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.

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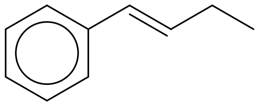
Section A

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]

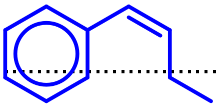
(iii) Draw the structure of a constitutional isomer of **M** that fulfils the following criteria:

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

(i) *cis-trans* isomerism ....

....

(ii)



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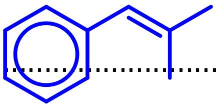
(iii)



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(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**.

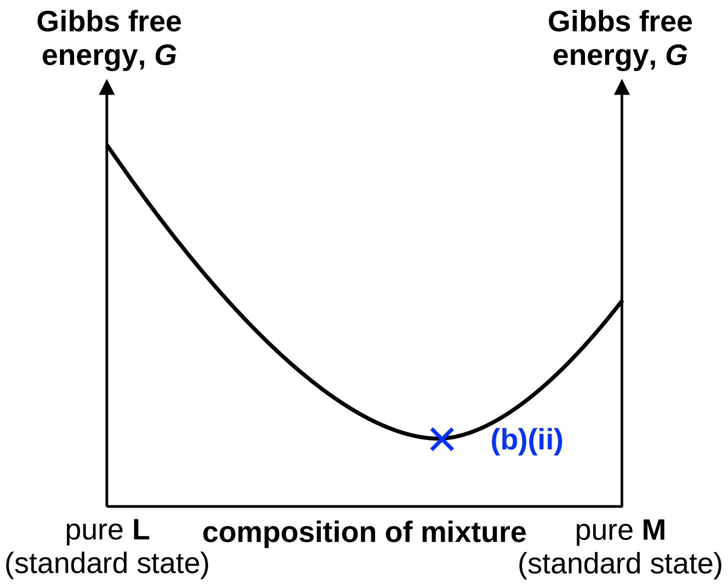


Fig. 1.1

(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]

(i)	L	$\rightleftharpoons$	M
initial conc / mol dm^{-3}	1.30		0
change in conc / mol dm^{-3}	$-x$		x
equilibrium conc / mol dm^{-3}	$1.30-x$		x

$$5.25 = \frac{x}{1.30-x}$$

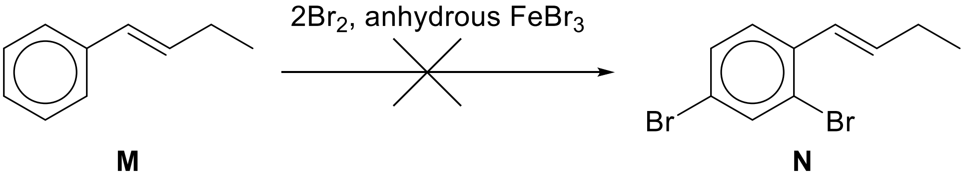
$x = 1.092$ mol dm^{-3}

equilibrium concentration of **L** = 1.30 – 1.092 = **0.208 mol dm^{-3}**

(iii) **M**, the *trans* isomer, has **less steric strain** than **L**, the *cis* isomer .

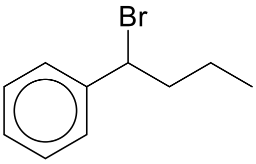
M is thus **more stable** than **L**, causing the minimum point to lie closer to **M**.

(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.



(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.

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]

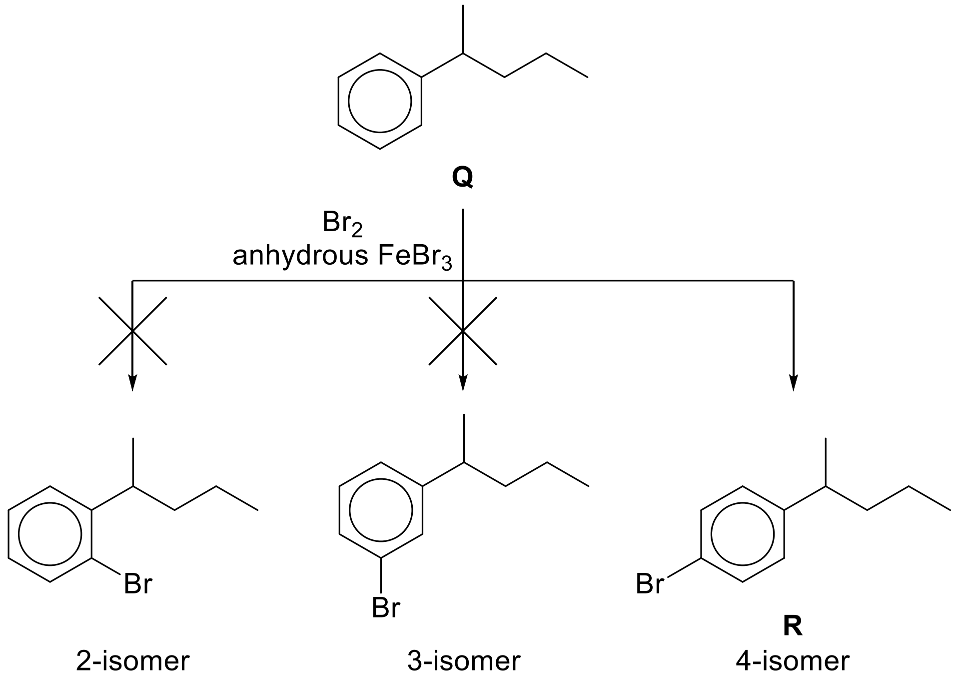


Fig. 1.2

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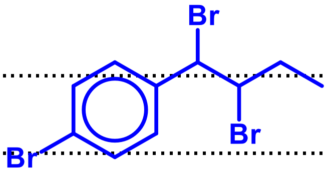
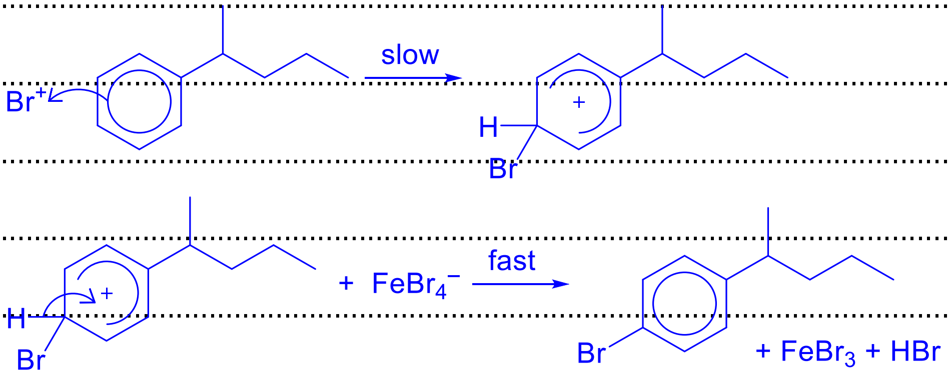
(i)



(ii) The **HBr formed in the formation of the major product reacted with unreacted M** to give **P**.

(iii)



(iv) The **alkyl group is 2,4-directing**; hence **Q** will preferentially substitute either on the second or fourth carbon atom. However, the **alkyl group on Q is very bulky and presents significant steric hindrance** to incoming electrophiles. Hence, the fourth carbon atom is more accessible than the second carbon atom.

(v) **Yes**, it would occur. **Using Br_2 and $FeCl_3$ will still generate Br^+** as the electrophile.

$Br_2 + FeCl_3 \rightleftharpoons Br^+ + FeCl_3Br^-$

(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 $1s^2\ 2s^2\ 2p^1$.

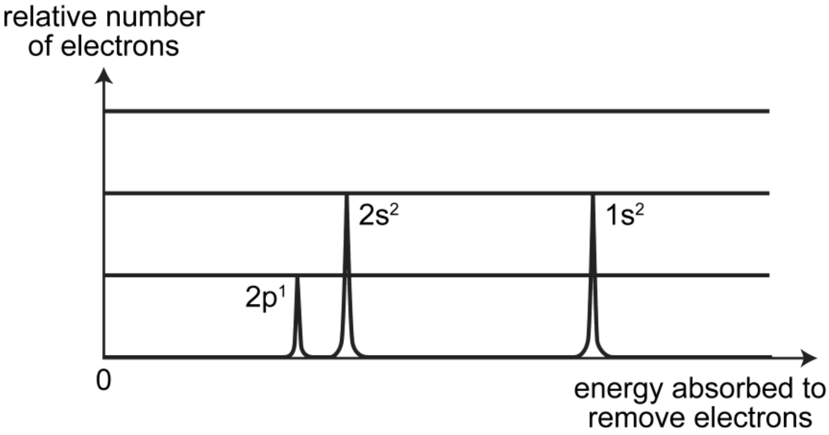


Fig. 1.3

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]

The **electrons in the 1s subshell are much closer to the nucleus than the 2s subshell**, hence 1s electrons experience **stronger electrostatic forces of attraction**, thus requiring **more energy to remove**. **Electrons in the 2s and 2p subshells** are in the **same principal quantum shell**, hence the **energy difference** between them **is smaller**, thus the gap between the peaks is smaller.

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.

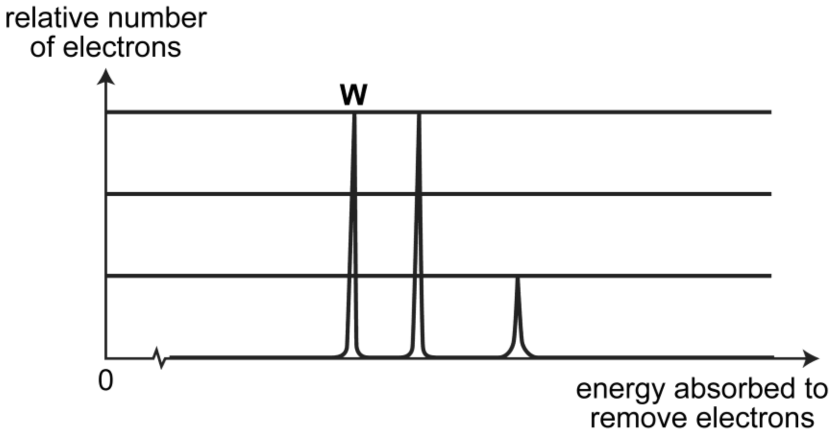


Fig. 1.4

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

$3d_{z^2}$ and the name of any other 3d orbital.

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

The ion is **Fe^{2+}**. The **3p subshell is filled first with 6 electrons before the 3d and 4s subshells**. Since **the middle and leftmost peaks are of the same height**, the **3p and 3d subshells must contain the same number of electrons**, implying a $3s^2\ 3p^6\ 3d^6$ electron configuration.

(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]

Ru^{2+}

[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.

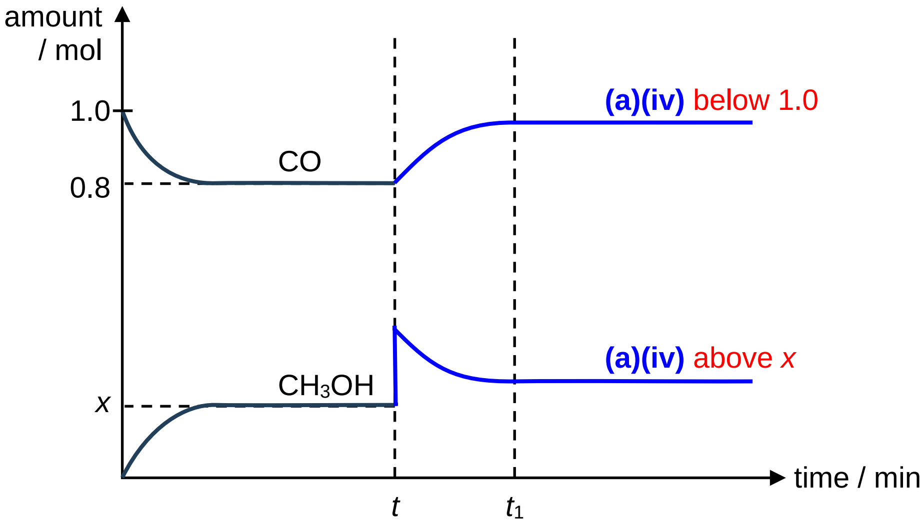


Fig. 2.1

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 °C 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]

(i) $K_p = \dfrac{p_{CH_3OH}}{p_{CO}\left(p_{H_2}\right)^2}$

(ii)

	$CO(g)$	$+$	$2H_2(g)$	$\rightleftharpoons$	$CH_3OH(g)$
initial amt / mol	1		2		0
change in amt / mol	–0.2		–0.4		+0.2
equilibrium amt / mol	0.8		1.6		0.2

x = **0.200 mol**

(iii) $p_{\text{CO}} = \frac{0.8}{2.6} \times 85 = 26.15 \text{ atm}$

$p_{\text{H}_2} = \frac{1.6}{2.6} \times 85 = 52.31 \text{ atm}$

$p_{\text{CH}_3\text{OH}} = \frac{0.2}{2.6} \times 85 = 6.54 \text{ atm}$

$$K_p = \frac{p_{\text{CH}_3\text{OH}}}{p_{\text{CO}}\left(p_{\text{H}_2}\right)^2} = \frac{6.54}{(26.15)(52.31)^2} = 9.14 \times 10^{-5} \text{ atm}^{-2}$$

(v) Effect on rate of producing methanol:

The bigger volume of the reactor **decreases the concentration** of the reactants. This results in the decrease in the frequency of effective collisions, hence **rate of producing methanol decreases.**

Effect on yield of methanol:

Increasing the volume of the reactor **decreases the total pressure**. By Le Chatelier's Principle, the **backward reaction is favoured** to increase the pressure by **producing greater amount of gas particles**. Hence the **position of equilibrium will shift to the left**, **decreasing the yield of methanol**.

(v) Effect on the value of K_p:

Since there is **no change in temperature**, $\boldsymbol{K_p}$ **remains constant**.

(vi) The catalysts are in solid state and function as **heterogeneous catalyst** since they are in a **different phase** from CO(g) and H_2(g)

- CO(g) and H_2(g) are **adsorbed to the surface** of the catalyst.
- This adsorption increases the concentration of the CO(g) and H_2(g) molecules at the catalyst surface and **weakens the covalent bonds** within the CO(g) and H_2(g) molecules, thereby reducing the activation energy for the reaction.
- The CH_3OH formed is subsequently desorbed from the surface of the catalyst.

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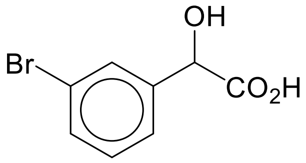
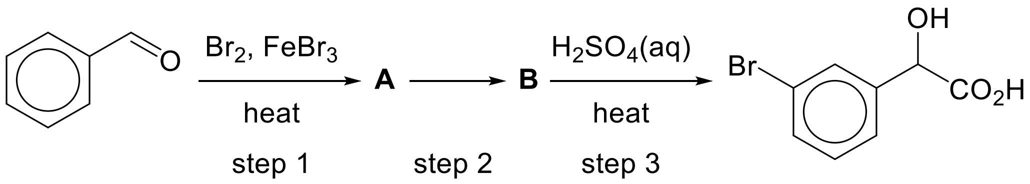
(b) Mandelic acid derivatives, including brominated forms like 3-bromomandelic acid, are used in the synthesis of chiral compounds.



3-bromomandelic acid

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



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

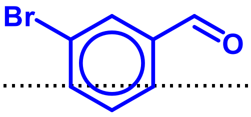
(ii) State the reagents and conditions for step 2. [1]

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

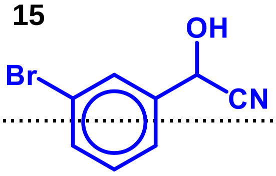
(iv) Suggest a chemical test to distinguish between benzaldehyde and 3-bromomandelic acid. Include the reagents and conditions used, and the observations for each compound. [2]

(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]

(i) **A**:



B:



(ii) **HCN, trace NaCN, cold**

(iii) **acidic hydrolysis**

(iv) To separate test-tubes containing each compound, add **Tollens' reagent and heat**. The one **containing benzaldehyde will give a silver mirror** while the **one containing 3-bromomandelic acid will not give a silver mirror**. (other suitable tests are also accepted)

(v) This conversion **will not take place** for 3-bromomandelic acid. The **4p orbital of Br overlaps with the π electron cloud of the benzene ring**, resulting in the **strengthening of C–Br bond** due to the **partial double bond character**. This makes it harder to break the C–Br bond.

[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.

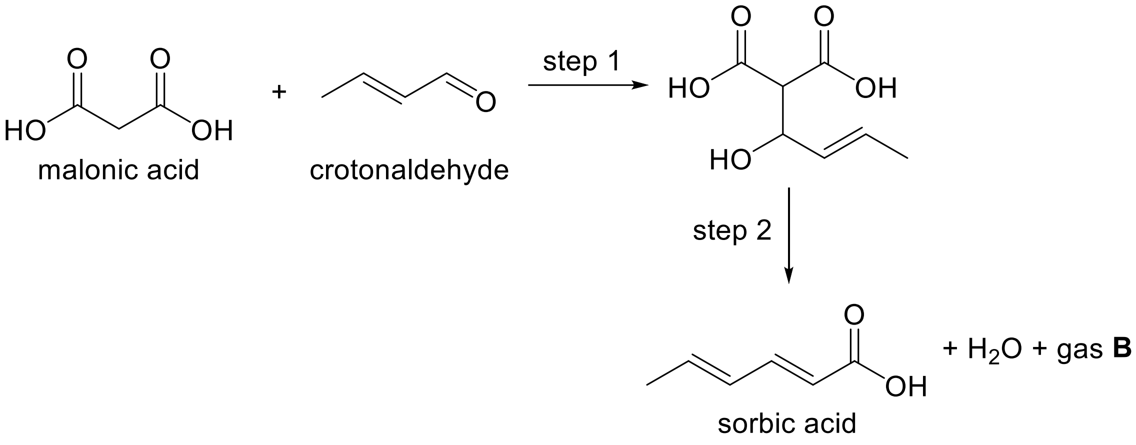


Fig. 3.1

(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]

K_{a1} of malonic acid is larger because the **conjugate base, $HO_2CCH_2CO_2^-$, is more stabilised** due to the **electron-withdrawing –CO_2H group dispersing the negative charge on the –CO_2^- group.**

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

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

(i) Nucleophilic addition

(ii) CO_2

(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]

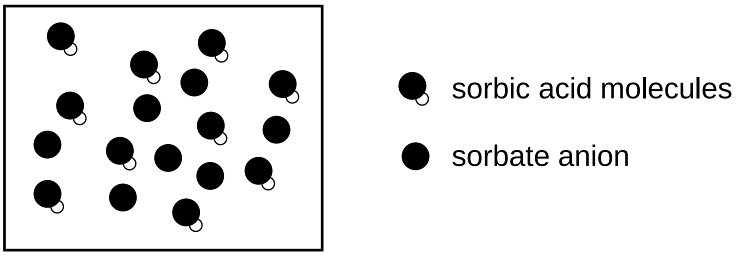


Fig 3.2

(i) NaOH will neutralise some of the **sorbic acid, $CH_3(CH)_4CO_2H$, to produce sorbate ion, $CH_3(CH)_4CO_2^-$.** The resulting solution contains **a mixture of a weak acid and its conjugate base** which is a buffer solution.

(ii) At pH = pK_a, means [acid] = [conjugate base].

The student should **add 50.0 cm^3** of 0.100 mol dm^{-3} NaOH(aq).

When half of the sorbic acid is converted to the conjugate base, **[sorbic acid] = [sorbate ion],** therefore the buffer has a pH equal to pK_a.

(Candidates can use the Henderson-Hasselbach equation to show)

(iii) The buffer in **(c)(ii)** is more resistant to changes in pH because it contains a **higher [sorbic acid] and [sorbate ion]** to react with added H^+ or OH^- ions.

(iv) At pH = pK_a = 4.75 [conjugate acid] = [conjugate base].

Since **[sorbic acid] > [sorbate ion]**, as represented in the diagram, the solution has a **pH < 4.75.** (Candidates can also use the Henderson-Hasselbach equation to show)

(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]

CH_3CO_2H

(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]

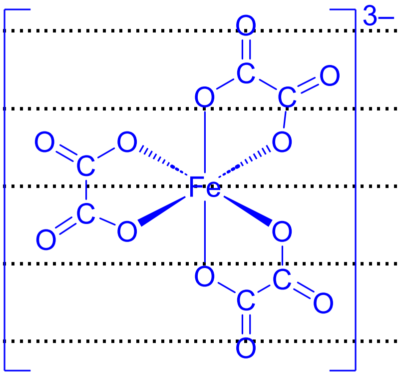
(i) **Ligand exchange**

(ii) **$[Fe(H_2O)_6]^{3+} + 3C_2O_4^{2-} \rightarrow [Fe(C_2O_4)_3]^{3-} + 6H_2O$**

More particles is produced after the reaction, resulting in an **increase in the degree of disorderliness.** Hence, entropy increases.

(iii) Spontaneity for a process at standard conditions is determined by the sign of $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$. Since $\Delta S^{\ominus}$ is positive, **the $-T\Delta S^{\ominus}$ term makes the value of $\Delta G^{\ominus}$ more negative** and thus makes the reaction more spontaneous.

(iv)



The O–Fe–O bond angle is **90°** and **180°**

(v) **Enantiomerism**

(vi) Iron(III) has an incomplete 3d subshell. The **ligands splits the d orbitals of the transition metal ion into two different energy levels.** An **electron in the lower energy d orbital absorbs certain wavelengths of light energy from the visible region of the electromagnetic spectrum,** and is promoted to a higher energy d orbital. This is called d-d transition. The remaining wavelengths are transmitted and the **complementary colour** is observed.

[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]

(i) **Thermal stability** of Group 2 peroxides **increases down the group,** hence there is increased tendency to form metal peroxides.

Down Group 2, the cationic radius increases from Mg^{2+} to Ba^{2+}. **The charge density and thus polarising power of the cations decreases down the group**. The ability of the cation to polarise and **distort the anionic electron cloud decreases down the group**, and hence the O–O in the peroxide is weakened to a lesser extent, leading to increase in thermal stability of the Group 2 peroxides down the group.

(ii) The combustion of Mg to form MgO is **highly exothermic**, and provides the energy to break the triple bond in nitrogen

(iii) $Mg_3N_2(s) + 6H_2O(l) \rightarrow 3Mg(OH)_2(s) + 2NH_3(g)$ ***or***

$Mg_3N_2(s) + 3H_2O(l) \rightarrow 3MgO(s) + 2NH_3(g)$

(b) Ammonia is produced via the Haber Process, in which a temperature of 450 ºC 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]

(i) At a **higher temperature** (of 450 ºC), the ammonia particles have **greater kinetic energy**, and can **overcome the existing** intermolecular **hydrogen bonding in NH_3.**

(ii) Let initial amount of $N_2(g)$ present be x mol.

	$N_2(g)$	+	$3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
initial amt / mol	x		$3x$		–
change in amt / mol	$-0.15x$		$-0.45x$		$+0.30x$
eqm amt / mol	$0.85x$		$2.55x$		$0.30x$

$$\text{partial pressure of } NH_3(g) = \frac{0.30x}{0.85x + 2.55x + 0.30x} \times 250 \text{ bar}$$

$$= 20.27 \text{ bar}$$

$$= 20.3 \text{ bar (to 3 s.f.)}$$

(iii) $pV = nRT$

$$pV = \left(\frac{m}{M_r}\right)RT$$

$$\frac{m}{V} = \frac{pM_r}{RT}$$

$$= \frac{(20.27 \times 10^5)(14.0 + 3.0)}{8.31 \times (450 + 273)}$$

$$= 5740 \text{ g m}^{-3} \text{ (to 3 s.f.)}$$

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

In order of increasing basicity in aqueous medium:

$\mathbf{CH_3CONH_2 < C_6H_5NH_2 < NH_3 < C_2H_5NH_2}$

Ethanamide is neutral, as the **lone pair of electrons on the nitrogen is delocalised into the C=O**, rendering the **lone pair unavailable** for donation to a proton. Phenylamine is the least basic, as the **lone pair of electrons** on nitrogen in phenylamine is partially **delocalised into the benzene ring**, rendering the **lone pair less available for donation** to a proton.

Ethylamine is the most basic (more basic than ammonia), as the **ethyl group is an electron-donating group** that increases the electron density on the nitrogen atom, which makes the **lone pair of electrons on the nitrogen most readily available for** donation to a proton.

(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.

(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]

step 1: nucleophilic addition

step 2: proton transfer

step 3: protonation

step 4: elimination of water

step 5: deprotonation

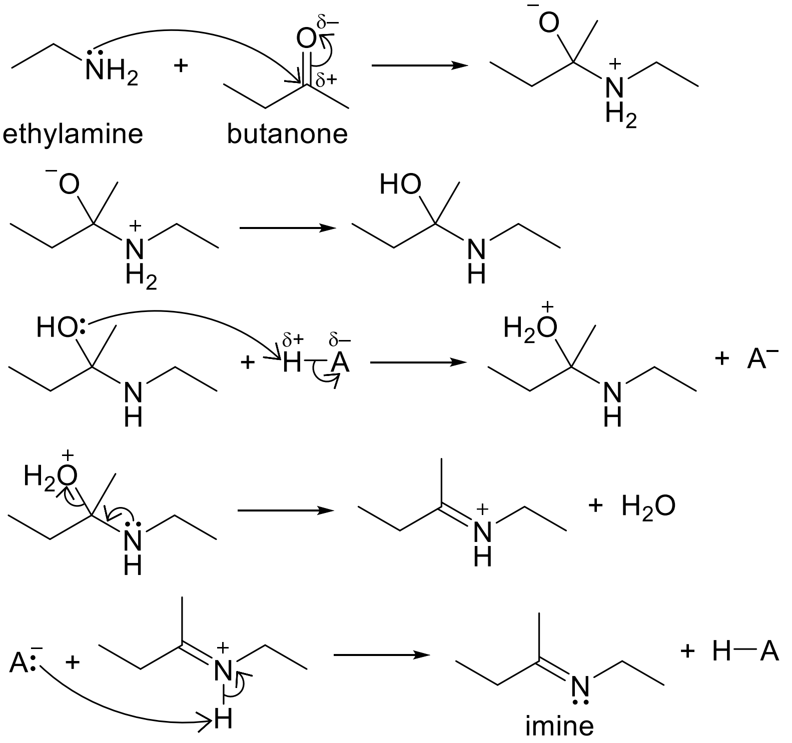


Fig. 4.1

(i) **Chloroethane** in **ethanol**, **heat in sealed tube** with excess ammonia.

(ii) At low pH, the **nitrogen** in ethylamine **is protonated** and **does not have a lone pair of electrons available** for nucleophilic addition. This leads to a slower rate of reaction as there is **lesser ethylamine** available.

(iii) The hydroxide group is a **poor leaving group** as it is a strong base. Protonation converts the leaving group to water instead. ***or*** The **carbon will be more electron deficient** due to the positively charged oxygen.

(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]

(i) **Cu is preferentially oxidised at the anode** and Cu^{2+} is **preferentially reduced at the cathode**. Since the current passing through the circuit is constant, the amount of Cu^{2+} entering and exiting the solution is the same and there is **no net change** in the concentration of the $CuSO_4$ electrolyte.

(ii)

$$It = n_e F$$

$$1.20 \times 20 \times 60 = n_e (96500)$$

$$n_e = 0.01492 \text{ mol}$$

$$n_{Cu} \text{ deposited} = 0.01492 \div 2 = 0.00746 \text{ mol}$$

$$\text{expected increase in mass} = 0.0746 \times 63.5 = 4.74 \text{ g}$$

(iii) $E^{\ominus}_{cell} = E^{\ominus}_{reduction} - E^{\ominus}_{oxidation}$

$= E^{\ominus}(Cu^{2+}|Cu) - E^{\ominus}(Cu^{2+}|Cu)$

$= +0.34V - (+0.34V) = 0 \text{ V}$

The voltage of the external circuit must be **higher than 0 V**.

[Total: 20]

5 **(a)** Describe the reactions, if any, of the chlorides $NaCl$, $MgCl_2$ and $AlCl_3$ 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]

$NaCl$ has a **giant ionic structure**, held together by electrostatic attraction between oppositely charged Na^+ and Cl^- ions. As a result, $NaCl$ **dissolves in water**, where the ions undergoes hydration:

$$NaCl(s) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq)$$

Due to the very low charge density of the hydrated $Na^+(aq)$ ion, no hydrolysis takes place and the pH of the resulting solution is **7**.

$MgCl_2$ also has a **giant ionic structure**, held together by electrostatic attraction between oppositely charged Mg^{2+} and Cl^- ions. $MgCl_2$ dissolves in water, where the ions undergoes hydration.

$$MgCl_2(s) \xrightarrow{H_2O} Mg^{2+}(aq) + 2Cl^-(aq)$$

Due to the higher charge density of the hydrated Mg^{2+} ion, slight hydrolysis takes place and the pH of the resulting solution is **6.5**.

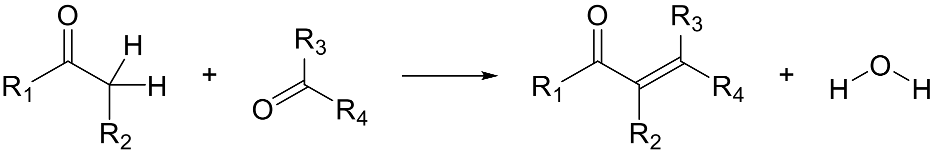
$$[Mg(H_2O)_6(aq)]^{2+} \longrightarrow [Mg(H_2O)_5OH(aq)]^{+} + H^+(aq)$$

$AlCl_3$ has a **simple molecular structure**, consisting of dimeric Al_2Cl_6 molecules containing intramolecular polar $Al–Cl$ covalent bonds. As a result, $AlCl_3$ **reacts violently** with water, liberating much **heat**. It undergoes **hydrolysis** to give white fumes of HCl, leaving behind white solid Al_2O_3:

$$2AlCl_3(s) + 3H_2O(l) \rightarrow Al_2O_3(s) + 6HCl(g/aq)$$

Some of the HCl dissolves in water to give a pH of **3** for the resulting solution.

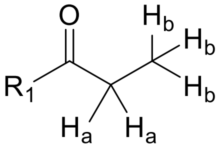
(b) Aldol condensation can occur between two carbonyl molecules, of which one of the molecules must possess at least one hydrogen on the neighbouring carbon atom to the carbonyl group.



(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.

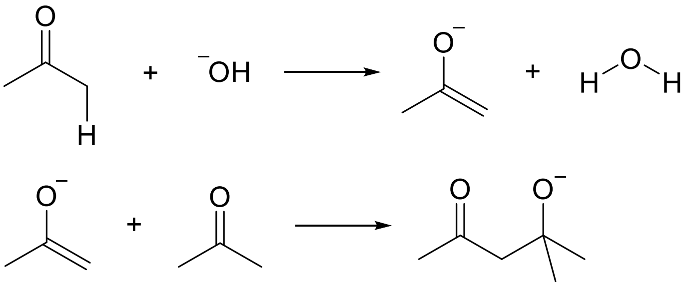
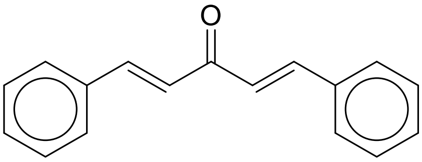


Fig. 5.1 [2]

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

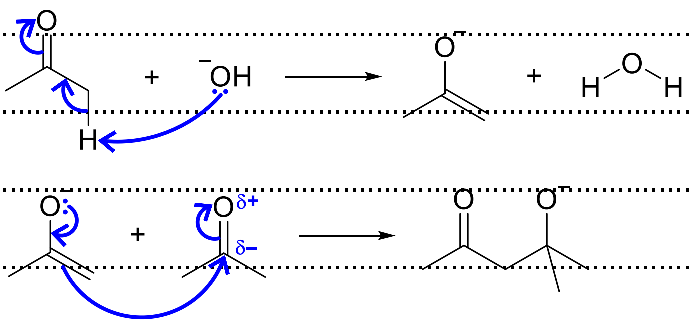


[1]

(i) When H_a is removed, the **negative charge** on the carbon atom of the conjugate base **may delocalise into the C=O bond**, hence the conjugate base formed is resonance stabilised and dissociation of H_a is preferred. This does not occur for H_b.

(ii) Potassium methoxide is **less basic** than potassium *tert*-butoxide. The **lone pair of electrons** on the oxygen of *tert*-butoxide is **more readily available** for donation to a proton due to the **greater number of alkyl donating groups attached**, which **increases the electron density** on the oxygen atom.

(iii)



(iv) Propanone and (2 equiv). **benzaldehyde**

(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]

(i) From experiment 1,

rate of reaction = rate of decrease of $[I_2]$

$$= \frac{0.05 \times 1 \times 10^{-3}}{110}$$

$= 4.50 \times 10^{-7}$ mol dm^{-3} s^{-1}

(ii) $-\dfrac{\Delta[\mathrm{I_2}]}{\Delta t} = k\left[\mathrm{CH_3COCH_3}\right]^{a}\left[\mathrm{I_2}\right]^{b}\left[\mathrm{H^+}\right]^{c}$

From experiment 1, $\dfrac{0.05\times1\times10^{-3}}{110} = k\left(0.2\right)^{a}\left(1\times10^{-3}\right)^{b}\left(0.1\right)^{c}$

From experiment 2, $\dfrac{0.05\times5\times10^{-4}}{55.1} = k\left(0.2\right)^{a}\left(5\times10^{-4}\right)^{b}\left(0.1\right)^{c}$

Comparing experiments 1 and 2, thus **b = 0**

From experiment 3, $\dfrac{0.05\times5\times10^{-4}}{110} = k\left(0.2\right)^{a}\left(5\times10^{-4}\right)^{0}\left(0.05\right)^{c}$

Comparing experiments 1 & 3, thus **c = 1**

From experiment 4, $\dfrac{0.05\times1\times10^{-3}}{440} = k\left(0.1\right)^{a}\left(1\times10^{-3}\right)^{0}\left(0.05\right)^{1}$

Comparing experiments 1 & 4, thus **a = 1**

The order of reaction with respect to $\mathrm{CH_3COCH_3}$ is **1**.

The order of reaction with respect to $\mathrm{I_2}$ is **0**.

The order of reaction with respect to $\mathrm{H^+}$ is **1**.

(iii) rate = $k[\mathrm{CH_3COCH_3}][\mathrm{H^+}]$

(iv) Since $\dfrac{0.05\times1\times10^{-3}}{110} = k\left(0.2\right)\left(0.1\right)$

$$k = 2.27\times10^{-5}\ \mathrm{mol^{-1}\ dm^{3}\ s^{-1}}$$

(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]

(i) **Cathode:** $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Anode: $CH_3OH + 8OH^- \rightarrow CO_3^{2-} + 6H_2O + 6e^-$

(ii) **Overall:** $CH_3OH + \frac{3}{2}O_2 + 2\ OH^- \rightarrow CO_3^{2-} + 3H_2O$

(iii) Since $E^\ominus_{cell} = E^\ominus_{reduction} - E^\ominus_{oxidation}$

$1.21\text{ V} = +0.40\text{ V} - E^\ominus_{oxidation}$

$E^\ominus_{oxidation} = -0.81\text{ V}$

The $E^\ominus$ of the anode is **–0.81 V**.

(iv) $\Delta G^\ominus = -nFE^\ominus_{cell}$

$= -6 \times 96500 \times 1.21 =$ **-701 kJ mol^{-1}**

[Total: 20]