RAFFLES INSTITUTION
2024 YEAR 6 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME			
CLASS		INDEX NUMBER	

CHEMISTRY 9729/02

Paper 2 Structured Questions **10 September 2024**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not open this question booklet until you are told to do so.

Write your name, class and index number in the spaces at the top of this page.
Write in dark blue or black pen.
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.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided. Do not write anything in it.
You are reminded of the need for good English and clear presentation in your answers.

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	
1	**/ 15**
2	**/ 19**
3	**/ 22**
4	**/ 19**
Total	**/ 75**

This document consists of **24** printed pages.

Answer **all** questions in the space provided.

1 Boron and its compounds have diverse applications across industries.

(a) **(i)** Write an equation to represent the fourth ionisation energy of boron.

……..…..... [1]

(ii) Explain why the fourth ionisation energy of boron is much higher than that of carbon.

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……..…..... [2]

(b) Borane, BH_3, is a useful compound of boron.

Borane undergoes complete combustion in excess oxygen to form boron trioxide, B_2O_3, as shown in equation 1.

equation 1

$$BH_3(g) + \frac{3}{2}\ O{=}O\ (g) \xrightarrow{\Delta H_r} \frac{1}{2}\ O{=}B{-}O{-}B{=}O\ (g) + \frac{3}{2}\ H{-}O{-}H\ (g)$$

(i) Draw a dot-and-cross diagram of the BH_3 molecule.

[1]

(ii) State the shape and bond angle in BH_3.

……..…..... [2]

(iii) Table 1.1 shows some bond energy data.

Table 1.1

bond	bond energy / kJ mol^{-1}
B–B	293
B–H	330
B–O	536
B=O	837

Use the data in Table 1.1, together with data from the *Data Booklet*, to calculate the enthalpy change, ΔH_r, for the reaction in equation 1.

[2]

(iv) Boron trioxide, B_2O_3, is a relatively inert glass-like solid at 298 K.

The standard enthalpy change of combustion of borane, $BH_3(g)$, is more exothermic than ΔH_r. Explain why.

……

……

…… [1]

(c) At certain temperatures, BH_3 dimerises into diborane, B_2H_6.
Similarly, $AlCl_3$ also dimerises to form Al_2Cl_6.

(i) Explain why $AlCl_3$ can undergo dimerisation.

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…… [1]

(ii) By considering the shape around the Al atom, state the change in hybridisation of the Al atom when $AlCl_3$ dimerises to Al_2Cl_6.

…… [1]

Fig. 1.1 shows the structure of B_2H_6.

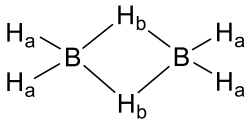


Fig. 1.1

(iii) The central hydrogen atoms, H_b, bond to both boron atoms. Two electrons are shared across the three atoms in $B{-}H_b{-}B$.

Explain why the $B{-}H_b$ bond is longer than $B{-}H_a$ bond.

……

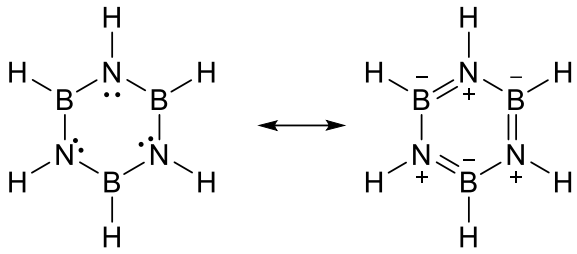
……

…… [1]

(d) Borazine, $B_3N_3H_6$, is similar in structure to benzene and consists of a six-membered ring with alternating boron and nitrogen atoms.

(i) The borazine structure can be represented by two different resonance structures, **X** and **Y**, as shown in Fig. 1.2. The arrow ⟷ indicates that the actual structure of borazine is somewhere in between these two structures.

Complete Fig. 1.2 by adding curly arrows to structure **X**.



X **Y**

Fig. 1.2

[1]

(ii) Explain why borazine is less resonance stabilised than benzene.

……

…… [1]

(iii) Borazine undergoes addition reactions due to the less resonance stabilised structure.

X accounts for the major products formed from addition reactions of borazine.

When one mole of **X** reacts completely with three moles of HC*l*, compound **Z** is formed as the only product. Draw the structure of **Z**.

[1]

[Total: 15]

2 Water chemistry plays a critical role in the well-being of fishes in an aquarium. Fish waste releases ammonia into water which is toxic to fish. During nitrification, ammonia is broken down by beneficial bacteria into less toxic nitrate ions as shown in Fig. 2.1.

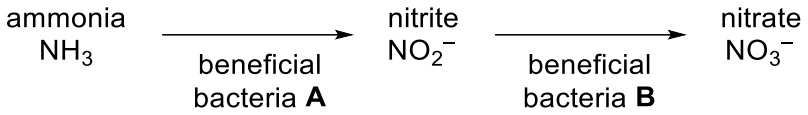


Fig. 2.1

(a) (i) Under acidic conditions, the equation for nitrification is shown.

$$NH_4^+ + 2O_2 \longrightarrow 2H^+ + NO_3^- + H_2O$$

Use relevant standard redox potentials from the *Data Booklet* to show that this reaction is spontaneous under standard conditions.

[1]

(ii) Despite nitrification being spontaneous under the conditions in an aquarium, the presence of beneficial bacteria is necessary for any appreciable breakdown of NH_4^+ to be observed.

Suggest the role of beneficial bacteria in the nitrification process.

…….…..... [1]

(b) Setting up a new aquarium involves establishing colonies of beneficial bacteria in the tank before fish are added. Ammonia is added daily and the concentrations of different water parameters are monitored. Fig. 2.2 shows a graph of some water parameters over 35 days.

The presence of the respective products in Fig. 2.1 indicates that the beneficial bacteria has been established.

Fish can only be safely added after the concentration of NO_2^- increases then decreases to 0 ppm as NO_2^- is also toxic to fish.

The total ammonia nitrogen, TAN, measured is the sum of the concentrations of NH_3 and NH_4^+.

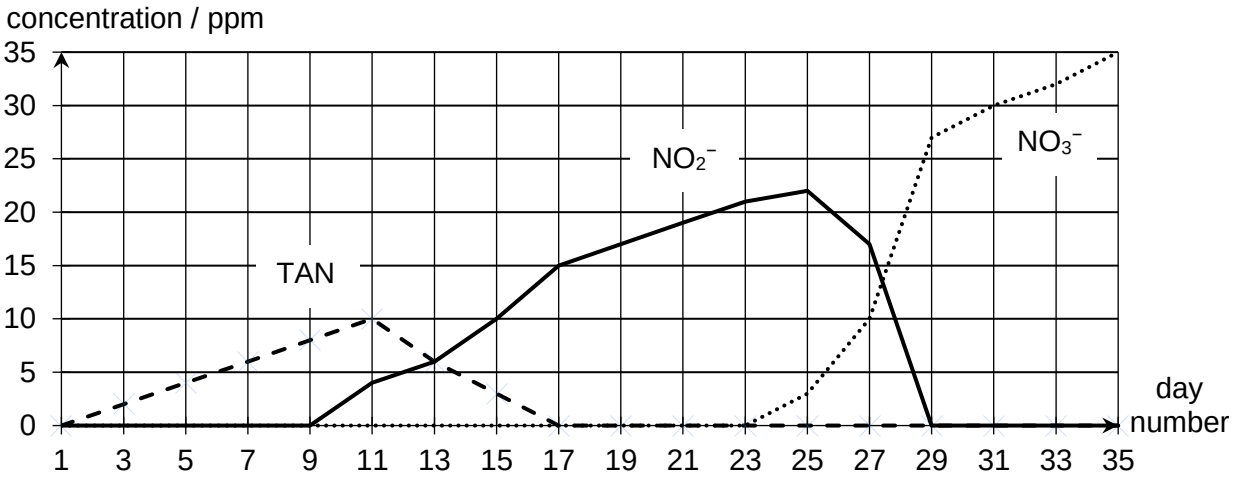


Fig. 2.2

(i) State the day number that first indicates that beneficial bacteria **A** is established.

……..…..... [1]

(ii) State the day number that is first safe for the addition of fish.

……..…..... [1]

(iii) On day 35, 25% of the tank water is replaced with water that is free of NO_3^-.

Calculate the new concentration of NO_3^-, in ppm.

[1]

(iv) At pH 7.4, ammonia released by fish waste exists as a mixture of NH_3 and NH_4^+. The mole fraction of ammonia in the mixture, z, can be calculated as follow.

$$z = \frac{[NH_3]}{TAN}$$

Calculate z for a sample of tank water at pH 7.4 on day 11.

The pK_a for NH_4^+(aq) is 9.25.

[2]

(c) In another aquarium, the tank water's buffering capacity is due to the presence of carbonate, CO_3^{2-}, and bicarbonate, HCO_3^-.

(i) Write two equations to show how the tank water behaves as a buffer when small amounts of OH^-(aq) and H_3O^+(aq) are separately added to it.

……

…… [2]

(ii) The nitrification process produces H^+ which can cause the pH of tank water to decrease.

Carbonate hardness is a measure of the total concentration of CO_3^{2-} and HCO_3^-.

Suggest why tank water with a higher carbonate hardness is better at maintaining its pH.

……

…… [1]

(d) The recommended range for the concentration of dissolved oxygen in aquarium water samples is 1.50×10^{-4} to 5.00×10^{-4} mol dm^{-3}.

The concentration of dissolved oxygen in aquarium water can be determined by first adding $Mn(OH)_2(s)$ to the water.

$$H_2O(l) + 2Mn(OH)_2(s) + \frac{1}{2}O_2(aq) \longrightarrow 2Mn(OH)_3(s)$$

Excess $I^-(aq)$ is then added and the following reaction occurs to produce I_2.

$$2Mn(OH)_3(s) + 2I^-(aq) + 6H^+(aq) \longrightarrow 2Mn^{2+}(aq) + I_2(aq) + 6H_2O(l)$$

The I_2 produced can then be titrated with a standard solution of sodium thiosulfate using starch as an indicator.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

(i) A 100 cm^3 of sample of aquarium water containing dissolved oxygen required 13.40 cm^3 of 0.0100 mol dm^{-3} sodium thiosulfate solution to reach the end point.

Calculate the concentration of dissolved oxygen in this sample, in mol dm^{-3}, and hence determine if it falls within the recommended range.

[3]

(ii) Azide, N_3^-, is added to the titration in **(d)(i)** to prevent NO_2^- in aquarium water from reacting with I^-. N_3^- reacts with NO_2^- to give nitrogen gas as the only nitrogen-containing product.

With the aid of half-equations, write a balanced equation for the reaction between N_3^- and NO_2^- under acidic conditions.

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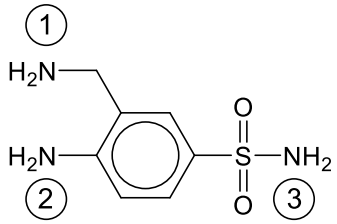
……

…… [2]

(e) Compound **P** can be used to test for NO_2^- and has a sulfonamide functional group, $-SO_2NH_2$, that has similar basicity to an amide.



compound **P**

Describe and explain the relative basicities of the three nitrogen-containing groups in compound **P**.

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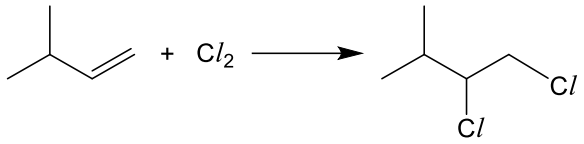
…… [4]

[Total: 19]

3 This question explores the reactions of short-chain hydrocarbons and halogenoalkanes.

(a) 3-Methylbut-1-ene reacts with chlorine gas in the dark to give compound **D**, as shown in Fig. 3.1.



D

Fig. 3.1

(i) Draw the three-dimensional structures of the two enantiomers of **D**.

[1]

(ii) By considering the shape of the intermediate formed during the reaction in Fig. 3.1, explain whether the product mixture rotates plane-polarised light.

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…… [2]

Fig. 3.2 shows the electrophilic addition of bromine to alkenes via a different type of intermediate from that in Fig. 3.1.

The stereochemistry of the product depends on the stereochemistry of the starting alkene.

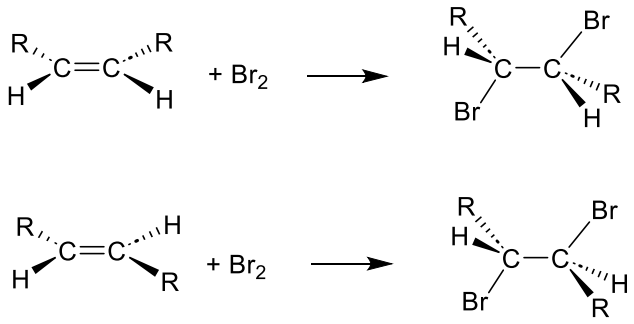

Fig. 3.2

(iii) A meso compound contains more than one chiral carbon with an internal plane of symmetry.

When an alkene **E**, C_4H_8, reacts with liquid bromine in the dark, a meso compound is produced.

With reference to Fig. 3.2, deduce the three-dimensional structures of **E** and the product.

E	product

[2]

(b) Rearrangement may occur when a carbocation is formed in a reaction. This typically involves the migration of a hydride or an alkyl group from a carbon adjacent to the positively charged carbon.

Fig. 3.3 shows the reaction between 3-methylbut-1-ene and hydrogen bromide.

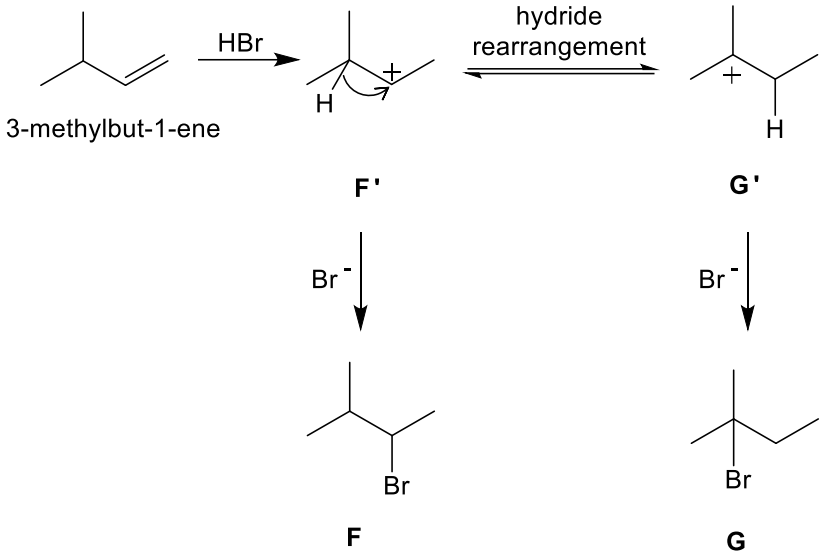

Fig. 3.3

(i) Using the concept of electronic effect, explain why **G** is produced in a larger proportion.

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…… [2]

The reaction in Fig. 3.4 proceeds via the S_N1 mechanism. Alkyl rearrangement results in the formation of **K** and **L**.

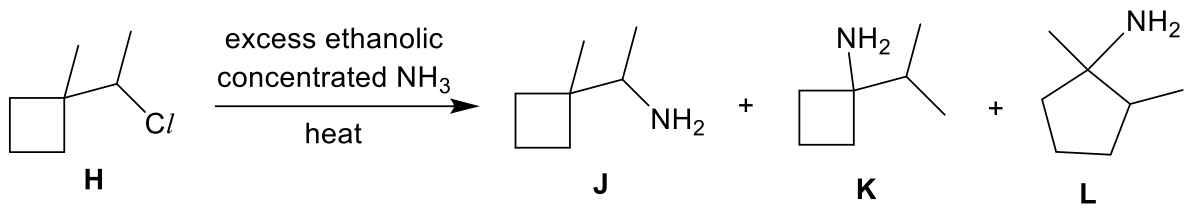

Fig. 3.4

(ii) On Fig. 3.5, draw a curly arrow for step B to show the alkyl rearrangement. [1]

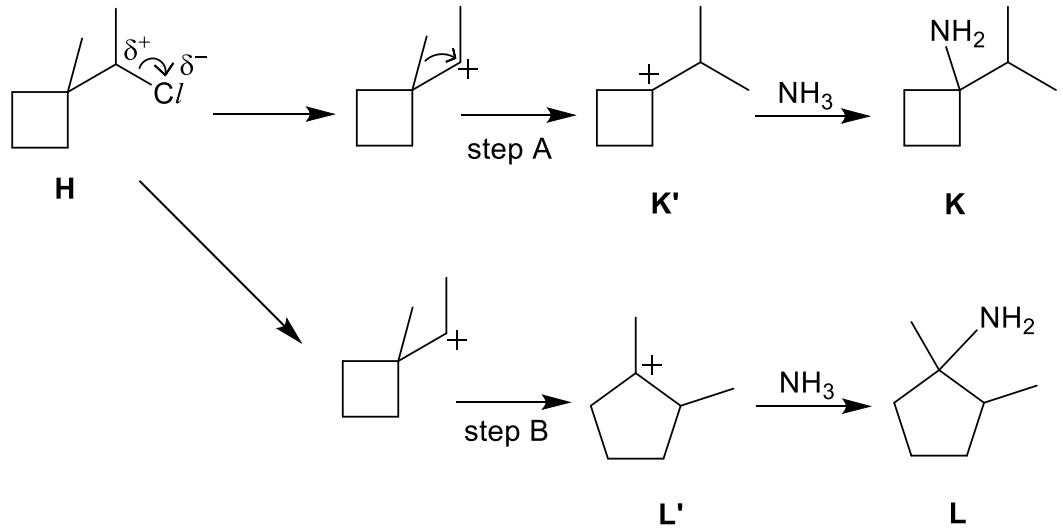

Fig. 3.5

(iii) Deduce whether **K** or **L** is the major product. Explain your answer.

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…… [1]

(c) Alkenes react with borane, BH_3, in the presence of hydrogen peroxide to give an alcohol, as shown in Fig. 3.6.

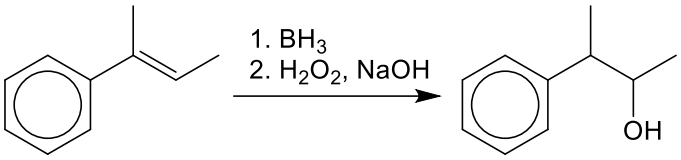


Fig. 3.6

(i) Use this information to complete the reaction scheme involving 3-methylbut-1-ene in Fig. 3.7. Draw the structures of **M** and **P** and state the reagent for step 2.

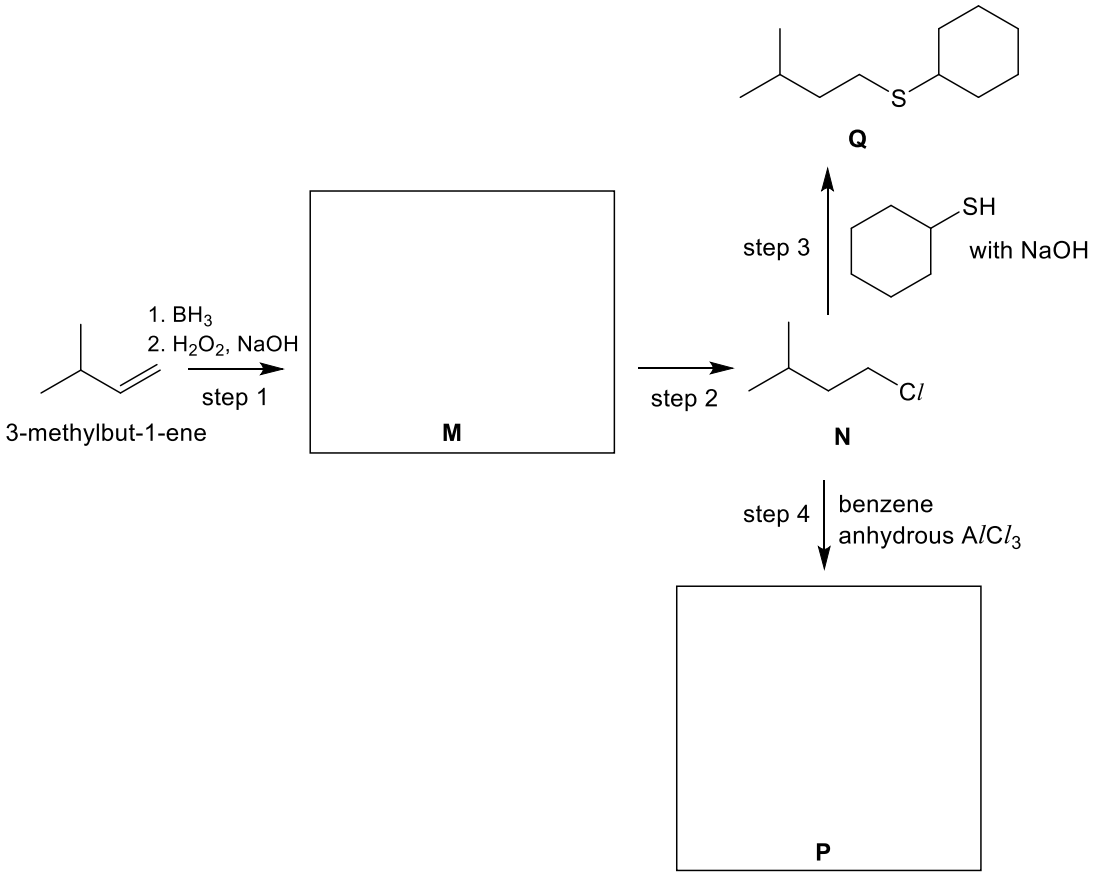


Fig. 3.7

reagent for step 2: ……. [3]

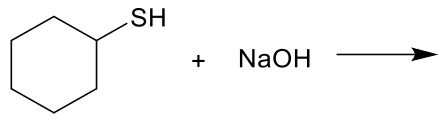
(ii) Give the systematic name for compound **N**.

…… [1]

(iii) State the type of reaction occurring in step 4.

…… [1]

(iv) The reagents used in step 3 are involved in an acid-base reaction.
Complete the equation below.



[1]

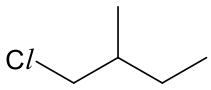
(v) Based on your answer in **(c)(iv)**, describe the mechanism to show the formation of **Q** from **N**.

Show all the partial charges, relevant lone pairs and show the movement of electron pairs by using curly arrows.

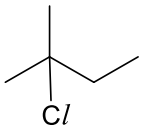
You may represent **N** as R−CH_2Cl.

[3]

3-Methylbut-1-ene can react to form compounds **S** and **T**.



S



T

(vi) Suggest a simple chemical test to distinguish between **S** and **T**.

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…… [2]

(d) 3-Methylbut-1-ene is a precursor to the production of chlorofluorocarbons, CFCs, which were once used as refrigerant fluids and propeller aerosols.

(i) Indiscriminate use of CFCs has resulted in ozone depletion.

Briefly explain how CFCs contribute to ozone depletion.

……

……

…… [1]

CFCs have been gradually replaced by hydrofluorocarbons, HFCs.

Table 3.1 provides some information regarding CFC−11 and HFC−23.

Table 3.1

name	structure	GWP
HFC−23	CHF_3	14800
CFC−11	$CFCl_3$	4750

Global warming potential, GWP, indicates the amount of heat trapped by 1 tonne of a gas relative to the amount of heat trapped by 1 tonne of CO_2 over a specified period.

(ii) Explain how the replacement of CFCs by HFCs is detrimental to the environment.

……

…… [1]

[Total: 22]

4 (a) (i) Define the terms *order of reaction* and *rate constant*.

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……

…… [2]

Question 4 continues on page 20.

When ethanal, CH_3CHO, reacts with hydroxyl radicals, •OH, the reaction shown in equation 1 takes place.

equation 1 $\quad CH_3CHO + \bullet OH \rightarrow CH_3\dot{C}O + H_2O$

The reaction was studied at 298 K and the initial $[CH_3CHO]$ was much higher than $[\bullet OH]_0$, the initial concentration of •OH.

In this experiment, the ratio of concentration of •OH at a particular time, relative to its initial concentration, is represented by $\frac{[\bullet OH]}{[\bullet OH]_0}$.

Fig. 4.1 shows the graph of $\frac{[\bullet OH]}{[\bullet OH]_0}$ against time for this experiment.

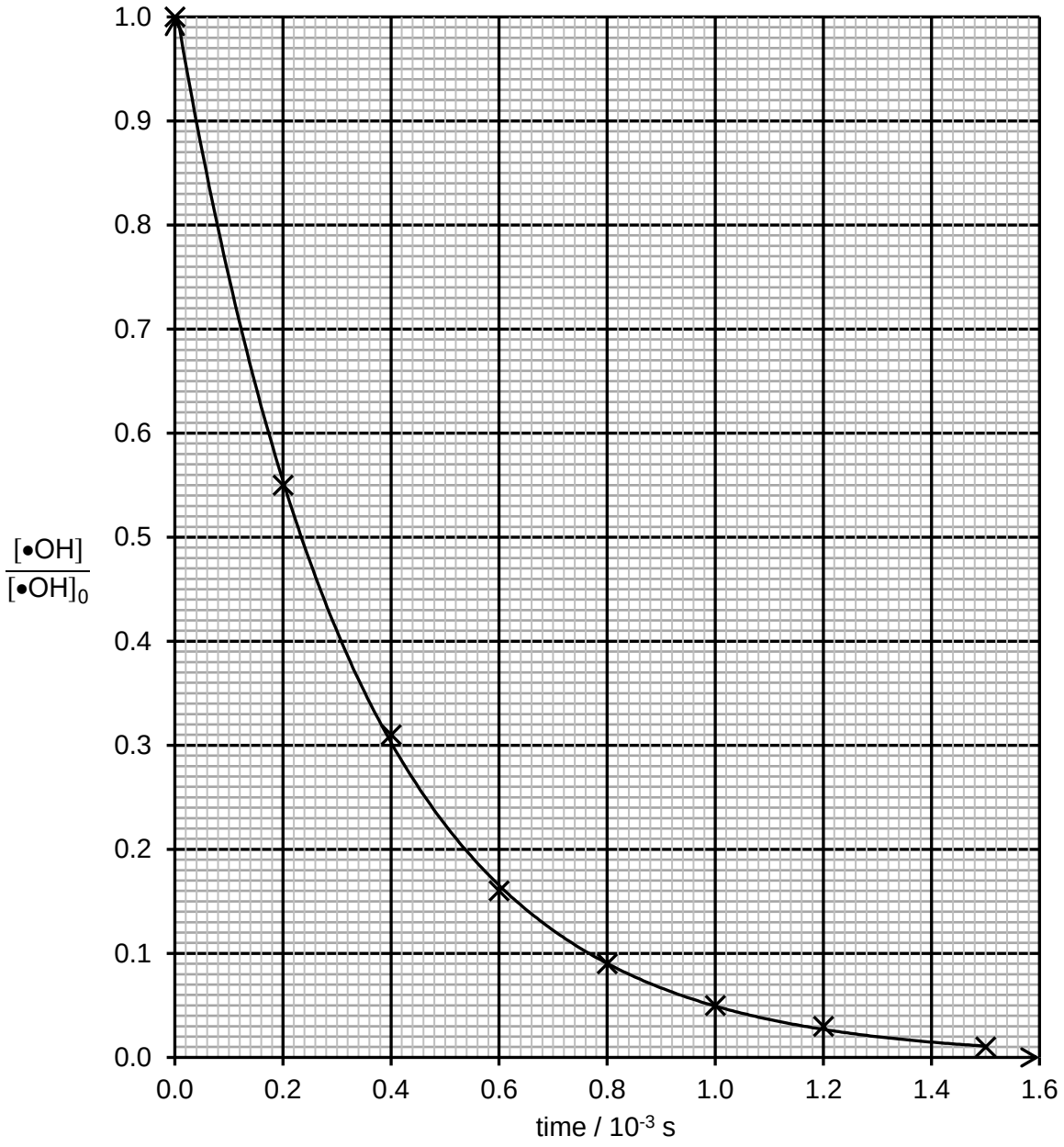

Fig. 4.1

(ii) Use Fig. 4.1 to determine the order of reaction with respect to •OH.

Assume that $\frac{[\bullet OH]}{[\bullet OH]_0}$ is equivalent to the concentration of •OH.

[2]

The reaction is known to follow pseudo–order kinetics, where the pseudo–order rate constant, $k' = k[CH_3CHO]^n$.

More experiments were conducted to explore the relationship between k' and the concentration of CH_3CHO. The results of these experiments are shown in Fig. 4.2.

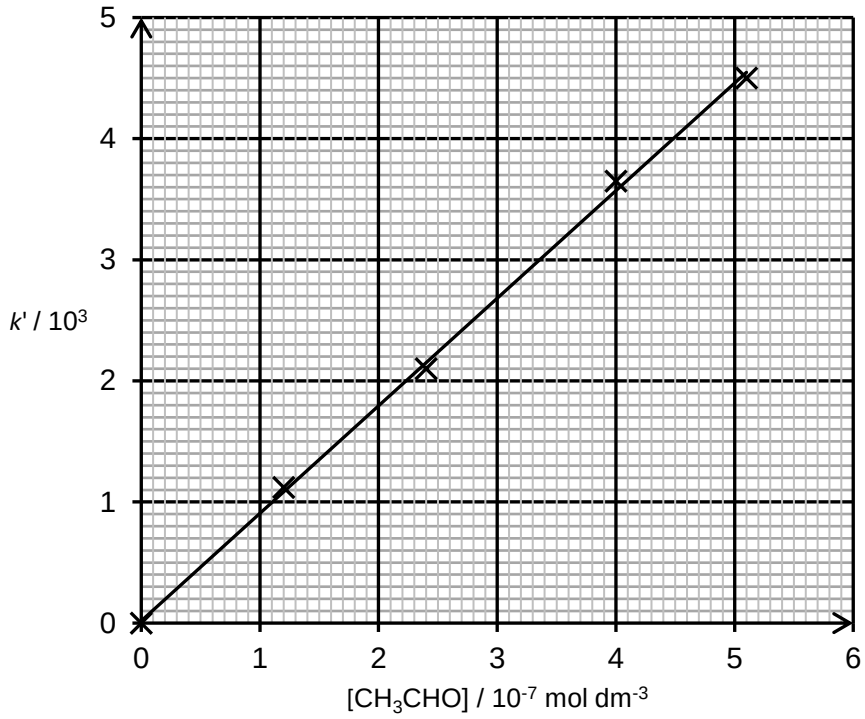

Fig 4.2

(iii) Use Fig. 4.2 to deduce the order of reaction with respect to CH_3CHO, and hence determine the value of the rate constant, *k*, for the reaction.

[2]

(iv) Hence, write the rate equation for the reaction in equation 1.

……..…..... [1]

(v) It is proposed that the reaction shown in equation 1 takes place in a single, elementary step. Using your answer in **(a)(iv)**, suggest if you agree with this proposal, giving your reasons.

……..….....

……..….....

……..…..... [1]

(vi) Suggest how the presence of a catalyst would affect the magnitudes of the rate constant, *k*, and activation energy, E_a, of the reaction in equation 1.

……..….....

……..…..... [1]

(b) The hydroxyl radical, •OH, is often referred to as the "detergent" of the atmosphere, as it eliminates pollutants and greenhouse gases like CH_4 by reacting with them via free radical substitution.

- The first step of this reaction involves the removal of a hydrogen atom from CH_4 by •OH, forming water and a methyl radical.
- The second step involves the reaction of the methyl radical with O_2, forming a radical with an O–O single bond as the only product.

The radical formed then undergoes further reactions to form more stable molecules such as CH_3OH and HCHO.

(i) Use the information given above to draw the first and second steps of the mechanism for the reaction between •OH and CH_4. Use curly arrows to show movement of electrons.

[4]

(ii) Draw the labelled energy profile diagram for the first two steps of the reaction between •OH and CH_4, given that the overall enthalpy change for the first and second steps is exothermic. Label the overall enthalpy change, ΔH, on your diagram.

[2]

(c) •OH may be generated by Fenton's reagent, which is an aqueous mixture of hydrogen peroxide, H_2O_2, and iron(II) sulfate, $FeSO_4$. The reactions shown in equations 2 and 3 take place in the mixture.

equation 2 $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^-$
equation 3 $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\bullet + H^+$

(i) Write the equation for the overall reaction.

……..…..... [1]

(ii) Using equations 2 and 3, deduce the role of Fe^{2+} in the overall reaction. Explain your reasoning.

……..….....

……..….....

……..…..... [2]

(iii) Fenton's reagent is used to generate •OH in the study of organic reactions.

However, after a small amount of •OH is generated, "quenching" or stopping of the reaction progress is sometimes required.

Suggest a method of "quenching" the reaction, without changing the temperature.

……..….....

……..…..... [1]

[Total: 19]