this was probably a 'button pressing error' in the use of the calculator. It scored 3 marks.



Check your calculations more than once. It is easy to make the same mistake twice!

Question 21 (c) (i)

This synthetic route question, with only two steps, was relatively straightforward for candidates to score some marks on. There were difficulties, however, with the reagents and conditions in step 1, with candidates mixing up the different options available to them for the nucleophilic addition of HCN. In step 2 the reagent, usually aqueous acid rather than alkali followed by acid, was commonly known but unfortunately many did not heat the mixture. Common mistaken options were to start by oxidizing or reducing the ethanal.

(i) Devise a two-step synthesis to produce lactic acid from ethanal. Include the reagents and conditions for each step, and the structure of the intermediate compound.

Step 1: production of @ 2-hydroxy propare nitroile from ethanal

Reagent: HCN

Condition: in the presence of KCN

Intermediate

Step 2 Hydriolysis of 2-hydroxy preopane notrcile to 2-hydroxy - proponoie 4

Reagent: Hel Condition: Head under reflux



This is an example of the expected response giving all the necessary detail for the two steps and gained full marks.



While it is good to be aware of the different options for step 1, learn and use one of them when you have a step in a synthesis to describe.

Question 21 (c) (ii)

The correct answer for the number of peaks in the nmr spectrum of lactic acid was 4. Many candidates found this a relatively easy question and scored well.

Question 21 (c) (iii)

Some candidates confused the alcohol group with the hydroxyl group in the carboxylic acid and gave the range for that of hydrogen instead. Of the correct answers, many were the expected range from the data booklet, though some candidates gave a single value within that range and scored the mark. 3.5 ppm was a commonly seen value.

(iii) The hydrogen of the alcohol group in <u>lactic acid</u> produces a single peak in the proton nmr spectrum.

Give the chemical shift you would expect for this peak.

(1)

12.0-10.0 6/ppm



This was the most common incorrect answer. It is the position of the proton for the carboxylic acid group rather than the alcohol on carbon 2.



Practice using the data booklet. There is a lot of information to sort through so make sure you know where the most useful information is.

Question 21 (c) (iv)

This was one of a small number of structures of unusual compounds that needed to be deduced. This one was particularly challenging, with common mistakes including diagrams of polyesters, linear esters with a single ester group or acid anhydrides. The latter perhaps resulted from candidates thinking they needed to link the two ester groupings together rather than to have them in separate parts of the ring system.

(iv) Two molecules of lactic acid react to form one molecule of a cyclic di-ester.

The structure of lactic acid is shown below

Draw the structure of the cyclic di-ester.
$$-\frac{1}{4}$$
 $\frac{1}{4}$ $\frac{1}{4}$



One of the typical errors - an acid anhydride structure rather than a cyclic di-ester.



It is a good idea on a question like this to do rough work to figure out the answer. Remember to cross out the bits you do not want to be marked.

(iv) Two molecules of lactic acid react to form one molecule of a cyclic di-ester.

The structure of lactic acid is shown below

Draw the structure of the cyclic di-ester.

 $H = \frac{1}{C_{1}} \left(\frac{1}{2} \right)^{2} \left(\frac{1}{2} \right$

HC C-H



Another common mistake was to create a ring including all the carbons as well as the ester bonds, as in this example.

(iv) Two molecules of lactic acid react to form one molecule of a cyclic di-ester.

The structure of lactic acid is shown below

Draw the structure of the cyclic di-ester.



One example of a correct answer, this partially displayed formula shows all the atoms including the single Hs, shown here in the middle of the ring. These were sometimes omitted.



Count the bonds to each carbon atom on structures other than skeletal to ensure you have the correct number of carbons.

Question 21 (d) (i)

The mechanism here was quite well understood by some, with marks most commonly being lost for not showing the presence of the chloride ion as one of the products. Other candidates really struggled to know what to do here, though some thought an S_N^2 mechanism was required and so scored a maximum of one mark.

(d) 2-hydroxy-2-phenylethanoic acid is more commonly known as mandelic acid. It has antibacterial properties.

(i) Mandelic acid is made when 2-chloro-2-phenylethanoic acid reacts with hydroxide ions.

Draw the S_{N1} mechanism for this reaction.

(3)

$$\begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \\ \\ \end{array} \end{array} \end{array} \end{array} \begin{array}{c} \begin{array}{c} \\ \\ \end{array} \end{array} \begin{array}{c} \\ \\ \end{array} \end{array} \begin{array}{c} \begin{array}{c} \\ \\ \end{array} \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} \\ \\ \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \\ \\ \end{array} \begin{array}{c} \\ \\ \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \\ \\ \end{array} \begin{array}{c} \\ \\ \\ \end{array} \begin{array}{c} \\ \\ \\ \end{array} \begin{array}{c} \\ \\ \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}$$



This example of a fully correct S_N^2 type mechanism including the transition state scored 1 mark.



Mechanisms are very common examination questions. Learning what the arrows mean will save you from making mistakes.

(d) 2-hydroxy-2-phenylethanoic acid is more commonly known as mandelic acid. It has antibacterial properties.

(i) Mandelic acid is made when 2-chloro-2-phenylethanoic acid reacts with hydroxide ions.

Draw the S_N1 mechanism for this reaction.

$$\frac{cl}{oH} = \frac{cl}{oH} = \frac{cl$$



This example was missing the arrow in the first step of the mechanism, but scores two out of three.

Question 21 (d) (ii)

Candidates understood this item very well, but they rarely included sufficient detail to score all 3 marks. Recognition of the importance of the bonds around the positive carbon of the carbocation intermediate being planar were key, with many candidates simply referring to a planar molecule, confusing this question with the reaction of hydrogen cyanide with an aldehyde or ketone. The idea about the addition of the OH ion from above and below this planar cation and the resulting formation of a racemic mixture were well understood.

*(ii) Explain why the mandelic acid, produced by the S_N1 mechanism from a single optical isomer of 2-chloro-2-phenylethanoic acid, is **not** optically active.

-The bonds around the intermediate carbo cation

is planar:
-So Therefore the neve nucleophile can attack from either side in equal amounts forming racemic mixture.



This is a good example of a response which nearly scores 3 marks. This one is just missing the idea of the bonds around the positive carbon in the carbocation being planar, rather than just the carbocation. As a result this scored two.



Look for opportunities to explain in detail. Particularly on 3 and 4 mark questions some level of detail will be required.

Question 21 (d) (iii)

This question required the candidates to identify five important points associated with recrystallisation. Help was provided by emboldened words in the question which gave hints as to what was required for the five marks. Those that tried to follow this usually scored well. Some even highlighted or underlined the words as well so it was clear they were reading the question with care.

(iii) An impure sample of mandelic acid can be recrystallised using methanol as the solvent.

The steps of the recrystallisation are summarised below. In the spaces provided, explain the purpose of each step, referring particularly to any words in **bold** type.

(5)

Step 1	-	•		ved in the						^	>>>>>dddddddddii
Step 2	The I	not soluti	on was f	iltered. A	de)			nsoluble		mpn.bics	
· (un	d	SO	the	Mix	lwc	duest	v4	crysti	Mize	before	
(h	tille	nution	1 (10	uson	why	Ы	s he	ot).		
•				in an ice ry ({ c		Can		for m	q/	aichly.	
Step 4				ed using:			\ C	an bi	. Sup	unted	
4	and									crystals	4



This candidate has not quite got the right idea about the use of an ice bath, needing to comment about the amount of mandelic acid recovered from the solution when one is used. The other parts of the question have been well answered so this scored four marks.



Very similar questions to this one have been asked before. Practise plenty of past paper questions to familiarise yourself with the requirements of the more common types of question.

(iii) An impure sample of mandelic acid can be recrystallised using methanol as the solvent.

alows discound in the minimum amount of bot mothanol

The steps of the recrystallisation are summarised below. In the spaces provided, explain the purpose of each step, referring particularly to any words in **bold** type.

(5)

step i	the sample was dissolved in the minimum amount of not methanol.
	Least insoluble impurities involved when all mandelic acid is
	dissolved. Methand is sorthated of mandelic acid.
Step 2	The hot solution was filtered .
***************************************	Keep the solution hot so no mandelic acid is wasted.
	Insoluble impurities are removed by filtering.
Step 3	The filtrate was cooled in an ice bath .
	when temperature decrease, the solubility decrease.
	Mandelic acid is czystallized and soluble impuries remain in ethanol.

(iii) An impure sample of mandelic acid can be recrystallised using methanol as the solvent.

The steps of the recrystallisation are summarised below. In the spaces provided, explain the purpose of each step, referring particularly to any words in **bold** type.

(5)

Step 1	The sample was dissolved in the minimum amount of hot methanol.					
	Least insoluble impurities involved when all mandelic acid is					
	dissolved. Meshant is sorthated of mandelic acid.					
Step 2	The hot solution was filtered .					
***************************************	Keep the solution hot so no mandelic acid is wasted.					
444444444444444444444444444444444444444	Insoluble impurities one removed by filtering.					
Step 3	The filtrate was cooled in an ice bath .					
***************************************	when temperature decrease, the solubility decrease.					
	Mandelic acid is czystallized and soluble impurites remain in exhand.					



This candidate had very much the right idea, but the comments lack sufficient depth to get all the marks. This scored 3 out of 5, scoring marks for the removal of both lots of impurities and for the idea of a saturated methanol solution.



Practical processes are another fruitful area for revision for this unit.

Question 22 (a)

These two items proved not as straightforward as was perhaps expected. The first has been asked many times recently. Candidates often commented on the electronic structures of the copper atom, regularly mentioning the similar energies of the 4s and 3d orbitals, but did not say why an electron was found in the 3d-subshell when it would be expected to be in the 4s. A comment as simple as 'a full 3d-subshell is more stable' was enough here. In part (ii), some candidates seemed to be writing about the strength of metallic bonding rather than the atomic radius, perhaps confused by the introductory comment concerning the number of electrons in the atom.

- 22 This question is about some metals and their compounds.
 - (a) Potassium and copper form ions with a single positive charge. Some information about these metals is given in the table.

18 H.	Potassium	Copper
Electronic configuration	[Ar]4s ¹	[Ar]3d ¹⁰ 4s ¹
Metallic radius / nm	0.235	0.128

(i) Most transition metals in Period 4 have two electrons in the 4s orbital of their atoms. State why copper atoms have one electron in their 4s orbitals.

Because it creates a half-filled attached that subshell which is more stable than having a partially filled 3d subshell with 3d6 45° (4s1 3d5)

(ii) Copper atoms have more electrons than potassium atoms. Explain why the metallic radius of copper is smaller than that of potassium.

Because the new mucleus of Because Copper hows a operater charge density than potassium and copper is to the left of the periodic debte compared to potassium



For (i) this answer is excellent, except that it refers to a 'half filled 3d-subshell' rather than a full 3d-subshell, presumably confusing copper with chromium, for which this answer would be correct. In (ii) the candidate justifies the size in terms of charge density, which is not enough to gain credit. 0 marks.



Be very careful that you understand and use the terms shell, sub-shell and orbital correctly.

Question 22 (b)

This unusual question was answered very well by most candidates. Whilst it has previously been part of A level specifications, remembering the Nernst equation, which links the standard electrode potential to the observed potential under different conditions, is no longer expected. Presented with the equation to use, however, the candidates mostly were able to produce an appropriate equation, substitute into it and produce the correct answer. Very few attempted to calculate without quoting the equation, so most scored at least 1.

(b) The standard electrode potential of the copper(II) / copper half-cell is $E^{\ominus} = +0.34 \text{ V}$.

$$Cu^{2+}(aq) + 2e^{-} \rightleftharpoons Cu(s)$$

The effect of changing the concentration of the ions is calculated using the equation

$$E = E^{\oplus} + \frac{RT}{96500 \times n} \ln [Cu^{2+}(aq)]$$

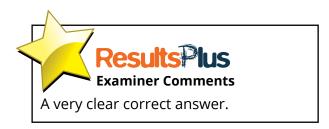
where n is the number of electrons in the half-equation, T is the temperature in kelvin and R is the gas constant.

Calculate the electrode potential of the half-cell at 298 K when the concentration of copper(II) ions is 0.100 mol dm⁻³.

[Gas constant, $R = 8.31 \,\mathrm{J}\,\mathrm{mol}^{-1}\,\mathrm{K}^{-1}$]

$$E = +0.34 + \frac{8.31(298)}{96500 \times 2} \ln(0.100)$$

(2)





On this question with a very unfamiliar equation most candidates wrote it out and substituted numbers in before calculation. This seemed to help as most got the answer correct.

Question 22 (c) (i)

The equation quoted in part (b) might have helped some candidates with this part of the question, hinting as it does on changing values of the actual electrode potential depending on conditions. The reaction being discussed goes very well because the electrode potential value under these conditions is positive so the reaction is thermodynamically feasible. However the standard electrode potential, measured under standard conditions, is not. Some candidates recognised this and were able to give good suggestions as to why conditions were not standard, though a resort to just 'the conditions are not standard' was insufficient. The expected response was that the copper salt formed is insoluble and so copper(I) is a solid here rather than in solution as given by the standard electrode potential value quoted.

(c) An aqueous solution of copper(II) ions reacts with excess iodide ions to form a white precipitate of copper(I) iodide.

$$2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow 2CuI(s) + I_2(aq)$$

(i) The relevant standard electrode potentials are given.

$$Cu^{2+}(aq) + e^{-} \rightleftharpoons Cu^{+}(aq)$$
 $E^{\ominus} = +0.15V$ $0.15 - 0.54$.
 $I_{2}(aq) + 2e^{-} \rightleftharpoons 2I^{-}(aq)$ $E^{\ominus} = +0.54V$

 $I_2(aq) + 2e^- \Rightarrow 2I^-(aq)$ $E^+ = +0.54V$ Calculate the value for E^+_{cell} for the reaction between copper(II) ions and iodide ions and suggest why the reaction takes place.

the E value of E°cell 13 negative, so the reaction B the not feasible. The reaction still takes place as the it is kinetically unstable



This candidate recognised that under these conditions the reaction is not feasible, as the electrode potential is negative but has not suggested how the value might become positive. This scored two.

(3)



Read carefully in reliable sources, such as approved text books, about the meanings of kinetic and thermodynamic feasibility so that these terms can be used accurately and at appropriate times.

(c) An aqueous solution of copper(II) ions reacts with excess iodide ions to form a white precipitate of copper(I) iodide.

$$2Cu^{2+}(ag) + 4I^{-}(ag) \rightarrow 2CuI(s) + I_{2}(ag)$$

(i) The relevant standard electrode potentials are given.

$$Cu^{2+}(aq) + e^{-} \rightleftharpoons Cu^{+}(aq)$$
 $E^{\ominus} = +0.15V$
 $I_{2}(aq) + 2e^{-} \rightleftharpoons 2I^{-}(aq)$ $E^{\ominus} = +0.54V$

Calculate the value for $E_{\text{cell}}^{\ominus}$ for the reaction between copper(II) ions and iodide ions and suggest why the reaction takes place.

(3)

" EGCEN = +0.15 - 0.54 2-0.39 V

· Although the Ecell value is negative indication that the reaction is not thermodynamically feasible, CuI is precipitated.

This means that the reaction tends togo to the right hand side such that have per Egy - Ered - Eard Egell = TEred - Eaxely, reduction increases and hences Eggell value increases.



Here we see an excellent attempt at the answer; although not entirely complete in so much as it does not say the $\rm E_{cell}$ becomes positive, it is enough for all three marks.

Question 22 (c) (ii)

This question proved a very good one for many candidates. Most approached the calculation logically and laid their work out well, showing their working clearly. This made it easy to award marks, and helped them work their way to the answer. Fully correct responses were common, as were those scoring three marks where just one step was missed out.

(ii) Many coins are made of alloys containing copper and other metals.

A coin was treated with concentrated nitric acid to convert all the copper atoms into copper(II) ions. The solution was neutralised, made up to 1.00 dm³ and mixed thoroughly. Excess potassium iodide was added to 25.0 cm³ portions of this solution and the liberated iodine was titrated with sodium thiosulfate solution of concentration 0.150 mol dm⁻³.

The mean titre was 10.90 cm³.

The equations for the reactions are

$$2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow 2CuI(s) + I_{2}(aq) + 2S_{2}O_{3}^{2-}(aq) + I_{2}(aq) \rightarrow S_{4}O_{6}^{2-}(aq) + 2I^{-}(aq)$$

Calculate the mass of copper in the coin. Give your answer to **three** significant figures.

$$n \cdot of 5_2 0_3^{2-} = 0.0150 \times 0.01090$$

$$= 1.635 \times 10^5 \text{ mol}.$$
(4)



This well set out example scored full marks.



Laying calculations out neatly and including a description of what is being calculated is not particularly time consuming but is very helpful, especially if you are not entirely sure how to approach the calculation. It allows you to review your work accurately when checking your answer.

(ii) Many coins are made of alloys containing copper and other metals.

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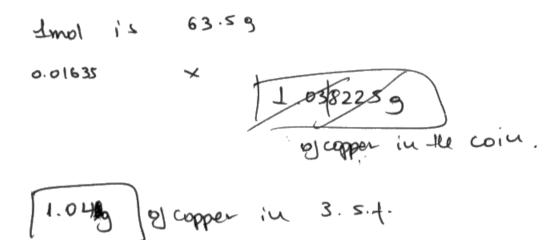
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Calculate the mass of copper in the coin. Give your answer to **three** significant figures.

10.150 in 1000 X 10.9 Molsofthiosulfer = 1.635 X10 -3 Mols of iodine = 8.175 X10 -4 mass of cooper = 4.0875 X10 -4 1000=40 40 X 4.0875 X10 -4 25

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(4)





This candidate has done the first two steps as outlined in the mark scheme, and has then done the third step in both of the methods suggested in the mark scheme, without doing the final step for either. This therefore scored three.



Underlining or putting your answer in a box is helpful as it will help to organise your work.

Question 22 (d) (i)

Some candidates found adding these two half equations surprisingly difficult, usually leaving electrons in the final equation or only having one Ag⁺ ion. Probably more candidates believed the reaction was a disproportionation than did not, confused by the different oxidation states of silver and not being entirely sound in their understanding of its definition.

- (d) Silver and gold are below copper in the Periodic Table.
 - (i) The standard electrode potential values involving silver ions are given.

$$Ag^{+}(aq) + e^{-} \rightleftharpoons Ag(s)$$
 $E^{\ominus} = +0.80V$
 $Ag^{2+}(aq) + e^{-} \rightleftharpoons Ag^{+}(aq)$ $E^{\ominus} = +1.98V$

Write the equation for the reaction involving these species that is thermodynamically feasible under standard conditions. Explain whether or not this reaction is a disproportionation.

2 Agt ->
Ag + + Ag -> 2 Ag + E reation - + 1.18 V

This is disproportionation as the same element (Ag)
is being both accidised and reduced (oxidation
much from +2 to +1 (reduction) and from 0 to +1 (oxidation)



Many candidates believed this reaction was a disproportionation. This is a typical example. One mark was scored for a correct equation.

Question 22 (d) (ii)

This question was well answered by many candidates. Some lost marks through omission of important information, like the oxidation state of Au in elemental Au. In questions of this type the element within the species that were being reduced or oxidised also needs to be identified which was not always the case here, particularly for the nitrogen in HNO₃.

(ii) Chloroauric acid, HAuCl₄, is used in the production of gold nanoparticles. It is formed when gold reacts with aqua regia, a mixture of concentrated nitric and hydrochloric acids.

$$Au + HNO_3 + 4HCl \Rightarrow HAuCl_4 + NO + 2H_2O$$

Explain, in terms of oxidation numbers, why this is a redox reaction.

(2)

N in HNO, her exidetion number +5

N in NO has exidetion number +2

Nitrogen is therefore reduced. Therefore, another element
is exidered and so is Redex



This has half of the information and explanation required so scores 1 mark. The nitrogen in the HNO₃ and NO is clearly identified.



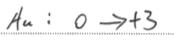
It is only ever one element in a species that is oxidised or reduced and it is important to identify which one. Numbering the oxidation number under the equation can be a great help.

(ii) Chloroauric acid, HAuCl₄, is used in the production of gold nanoparticles. It is formed when gold reacts with aqua regia, a mixture of concentrated nitric and hydrochloric acids.

$$Au + HNO_3 + 4HCl \Rightarrow HAuCl_4 + NO + 2H_2O$$

Explain, in terms of oxidation numbers, why this is a redox reaction.

(2)





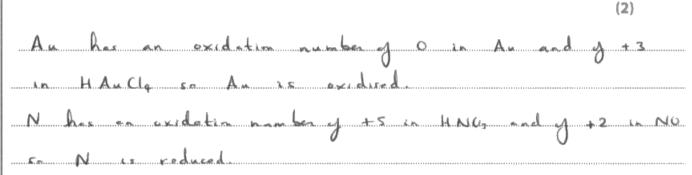
This one correctly identifies the oxidation numbers but makes no attempt to explain why it is a redox reaction so again scores 1.



Sometimes a concise answer is the best answer.

(ii) Chloroauric acid, HAuCl₄, is used in the production of gold nanoparticles. It is formed when gold reacts with aqua regia, a mixture of concentrated nitric and hydrochloric acids.

Explain, in terms of oxidation numbers, why this is a redox reaction.





This time all the necessary information and explanation is given, so this scores both marks.

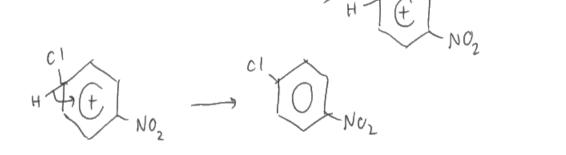
Question 23 (a) (i)

This is a very familiar question to candidates in this paper, being asked often in its various forms. The mechanism looks for some very specific things and is easily learnt and practised. The reasons for dropping marks in the mechanism are the position of the arrows and the structure of the intermediate. The orientation of the delocalised 'horseshoe' and the position of the positive charge are both in the intermediate structure.

(i) Give the mechanism for the formation of 1-chloro-4-nitrobenzene from nitrobenzene. Include an equation to show the formation of the electrophile.

(4)

(4)





This intermediate does not have the gap in the horseshoe pointing towards the tetrahedral carbon, suggesting it is still involved in the delocalised ring so this only scored three out of four.



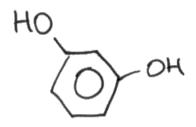
Practicing these mechanisms is the secret to success.

Question 23 (a) (ii)

As well as the identification of the necessary compound, the correct connectivity of the bonds in benzene-1,3-diol was tested. The expected compound was the negative ion formed by the action of the phenol OH group as an acidic group and releasing hydrogen, though this was rarely seen. The next best answer was benzene-1,3-diol.

(ii) Draw the structure of the organic species needed for Step 4.

(1)







Do not be afraid to 'turn around' functional groups like -OH and -NH $_{\! 2}$ so that the correct bonds are formed.

(ii) Draw the structure of the organic species needed for Step 4.



This is incorrect for two reasons, firstly there is an additional OH group present in this triol, and secondly the extreme left hydroxy- group is bonded through the H rather than the O. Either of these on their own would lose the mark.

(1)

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Question 23 (a) (iii)

Counting the hydrogen atoms on a skeletal structure can be quite challenging, and many candidates found they did not have this quite correct. Some also gave structural rather than molecular formulae.

(iii) Give the molecular formula for azo violet.

(1)

C6H502N2C6H5NO2 or G2 H10 O4 N3



The structural formula here is not quite correct, and a structural formula has also been offered as an answer. Again, either one of these would lose the mark.



It is quite dangerous to give more answers than are required because if one is wrong you may lose marks.

Question 23 (b)

This proved challenging with a number of common mistakes resulting in a spread of marks here. Missing or additional oxygen atoms were two possible mistakes, but the most common was to replace the methyl group on the amine with an ethanoyl group.

(b) Draw the structure of the product formed when phenylephrine reacts with **excess** ethanoyl chloride.

-12 - 5 - 7 - 7



This did not score as the methyl group has been substituted rather than the hydrogen on the amine nitrogen. This scored zero.

(b) Draw the structure of the product formed when phenylephrine reacts with **excess** ethanoyl chloride.



Two of the three groups have been ethanoylated here, and as one is the amine and one a phenol group this scores both marks.

Question 23 (c) (i)

A good diagram here with appropriate labels could score all the marks in this item. The idea of hydrogen bonds forming was required for one mark, the position of the hydrogen bonds gained a second and the orientation of the hydrogen bond lead to the third.

(c) (i) Suggest, with the aid of a diagram, why urea, $(H_2N)_2CO$, is soluble in water.

(3) H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H - N H = 0 - H H = 0 - H H = 0 - H H = 0 - H H = 0 - H H = 0 - H H = 0 - H H = 0 - H H = 0 - H H = 0 - H H = 0 - H H = 0 - H H = 0 - H H = 0 - H H = 0 - H H = 0 - H H = 0 - H H = 0 - H H = 0



The diagram on its own here shows all three marks, with hydrogen bonds, traditionally labelled as dashed lines, present between the hydrogen and oxygens in the water. The bond angle of 180° is labelled, and there is additional explanation in the written section. This scored all three marks.



Try to match your diagrams to known bond angles. This has very clear 180° angles both labelled and drawn at about 180°.

Question 23 (c) (ii)

This equation proved to be challenging for some, with unbalanced equations and ones with water being the most likely mistakes.

(ii) Urea is made by reacting ammonia and carbon dioxide at 200 °C and 200 atm pressure.

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

(1)







Your equations should always balance as this one does.

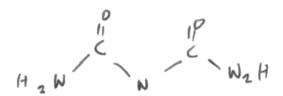
Question 23 (c) (iii)

This was a challenging structure which some candidates did not really know how to approach. Others were very close to the right answer but missed out through small errors, e.g. missing one hydrogen.

(iii) Biuret is formed when urea is heated above its melting temperature. A molecule of biuret is made when two molecules of urea react together with the loss of ammonia.

Suggest the displayed formula of a molecule of biuret.

(1)





This example is missing a hydrogen from the central nitrogen.



Counting bonds again would have been of benefit here. Remember carbon should generally have four bonds, nitrogen, three and oxygen, two.

Question 23 (c) (iv)

This proved the more straightforward of the structures in this question. Candidates needed to read the question to ensure they did the correct type of structure.

(iv) Barbiturate drugs are derivatives of barbituric acid.

Barbituric acid is formed from urea and a dicarboxylic acid in a condensation reaction.

Draw the skeletal formula of the dicarboxylic acid.

(1)



This is an excellent diagram of the correct displayed formula. The candidate would have benefited from reading the question more thoroughly as it asks for the skeletal structure, not displayed formula.



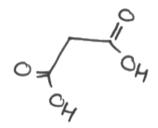
Make sure you know what the different types of formula are and how they represent the molecules.

(iv) Barbiturate drugs are derivatives of barbituric acid.

Barbituric acid is formed from urea and a dicarboxylic acid in a condensation reaction.

Draw the **skeletal** formula of the dicarboxylic acid.

(1)

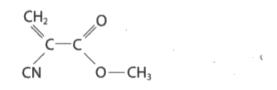




Question 23 (d) (i)

A wide variety of answers were given here. The expected answer was the three functional groups of alkene, nitrile and ester. A number of additional things were ignored including alkane and cyanide, but some others resulted in marks being lost, including carbonyl. The three correct groups scored two marks and any two of the correct ones scored one.

(d) (i) Name the functional groups present in methyl 2-cyanopropenoate.



nitrile, alkene, ester



This was the expected response so scored 2 marks.

(2)

Question 23 (d) (ii)

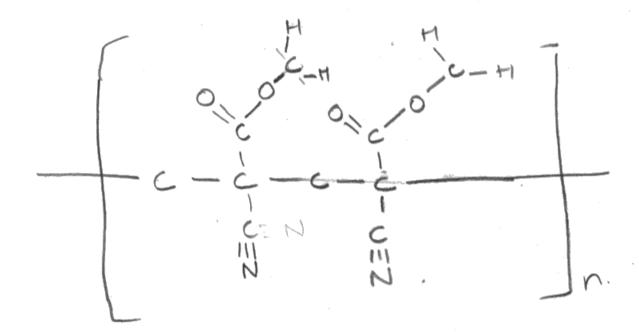
In most cases candidates knew that the type of polymerisation was addition. Where they could not give the full structure for the two repeat units they were still usually able to score 1 mark for having four carbons in a chain and the necessary extension bonds.

(ii) Methyl 2-cyanopropenoate polymerises.

Name the type of polymerisation and draw **two** repeat units of the polymer.

(3)

Type addition soly merisation





This was an extremely good effort, but unfortunately the hydrogens are missing from the -CH₂- parts of the structure. It scored 2 marks.



This was another opportunity to save marks by counting the number of bonds. There should be four around each carbon, three round each nitrogen and two round each oxygen. If there are fewer bonds, there are probably hydrogens missing.

Paper Summary

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

- Remember that AS content will be examined in this paper as you build on your AS foundations.
- Read the question carefully, try to identify what is required, then reread it with your answer to ensure you have covered all the required points.
- Be careful with the use of specific terminology such as shell, subshell and orbital. A glossary of definitions is useful in this regard.
- Using some indication of what is being calculated in the longer calculations will help your organisation of your answer and ensure that you are working towards the right end point.

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