EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2024
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	

CIVICS GROUP	2	3	–				INDEX NUMBER		

CHEMISTRY

9729/03

Paper 3 Free Response

12 September 2024
2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, civics group, index number on all the work you hand in.
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. If addition 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	
Paper 3	
Section A	
1	/20
2	/20
3	/20
Section B	
4	/20
5	/20
Total	**/80**

This document consists of **31** printed pages and **1** blank page.

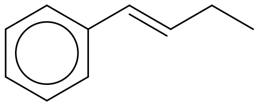
BLANK PAGE

Section A

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

1 Alkenylbenzene molecules are secondary plant metabolites with certain levels of toxicity, despite their presence in herbs and spices. One type of alkenylbenzene is (2-ethylethenyl)benzene.

(a) (2-ethylethenyl)benzene exhibits stereoisomerism and exists as a pair of stereoisomers **L** and **M**. The structure of **M** is as shown.



compound **M**

(i) State the type of stereoisomerism exhibited by (2-ethylethenyl)benzene. [1]

(ii) Draw the skeletal structure of **L**. [1]

(iii) Draw the structure of a constitutional isomer of **M** that fulfils the following criteria:

- does not exhibit the stereoisomerism stated in **(a)(i)**
- has a non-terminal alkene [1]

....

....

....

....

....

....

....

....

....

....

....

....

(b) When a pure sample of **L** is left to stand, a portion of it converts to **M**. The mixture will then eventually achieve equilibrium, as illustrated in the following equation.

$$\mathbf{L} \rightleftharpoons \mathbf{M}$$

Fig. 1.1 shows a sketch of how the Gibbs free energy of the mixture of **L** and **M** varies with the composition of the mixture at a particular temperature. The slope of the graph at each point corresponds to ΔG of the conversion of **L** to **M**.

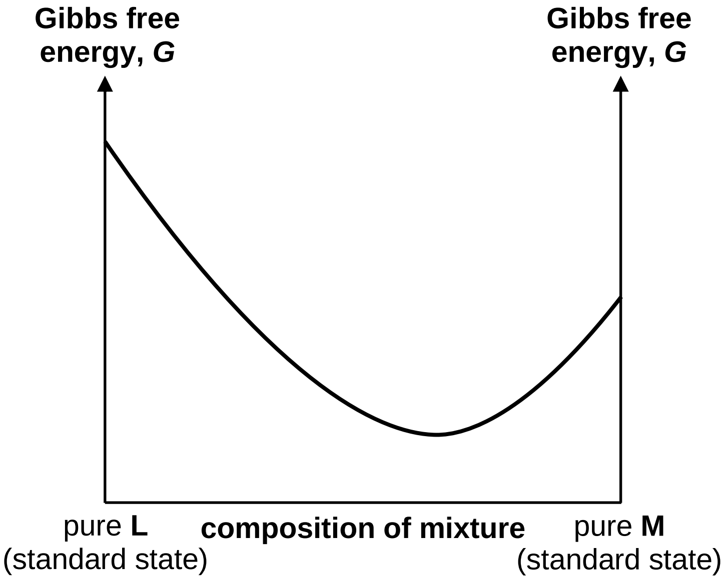


Fig. 1.1

(i) Given that the K_c value of this equilibrium at the temperature given is 5.25, calculate the equilibrium concentration of **L** when 1.30 mol dm^{-3} of pure **L** was placed in an empty reaction chamber and allowed to reach equilibrium. [2]

(ii) Label Fig. 1.1 with a cross (×) to show the composition of the mixture of **L** and **M** at equilibrium. [1]

(iii) With reference to the structures of **L** and **M**, explain why the minimum point of the graph in Fig. 1.1 lies closer to the point of pure **M**. [1]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

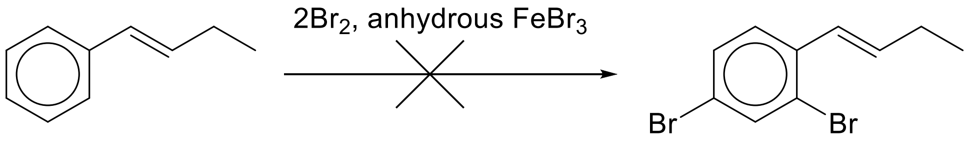
....

....

....

....

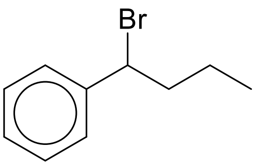
(c) An attempt to synthesise **N** by mixing one mole of **M** with **two moles** of Br_2 in the presence of anhydrous $FeBr_3$ in the dark, was not successful.



M **N**

(i) Draw the skeletal structure of the major product obtained instead. [1]

(ii) A trace amount of **P** was obtained as a by-product. Suggest how **P** was formed during the reaction. [1]



P

The student then changed **M** to **Q** and changed the amount of **Q** and Br_2 used to one mole each, while keeping the other conditions the same. This caused the student to obtain **R**, the 4-bromo product, as the major product, as shown in Fig. 1.2.

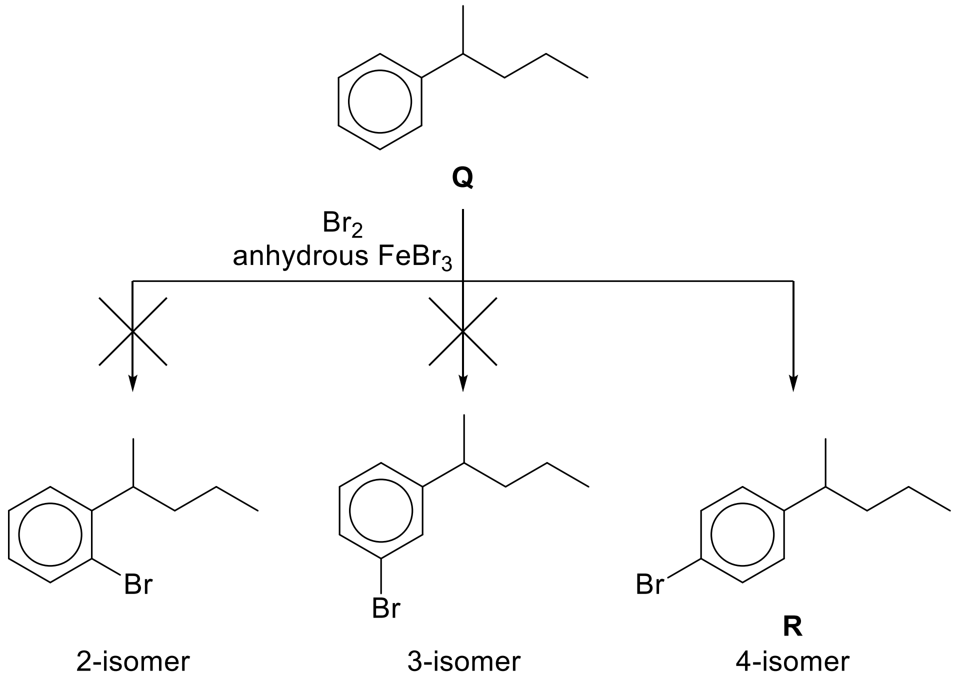


Fig. 1.2

The generation of the electrophile for this reaction is as shown.

$$Br_2 + FeBr_3 \rightleftharpoons Br^+ + FeBr_4^-$$

(iii) Draw the mechanism for the reaction between **Q** and Br_2 to form **R**. [2]

(iv) Explain why **R** is preferentially formed over the 2-isomer and 3-isomer. [2]

(v) With the aid of an equation, explain if **R** can be formed when Br_2 and anhydrous $FeCl_3$ were used instead. [1]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

(d) Photoelectron spectroscopy is an experimental technique used to measure the energies of electrons in atoms and ions, such as Cr and Ag^+. A typical photoelectron spectrum plots the relative number of electrons against energy absorbed to remove the electrons, as exemplified by the photoelectron spectrum of boron in Fig. 1.3, which has the electronic configuration $1s^2\ 2s^2\ 2p^1$.

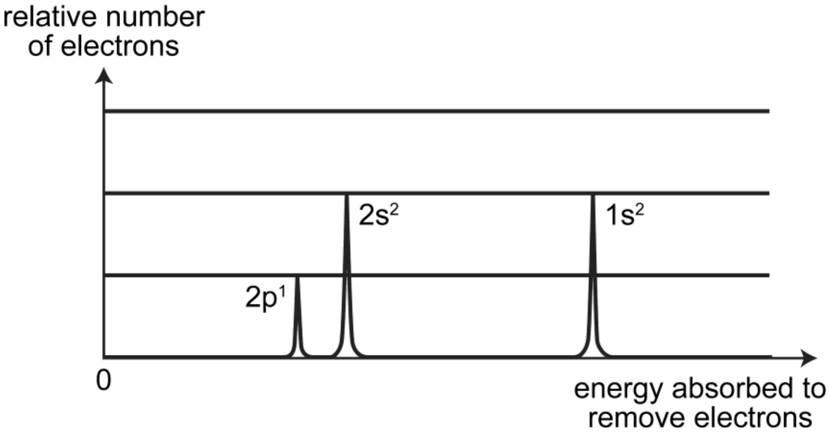


Fig. 1.3

The relative height of each peak corresponds to the number of electrons in that subshell.

(i) Explain why the gap between the peaks corresponding to the 1s and 2s subshells is much larger than the gap between the peaks corresponding to the 2s and 2p subshells. [2]

....

....

....

....

....

....

....

....

Fig. 1.4 shows a sketch of the photoelectron spectrum of the **valence shell** of **X**$^{2+}$, where **X** is a first-row transition element.

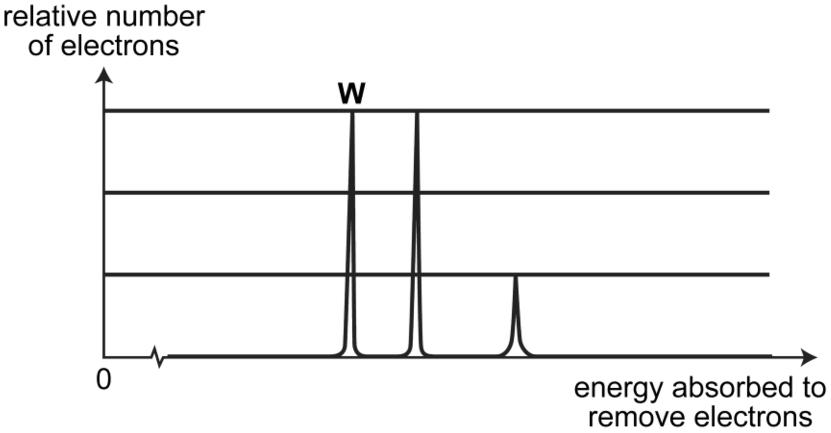


Fig. 1.4

(ii) State two orbitals in the subshell corresponding to peak **W** that have different shapes from each other. [1]

(iii) Identify **X**$^{2+}$ and explain your answer briefly using Fig. 1.4. [2]

(iv) Identify another ion with a 2+ charge that is a second-row transition element and has a valence shell photoelectron spectrum with the same peak heights as Fig. 1.4. [1]

....

....

....

....

....

....

....

....

....

....

....

[Total: 20]

2 **(a)** The industrial synthesis of methanol involves heating carbon monoxide and hydrogen under controlled conditions in the presence of catalysts.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

temperature / °C	200 to 300
pressure / atm	50 to 100
catalysts	mixture of Cu, ZnO and Al_2O_3

(i) Write the expression for the equilibrium constant, K_p, for this reaction. [1]

(ii) In one of the synthesis, CO and H_2 were added in the molar ratio 1:2. Fig. 2.1 shows the change in the amounts of CO and CH_3OH with time. The temperature was maintained at a temperature of 250 °C and the total pressure at equilibrium is 85 atm.

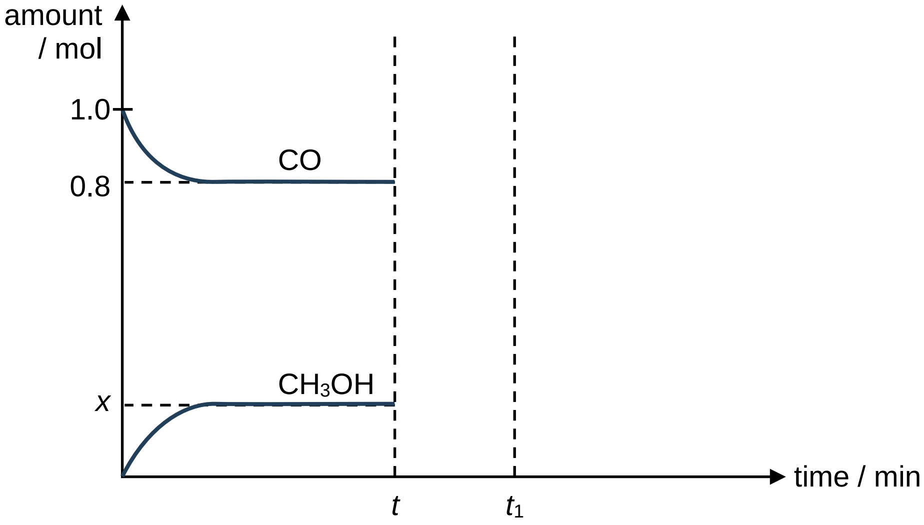


Fig. 2.1

Use the information provided and data from Fig. 2.1 to calculate the equilibrium amount of methanol, x, at 250 °C. [1]

(iii) Hence, calculate the value of K_p for the equilibrium at 250 °C, giving its units. [2]

(iv) At time t, 0.2 mol of $CH_3OH(g)$ was added. Assuming that the volume and temperature in the sealed vessel remains unchanged, sketch the changes in amount of CO and CH_3OH that would be observed from t min in Fig. 2.1 until the new equilibrium is reached at t_1 min. [2]

(v) The reaction to produce CH_3OH is repeated with the same amounts of CO and H_2 at 250 ºC in a bigger vessel. State and explain the effects, if any, of this change on

- rate of producing methanol
- the equilibrium yield of methanol
- the value of K_p [3]

(vi) State the type of catalysis and outline the mode of action of the catalysts in the synthesis of methanol. [3]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

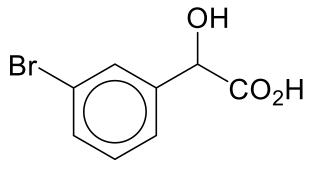
....

....

....

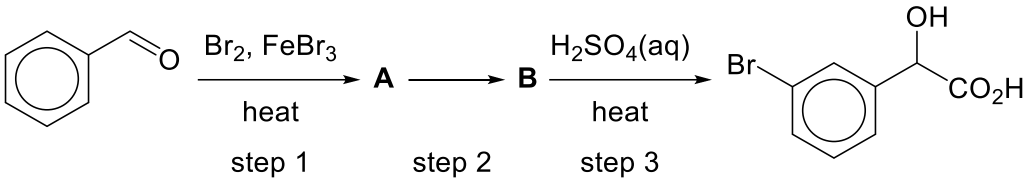
....

(b) Mandelic acid derivatives, including brominated forms like 3-bromomandelic acid, are used in the synthesis of chiral compounds.



3-bromomandelic acid

3-bromomandelic acid can be formed from benzaldehyde in 3 steps.



(i) Suggest the identity of intermediates **A** and **B**. [2]

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

(iii) State the type of reaction in step 3. [1]

(iv) Suggest a chemical test to distinguish between benzaldehyde and 3-bromomandelic acid. Include the reagents and conditions used, and the observations for each compound. [2]

(v) In many brominated organic compounds, the Br will be converted to a hydroxy group in the presence of hot aqueous sodium hydroxide. Explain whether this conversion will take place for 3-bromomandelic acid. [2]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

[Total: 20]

3 Sorbic acid is a natural organic compound used as a food preservative. The traditional route to sorbic acid involves the reaction of malonic acid and crotonaldehyde as shown in Fig. 3.1.

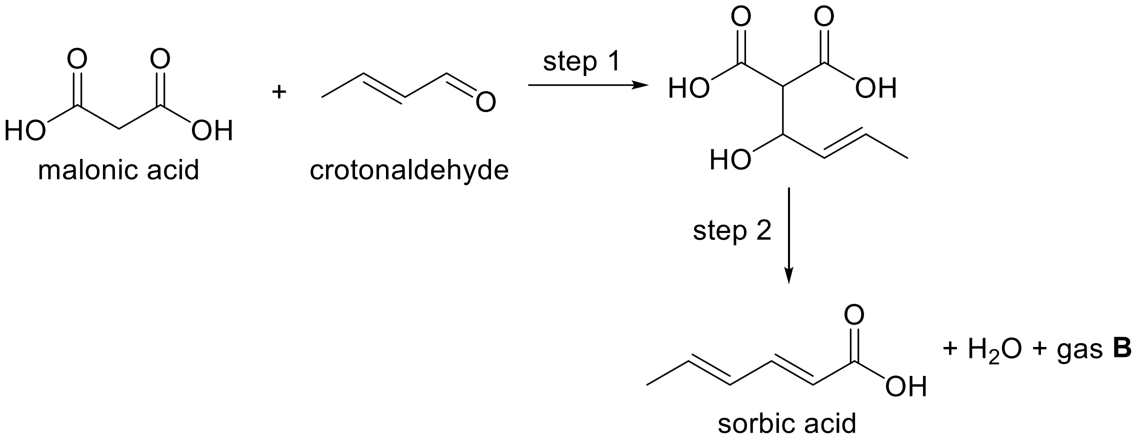


Fig. 3.1

(a) Malonic acid has a K_{a1} of 1.48×10^{-3} mol dm^{-3}, while sorbic acid has a K_a of 1.74×10^{-5} mol dm^{-3}. Explain why K_{a1} of malonic acid is larger than the K_a of sorbic acid. [2]

....

....

....

....

....

(b) **(i)** State the type of reaction for step 1. [1]

(ii) State the identity of gas **B**. [1]

....

....

....

....

(c) **(i)** Explain why the addition of NaOH(aq) to aqueous sorbic acid can result in the formation of a buffer solution. [1]

(ii) Sorbic acid has a pK_a of 4.75.

Deduce the volume of 0.100 mol dm^{-3} NaOH(aq) that must be added to 100 cm^3 of 0.100 mol dm^{-3} sorbic acid to make a buffer solution with a pH of 4.75. [2]

(iii) Another buffer is made by dissolving 0.100 mol of solid sodium sorbate in 100 cm^3 of 1.00 mol dm^{-3} aqueous sorbic acid.

Comparing this buffer with the buffer in **(c)(ii),** explain which buffer is more resistant to changes in pH when a strong acid or a strong base is added. [1]

(iv) A particulate representation of another sorbic acid / sodium sorbate buffer solution is shown in Fig. 3.2.

Is the pH of this buffer greater than, less than, or equal to 4.75? Justify your answer. [1]

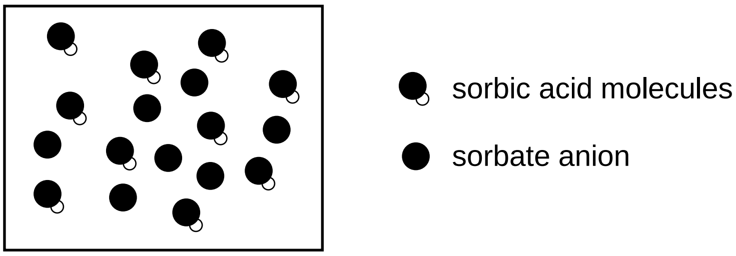


Fig 3.2

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

(d) When sorbic acid reacts with excess hot acidified potassium manganate(VII), only one organic product is formed. Write the structural formula of the organic product. [1]

....

....

Question 3 continues on the next page.

(e) Sorbic acid undergoes controlled oxidation in alkaline potassium manganate(VII) producing ethanedioate ion, $^{-}O_2C–CO_2^{-}$. Ethanedioate ions react with aqueous iron(III) ions to form a green iron(III) complex.

(i) Name the reaction between aqueous iron(III) ion and ethanedioate ions. [1]

(ii) Write an equation for the reaction between aqueous iron(III) ion and ethanedioate ions. Hence, explain why the $\Delta S^\ominus$ of reaction is positive. [2]

(iii) Explain how the positive $\Delta S^\ominus$ of reaction contributes to the spontaneity of the reaction in **(e)(ii)**. [1]

(iv) Draw the structure of the green iron(III) complex ion formed in **(e)(ii)**. State the value of the O–Fe–O bond angle. [2]

(v) State the type of isomerism exhibited by the iron(III) complex ion. [1]

(vi) Explain why the iron(III) complex ion is coloured. [3]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

[Total: 20]

Section B

Answer **one** question from this section.

4 (a) Group 2 metals can react with nitrogen and oxygen to form different compounds.

(i) On heating with oxygen, Group 2 metals have an increasing tendency to form metal peroxides, $M^{2+}O_2^{2-}$, down the group from magnesium to barium.

Describe and explain this tendency in terms of the variation in thermal stability of the Group 2 peroxides. [3]

(ii) Nitrogen is typically inert due to the large amount of energy needed to break N≡N bond, but magnesium produces trace Mg_3N_2, in addition to MgO, when burnt in atmospheric air. Suggest a reason that allows the formation of Mg_3N_2. [1]

(iii) Mg_3N_2 dissolves in water to give a white solid and ammonia gas. Write an equation, with state symbols, that describes this reaction. [1]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

(b) Ammonia is produced via the Haber Process, in which a temperature of 450 °C is used, and nitrogen and hydrogen are mixed in a molar ratio of 1:3 at 250 bar in a reaction vessel.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(i) Suggest why ammonia behaves as an ideal gas despite the high pressure used in the Haber Process. [1]

(ii) Given that 15% yield of ammonia is obtained from the process, calculate the partial pressure of the ammonia produced. [2]

(iii) Hence, assuming ammonia is an ideal gas, calculate the density of ammonia produced, in g m^{-3}, in the reaction vessel. [2]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

(c) Describe and explain the relative basicities of ethanamide, ethylamine, phenylamine, and ammonia, in aqueous medium. [3]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

(d) Primary amines can react with aldehydes and ketones to yield imines, containing C=N bond, which are common as intermediates in biological pathways. The mechanism for the reaction between ethylamine and butanone is shown in Fig. 4.1.

step 1: nucleophilic addition

step 2: proton transfer

step 3: protonation

step 4: elimination of water

step 5: deprotonation

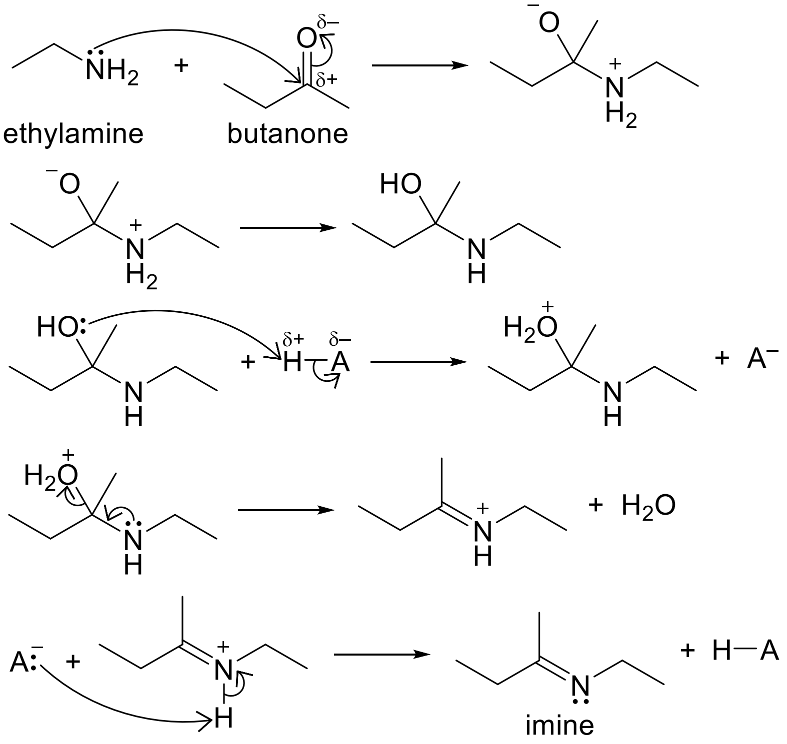


Fig. 4.1

(i) State the reagents and condition required to form ethylamine from ammonia. [1]

(ii) By considering step 1, suggest why the reaction is slow at a low pH. [1]

(iii) Explain why protonation in step 3 favours the elimination of water in step 4. [1]

....

....

....

....

....

....

....

....

....

(e) An electrolysis cell was set up to coat a zinc disc with copper. The zinc disc with a surface area of 25 cm^2 was used as the cathode with 1 mol dm^{-3} $CuSO_4(aq)$ as the electrolyte at 298 K. The anode is a 10 g copper ore with silver impurities.

A current of 1.20 A was passed through the electrolysis cell for 20 minutes. At the end of the electrolysis, there was a deposit under the anode.

(i) Explain why the concentration of the electrolyte remains constant. [1]

(ii) Calculated the expected increase in mass of the circular zinc disc at the end of 20 minutes. [2]

(iii) Calculate a minimum value for which the voltage of the external circuit must be higher than, so that electrolysis can occur. [1]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

[Total: 20]

5 **(a)** Describe the reactions, if any, of the chlorides $\mathrm{NaC}l$, $\mathrm{MgC}l_2$ and $\mathrm{A}l\mathrm{C}l_3$ with water. Write equations for all reactions that occur, and suggest the pH of the resulting solutions. Relate the reactivity of these chlorides to their structure and bonding. [4]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

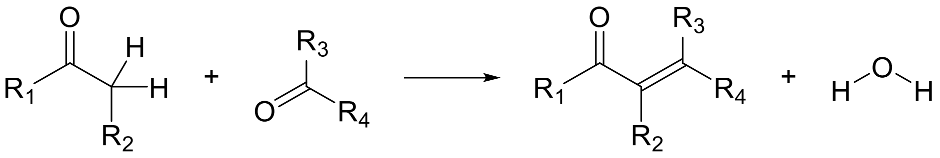
....

....

....

....

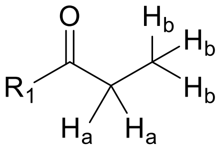
(b) Aldol condensation can occur between two carbonyl molecules, of which one of the molecules must possess at least one hydrogen on the neighbouring carbon atom to the carbonyl group.



(where R_1, R_2, R_3 and R_4 can be H, alkyl or aryl groups)

The first step of the aldol condensation involves the generation of a nucleophile, which occurs in the presence of strong bases, such as potassium hydroxide, potassium methoxide, CH_3OK, or potassium *tert*-butoxide, $(CH_3)_3COK$.

In the carbonyl molecule shown below, H_a is removed instead of H_b.



(i) Explain why H_a is more acidic than H_b. [1]

(ii) Compare and explain the basicities of potassium methoxide, CH_3OK, and potassium *tert*-butoxide, $(CH_3)_3COK$. [1]

(iii) The initial steps for aldol condensation of two propanone molecules are shown in Fig. 5.1, where OH^- is used to represent a strong base.

Copy and complete Fig. 5.1 to suggest a mechanism for these initial steps. Show all charges and relevant lone pairs, and show the movement of electron pairs by using curly arrows.

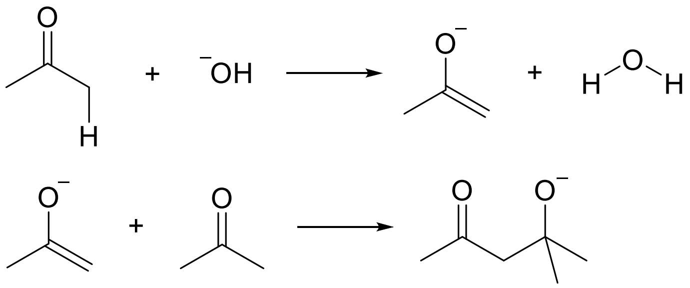
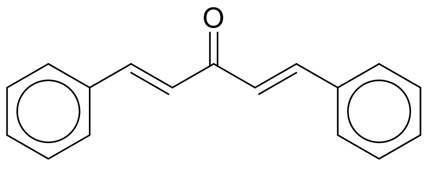


Fig. 5.1 [2]

(iv) Suggest the starting organic reactants required to form the following compound.



[1]

(c) The kinetics of acid-catalysed iodination of propanone was studied. Reaction mixtures with varying concentrations of iodine, propanone and H^+ were prepared, and the progress of the reaction was then followed by the use of a colourimeter.

The total volume of the reaction mixture was kept constant in all experiments. The time taken for a 5% decrease in $[I_2]$ was measured and the data in Table 5.1 was obtained at a fixed temperature of 298 K.

Table 5.1

experiment	$[CH_3COCH_3]$ / mol dm^{-3}	$[I_2]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	time taken for a 5% decrease in $[I_2]$ / s
1	0.2	1×10^{-3}	0.1	110
2	0.2	5×10^{-4}	0.1	55
3	0.2	5×10^{-4}	0.05	110
4	0.1	1×10^{-3}	0.05	440

(i) The rate of reaction is given by the rate of decrease of $[I_2]$.
Given that $[I_2]$ has decreased by 5% at the end-point, calculate the rate of reaction, in mol dm^{-3} s^{-1}, for experiment 1. [1]

(ii) Determine the order of the reaction with respect to each of the following reactants:

- CH_3COCH_3
- I_2
- H^+ [3]

(iii) Hence, write the rate equation for the reaction. [1]

(iv) Calculate the rate constant for the reaction, stating its units. [1]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

(d) Methanol can be used in direct-membrane alkaline fuel cells to generate electricity. At the anode, methanol is diluted in potassium hydroxide solution and undergoes oxidation to become carbonate, CO_3^{2-}, and water. At the cathode, oxygen gas is being supplied into water.

(i) Construct half equations for the cathode and anode reactions. [2]

(ii) Hence, write the overall equation. [1]

(iii) The cell is capable of producing an e.m.f of +1.21 V under standard conditions. By using relevant data from the *Data Booklet*, suggest a value for the $E^\ominus$ of the anode reaction. [1]

(iv) Calculate $\Delta G^\ominus$ for the oxidation of 1 mol of methanol. [1]

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

[Total: 20]

Additional answer space

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