

Answer ALL the questions. Write your answers in the spaces provided.

1. (a) Complete the electronic configurations of a copper ion, Cu^+ , and a copper ion, Cu^{2+} .

	1s	2s	2p	2p	2p	3s	3p	3p	3p	3d	3d	3d	3d	3d	4s
Cu^+	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓						
Cu^{2+}	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓						

(2)

- (b) (i) Copper compounds containing the copper 2+ ion are blue in aqueous solution. Explain the origin of the colour.

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(3)

- (ii) On heating, blue hydrated copper(II) sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, turns white. Suggest why the anhydrous salt, CuSO_4 , is white.

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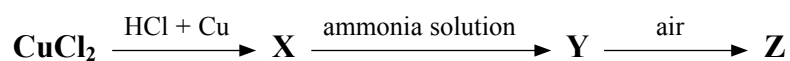
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(1)



(c) A green chloride of copper, CuCl_2 , was boiled with concentrated hydrochloric acid and metallic copper. After addition of a large volume of water, a white precipitate, **X**, was produced. The precipitate was washed with distilled water and dissolved in concentrated ammonia solution, giving a colourless solution of a copper complex, **Y**. When air was blown through the solution of **Y**, it turned dark blue producing a solution of a different complex of copper, **Z**.

Summary



(i) Identify **X** and write an equation for its formation.

Identity of X

Equation

(2)

(ii) What type of reaction is taking place in the formation of **X**?

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(1)

(iii) The complex copper ion, **Y**, is linear. Suggest the formula for **Y**.

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(1)

(iv) Explain why **Y** is **not** coloured.

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(1)

(v) Write the formula of **Z**.

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(1)

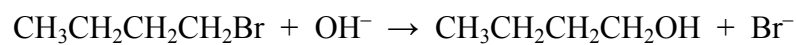
(Total 12 marks)

Q1

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2. The equation for the reaction between 1-bromobutane and hydroxide ions is



(a) Classify the reaction taking place.

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(1)

(b) Data for the reaction of 1-bromobutane with hydroxide ions are shown in the table.

Expt	Initial concentration of 1-bromobutane /mol dm ⁻³	Initial concentration of hydroxide ions /mol dm ⁻³	Initial rate /mol dm ⁻³ s ⁻¹
1	0.01	0.01	0.012
2	0.01	0.03	0.036
3	0.04	0.03	0.144

(i) Calculate, showing your working, the order of the reaction with respect to 1-bromobutane and to the hydroxide ion. Hence write the rate equation.

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(3)



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(ii) Write the mechanism for the reaction which is consistent with your rate equation.
You should use RCH_2Br to represent 1-bromobutane.

(3)

(c) (i) One optical isomer of a tertiary bromoalkane reacts with aqueous hydroxide ions to produce a mixture that does **not** rotate the plane of monochromatic plane-polarised light.

Explain how this information suggests the mechanism is $\text{S}_{\text{N}}1$ but **not** $\text{S}_{\text{N}}2$.

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(4)



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- (ii) The S_N1 mechanism is first order with respect to the **tertiary** bromoalkane and zero order with respect to the hydroxide ion. It takes place in two steps, one of which is rate-determining.

Explain what is meant by the term **rate-determining step** and explain what happens in this step. (You do **not** need to draw out the mechanism.)

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(2)

Q2

(Total 13 marks)



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3. Benzene and propene both react with electrophiles. Propene undergoes addition but benzene undergoes substitution.

(a) (i) Write the mechanism for the addition of hydrogen bromide to propene to form 2-bromopropane.

(3)

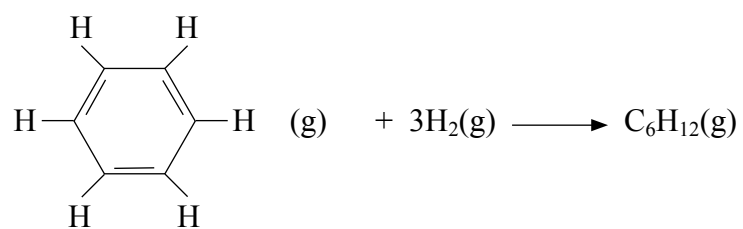
(ii) State why 2-bromopropane is the major product.

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(1)



- (b) Use the average bond enthalpy data below to calculate the enthalpy of hydrogenation of the hypothetical molecule cyclohexa-1,3,5-triene, C_6H_6 , to form cyclohexane, C_6H_{12} .



Bond	Average bond enthalpy / kJ mol^{-1}
C—C	347
C=C	612
C—H	413
H—H	436

(3)



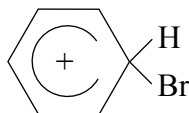
(c) The measured enthalpy change for the hydrogenation of benzene is -208 kJ mol^{-1} . The difference between this value and the answer in (b) is called the delocalisation (stabilisation) energy. The structure shown for cyclohexa-1,3,5-triene assumes three **localised** π -bonds.

(i) Explain how the **delocalised** π -bond system in benzene is formed. Include a diagram in your answer.

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(2)

(ii) The first step in the reaction of benzene with bromine, in the presence of a catalyst, is the addition of Br^+ to the benzene ring forming:



Explain why the second step results in the overall reaction being substitution rather than addition.

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(2)



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(d) An azo dye can be produced from benzene. The azo dye produced is very impure. It can be purified by recrystallisation as follows.

- Dissolve the solid azo dye in the minimum volume of hot ethanol.
- Filter the mixture while it is hot.
- Cool the filtrate in ice to crystallise the solid.
- Filter the mixture.
- Wash the solid with the minimum volume of ice-cold ethanol.
- Dry the solid.

(i) What essential property must be shown by a solvent for it to be suitable for use in recrystallisation?

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(1)

(ii) State which process removes insoluble impurities.

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(1)

(iii) Explain how soluble impurities are removed during the purification.

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(1)

(iv) Why is the solid washed with solvent after the second filtration?

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(1)

(v) State ONE feature of the procedure that ensures the maximum yield of pure azo dye at the end of the purification.

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(1)

(Total 16 marks)

Q3



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4. Draw a boiling temperature/composition diagram for a mixture of octane (boiling temperature $126\text{ }^{\circ}\text{C}$) and hexane (boiling temperature $69\text{ }^{\circ}\text{C}$) and then **use the diagram to explain** how fractional distillation of a mixture of 50% octane and 50% hexane can be used to produce pure hexane.



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(Total 5 marks)

Q4



5. (a) Cinnamon oil is an aromatic oil which has the following percentage composition by mass:

Carbon 81.82%: Hydrogen 6.06%: Oxygen 12.12%.

The molar mass of the compound is 132 g mol^{-1} .

Use this information to confirm that the molecular formula of cinnamon oil is $\text{C}_9\text{H}_8\text{O}$.

(3)

- (b) Cinnamon oil has the following reactions. For each reaction state what structural information is gained from the test result.

- (i) Cinnamon oil reacts with a solution of 2,4-dinitrophenylhydrazine to give a yellow precipitate.

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(1)

- (ii) Cinnamon oil reacts with ammoniacal silver nitrate solution to give a silver mirror.

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(1)

- (iii) Cinnamon oil reacts with excess hydrogen bromide to give a product which has a molecular formula $\text{C}_9\text{H}_9\text{OBr}$.

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(1)



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(c) Cinnamon oil's structure is based on a benzene ring with a single unbranched side chain.

(i) Use this information and your answers from (b) to suggest a structural formula for cinnamon oil.

(1)

(ii) Draw the structure of the product of the reaction between cinnamon oil and hydrogen bromide, HBr. Mark the chiral carbon atom with an asterisk (*).

(2)

(iii) Explain why, when cinnamon oil reacts with bromine in the presence of anhydrous aluminium chloride, several different compounds are formed.

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(2)

Q5

(Total 11 marks)

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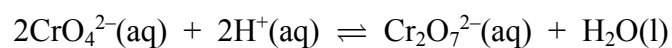
6. This question concerns the chemistry of chromium and its compounds.

(a) State what you would **see** when a solution of sodium hydroxide is added slowly, until in excess, to a solution containing chromium(III) ions.

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(2)

(b) Consider the following reaction:



(i) Explain the effect of changing the pH on the position of this equilibrium.

Higher pH.....

Lower pH.....

(2)

(ii) Explain, with reference to chromium, why this is **not** a redox reaction.

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(1)

(c) Use the information in the table below to answer the questions that follow.

	E^\ominus /V
$\text{Cr}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cr}(\text{s})$	-0.90
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$	-0.76
$\text{Cr}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Cr}^{2+}(\text{aq})$	-0.41



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(i) Write the equation for the reduction of Cr^{3+} ions to Cr^{2+} ions with zinc. State symbols are **not** required.

(1)

(ii) Write the equation for the reduction of Cr^{2+} ions to chromium metal with zinc. State symbols are **not** required.

(1)

(iii) Calculate the $E_{\text{cell}}^{\ominus}$ values for each of the above reactions.

State, with a reason, what the final product of the reaction between Cr^{3+} ions and zinc will be.

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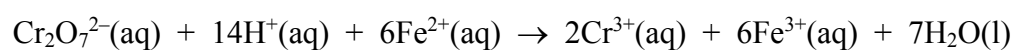
(2)



- (d) Standard potassium dichromate(VI) solution can be used to find the amount of iron(II) sulphate, FeSO_4 , in an iron(II) sulphate tablet.

A tablet of mass 4.00 g was dissolved in dilute sulphuric acid and the solution made up to 250 cm^3 with water. A 25.0 cm^3 portion of the solution was titrated with a solution of potassium dichromate(VI) of concentration $0.0136 \text{ mol dm}^{-3}$. The mean titre was 19.00 cm^3 .

The reaction is as follows:



Calculate the percentage of iron(II) sulphate in the tablet.

(5)



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