

Example Responses – Paper 4

Cambridge International AS & A Level Chemistry 9701

For examination from 2022



Cambridge
Pathway 

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Introduction

The main aim of this booklet is to exemplify standards for those teaching Cambridge International AS & A Level Chemistry 9701.

This booklet contains responses to all questions from June 2022 Paper 42, which have been written by a Cambridge examiner. Responses are accompanied by a brief commentary highlighting common errors and misconceptions where they are relevant.

The question papers and mark schemes are available to download from the [School Support Hub](#).

9701 June 2022 Question Paper 42

9701 June 2022 Mark Scheme 42

Past exam resources and other teaching and learning resources are available from the [School Support Hub](#).

Question 1

- 1 (a) The solubility of the Group 2 hydroxides increases down the group.

Explain this trend.

- Lattice energy and enthalpy change of hydration both decrease.
 - Lattice energy decreases more than enthalpy change of hydration.
 - Enthalpy change of solution becomes less endothermic.
- [3]

Examiner comment

It is correct to state that ΔH_{att} and ΔH_{hyd} become less exothermic.

Common errors included:

- confusing which quantity decreased more
- using enthalpy of solubility instead of enthalpy change of solution
- stating that the solution becomes more exothermic rather than the enthalpy of solution becomes more exothermic.

- (b) The solubility of $\text{Be}(\text{OH})_2$ in water is $2.40 \times 10^{-6} \text{ g dm}^{-3}$ at 298 K.

- (i) Write an expression for the solubility product, K_{sp} , of $\text{Be}(\text{OH})_2$ and state its units.

$$K_{\text{sp}} = [\text{Be}^{2+}][\text{OH}^-]^2$$

$$\text{units} = \text{mol}^3 \text{ dm}^{-9}$$

[2]

Examiner comment

- Use of square brackets is essential in the K_{sp} expression. Some candidates used curly brackets.
- A common error was to write $K_{\text{sp}} = [\text{Be}^{2+}][\text{OH}^-]^2$. This was not accepted.
- Each concentration in the solubility product expression has the unit mol dm^{-3} so the units for K_{sp} should be $\text{mol}^3 \text{ dm}^{-9}$.

- (ii) Calculate the numerical value of K_{sp} for $\text{Be}(\text{OH})_2$ at 298 K.

$$\frac{2.4 \times 10^{-6}}{43} = 5.58 \times 10^{-8} \text{ mol dm}^{-3}$$

$$(5.58 \times 10^{-8}) (2 \times 5.58 \times 10^{-8})^2$$

$$= 6.95 \times 10^{-22}$$

$$K_{\text{sp}} = 6.95 \times 10^{-22} \quad [2]$$

Examiner comment

Common errors were:

- not to convert the solubility in g dm^{-3} to mol dm^{-3} .
- not to realise that for every one mole of $\text{Be}(\text{OH})_2$ there are two moles of OH^- ions, so the concentration of OH^- needed to be multiplied by two.

- (c) $\text{Be}(\text{OH})_2$ is soluble in aqueous solutions containing an excess of hydroxide ions and forms the complex ion $[\text{Be}(\text{OH})_4]^{2-}$. This complex ion has a similar shape to that of $[\text{CuCl}_4]^{2-}$.

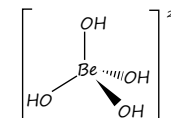
- (i) Define the term complex ion.

An ion formed by a central metal atom or ion surrounded by one or more ligands. [1]

Examiner comment

This definition appears in the syllabus and is one that candidates should learn precisely. Often, answers missed key words such as *metal* and *ligands*.

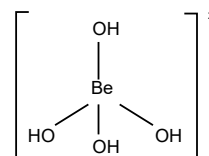
- (ii) Draw a three-dimensional diagram to show the structure of the complex ion $[\text{Be}(\text{OH})_4]^{2-}$. Name the shape of the $[\text{Be}(\text{OH})_4]^{2-}$ complex ion.



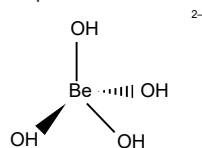
shape *tetrahedral* [1]

Examiner comment

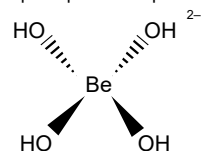
- The question asks for a three-dimensional diagram, which must be correct.
- Common errors in the drawings were:
 - all the bonds in the plane of the paper.



- an in-plane bond between the two out-of-plane bonds.



- a square planar shape.



- Sometimes the correct three-dimensional shape was drawn, but the shape was described as square planar.

- (d) (i) Explain why transition elements can form complex ions.

They have vacant d-orbitals that are energetically accessible.

..... [1]

Examiner comment

- Candidates frequently referred to transition elements as having partially filled, or incomplete, d orbitals. This explanation was not sufficient to explain why transition elements can form complex ions.
- It was also not enough to state that transition metals have empty or vacant d-orbitals, since many elements have empty d orbitals which are not energetically accessible. However, explaining that transition metals have empty or vacant d-orbitals which can form dative bonds with ligands was an acceptable alternative response.

- (ii) Complete Table 1.1 to show the coordination number of each metal ion, and the shapes and overall polarities of the complex ions listed.

Table 1.1

complex ion	shape	coordination number	polar or non-polar
<i>cis</i> -[Pt(H ₂ NCH ₂ CH ₂ NH ₂)Cl ₂]	square planar	4	polar
[Ag(NH ₃) ₂] ⁺	linear	2	non-polar
[Fe(C ₂ O ₄) ₃] ³⁻	octahedral	6	non-polar

[2]

Examiner comment

The most common incorrect answer was to state that [Fe(C₂O₄)₃]³⁻ was polar.

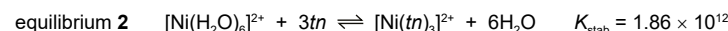
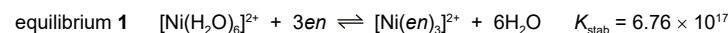
- (e) (i) Define stability constant, K_{stab} .

The equilibrium constant for the formation of the complex ion in a solvent from its constituent ions or molecules...... [1]

Examiner comment

- This definition appears in the syllabus.
- A common response was to state that K_{stab} was the ratio of [products] to [reactants]. This was not sufficient to define the stability constant and was ignored.

- (ii) Nickel can form complexes with the ligands *en*, H₂NCH₂CH₂NH₂, and *tn*, H₂NCH₂CH₂CH₂NH₂, as shown.



Construct an expression for the stability constant, K_{stab} , for equilibrium 1.

State the units for K_{stab} .

$$K_{\text{stab}} = \frac{[\text{Ni}(\text{en})_3]^{2+}}{[\text{Ni}(\text{H}_2\text{O})_6]^{2+} [\text{en}]^3}$$

units = mol⁻³ dm⁹..... [2]

Examiner comment

Common incorrect responses were:

- to use curly brackets instead of square brackets. Candidates must remember that for expressions involving stability constants and equilibrium constants, the use of square brackets is essential because they show that concentrations of the species are required. Here is an example where curly brackets were used:

$$K_{\text{stab}} = \frac{(\text{[Ni(en)}_3\text{]}^{2+})}{(\text{[Ni(H}_2\text{O)}_6\text{]}^{2+})(\text{[en]})^3}$$

- put into the expression [3en] instead of [en]³.
- to include water in the expression:

$$K_{\text{stab}} = \frac{[\text{Ni}(\text{en})_3]^{2+} [\text{H}_2\text{O}]^6}{[\text{Ni}(\text{H}_2\text{O})_6]^{2+} [\text{en}]^3}$$

It is specifically mentioned in the syllabus that [H₂O] should not be included. This is because water is in such large excess that its concentration is assumed to be constant.

- (iii) Describe what the K_{stab} values indicate about the position of equilibrium for equilibrium 1 and 2. Use the K_{stab} values to deduce which complex, $[\text{Ni}(\text{en})_3]^{2+}$ or $[\text{Ni}(\text{tn})_3]^{2+}$, is more stable.

Both equilibria lie to the right.

$[\text{Ni}(\text{en})_3]^{2+}$ is more stable because it has the larger K_{stab} value. [1]

Examiner comment

Common errors included:

- candidates stating that the equilibrium shifts to the right. This was incorrect because the K_{stab} values show the position of the equilibria at a particular temperature and this does not shift.
- stating that the position of equilibrium is forwards. This was not sufficient; candidates needed to indicate that the positions of both equilibria are to the right.
- stating that the position of equilibrium 2 lies to the left, when its K_{stab} value is so large.
- omitting the second part of the answer by not deducing which complex was the more stable.

Question 2

- 2 (a) Explain why transition elements have variable oxidation states.

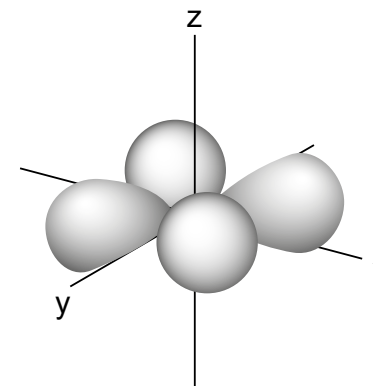
The 3d and 4s sub-shells are similar in energy.

[1]

Examiner comment

- A common error was to suggest that the d and s orbitals were incompletely filled.
- It was insufficient to say that electrons can be lost from the s and d orbitals. Candidates needed to indicate that the d and s orbitals have similar energy.

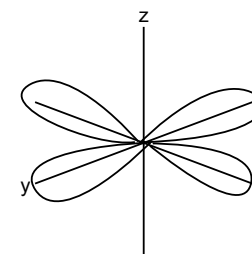
- (b) Sketch the shape of a $3d_{xy}$ orbital.



[1]

Examiner comment

Many candidates drew this incorrect shape, with the lobes of the d-orbital going along the x- and y- axes.



- (c) Explain why transition elements form coloured compounds.

The degenerate d orbitals are split into two non-degenerate sets of d orbitals of higher energy.

An electron is promoted between two non-degenerate d-orbitals by absorbing a frequency of light.

The colour seen is complementary to the frequency of light absorbed.

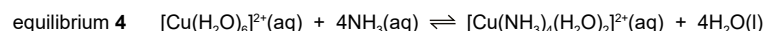
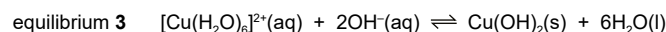
[3]

Examiner comment

- If a candidate stated that an electron 'jumps', they needed to make it clear that this is to a higher d-orbital. Electrons could jump to the same energy level, which would not be correct.
- Alternative words for frequency, such as wavelength or photon, were correct.
- 'Adsorbed' was not accepted instead of absorbed.
- It was not sufficient to state that colour was absorbed.
- Occasionally, candidates explained that colour was emitted. This was not accepted.

- (d) Aqueous solutions of copper(II) salts contain $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ions.

Equilibrium 3 and equilibrium 4 show two reactions of these ions.



- (i) State the colour of $\text{Cu}(\text{OH})_2(\text{s})$ and $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}(\text{aq})$.

colour of $\text{Cu}(\text{OH})_2(\text{s})$ *pale blue*

colour of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}(\text{aq})$ *dark blue*

[1]

Examiner comment

- The question only asked for colours to be given.
- While the vast majority of candidates gave both colours correctly, others gave a range of colours from yellow to black.
- Answers that gave a mix of colours, such as blue-green for $\text{Cu}(\text{OH})_2(\text{s})$, were not awarded the mark.
- Candidates should be encouraged to memorise the colours given in the qualitative analysis notes in the syllabus for the various reactions specified.

- (ii) Use Le Chatelier's principle to explain why a precipitate is formed when $\text{NaOH}(\text{aq})$ is added dropwise to $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$.

The concentration of OH^- ions increases and shifts equilibrium 3 to the right.

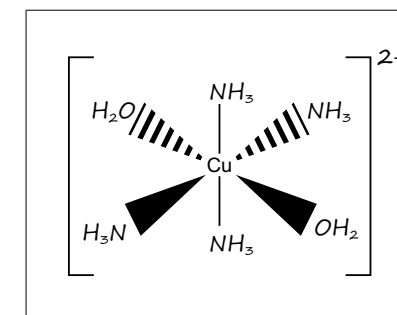
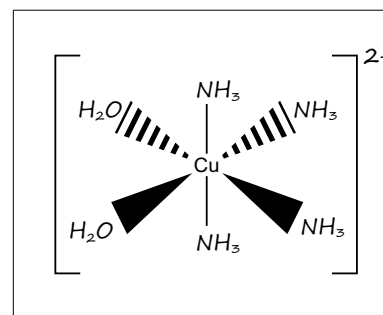
[1]

Examiner comment

The question asks candidates to use Le Chatelier's principle, so answers based on the amount of OH^- increasing, or the common ion effect, were ignored.

- (e) There are two possible stereoisomers with the formula $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$.

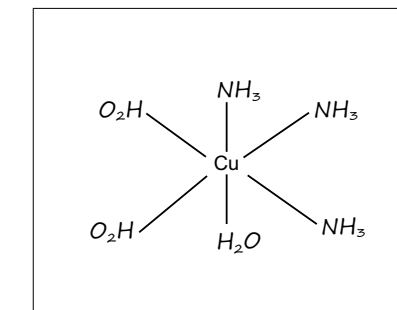
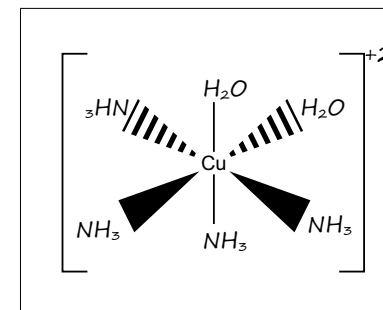
Draw three-dimensional diagrams to show the two stereoisomers.



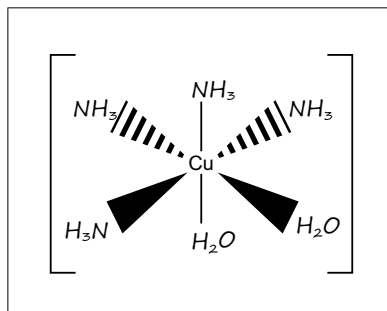
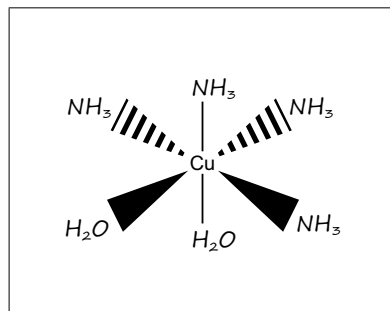
[2]

Examiner comment

- The diagrams needed to indicate correct three-dimensional structures and the convention for drawing these can be found in the syllabus.
- The formulae of the ligands must be correct: O_2H and NH_3 were not accepted. For example, both these diagrams are incorrect:



- Candidates sometimes drew two diagrams that were of the same isomer. In the example below, both the isomers drawn are the same *cis*-isomer:



Question 3

- 3 (a) (i) Define first electron affinity.

The enthalpy change when one mole of electrons is gained by one mole of gaseous atoms to form one mole of gaseous 1- ions.

[2]

- (ii) The first electron affinity of an atom is usually an exothermic process, whereas the second electron affinity is an endothermic process.

Suggest why.

The first electron affinity releases energy because there is attraction between the positive nucleus and the incoming electron. The second electron affinity requires energy to overcome the repulsion between the negative ion and the electron.

[1]

Examiner comment

Candidates needed to clearly state that the repulsion for the second electron affinity was between the electron and the negatively charged anion. It was not sufficient to describe repulsion between an incoming electron and the electrons already present.

- (iii) Describe the general trend in first electron affinities for Cl, Br and I. Explain your answer.

The general trend is less exothermic down the group because of the increasing distance between the nucleus and the outer electron shell. This means there is less attraction between the nucleus and the incoming electron, so less energy is released.

[2]

Examiner comment

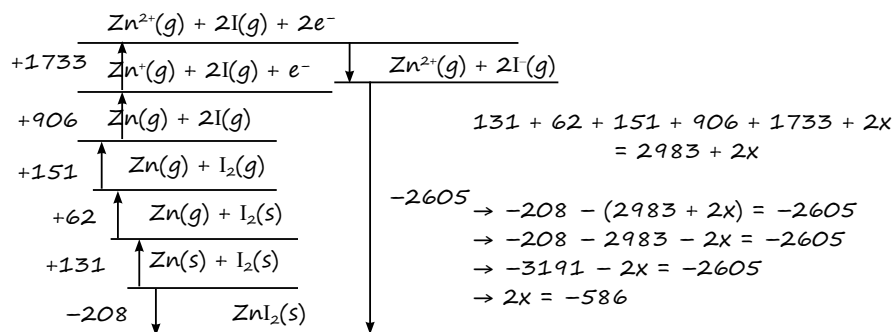
Explanations often did not state that the attraction between nucleus and the incoming electron decreases.

(b) Table 3.1 shows energy changes to be used in this question and in (c).

Table 3.1

energy change	value / kJ mol ⁻¹
standard enthalpy change of atomisation of zinc	+131
first ionisation energy of zinc	+906
second ionisation energy of zinc	+1733
standard enthalpy change of formation of ZnI ₂ (s)	-208
lattice energy, $\Delta H_{\text{latt}}^{\circ}$ of zinc iodide, ZnI ₂ (s)	-2605
first ionisation energy of iodine	+1008
second ionisation energy of iodine	+1846
I-I bond energy	+151
enthalpy change of sublimation of iodine, I ₂ (s) → I ₂ (g)	+62

Calculate the first electron affinity for iodine. Use relevant data from Table 3.1 in your working. It may be helpful to draw a labelled energy cycle. Show all working.



first electron affinity for iodine =-293..... kJ mol⁻¹ [3]

Examiner comment

- The question asks candidates to show all working. Many candidates made at least one error, but they still received some marks through applying error carried forward based on the errors they had made.
- Common errors were:
 - a final answer of -586 kJ mol⁻¹. This was obtained because candidates did not realise that there were two moles of iodide ions in ZnI₂, so 2 × the electron affinity was required in the calculation.
 - a final answer of -262 kJ mol⁻¹. This resulted from not using +62 kJ mol⁻¹, the enthalpy change of sublimation of iodine.

(c) Predict how $\Delta H_{\text{latt}}^{\circ}$ of CdI₂(s) differs from $\Delta H_{\text{latt}}^{\circ}$ of ZnI₂(s). Place a tick (✓) in the appropriate box in Table 3.2.

Table 3.2

$\Delta H_{\text{latt}}^{\circ}$ of CdI ₂ (s) is less negative than $\Delta H_{\text{latt}}^{\circ}$ of ZnI ₂ (s)	$\Delta H_{\text{latt}}^{\circ}$ of CdI ₂ (s) is the same as $\Delta H_{\text{latt}}^{\circ}$ of ZnI ₂ (s)	$\Delta H_{\text{latt}}^{\circ}$ of CdI ₂ (s) is more negative than $\Delta H_{\text{latt}}^{\circ}$ of ZnI ₂ (s)
✓		

Explain your answer.

Cd²⁺ is larger than Zn²⁺. There is less attraction between Cd²⁺ ions and I⁻ ions in the lattice. [1]

[Total: 9]

Examiner comment

Many candidates recognised that Cd²⁺ was larger than Zn²⁺ but did not mention that there was less attraction between Cd²⁺ ions and I⁻ ions in the lattice.

Question 4

- 4 (a) Calcium carbonate decomposes on heating.

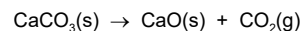


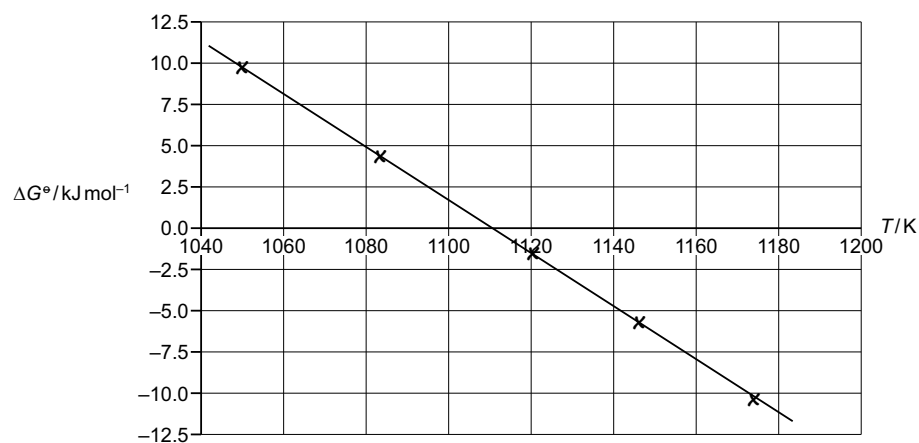
Table 4.1 shows the values of the Gibbs free energy change, ΔG° , for this reaction at various temperatures.

Table 4.1

T/K	$\Delta G^\circ/\text{kJ mol}^{-1}$
1050	9.9
1085	4.3
1120	-1.3
1148	-5.8
1176	-10.3

Assume the standard enthalpy change, ΔH° , and the standard entropy change, ΔS° , for this reaction remain constant over this temperature range.

- (i) Use the data in Table 4.1 to plot a graph of ΔG° against T on the grid.

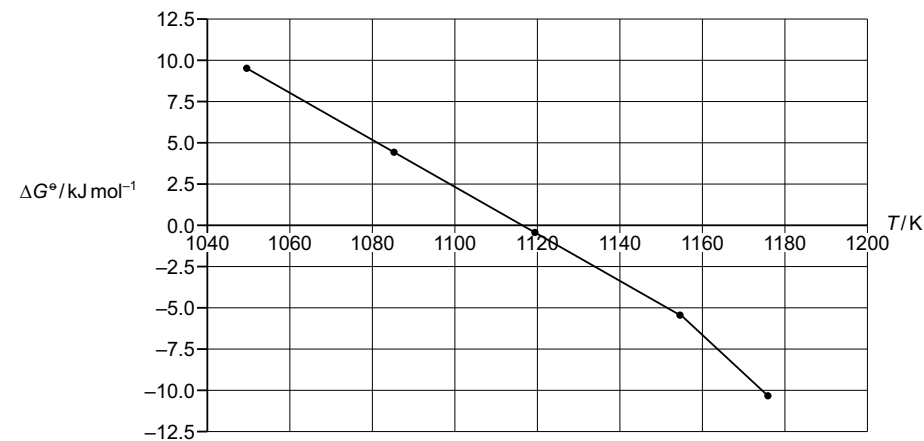


[2]

Examiner comment

Common errors were:

- not using a ruler to draw the line of best fit
- to plot points incorrectly and then not draw a line of best fit, which would have received an error carried forward mark. For example:



[2]

- (ii) Calculate the gradient of your graph. Determine the ΔS° in $\text{JK}^{-1} \text{mol}^{-1}$ for this reaction. Show all working.

coordinates: (1080, 4.8) (1180, 11.2)

$$\text{gradient} = \frac{4.8 - (-11.2)}{1080 - 1180} = -0.160$$

$$\text{gradient} = -\Delta S^\circ \quad \Delta S^\circ = 0.160 \times 1000$$

$$\Delta S^\circ = \dots\dots\dots +160 \text{ JK}^{-1} \text{mol}^{-1} \quad [2]$$

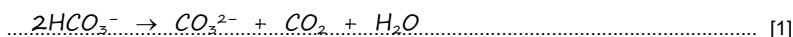
Examiner comment

Common errors were:

- using values from Table 4.1 which did not lie on the line of best fit
- not understanding that the gradient gave $-\Delta S^\circ$ and calculating a negative value for the entropy
- not converting the entropy value to $\text{JK}^{-1} \text{mol}^{-1}$ by multiplying by 1000.

- (b) Group 1 hydrogencarbonates, MHCO_3 , decompose on gentle heating to give the corresponding metal carbonate, carbon dioxide and water vapour.

- (i) Write an ionic equation for the decomposition of the hydrogencarbonate ion.



Examiner comment

- Candidates needed to read the question carefully. They needed to give an ionic equation which shows the decomposition of the hydrogen carbonate ion and the formation of a carbonate ion, carbon dioxide and water.
- Common errors were:
 - $2\text{MHCO}_3 \rightarrow \text{M}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ This is not an ionic equation.
 - $\text{HCO}_3^- \rightarrow \text{H}^+ + \text{CO}_3^{2-}$ This does not show the formation of carbon dioxide and water.

- (ii) The thermal stability of Group 1 hydrogencarbonates increases down the group.

Suggest an explanation for the trend in thermal stability of the Group 1 hydrogencarbonates.

The ionic radius of M^+ increases down the group.

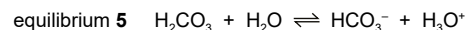
There is less polarisation of the HCO_3^- anion by the M^+ ion.

[2]

Examiner comment

- Answers which referred to decreasing charge density of the cation down the group were an acceptable alternative to increasing cation size.
- Many candidates did not explain that the hydrogencarbonate ion would be less polarised as the metal ions became larger.
- Some candidates used the term 'depolarisation' instead of polarisation. This was ignored.
- Some candidates stated that the ion becomes less polarised. It is essential that candidates refer to the **anion** being less polarised.

- (c) The buffer system in seawater contains a mixture of HCO_3^- and H_2CO_3 .



- (i) Define a buffer solution.

A solution which resists changes in pH when small amounts of acid

or alkali are added to it.

[2]

Examiner comment

- Many candidates described the buffer solution as 'keeping the pH constant' or 'maintaining the pH' and omitted the word 'small' when referring to the amounts of acid and alkali added.
- Answers such as 'it is a solution which keeps the pH constant when any acid or base is added to it' contained both of the common errors and was not awarded either of the two marks available.

- (ii) Construct **two** equations to show how equilibrium 5 acts as a buffer solution.

with acid: $\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{CO}_3$

with alkali: $\text{H}_2\text{CO}_3 + \text{OH}^- \rightarrow \text{HCO}_3^- + \text{H}_2\text{O}$ [2]

Examiner comment

- This is also a correct equation: $\text{HCO}_3^- + \text{H}_3\text{O}^+ \rightarrow \text{H}_2\text{CO}_3 + \text{H}_2\text{O}$.
- These incorrect equations were frequently seen:
 - $\text{H}_2\text{CO}_3 + \text{OH}^- \rightarrow \text{HCO}_3 + \text{H}_2\text{O}$. HCO_3 should have a minus charge. It is worth emphasising to learners the importance of balancing equations for charges as well as species. If the candidate had done this they would have detected this error.
 - $\text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2$. Although this reaction can occur, it is an equilibrium that lies well to the left. It was ignored and candidates did not receive a mark for this.

- (iii) The $[\text{HCO}_3^-]/[\text{H}_2\text{CO}_3]$ ratio in a sample of seawater is 14.1.

Calculate the pH of this sample.

$[\text{p}K_a: \text{H}_2\text{CO}_3, 6.35]$

$$K_a = 10^{-6.35} = 4.47 \times 10^{-7}$$

$$[\text{H}^+] = \frac{4.47 \times 10^{-7}}{14.1} = 3.17 \times 10^{-8}$$

$$\text{pH} = -\log [\text{H}^+] = 7.5 \quad [3]$$

[Total: 14]

Examiner comment

An alternative calculation involved the Henderson–Hasselbalch equation.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\text{pH} = 6.35 + \log (14.1)$$

$$\text{pH} = 7.50$$

Question 5

- 5 (a) Complete Table 5.1 to predict the substance liberated at each electrode during electrolysis of the indicated electrolyte with inert electrodes.

Table 5.1

electrolyte	substance liberated at the anode	substance liberated at the cathode
PbBr ₂ (l)	<i>bromine</i>	<i>lead</i>
concentrated NaCl(aq)	<i>chlorine</i>	<i>hydrogen</i>
Cu(NO ₃) ₂ (aq)	<i>oxygen</i>	<i>copper</i>

[3]

Examiner comment

- Candidates could use formulae instead of names, provided the formulae were correct, e.g. Br₂ was correct but Br was not.
- Many candidates gave ions. These are not substances liberated and were ignored.
- There were many incorrect substances given, these included Na from concentrated NaCl(aq) and NO₃⁻ from Cu(NO₃)₂(aq).
- Water was ignored as a substance liberated from Cu(NO₃)₂(aq). Oxygen was the response required.
- Some candidates gave the correct substances but assigned them to the incorrect electrode.

- (b) An electrolytic cell is set up to determine a value for the Avogadro constant, L . The electrolyte is dilute sulfuric acid and both electrodes are copper.

When a current of 0.600 A is passed through the acid for 30.0 minutes, the anode decreases in mass by 0.350 g.

- (i) State the relationship between the Faraday constant, F , and the Avogadro constant, L .

$F = Le$ [1]

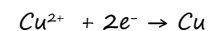
- (ii) Use the experimental information in (b) and data from the table on page 23 to calculate a value for the Avogadro constant, L .

Show all working.

$$\text{Amount of Cu}^{2+} \text{ formed} = \frac{0.35}{63.5} = 5.5111811 \times 10^{-3} \text{ mol}$$

$$Q = I \times t = 0.60 \times 30 \times 60 = 1080 \text{ C}$$

$$\text{Number of electrons} = \frac{1080}{1.6 \times 10^{-19}} = 6.75 \times 10^{21}$$



$$\text{Number of Cu}^{2+} \text{ ions} = \frac{6.75 \times 10^{21}}{2} = 3.375 \times 10^{21}$$

$$\text{Number of Cu}^{2+} \text{ ions per mole (L)} = \frac{3.375 \times 10^{21}}{5.51 \times 10^{-3}} = 6.123914164 \times 10^{23}$$

$$\text{Avogadro constant, } L = \frac{6.12 \times 10^{23}}{1} \text{ [4]}$$

[Total: 8]

Examiner comment

- There were alternative calculations which were valid and could be awarded marks.
- The most common error was to use 96 500 C and divide this by 1.6×10^{-19} to give a value for L of 6.022×10^{23} . This approach did not use the experimental information given.
- Many candidates rounded too early in the calculation and obtained an incorrect value for L .

Question 6

- 6 (a) The reagent and conditions required for the nitration of benzene, benzoic acid and phenol are shown in Table 6.1.

Table 6.1

compound	reagents and conditions for nitration
benzene	concentrated HNO_3 , 50°C , concentrated H_2SO_4 catalyst
benzoic acid	concentrated HNO_3 , 100°C , concentrated H_2SO_4 catalyst
phenol	dilute $\text{HNO}_3(\text{aq})$, 20°C

Concentrated HNO_3 reacts with concentrated H_2SO_4 to generate the electrophile NO_2^+ .

- (i) Complete Fig. 6.1 to show the mechanism of the reaction between benzene and NO_2^+ . Include all relevant curly arrows and charges.

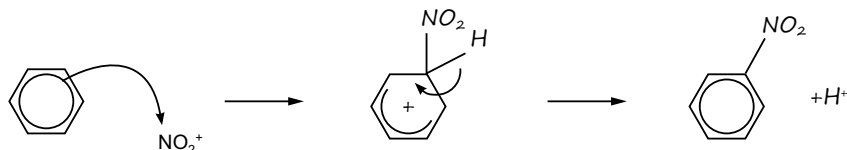
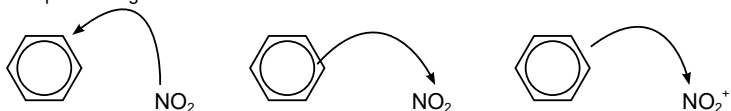


Fig. 6.1

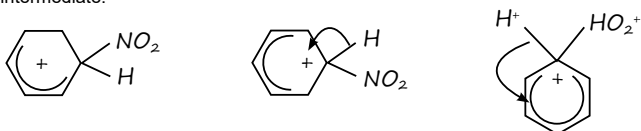
[3]

Examiner comment

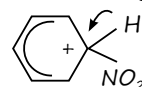
- The first curly arrow must come from within the hexagon of the benzene ring and go to the N of NO_2^+ . These are examples of diagrams which could not be awarded marks:



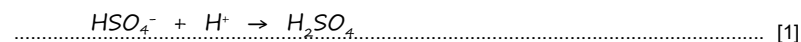
- The diagram for the intermediate must:
 - show the delocalised system as a 'horseshoe' shape which includes carbon 3 (C3), C4 and C5, and preferably extends up to C2 and C6. The horseshoe should not go beyond either C2 or C6.
 - show the + charge below an imaginary line which connects C2 and C6. Ideally, the + charge should lie within the horseshoe. If + was drawn above the imaginary line then it implied that C1 had a + charge, which cannot be the case as it is surrounded by four single bonds.
 - not show any other charges.
- These diagrams of the intermediate did not receive marks. The curly arrows were ignored when considering the intermediate.



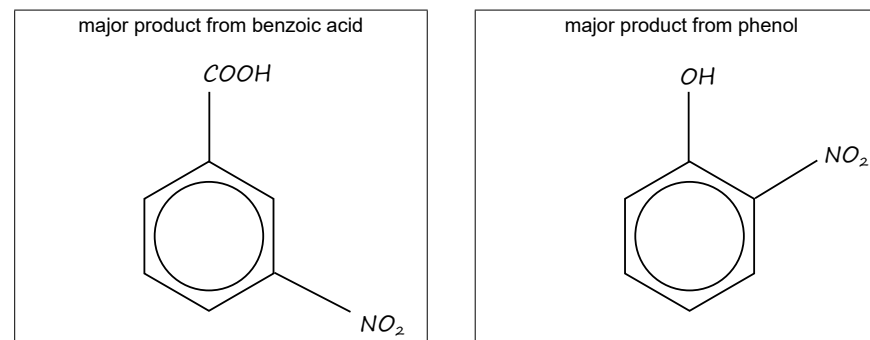
- The second curly arrow must come from the C—H bond and go into the hexagon of the benzene ring. Also, the H^+ ion lost must be shown.
- This diagram was not awarded marks for the curly arrow because it did not come from the bond and did not enter the benzene ring:



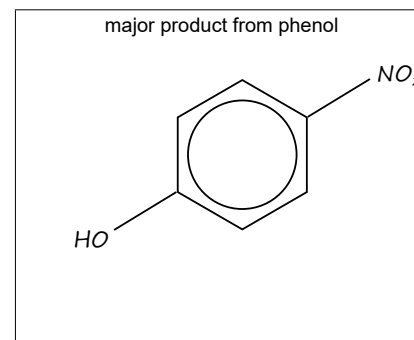
- (ii) Write an equation to show how H_2SO_4 is regenerated.



- (b) Draw the major products from the mononitration of benzoic acid and of phenol.



[2]



Examiner comment

- Only one major product from phenol was required and either of the structures shown were awarded marks.
- Displayed formulae could also be drawn, but candidates needed to take care to ensure that the bonds connected to the correct atoms.
- Some candidates drew the substituents in the incorrect positions on the benzene ring, e.g. 3-nitrophenol.

- (c) Compare the relative ease of nitration of benzene, benzoic acid and phenol. Explain your reasoning; include reference to the structures of the three compounds in your answer.

..... phenol > benzene > benzoic acid
 easiest least easy

One of the lone pairs on the oxygen atom of the OH group of phenol overlaps with the π -delocalised ring system. This increases electron density in the ring and makes phenol more likely to be attacked by NO_2^+ compared to benzene. The COOH group in benzoic acid is electron withdrawing. This decreases electron density in the ring so it is less likely to be attacked by an electrophile when compared to benzene. [4]

Examiner comment

- Another way of explaining why phenol is the easiest to nitrate is to refer to the p-orbital on oxygen overlapping with the π -delocalised ring and thus decreasing electron density.
- The lone pair which overlaps with the delocalised ring in phenol must be linked to the oxygen atom.
- It was not sufficient to use the term 'charge density' instead of 'electron density'.
- Some candidates omitted the + charge on NO_2 . This was not accepted.
- The OH group was sometimes described as electron withdrawing, which is incorrect.

- (d) The azo compound Congo Red is used as an acid–base indicator and can be made by the route shown in Fig. 6.2.

In step 3 of this synthesis, compound **Y** reacts with compound **Z**. Compound **Z** is made from compound **X**. Assume that the $-\text{SO}_3^-\text{Na}^+$ groups do not react.

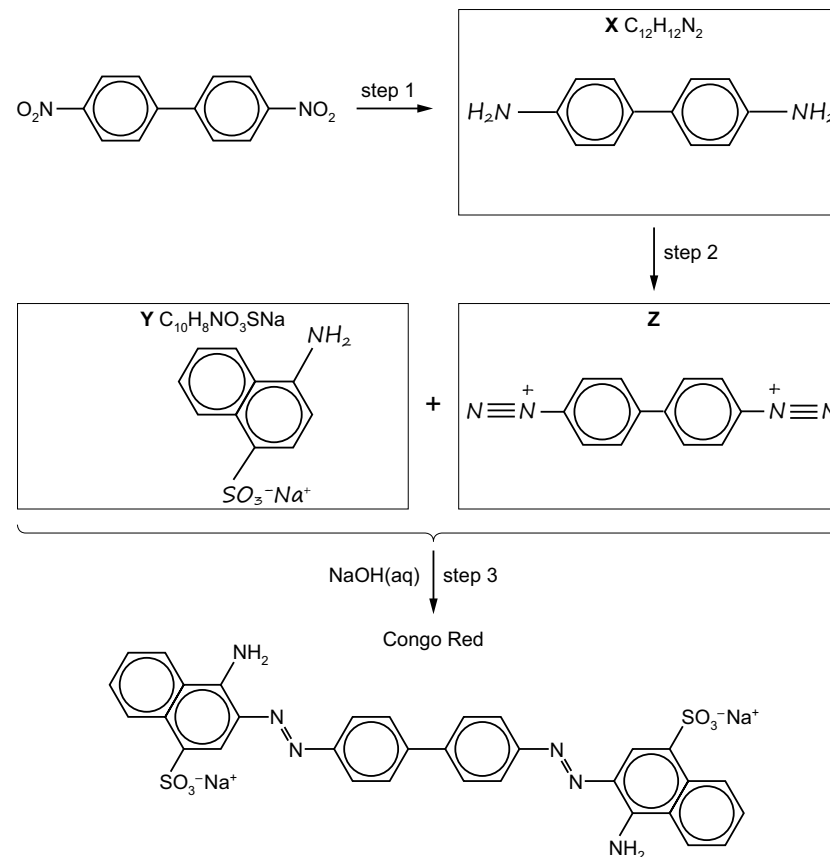
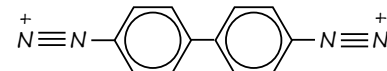


Fig. 6.2

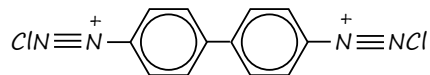
- (i) Suggest structures for compounds **X**, **Y** and **Z** and draw them in the boxes in Fig. 6.2. [3]

Examiner comment

- This structure for **Z** is incorrect because the + charges are on the wrong nitrogen atoms.



- Some candidates showed the chloride ions at both ends of Z. This was awarded as it shows the neutral compound. However, the structure shown below was incorrect because the chloride ions should be shown with minus charges.



(ii) Give the reagents and conditions for step 1 and step 2.

step 1 *Sn and concentrated HCl are heated under reflux, followed by the addition of NaOH(aq).*

step 2 *HNO₂ (or NaNO₂ and dilute acid) below 10°C.*

[3]

Examiner comment

Common errors were to:

- describe tin as a catalyst. It is a reactant and this contradicts the mark for reactants in step 1.
- reflux the reactant mixture together with NaOH(aq) in step 1. NaOH(aq) is added to the cooled mixture after the reaction with HNO₂ has finished.
- miss out a reaction condition such as concentrated for HCl.

[Total: 16]

Question 7

7 (a) State the uses of TMS and D₂O in NMR spectroscopy.

TMS *the standard for chemical shift measurements.*

D₂O *it is a solvent that does not contain any H atoms so does not produce peaks which interfere with the NMR spectrum.* [1]

Examiner comment

- D₂O could also be used to identify O–H and N–H protons by removing their peaks.
- A common error was to describe TMS as a solvent.

(b) The three isomeric ketones with molecular formula C₅H₁₀O are:

- pentan-2-one
- pentan-3-one
- 3-methylbutanone.

(i) Complete Table 7.1 to show the number of peaks observed in the proton (¹H) NMR spectrum and in the carbon-13 NMR spectrum for each compound listed.

Table 7.1

ketone	number of peaks observed in the proton (¹ H) NMR spectrum	number of peaks observed in the carbon-13 NMR spectrum
pentan-2-one	4	5
pentan-3-one	2	3
3-methylbutanone	3	4

[2]

(ii) State **all** the ketones with molecular formula C₅H₁₀O that have:

a doublet in their proton (¹H) NMR spectrum

3-methylbutanone

a singlet in their proton (¹H) NMR spectrum.

3-methylbutanone and pentan-2-one

[2]

- (c) Cortisone, $C_{21}H_{28}O_5$, is a naturally occurring chemical that contains chiral carbon atoms.

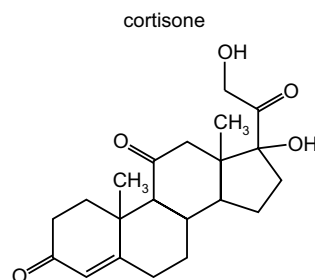


Fig. 7.1

- (i) Deduce the number of chiral carbon atoms in one molecule of cortisone.

six [1]

- (ii) Cortisone is reacted with an excess of $NaBH_4$.

State the molecular formula of the organic compound formed.

$C_{21}H_{34}O_5$ [1]

Examiner comment

Common errors were to:

- work out an incorrect number of hydrogen atoms
- put a sodium atom in the formula.

- (iii) Cortisone is an optically active molecule.

Explain what is meant by optically active.

A molecule that is able to rotate the plane of polarised light.
.....
..... [1]

Examiner comment

This question was not well understood by many candidates. Common errors were to:

- miss out at least one of the key words 'rotate' and 'polarised'.
- state that the molecule had optical isomers.
- explain that the molecule contained a chiral carbon.

Question 8

- 8 (a) Compare the relative acidities of ethanol, ethanoic acid, chloroethanoic acid and phenol. Explain your reasoning.

chloroethanoic acid > *ethanoic acid* > *phenol* > *ethanol*
most acidic least acidic

Chloroethanoic acid > ethanoic acid because it contains an electronegative Cl. This withdraws electrons from the O—H bond, weakening it so that H^+ is more easily lost. It also stabilises the conjugate base.

Ethanoic acid > phenol due to the negative inductive effect of $C=O$ which weakens the O—H bond.

Phenol > ethanol because one of the lone pairs on the oxygen atom of the OH group of phenol is delocalised into the benzene ring. This means that H^+ is more easily lost.

Ethanol is the least acidic because its alkyl group has a positive inductive effect which strengthens the O—H bond so that H^+ is most difficult to lose.

Examiner comment

- This question asks candidates to explain the relative acidities of the compounds so explanations in terms of the ability of the anions to accept protons could not be awarded marks.
- There was often no reference made to weakening the O—H bond, allowing a proton to be lost more easily.
- It was not sufficient to describe the O atom in ethanoic acid as electronegative because all the compounds contain an O atom.

- (b) An excess of ethanedioic acid, $\text{HOOC}\text{COOH}(\text{aq})$, is reacted with warm acidified $\text{KMnO}_4(\text{aq})$.

State the type of reaction undergone by ethanedioic acid.

Describe what you would observe.

Write an equation for this reaction.

Your equation can use [O] or [H] as necessary.

type of reaction *oxidation*.....

observations *bubbles and the purple solution decolourises*.....

equation *$\text{HOOC}\text{COOH} + [\text{O}] \rightarrow 2\text{CO}_2 + \text{H}_2\text{O}$*

[2]

Examiner comment

- The equation $5\text{HOOC}\text{COOH} + 2\text{MnO}_4^- + 6\text{H}^+ \rightarrow 10\text{CO}_2 + 8\text{H}_2\text{O} + 2\text{Mn}^{2+}$ is also correct.
- Redox is insufficient for the type of reaction because the question specifically asks for the reaction undergone by ethanedioic acid.
- Gas given off is not an observation; it is a conclusion based on the observation that effervescence is occurring.
- Some candidates put [O] above the reaction arrow instead of on the left of the equation. This was not accepted as showing a balanced equation.

- (c) A section of a polyester is shown.

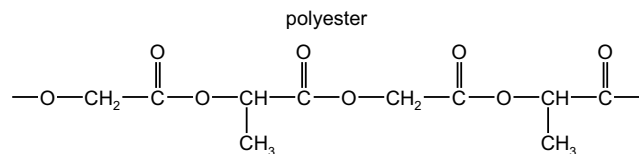
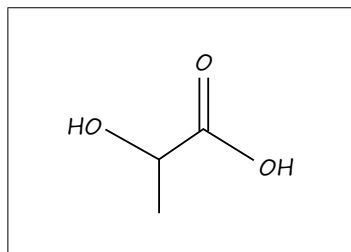
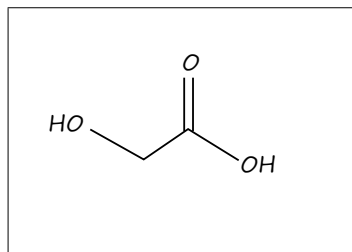


Fig. 8.1

Draw the structures of the two monomers that form this polyester.



[2]

Examiner comment

- Structural or displayed formulae were accepted. Displayed formulae needed to show the correct connectivity between atoms.
- Instead of a carboxylic acid group, an acyl chloride group was also accepted i.e. HOCH_2COCl and $\text{HOCH}(\text{CH}_3)\text{COCl}$.

- (d) Serine can polymerise to form two different types of condensation polymer; a polyester and a polypeptide.

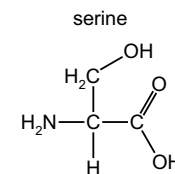
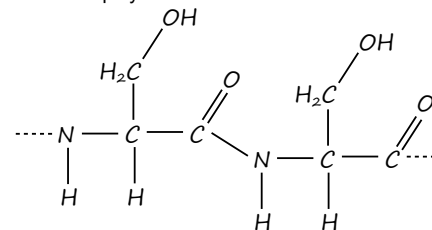


Fig. 8.2

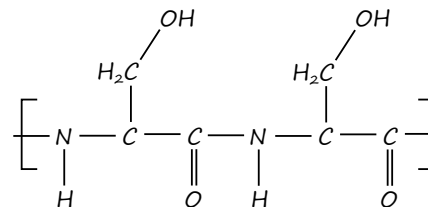
Draw the structure of the polypeptide showing **two** repeat units. The peptide linkage should be shown displayed.



[2]

Examiner comment

- Many candidates did not read the question carefully enough and drew three or more repeat units.
- The continuation bonds were frequently missing.
- Candidates who drew skeletal formulae needed to show the continuation bonds clearly as dashed lines. A solid line at either end of a skeletal formula indicates a methyl group.
- Many candidates drew trivalent carbon atoms. Learners should be reminded to check their structures to ensure that each carbon atom has four bonds around it. This diagram is incorrect:



- (e) Explain why condensation polymers normally biodegrade more readily than addition polymers.

Condensation polymers can hydrolyse in acidic or alkaline conditions......

Addition polymers are chemically inert...... [1]

[Total: 11]

Question 9

- 9 The structure of cyclohexylamine is shown in Fig. 9.1.

cyclohexylamine

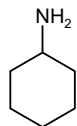


Fig. 9.1

- (a) Compare the relative basicities of ammonia, cyclohexylamine and phenylamine. Explain your reasoning.

cyclohexylamine > ammonia > phenylamine
 most basic least basic

Cyclohexylamine has an alkyl group which has a positive inductive effect.

This pushes electrons towards the N, increasing its electron density and so it accepts a proton most easily.

Phenylamine has a lone pair on N which delocalises into the π -ring. This decreases electron density on N so it accepts a proton least easily.

[3]

Examiner comment

- Candidates must have explained clearly that the order of basicity was linked to the ability of N to accept a proton, or donate its lone pair to a proton. Many answers were too vague, e.g.:
 - ‘basicity is linked to the ability of the NH_2 group to accept a proton’. This does not tell us that it is the N atom that accepts the proton or donates its lone pair.
 - ‘the lone pair on N is more available in cyclohexylamine’. This does not mention gaining a proton more easily.
- Candidates could state that the p orbital from N overlaps with the delocalised π -ring instead of the lone pair.
- For phenylamine the lone pair that is delocalised needed to be identified as belonging to N.

- (b) Cyclohexylamine reacts with ethanoyl chloride to form the corresponding amide, L.

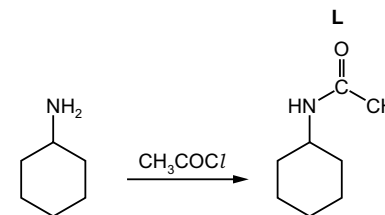


Fig. 9.2

- (i) Name the mechanism for the reaction shown in Fig. 9.2.

Addition-elimination [1]

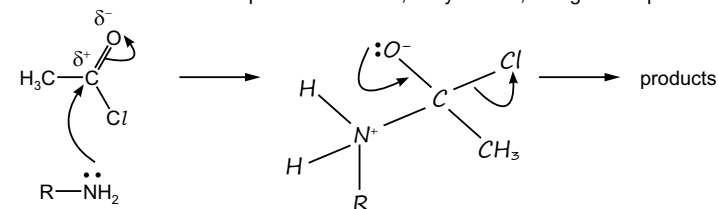
Examiner comment

‘Condensation’ was ignored as it does not accurately describe the mechanism.

- (ii) Complete the mechanism of the reaction between cyclohexylamine and CH_3COCl .

R-NH_2 is used to represent cyclohexylamine.

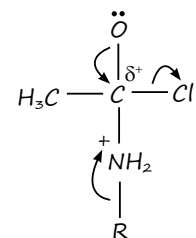
Include all relevant lone pairs of electrons, curly arrows, charges and partial charges.



[4]

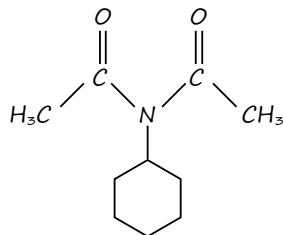
Examiner comment

- The lone pair should be clearly shown on the N of RNH_2 . This diagram is incorrect:
 $\text{R}-\text{NH}_2$
- The partial charges were often omitted from $\text{C}=\text{O}$.
- This candidate's diagram of the intermediate showed several common errors:
 - there was no minus sign on the O atom.
 - the curly arrow should have been shown coming from the lone pair of O.
 - the curly arrow on $\text{N}-\text{R}$ was incorrect.



- (iii) The reaction between cyclohexylamine and an excess of CH_3COCl forms compound **M**. Compound **M** has the molecular formula $\text{C}_{10}\text{H}_{17}\text{NO}_2$.

Suggest and draw the structure of **M**.



[1]

Examiner comment

- Skeletal or displayed structures could be drawn.
- This was a common incorrect structure:

