



ANDERSON SERANGOON JUNIOR COLLEGE

2025 JC 2 PRELIMINARY EXAMINATION PAPER 2 SUGGESTED SOLUTIONS

NAME: _____ () CLASS: 25 / _____

- (a) Mild steel is an alloy that contains iron and carbon. A sample of mild steel was analysed, and four different types of atoms were identified; **A**, **B**, **C** and **D**. Table 1.1 shows information about the four types of atoms found in the sample.

Table 1.1

atom	relative mass	relative % abundance
A	12.00	0.238
B	13.00	0.012
C	53.94	5.79
D	55.93	93.96

- (i) Calculate the relative atomic mass of carbon in this sample to four significant figures. Show your working. [1]

Relative atomic mass of carbon

$$= \frac{12 \times 0.238 + 13 \times 0.012}{0.238 + 0.012} = \underline{12.05} [1]$$

- (ii) In an experimental set-up, beams of particles travelling at the same speed from different sources are subjected to an electric field as shown in Fig. 1.1.

A beam of protons with an angle of deflection of 60° has already been drawn.

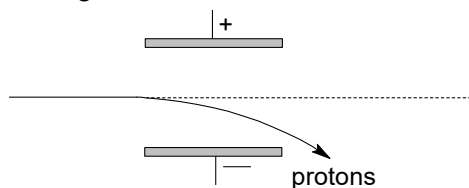


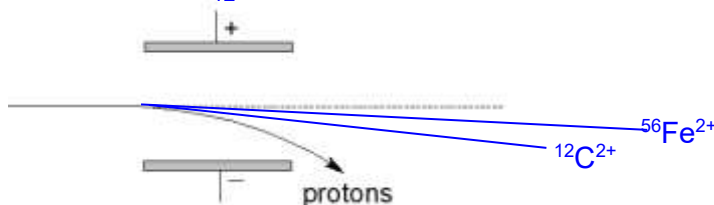
Fig. 1.1

Under identical conditions, beams of particles $^{12}\text{C}^{2+}$ and $^{56}\text{Fe}^{2+}$ were subjected to the same electric field.

Calculate the angle of deflection of $^{12}\text{C}^{2+}$ and $^{56}\text{Fe}^{2+}$ particles under the electric field and sketch the beams of $^{12}\text{C}^{2+}$ and $^{56}\text{Fe}^{2+}$ on Fig. 1.1. Label the beams clearly. [2]

$$\text{Angle of } ^{12}\text{C}^{2+} = \frac{2}{12} \times 60^\circ = \underline{+10.0^\circ}$$

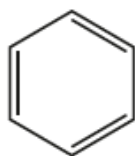
$$\text{Angle of } ^{56}\text{Fe}^{2+} = \frac{2}{56} \times 60 = \underline{+2.14^\circ} [1] \text{ for both}$$



[1] for both beams

- (b) The compound C_6H_6 has many possible structural isomers. Three suggested structures of C_6H_6 are shown in Fig. 1.2.

Kekulé benzene



Dewar benzene



Ladenburg benzene



Fig. 1.2

- (i) Using Fig. 1.2, complete Table 1.2 to predict the number of carbon atoms that have sp , sp^2 and sp^3 hybridisation in Kekulé benzene, Dewar benzene and Ladenburg benzene.

Table 1.2

C_6H_6 structure	sp hybridised	sp^2 hybridised	sp^3 hybridised
Kekulé benzene			
Dewar benzene			
Ladenburg benzene			

[2]

	sp	sp^2	sp^3
Kekulé benzene	0	6	0
Dewar benzene	0	4	2
Ladenburg benzene	0	0	6

[1] row 1 and 2 correct; [1] row 3 correct

- (ii) Dewar benzene contains both σ bonds and π bonds. By reference to the hybridisation of the carbon atoms and orbital overlap, describe the covalent bonding in Dewar benzene.

[2]

σ bonds: [1]

- Head-on overlap of the sp^2 orbital of C with sp^2 orbital of adjacent C
- Head-on overlap of sp^3 orbital of C with sp^3 orbital of adjacent C
- Head-on overlap of sp^2 orbital of C with sp^3 orbital of adjacent C
- Head-on overlap of the sp^2 orbital of C with the s orbital of H
- Head-on overlap of the sp^3 orbital of C with the s orbital of H

π bonds: [1]

- Side-way overlap of two unhybridised 2p orbital of sp^2 C

- (iv) Suggest why Dewar benzene and Ladenburg benzene are unstable isomers of C_6H_6 .

[1]

Bond strain or ring strain [1]

[Total: 8]

- 2 Aluminum is the most abundant metal in the earth's crust and has been produced commercially since 1888. It is now the second most used metal in the world after iron.

Approximately 75% of aluminum ever produced is still in use today, as it can be recycled endlessly without compromising any of its unique properties or quality.

- (a) Aluminum objects that have had the aluminum oxide layer removed may be anodised.
- (i) Complete Table 2.1 to show the relevant half-equations, during the anodisation of an aluminum object.

Table 2.1

	half-equation
anode Al + H ₂ O → Al ₂ O ₃ + H ⁺ + e
cathode	

[2]

Table 2.1

	half-equation
anode	$2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3(\text{s}) + 6\text{H}^+ + 6\text{e}^-$ [1]
cathode	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ [1]

- (ii) During the anodisation of an aluminum object, 3.50 g of a protective layer aluminum oxide is formed in 2 hours.
Calculate the value of the current used.

[2]

$$\text{Amount of Al}_2\text{O}_3 = \frac{3.50}{2 \times 27.0 + 3 \times 16.0} = 0.034313 \text{ mol}$$

$$\begin{aligned} \text{Amount of electrons passed} &= 0.034313 \times 6 \\ &= 0.2059 \text{ mol} \quad [1] \end{aligned}$$

$$n_e \times F = I \times t$$

$$0.20588 \times 96500 = I \times (2 \times 60 \times 60)$$

$$I = 2.76 \text{ A}$$

[1]

(b) Fig. 2.1 shows an **incomplete** energy cycle involving aluminium oxide, Al_2O_3 .

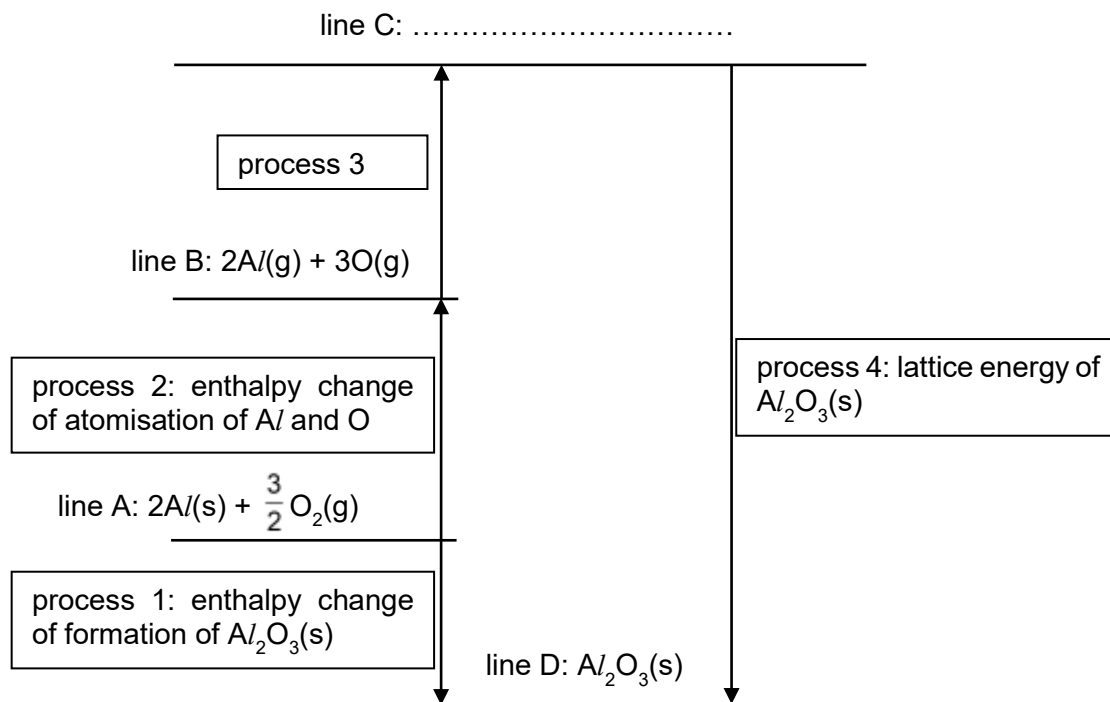
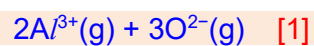


Fig. 2.1

(i) Complete line C. Include state symbols.

[1]



- (ii) Using Fig 2.1, the data in Table 2.2, together with data from the *Data Booklet*, to calculate the lattice energy of $\text{Al}_2\text{O}_3(\text{s})$.

Table 2.2

	$\Delta H^\ominus / \text{kJ mol}^{-1}$
1 st electron affinity of oxygen, $\text{O}(\text{g}) + \text{e}^- \rightarrow \text{O}^-(\text{g})$	−141
2 nd electron affinity of oxygen, $\text{O}^-(\text{g}) + \text{e}^- \rightarrow \text{O}^{2-}(\text{g})$	+790
standard enthalpy change of atomisation of $\text{Al}(\text{s})$	+326
standard enthalpy change of formation of $\text{Al}_2\text{O}_3(\text{s})$	−1676

[2]

$$\Delta H_f^\ominus = 326 \times 2 + 3/2 \times 496 + 2(577+1820+2740) + 3 \times (-141) + 3 \times 790 + \text{LE} \quad [1]$$

$$= -1676$$

$$\text{LE} = -15293 \text{ kJ mol}^{-1} [1]$$

- (iii) Explain why the first electron affinity of oxygen is exothermic, but the second electron affinity is endothermic. [2]

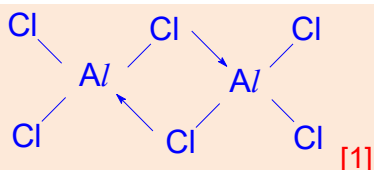
First EA is exothermic as **energy is released when an electron is attracted to the neutral oxygen atom by its nucleus.** [1]

Second EA is endothermic as **energy is required to overcome the repulsion between the added electron and the negatively charged O^- ion.** [1]

(c) When aluminum reacts with dry chlorine, aluminum chloride, AlCl_3 , is formed.

(i) AlCl_3 can undergo dimerisation to form Al_2Cl_6 .

With the aid of a diagram, name the type of bond formed during dimerisation and explain why this bond is formed. [2]



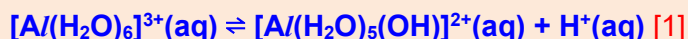
In forming the Al_2Cl_6 dimer, two AlCl_3 molecules are joined by dative bonds. Reason: Al is electron deficient and can accept lone pair of electron from chlorine forming octet structure [1] name and reason

(ii) When AlCl_3 is dissolved in water, a solution of pH 3.0 is formed.

Explain with the aid of a balanced equation why the solution has a pH of 3.0. [2]

$\text{AlCl}_3(\text{s})$ dissolves in water to form hydrated $[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$.

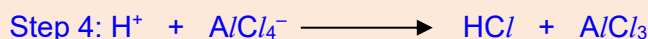
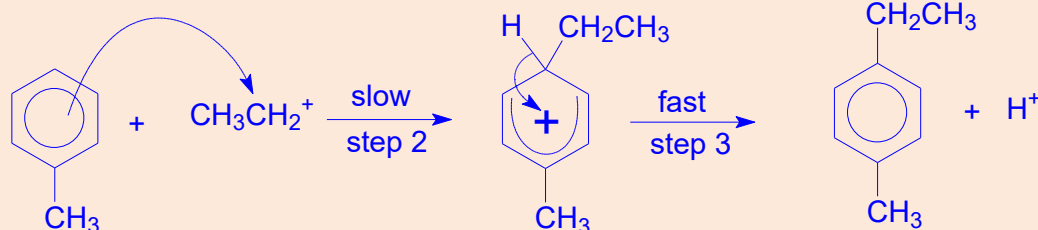
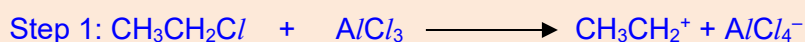
Due to **high charge density of Al^{3+}** , it is able to **polarise** the neighbouring **water molecule**, which **further breaks the O-H bonds**, thereby **producing H^+** in the solution. Hence, AlCl_3 undergoes hydrolysis in water to form an acidic solution. [1]



(iii) AlCl_3 can be used as a catalyst in the reaction of methylbenzene with chloroethane to form 4-ethylmethylbenzene.

Describe the mechanism of this reaction. [3]

Electrophilic Substitution



[1] name of mechanism

[1] for correct intermediates (carbocation and H^+) and regeneration of catalyst

[1] for correct arrows and charges

[Total: 16]

- 3 (a) The acid strength of a carboxylic acid is measured by its pK_a value. Table 3.1 shows pK_a of ethanoic acid, chloroethanoic acid and fluoroethanoic acid.

Table 3.1

carboxylic acid	pK_a
ethanoic acid, CH_3COOH	4.76
chloroethanoic acid, ClCH_2COOH	2.87
fluoroethanoic acid, FCH_2COOH	2.60

- (i) Explain the difference in pK_a values for ethanoic acid, chloroethanoic acid and fluoroethanoic acid. [3]

pK_a in the order:

$\text{CH}_3\text{COOH} > \text{ClCH}_2\text{COOH} > \text{FCH}_2\text{COOH}$
hence acid strength in the order:

ethanoic acid < chloroethanoic acid < fluoroethanoic acid.

- CH_3 group is electron-donating, intensifies the negative charge on the carboxylate group ($-\text{COO}^-$) destabilises the anion, ethanoic acid is the weakest acid. [1]
- Cl is electron-withdrawing, disperses the negative charge on the carboxylate group ($-\text{COO}^-$), stabilises the ion to a greater extent, chloroethanoic acid is **stronger** than ethanoic acid. [1]
- F is more electronegative than Cl , stronger electron-withdrawing effect on the carboxylate ion, greater negative charge dispersal leading to greater stabilisation of the ion, fluoroethanoic acid is the strongest acid. [1]

- (ii) Calculate the $\frac{[\text{anion}]}{[\text{acid}]}$ ratio for each of the following acids when it is placed in a buffer solution kept at pH 3.8. Give your answer to **three** significant figures. [1]

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

For $\text{CH}_3\text{CO}_2\text{H}$:

$$\frac{[\text{A}^-]}{[\text{HA}]} = \frac{10^{-4.76}}{10^{-3.8}}$$

$$\frac{[\text{A}^-]}{[\text{HA}]} = \underline{0.110}$$

For $\text{ClCH}_2\text{CO}_2\text{H}$:

$$\frac{[\text{A}^-]}{[\text{HA}]} = \frac{10^{-2.87}}{10^{-3.8}}$$

$$\frac{[\text{A}^-]}{[\text{HA}]} = \underline{8.51}$$

[1] for both values

- (iii) Hence, using your answer from (a)(ii), explain if ethanoic acid or chloroethanoic acid, and its conjugate base forms a more effective buffer in removing the small amount of H^+ added at pH 3.8. [1]

At pH 3.8, the ratio of $[\text{A}^-]$ to $[\text{HA}]$ for chloroethanoic acid is much greater (8.51) than for ethanoic acid (0.110).

This means a higher concentration of conjugate base ($\text{ClCH}_2\text{COO}^-$) is present to remove added H^+ , so chloroethanoic acid forms a buffer with a greater capacity to resist pH change. [1]

- (b) Both ethanoic acid, CH_3COOH , and lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}$, can be synthesised from ethanol, $\text{C}_2\text{H}_5\text{OH}$, in the laboratory via different routes, as shown in Fig. 3.1.

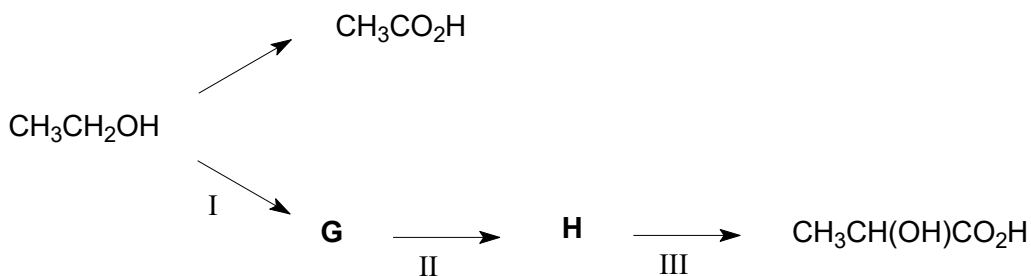
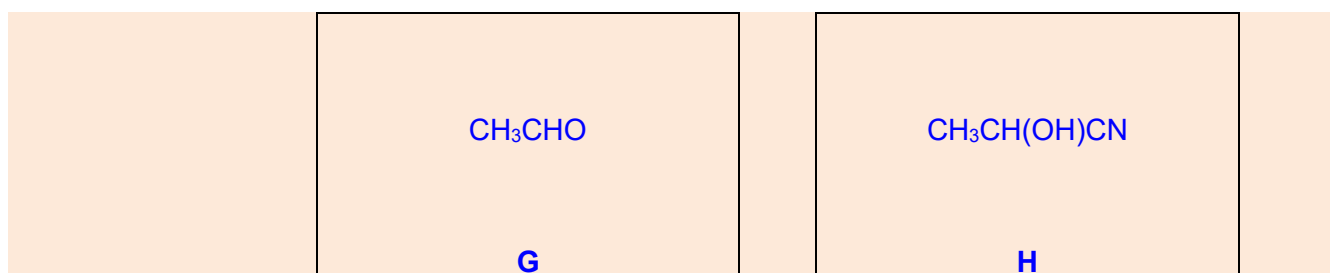


Fig. 3.1

- (i) Suggest structures for compounds **G** and **H**.

[2]



- (ii) Suggest reagents and conditions for each of the steps I and II.

step I

step II

[2]

step I $\text{K}_2\text{Cr}_2\text{O}_7$, dilute H_2SO_4 , warm/heat with (immediate) distillation
 (accept acidified $\text{K}_2\text{Cr}_2\text{O}_7$ but not KMnO_4)

step II HCN , KCN (as catalyst), cold
 (accept trace of $\text{NaOH}(\text{aq})$ as catalyst or KCN , dilute acid, cold)

- (iii) It is found that lactic acid synthesised in the lab do not rotate plane polarised light while naturally occurring lactic acid found in goat milk exhibits optical activity. Explain why such observation is made.

[2]

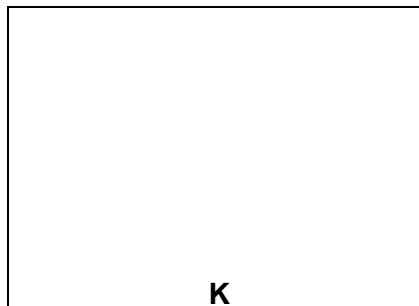
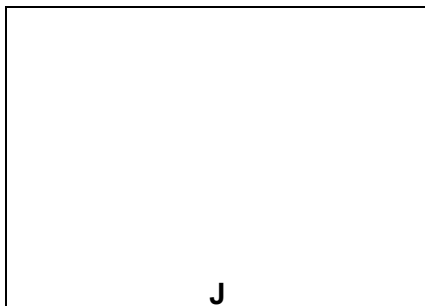
In the synthesis, the carbonyl carbon is trigonal planar, so nucleophilic attack occurs from the top and bottom with equal probability. This produces a racemic mixture/ equal amounts of both enantiomers, The enantiomers cancel each other's optical activity, so the product is optically inactive

Naturally occurring lactic acid exists as a pure enantiomer. Its central carbon is chiral, bonded to four different substituent groups and lacking an internal plane of symmetry, hence it exhibits optical activity. [1]

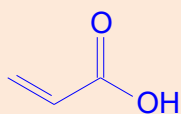
(c) Lactic acid reacts in the presence of hot, concentrated sulfuric acid to form two different compounds, **J** and **K**.

- **J** has a molecular mass 72.0 g mol^{-1}
- **K** is a cyclic compound and has a molecular formula $\text{C}_6\text{H}_8\text{O}_4$.

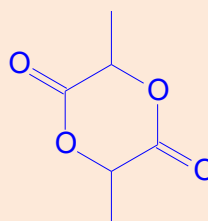
Draw the skeletal formula of **J** and **K**.



[2]



J [1]



K [1]

(d) Table 3.2 shows the solubility of various calcium salts in water.

Table 3.2

calcium salt	solubility / mol dm ⁻³	colour
CaC ₂ O ₄	4.8 x 10 ⁻⁵	white
Ca ₃ (PO ₄) ₂	1.6 x 10 ⁻⁷	white
CaCrO ₄	2.7 x 10 ⁻²	bright yellow

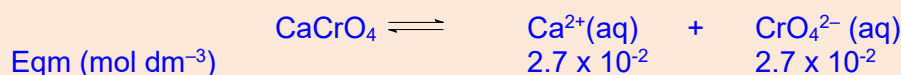
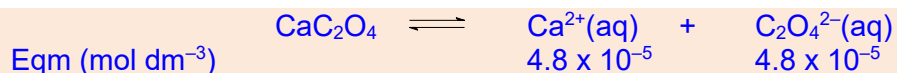
(i) Write an expression for the solubility product of Ca₃(PO₄)₂. [1]

$$K_{sp} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2 \quad [1]$$

(ii) Calculate the solubility product, K_{sp} , for Ca₃(PO₄)₂, giving its units. [1]

$$\begin{aligned} K_{sp} &= [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2 \\ &= (3 \times 1.6 \times 10^{-7})^3 (2 \times 1.6 \times 10^{-7})^2 \\ &= \underline{1.13 \times 10^{-32} \text{ mol}^5 \text{ dm}^{-15}} \quad [1] \text{ including units} \end{aligned}$$

(iii) Describe what you would observe if equal volumes of saturated solutions of CaC₂O₄ and CaCrO₄ were mixed. Explain your answer using calculations. [3]



When **equal volumes** of the 2 saturated solutions are mixed, **concentration** in mol dm⁻³ of all ions will be **halved**:

$$\begin{aligned} [\text{Ca}^{2+}]_{\text{total}} &= \frac{1}{2}(4.8 \times 10^{-5} + 2.7 \times 10^{-2}) \\ &= 0.013524 \end{aligned}$$

$$[\text{C}_2\text{O}_4^{2-}] = \frac{1}{2}(4.8 \times 10^{-5}) = 2.4 \times 10^{-5}$$

$$[\text{CrO}_4^{2-}] = \frac{1}{2}(2.7 \times 10^{-2}) = 0.0135$$

[1] for correct concentrations of all ions after mixing

$$\begin{aligned} \text{Ionic product of CaC}_2\text{O}_4 &= [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] \\ &= (0.013524) \times (2.4 \times 10^{-5}) = 3.246 \times 10^{-7} \\ &> K_{sp} \text{ of CaC}_2\text{O}_4 \end{aligned}$$

$$\begin{aligned} \text{Ionic product of CaCrO}_4 &= [\text{Ca}^{2+}][\text{CrO}_4^{2-}] \\ &= (0.013524) \times (0.0135) = 1.826 \times 10^{-4} \\ &< K_{sp} \text{ of CaCrO}_4 \end{aligned}$$

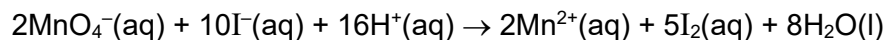
[1] for correct IP calculations for both

Hence, a **white precipitate** of CaC₂O₄ would be observed. [1] ecf based on IP calculation (no calculation no marks)

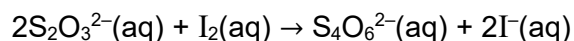
- (e) An iodometric titration can be used to determine the percentage purity of calcium oxalate crystals, CaC_2O_4 .

A 3.20 g impure sample of CaC_2O_4 is shaken with 100.0 cm^3 of 0.10 mol dm^{-3} aqueous acidified MnO_4^- ions. One of the products of this reaction is CO_2 .

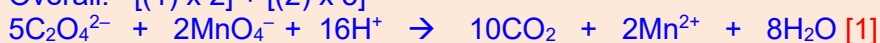
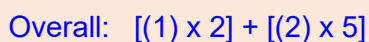
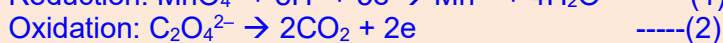
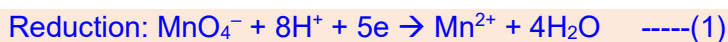
The remaining MnO_4^- is reacted with an excess of iodide solution to liberate $\text{I}_2(\text{aq})$.



A 25.0 cm^3 aliquot requires 24.50 cm^3 of 0.2 mol dm^{-3} $\text{S}_2\text{O}_3^{2-}$ for this titration.



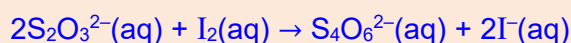
- (i) Construct an equation for the reaction between MnO_4^- ions and $\text{C}_2\text{O}_4^{2-}$ ions. [1]



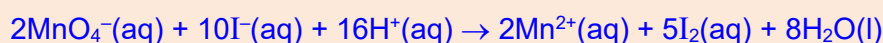
(ii) Calculate the percentage purity of the sample of CaC_2O_4 .

[3]

$$\begin{aligned}\text{amount of } \text{S}_2\text{O}_3^{2-} \text{ required} &= \frac{24.50}{1000} \times 0.20 \\ &= 4.90 \times 10^{-3} \text{ mol}\end{aligned}$$



$$\begin{aligned}\text{amount of } \text{I}_2 \text{ that reacted with } \text{S}_2\text{O}_3^{2-} &= \frac{1}{2} \times 4.90 \times 10^{-3} \\ &= 2.45 \times 10^{-3} \text{ mol}\end{aligned}$$



$$\begin{aligned}\text{amount of remaining } \text{MnO}_4^- &= \frac{2}{5} \times 2.45 \times 10^{-3} \\ &= \underline{9.80 \times 10^{-4} \text{ mol}} \quad [1]\end{aligned}$$

$$\begin{aligned}\text{Amount of remaining } \text{MnO}_4^- \text{ in } 100 \text{ cm}^3 \text{ of solution} &= 9.80 \times 10^{-4} \times 100/25 \\ &= 0.00392 \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{initial amount of } \text{MnO}_4^- &= \frac{100.0}{1000} \times 0.10 \\ &= 0.0100 \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{amount of } \text{MnO}_4^- \text{ that reacted with } \text{C}_2\text{O}_4^{2-} &= 0.0100 - 0.00392 \\ &= \underline{0.00608 \text{ mol}} \quad [1]\end{aligned}$$



$$\begin{aligned}\text{amount of } \text{C}_2\text{O}_4^{2-} \text{ in sample} &= \text{amount of } \text{CaC}_2\text{O}_4 \text{ in sample} \\ &= \frac{5}{2} \times 0.00608 \\ &= \underline{0.0152 \text{ mol}}\end{aligned}$$

$$\begin{aligned}\text{mass of pure } \text{CaC}_2\text{O}_4 &= 0.0152 \times [40.1 + 2(12.0) + 4(16.0)] \\ &= 1.95 \text{ g}\end{aligned}$$

$$\begin{aligned}\text{Percentage by mass of } \text{CaC}_2\text{O}_4 &= \frac{1.95}{3.20} \times 100\% \\ &= \underline{60.9 \%} \quad [1]\end{aligned}$$

- (f) The trend in the thermal stability of Group 2 oxalates, MC_2O_4 , is similar to that of Group 2 carbonates.

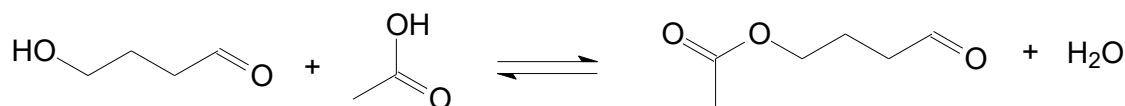
Suggest if MgC_2O_4 or CaC_2O_4 undergoes thermal decomposition at a lower temperature. Explain your answer. [3]

MgC_2O_4 decomposes at a lower temperature [1].

- ionic radius of Mg^{2+} is smaller so the charge density of the Mg^{2+} is larger and Mg^{2+} is more polarising. [1]
- The electron cloud of $\text{C}_2\text{O}_4^{2-}$ anion is more polarised / distorted [1]
- so the C-C / C-O covalent bond within the anion is weakened for MgC_2O_4 .

[Total: 25]

- 4 (a) 4-hydroxybutanal can undergo an esterification reaction with a carboxylic acid. In a controlled experiment, 4-hydroxybutanal and ethanoic acid were heated under reflux with a small amount of concentrated sulfuric acid as a catalyst.



The following information was recorded from the experiment at 298 K.

- initial amount of 4-hydroxybutanal: 0.500 mol
- initial amount of ethanoic acid: 0.400 mol
- total volume of solution: 2.00 dm³
- at equilibrium, 60% of 4-hydroxybutanal has reacted

- (i) Write the expression for the equilibrium constant, K_c , for this reaction. Use your expression to calculate the value of K_c for this reaction. [3]

	$\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CHO} + \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CHO} + \text{H}_2\text{O}$			
Initial (mol)	0.50	0.40	0	0
Change (mol)	$-(\frac{60}{100} \times 0.50 = 0.30)$	-0.30	+0.30	+0.30
Eqm (mol)	0.20	0.10	0.30	0.30
Conc (mol dm ⁻³)	$\frac{0.20}{2} = 0.10$	$\frac{0.10}{2} = 0.05$	$\frac{0.30}{2} = 0.15$	$\frac{0.30}{2} = 0.15$

Working for correct concentration [1]

$$K_c = \frac{[\text{ester}][\text{H}_2\text{O}]}{[\text{4-hydroxybutanal}][\text{ethanoic acid}]} \quad [1]$$

$$K_c = \frac{(0.15)(0.15)}{(0.05)(0.10)} = 4.5 \quad [1]$$

- (ii) Aqueous potassium hydroxide was added to the equilibrium mixture at 298 K. Suggest how the position of equilibrium might change and if the K_c will be affected. [2]

KOH undergoes acid-base reaction with CH₃COOH.

Adding KOH(aq) results in a decrease in [CH₃COOH]. Position of equilibrium of esterification reaction will shift left to increase the [CH₃COOH]. [1]

K_c will not change as it is temperature dependent. [1]

- (b) 4-hydroxybutanal can form a cyclic hemiacetal in the presence of an acid catalyst as shown in Fig. 4.1.

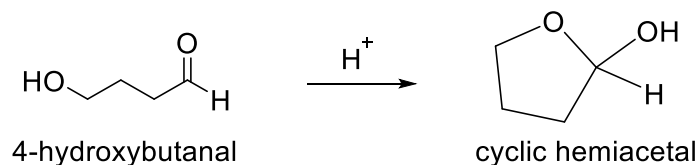


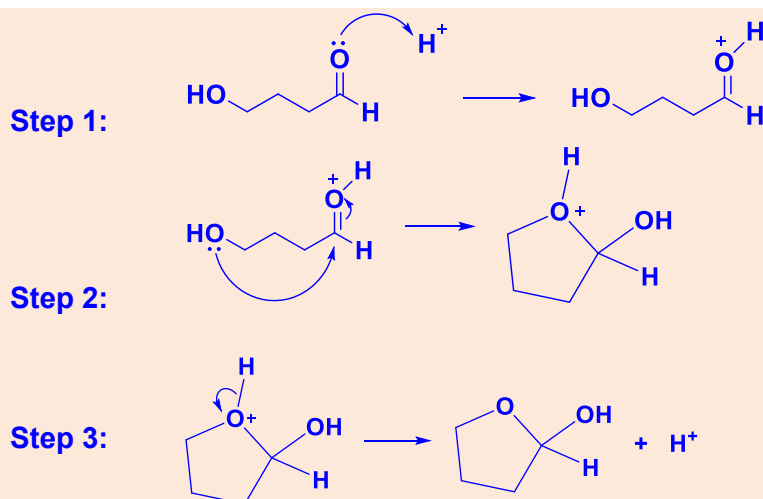
Fig. 4.1

- (i) The mechanism for the reaction in Fig. 4.1 is shown in Table 4.1.
Draw **four** curly arrows to complete the mechanism shown in Table 4.1.

[2]

Table 4.1

Step 1: The aldehyde is protonated by the acid catalyst to form a non-cyclic intermediate.	
Step 2: Nucleophilic attack by the alcohol to form a cyclic intermediate.	
Step 3: Deprotonation of the cyclic intermediate to form the product.	



[1]: 1 curly arrow in step 1 **and** 3 each

[1]: 2 curly arrows in step 2

- (ii) The reaction to form cyclic hemiacetal is completed when all the 4-hydroxybutanal is used up. Describe a chemical test to check the completion of the reaction.

Include the reagents and conditions for the test. Explain how the observations will be used to determine if the reaction has been completed. [3]

Add 2,4-DNPH to a sample of the reaction mixture. [1] for test

Students can propose Tollen's reagent and Felding reagent

Do not accept test involving cyclic hemiacetal (e.g. PCl_3 , PCl_5 , SOCl_2 , Na)

If traces of 4-hydroxybutanal is presence, an orange/yellow ppt. is observed [1] for observation from the test

The reaction will be completed when no orange ppt is observed in the sample of reaction mixture. [1] showing idea of how to ensure reaction has been completed.

- (c)** Koch reaction uses carbon monoxide to manufacture tertiary carboxylic acids as shown in Fig. 4.2.

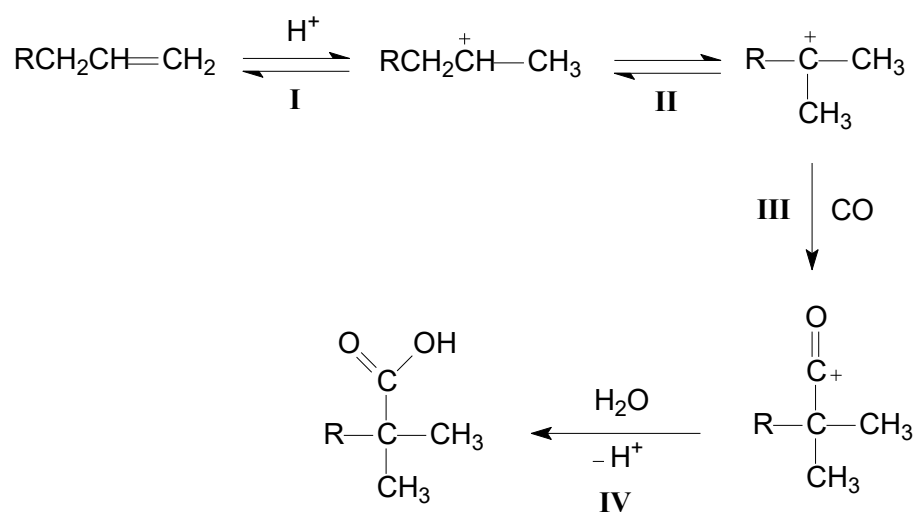
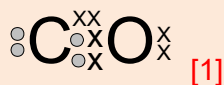


Fig. 4.2

- (i) Step II is known as a rearrangement reaction. With reference to the stability of the species involved, suggest a reason why such a reaction occurs. [1]

The 3° carbocation formed after step II is more stable than the 2° carbocation [1]

- (ii)** Draw the “dot-and-cross” diagram for carbon monoxide, CO. [1]



(iii) Hence, state the role of carbon monoxide, CO, in the mechanism of step III. [1]

Carbon monoxide acts as a nucleophile or Lewis base (due to the presence of a lone pair of electrons on the carbon atom. This lone pair of electrons is donated to an electron-deficient carbon in the carbocation) [1]

(iv) Acidic hydrolysis of an ester can be explained in terms of nucleophilic acyl substitution.

Besides electronic effect, suggest another reason why esters synthesised from tertiary carboxylic acids are stable when heated in the presence of acids. [1]

The steric hindrance due to the 3 bulky R groups present in 3° carboxylic acid prevents the attack of the nucleophile on the carbonyl carbon during the hydrolysis reaction. [1]

(do not accept: electron-donating effect of alkyl groups making the carbonyl carbon less electron deficient and hence less susceptible to nucleophilic attack by water as question already mentioned “beside electronic effect”).

For your information.

Under neutral conditions, the carbonyl carbon in esters is not reactive enough for water to attack efficiently.

Protonating the carbonyl oxygen with H^+ increases the electrophilicity of the carbonyl carbon, making nucleophilic attack more favourable. Thus, when 3 bulky R groups are present, beside electronic factor, steric factor is also considered.

3. Step-by-Step Mechanism (Nucleophilic Acyl Substitution)

1. *Activation of the electrophile*
 - H^+ protonates the carbonyl oxygen of the ester.
 - This makes the $C=O$ more positively polarised, increasing the δ^+ charge on the carbon.
2. *Nucleophilic attack*
 - Water acts as the nucleophile, attacking the carbonyl carbon.
 - This forms a tetrahedral intermediate.
3. *Proton transfers*
 - Within the tetrahedral intermediate, proton transfers occur to prepare the alkoxy group ($-OR'$) for departure.
 - One common path is protonating the $-OR'$ oxygen so it becomes a better leaving group ($-OH+R'$).
4. *Elimination of leaving group*
 - The $C-OR'$ bond breaks, reforming the $C=O$ and ejecting the alcohol.
5. *Deprotonation of product*
 - The protonated carboxylic acid loses a proton, regenerating the acid catalyst and yielding the neutral carboxylic acid.

[Total: 14]

- 5 (a) Volatile Organic Compounds (VOCs) are a group of organic chemicals that easily vaporise at room temperature. They are released by a wide range of products and processes, both indoors and outdoors.

Some VOCs can contribute to the formation of secondary pollutants like ozone and have adverse health effects. They are usually released from sources like vehicle exhaust, paint and solvents.

In the presence of sunlight, photochemical reaction is triggered between nitrogen oxides (NO and NO₂) and VOCs. The five stages of the reaction between formaldehyde, one of the common VOCs, with NO in the presence of sunlight leading to the formation of ozone, O₃, are described in Table 5.1.

Table 5.1

stage	description of stage	equation
1	*photolysis of formaldehyde	$\text{HCHO} \rightarrow \bullet\text{H} + \bullet\text{CHO}$
2	oxidation of formyl radical	$\bullet\text{CHO} + \text{O}_2 \rightarrow \text{CO} + \bullet\text{HO}_2$
3	oxidation of NO(g)	$\bullet\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \bullet\text{OH}$
4	photolysis of NO ₂ (g)	
5	formation of O ₃ (g)	

* photolysis is the decomposition of a molecule by the action of light.

After stage 3, NO₂ is photolysed by sunlight to generate NO and O atoms. The O atom formed then reacts with the oxygen gas in the air to form ozone.

- (i) Explain why the hydrogen atom produced in step 1 is described as a *free radical*. [1]

An hydrogen atom has one unpaired electron making them highly reactive. [1]

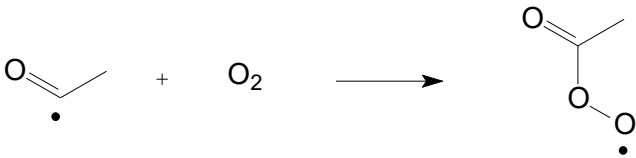
- (ii) Complete Table 5.1 by adding the two equations to represent stages 4 and 5. [1]

$\text{NO}_2 \rightarrow \text{NO} + \text{O}$ (not necessary to put $h\nu$)
 $\text{O} + \text{O}_2 \rightarrow \text{O}_3$ Two equations [1]

- (iii) Propanone, CH_3COCH_3 , undergoes a similar reaction to that shown for stages 1 to 3 in Table 5.1.

Complete Table 5.2 by adding the equations to represent stage 1 and 3.

Table 5.2

stage	description of stage	equation
1	photolysis of CH_3COCH_3 to generate two radicals, $\text{CH}_3\text{CO}\bullet$ being one of them	
2	oxidation of $\text{CH}_3\text{CO}\bullet$ radical to form peroxyacetyl radical	
3	oxidation of NO(g) by peroxyacetyl radical to form brown gas	

[2]

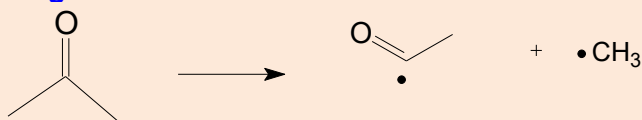
Stage 1: $\text{CH}_3\text{COCH}_3 \rightarrow \bullet\text{CH}_3 + \text{CH}_3\text{CO}\bullet$ [1]

Stage 2: $\text{CH}_3\text{CO}\bullet + \text{O}_2 \rightarrow \text{CH}_3\text{C(O)OO}\bullet$ (FYI not required)

Stage 3: $\text{CH}_3\text{C(O)OO}\bullet + \text{NO} \rightarrow \text{CH}_3\text{C(O)O}\bullet + \text{NO}_2$ [1]
(brown gas)

Or

Stage 1:



Stage 2: $\text{CH}_3\text{CO}\bullet + \text{O}_2 \rightarrow \text{CH}_3\text{C(O)OO}\bullet$ (FYI not required)

Stage 3:



- (b) In recent years, there is an increasing concern about the post renovation air quality in buildings. In 2018, the death of a flat-dweller in Beijing has been attributed to formaldehyde, a carcinogenic substance widely used in wood products due to its strong adhesive, preservative and binding properties. Similarly, homeowners in Singapore have also been seeking help as they experienced stinging sensation in their nose and eyes due to VOCs released from furniture in their newly-renovated houses.

The air quality of a newly renovated office with limited ventilation was studied over the course of one week. Table 5.3 shows the average concentrations, in parts per billion (ppb), of selected VOCs detected.

Table 5.3

VOCs detected in the air of the office	molar mass (g mol ⁻¹)	concentration (ppb)
Formaldehyde, HCHO	30.0	0.0692
Toluene, C ₆ H ₅ CH ₃	92.0	38.5
Xylene C ₆ H ₄ (CH ₃) ₂	106.0	12.7

- (i) State two basic assumptions of the kinetic theory as applied to an ideal gas. [2]

The volume of the gas molecules is negligible compared to the volume of the container. [1]

The forces of attraction between the gas molecules as well as between the gas molecules and walls of the container are negligible. [1]

- (ii) Explain, with reference to intermolecular forces, which VOC vapour in Table 5.3 will have the greatest deviation from ideal gas behaviour. [2]

Xylene (C₆H₄(CH₃)₂). [1]

Thus, it has— the most electrons and the instantaneous dipole–induced dipole between xylene molecules is the most extensive. [1]

- (iii) The concentration of VOC in the air is often represented in parts per billion (ppb). 1 ppb VOC means there should be 1 mole of VOC for every 1 000 000 000 moles of air.

Calculate the concentration, in mol dm^{-3} , of toluene in the sample of office air.

[Assume the sample of air is at room temperature and pressure conditions.] [1]

$$\begin{aligned} 38.5 \text{ ppb} &= 38.5 \text{ mole of toluene in } 1\,000\,000\,000 \text{ mole of air} \\ &= 38.5 \text{ mol of toluene in } 1\,000\,000\,000 \times 24 \text{ dm}^3 \text{ of air} \\ &= \frac{38.5}{24\,000\,000\,000} \text{ mol of toluene in } 1 \text{ dm}^3 \text{ of air} \end{aligned}$$

$$\text{concentration of toluene at } 38.5 \text{ ppb} = 1.60 \times 10^{-9} \text{ mol dm}^{-3} \text{ [1]}$$

- (iv) The indoor air quality is often measured by TVOC (Total Volatile Organic Compounds) levels. It is calculated as the sum of the concentrations of all measured VOCs, expressed in ppb.

Using Table 5.3, determine the TVOC level of the office. [1]

$$\text{TVOC} = 0.0692 + 38.5 + 12.7 = 51.3 \text{ ppb (3sf) [1]}$$

- (v) The World Health Organisation (WHO) recommends a target level of under 50 ppb for TVOC.

Explain if the TVOC level of the office is of concern and suggest a measure that can be taken to keep TVOC low in indoor spaces. [2]

The TVOC level in the office is 51.3 ppb, above the recommended level. Hence, it is of concern. [1]

Measure to keep TVOC level low (any of the below) [1]:

- increase ventilation by opening windows, turning on fan
- use air purifier with activated carbon
- use less/omit use of formaldehyde/toluene/xylene in furniture

[Total: 12]

END