YISHUN INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME			
CG		INDEX NO	

CHEMISTRY

9729/03

Paper 3 Free Response

12 September 2024

Candidates answer on the Question Paper.
Additional Materials: Data Booklet

2 hours

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** the questions.

Section B
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

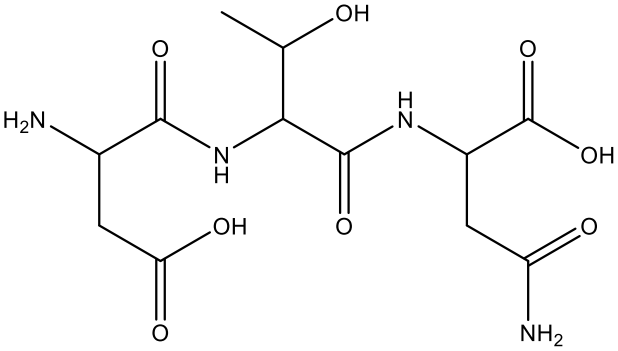
For Examiner's Use		
Section A		
1	**/ 21**	
2	**/ 18**	
3	**/ 21**	
Section B		
4 or 5	**/ 20**	
Penalty	**units**	**significant figures**
Overall	**/ 80**	

This document consists of **32** printed pages.

Section A

Answer **all** the questions in this section.

1 **(a)** The tripeptide **A** is made by reacting amino acids **B**, **C** and **D** together.



A

Table 1.1 shows the pK_a values of the different functional groups present on each amino acid.

Table 1.1

amino acid	pK_a of α–carbonyl group	pK_a of α–amino group	pK_a of side chain
B	2.09	9.10	–
C	1.88	9.60	3.65
D	2.02	8.80	–

(i) Explain the term *α-amino acid*. [1]

(ii) One of the amino acids, **B**, present in the tripeptide **A** contains more than one chiral carbon atom. Draw the displayed formula of **B**. [1]

(iii) Draw the predominant species of **C** at pH 4.0. [1]

(iv) Suggest a pH at which the predominant species of **C** is a zwitterion using the information in Table 1.1. [1]

(v) Explain why the side-chain of **D** does not have a K_a value. [1]

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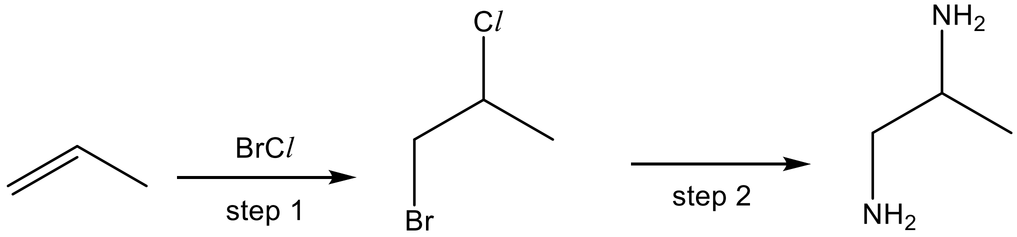
(b) 1,2-diaminopropane can be synthesised from propene by the following route.



propene 1-bromo-2-chloropropane 1,2-diaminopropane

(i) Outline the mechanism for step 1 to show the formation of 1-bromo-2-chloropropane. Show all charges, relevant lone pairs and show the movement of electron pairs using curly arrows. [2]

(ii) Use your mechanism to explain the preferential production of 1-bromo-2-chloropropane over 2-bromo-1-chloropropane. [1]

(iii) State the reagents and conditions for step 2. [1]

(iv) 1,2-diaminopropane can react with bromoethane to form compound **E**, $C_7H_{18}N_2$. Suggest the structure for **E**. [1]

(c) Alkanes are very unreactive. However, alkanes such as butane, C_4H_{10}, do react with chlorine. There are two possible monochloroalkanes that can be formed from butane. One of the monochloroalkanes exhibits stereoisomerism.

(i) Suggest two reasons why alkanes are generally unreactive. [2]

(ii) Predict the relative proportions of 1-chlorobutane and 2-chlorobutane that are likely to be produced from C_4H_{10}. Explain your answer. [2]

(iii) Draw three-dimensional structures for the two stereoisomers of the monochloroalkane formed from the chlorination of butane. [1]

(d) Use the data in Table 1.2, together with relevant data from the *Data Booklet*, to calculate the average bond energy of the Si-C*l* bond in SiC*l*$_4$. Show your working.

Table 1.2

enthalpy change of vaporisation of SiC*l*$_4$ molecules, SiC*l*$_4$(l) $\rightarrow$ SiC*l*$_4$(g)	=	+29 kJ mol^{-1}
standard enthalpy change of atomisation of Si(s)	=	+338 kJ mol^{-1}
standard enthalpy change of formation of SiC*l*$_4$(l)	=	–687 kJ mol^{-1}

[3]

(e) Describe the reaction of $SiCl_4$ with water, stating the pH of the resulting mixture. [1]

(f) Elements in Group 17 are known as the halogens.
State how the reactivity of the halogens as oxidising agents varies down the group, and relate this variation to relevant $E^\ominus$ values. [2]

[Total: 21]

2 **(a)** Alnico alloys are known for its strong magnetic properties and are commonly used in applications like permanent magnets and electronic devices.

Alnico alloys contain metals such as aluminum, magnesium, iron, and cobalt.

The densities of the four metals present in Alnico are given in Table 2.1.

Table 2.1

	metal 1	metal 2	metal 3	metal 4
density / g cm^{-3}	1.74	2.70	7.87	8.83

(i) Explain why iron and cobalt have a higher melting point than aluminium and magnesium.[1]

(ii) State which two of the metals, Mg, A*l*, Fe and Co, which are present in Alnico, are metals 3 and 4. Explain why. [2]

(b) The iron(II) complex, *ferrous bisglycinate hydrochloride* is sometimes prescribed, in capsule form, to treat iron deficiency or anaemia.

A capsule containing 500 mg of this iron(II) complex was dissolved in dilute H_2SO_4 and titrated with 0.0200 mol dm^{-3} $KMnO_4$. 18.10 cm^3 of $KMnO_4$ solution were required to oxidise all the Fe^{2+} present in the capsule.

Calculate the molar mass of the iron(II) complex given that the ratio of Fe^{2+} to the complex is 1:1. [2]

(c) $[Fe(H_2O)_6]^{3+}$ form a deep-red complex with thiocyanate ions, SCN^-, as shown in reaction 1, and a yellow complex with $EDTA^{4-}$ as shown in reaction 2.

reaction 1 $[Fe(H_2O)_6]^{3+}(aq) + SCN^-(aq) \rightleftharpoons [Fe(SCN)(H_2O)_5]^{2+}(aq) + H_2O(l)$ $K_c = 1.00 \times 10^3$

deep-red

reaction 2 $[Fe(H_2O)_6]^{3+}(aq) + EDTA^{4-}(aq) \rightleftharpoons [Fe(EDTA)]^-(aq) + 6H_2O(l)$ $K_c = 1.26 \times 10^{26}$

yellow

(i) Explain why transition element complexes are usually coloured. [3]

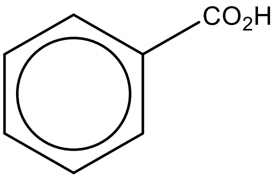
(ii) With reference to reaction 1 and 2, suggest and explain which reaction has a higher positive standard entropy change, $\Delta S^\ominus$. [2]

(iii) A few drops of KSCN was added to 5 cm^3 of $[Fe(EDTA)]^-$. Use the K_c values to predict and explain whether there is any colour change when a few drops of KSCN was added to 5 cm^3 of $[Fe(EDTA)]^-$. [2]

(d) Compound **F** has the molecular formula $C_{11}H_{15}Cl$ and contains a chiral centre.

One mole of compound **F** is reacted separately with

- Iodine in aqueous NaOH with heating, followed by acidification to form compound **G** and a yellow precipitate.
- ethanolic NaOH with heating forming a mixture of isomeric alkenes.
- anhydrous $FeCl_3$ forming one mole of compound **H**.
- hot acidified $KMnO_4$ forming benzoic acid.



benzoic acid

Suggest possible structures for compounds **F**, **G** and **H**, explaining the reactions described. [6]

[Total: 18]

3 **(a)** The equation for the complete combustion of one mole of ethanol is shown.

$$CH_3CH_2OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$$

The standard enthalpy change of combustion of ethanol, $\Delta H_c^\ominus$, is –1367 kJ mol^{-1}.
The standard entropy change, $\Delta S^\ominus$, for the same reaction is –140 J mol^{-1} K^{-1}.

(i) Calculate the standard Gibbs free energy change, $\Delta G^\ominus$, for the combustion of ethanol at 298K. [1]

(ii) Using the equation for the combustion of ethanol and your answer to **(a)(i)**, calculate $E^\ominus_{cell}$ for the ethanol/oxygen fuel cell. [2]

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(b) Separate acidified samples of $Cr^{2+}(aq)$ and $Mn^{2+}(aq)$ are left to stand in the air.
Use relevant $E^\ominus$ values from the *Data Booklet* to predict whether a reaction occurs in the samples after some time. [2]

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(c) At high temperatures, water and carbon monoxide undergoes the following reaction in the presence of nickel catalyst.

$$H_2O(g) + CO(g) \longrightarrow H_2(g) + CO_2(g)$$

(i) Deduce the type of catalysis and explain how some transition elements, such as nickel, can act as catalyst. [1]

(ii) Outline the mode of action of nickel catalyst in this reaction. [2]

(d) **I** and **J** are two elements in period 3.

When oxides of **I** and **J** are added to water separately, the pH of the resultant solutions is 7. When NaOH(aq) is added to each oxide, only the oxide of **I** dissolves to form a colourless solution.

Suggest the identity of **I** and **J** and write equations for any reactions that occurred. [3]

(e) Aldehydes can react with hydroxy compounds to form hemiacetals as shown in Fig. 3.1.

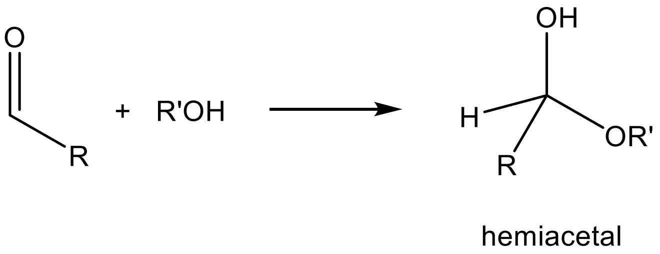

Fig. 3.1

The reaction between propanal and phenol in aqueous sodium hydroxide is a nucleophilic addition reaction. Phenol dissolves in aqueous sodium hydroxide to form phenoxide ions.

(i) Draw the mechanism for this reaction, assuming phenoxide ion as the nucleophile. Show curly arrows, charges, dipoles and any relevant lone pairs. [3]

(ii) Explain why the product cannot rotate plane of polarised light. [2]

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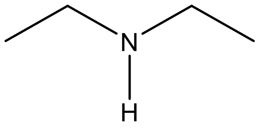
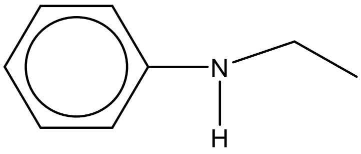
(f) Explain, with the aid of a labelled Boltzmann distribution diagram, the effect on a rate constant of increasing temperature from T_1 to T_2. [3]

(g) Describe and explain the relative basicities of N,N-diethylamine and N-ethylphenylamine. [2]



N,N-diethylamine



N-ethylphenylamine

[Total: 21]

Section B

Answer **one** question in this section.

4 **(a)** Sulfuryl chloride, SO_2Cl_2, is often used as a source of Cl_2 for various organic reactions. When heated, it decomposes as shown.

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

13.51 g of SO_2Cl_2(g) and 3.55 g of Cl_2(g) was introduced in a container at 550 K and left to equilibrate. The total amount of gases at equilibrium was found to be 0.225 mol, and the total pressure of gases was 5.00 atm.

(i) Write an expression for the equilibrium constant for the decomposition reaction, K_p, stating its units. [1]

(ii) Use your expression to calculate the value of K_p for this reaction. [4]

(b) Under industrial conditions, gases do not behave ideally.
Fig. 4.1 shows how one mole of an ideal gas, one mole of SO_2Cl_2, and one mole of SO_2 behave at a temperature of 550 K.

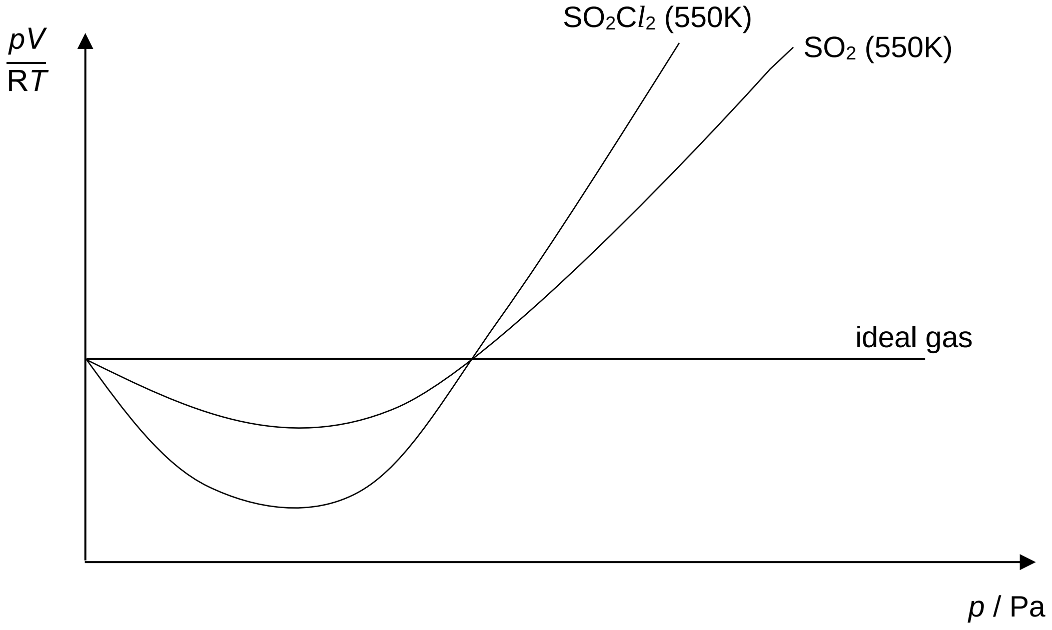


Fig. 4.1

(i) Explain the differences in the behaviour of SO_2 and SO_2Cl_2 at 550 K. [1]

(ii) Sketch how SO_2 will behave at 700 K in Fig. 4.1. Explain your answer. [2]

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(c) SO_3 dissolves in rainwater to form sulfate ions, which are absorbed into the soil.
The sulfate ions formed can react with calcium ions found in the soil. Calcium sulfate, $CaSO_4$, is sparingly soluble in water.

$$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$$

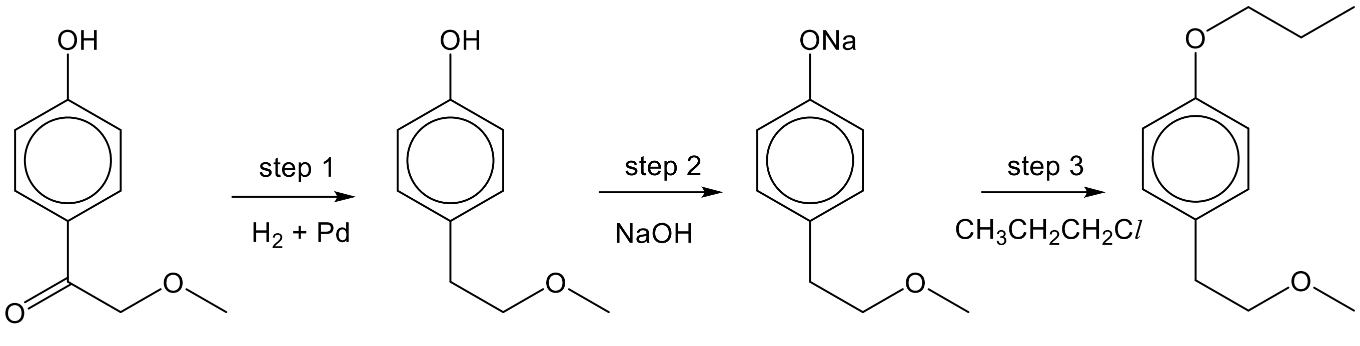
The numerical value of K_{sp} of $CaSO_4$ is 4.93×10^{-5}.

(i) Write an expression for the solubility product, K_{sp}, of $CaSO_4$, stating its units. [1]

(ii) A 20 cm^3 water sample from soil contains 0.010 mol dm^{-3} of calcium ions.
Calculate the minimum amount of sulfate ions that must be present in the soil for the precipitation of calcium sulfate to occur. [2]

(iii) Describe and explain, how the solubility of $CaSO_4$ is affected by adding Na_2SO_4(aq). [1]

(d) The synthesis of compound **K** is shown in Fig. 4.2



K

Fig. 4.2

(i) State the *types of reaction* that occur during each of the steps 1 and 2. [2]

(ii) In step 3, the phenoxide ion readily undergoes a nucleophilic substitution reaction with $CH_3CH_2CH_2Cl$ as shown in Fig 4.3.

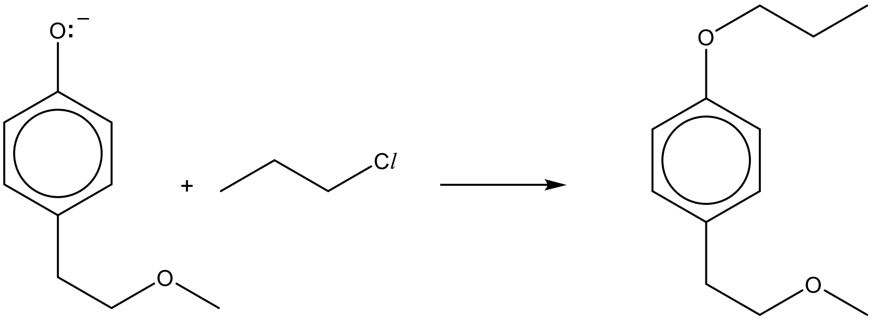


Fig 4.3

On Fig 4.3, draw curly arrows to show the mechanism for this reaction. Show all relevant dipoles in your answer. [1]

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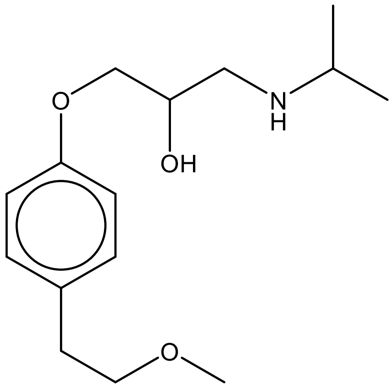
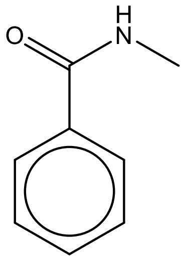
(e) *Metoprolol* and N-methylbenzamide are white solids and insoluble in water. A student accidentally added N-methylbenzamide to a sample of metoprolol.



metoprolol



N-methylbenzamide

(i) Outline how metoprolol can be obtained as a solid from the mixture. [2]

(ii) N-methylbenzamide can be synthesised from benzoic acid. Suggest reagents and conditions for each step. Draw the structure of the intermediate compound. [3]

[Total: 20]

5 **(a)** Methanoic acid can be oxidised by bromine to form carbon dioxide gas.

$$HCO_2H(aq) + Br_2(aq) \rightarrow CO_2(g) + 2H^+ + 2Br^-(aq)$$

The rate of the oxidation reaction can be followed by measuring the concentration of aqueous bromine remaining after various times at a constant temperature.

The following reaction mixture was prepared for this experiment.

initial $[Br_2]$ = 0.0500 mol dm^{-3}
initial $[HCO_2H]$ = 0.500 mol dm^{-3}

Fig 5.1 shows the graph obtained from the experiment.

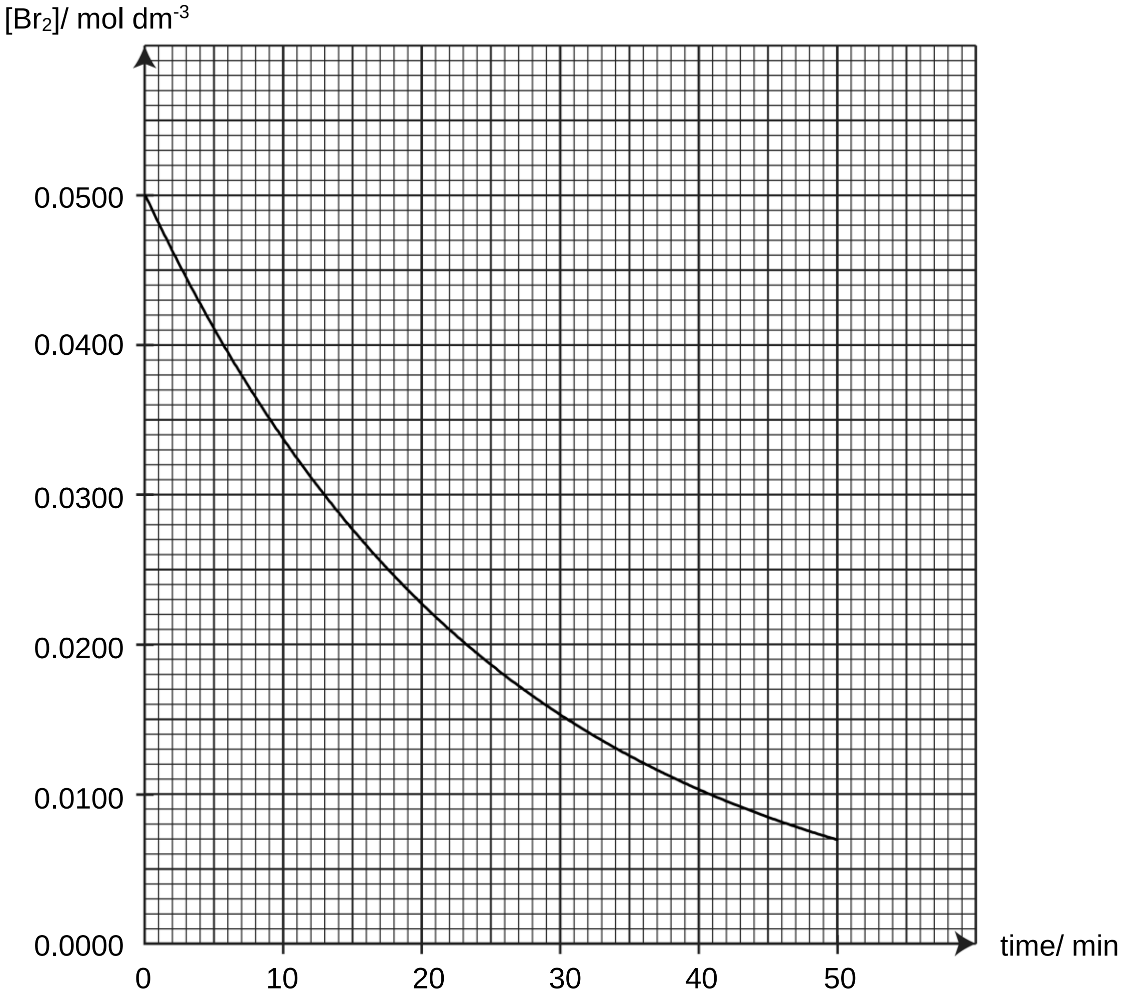


Fig. 5.1

(i) Using the graph in Fig 5.1, show that the order of reaction with respect to $[Br_2]$ is 1. Show all working and draw clearly any construction lines on Fig 5.1. [2]

(ii) The rate of the reaction is directly proportional to the $[HCO_2H]$. Use the information given to write the overall rate equation for the oxidation reaction. [1]

(iii) The experiment was repeated using 0.0400 mol dm^{-3} of Br_2 and 0.500 mol dm^{-3} of HCO_2H. The initial rate is found to be 1.54×10^{-3} mol dm^{-3} s^{-1}.
Use this information, and your answer in **(a)(ii)** to calculate the value for rate constant. State its unit. [2]

(b) Methanoic acid and sodium methanoate forms a buffer.

$$HCO_2H \rightleftharpoons HCO_2^- + H^+ \qquad K_a = 1.77 \times 10^{-4} \text{ at } 298K$$

Sodium methanoate is formed when methanoic acid reacts with NaOH(aq) as shown.

$$HCO_2H + NaOH \rightarrow HCO_2Na + H_2O$$

The above buffer of pH 3.85 is prepared using 45 cm^3 of 0.0200mol dm^{-3} HCO_2H and x mol of solid NaOH.

Assume that all the NaOH reacts with HCO_2H to form HCO_2Na.

(i) Explain what is meant by a *buffer* solution. [1]

(ii) Calculate the amount, x, of NaOH required to make a buffer solution of pH 3.85. [3]

(c) **(i)** In terms of structure and bonding, explain why HCO_2H is a liquid while HCO_2Na is a solid at room temperature. [2]

(ii) HCO_2H is soluble in water.
Draw a diagram to illustrate the type of interaction between HCO_2H and a water molecule.
Show any relevant dipoles. [1]

(d) Magnesium forms an important group of covalent compounds known as Grignard reagents. An example of a Grignard reagent is CH_3CH_2MgBr, which is a source of the carbanion, $CH_3CH_2^-$.

Grignard reagents can be used in the synthesis of butanone from nitrile compounds as shown in Fig. 5.2.

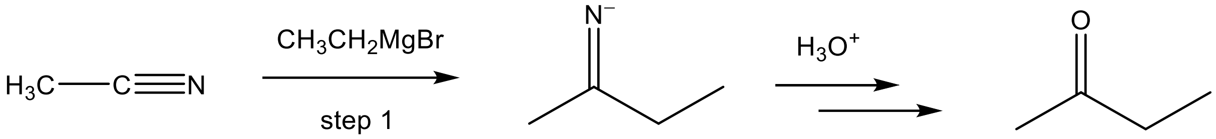


Fig. 5.2

(i) The reaction between CH_3CH_2MgBr and CH_3CN in step 1 is a nucleophilic addition reaction. Suggest why CH_3CH_2MgBr reacts with CH_3CN but does not react with propyne, $CH_3C{\equiv}CH$. [2]

(ii) The presence of butanone can be confirmed using alkaline aqueous iodine. State the expected observation and draw the structure of the organic products formed. [2]

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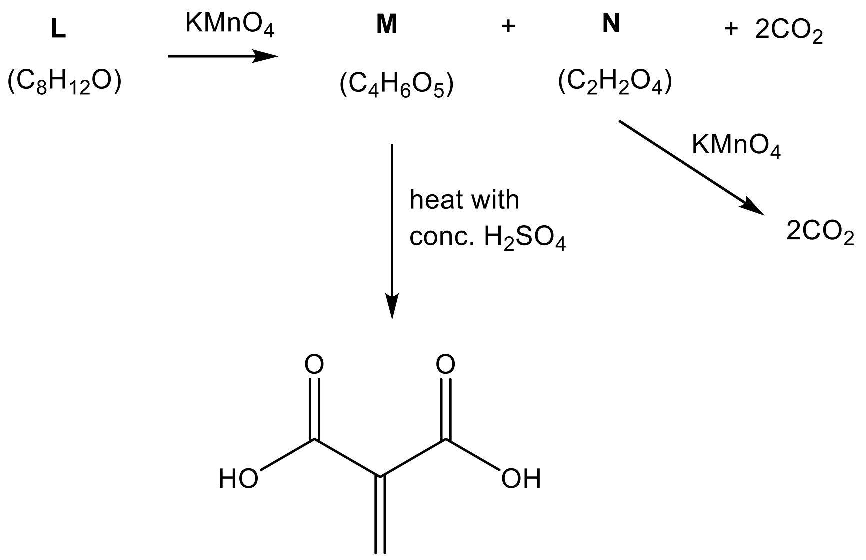
(e) Hot, concentrated potassium manganate(VII) oxidises organic compounds to ketones, carboxylic acids or carbon dioxide. By this means, the structures of compounds can be determined.

The following scheme shows the reactions of compounds **L** and its oxidation products.



(i) Compound **M** effervesces with sodium metal but does **not** react with warm acidified potassium dichromate(VI). Explain these observations. [1]

(ii) Suggest structures for compounds **L**, **M** and **N**. [3]

[Total: 20]

Additional Answer Space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.