



ANDERSON SERANGOON JUNIOR COLLEGE

2024 JC 2 PRELIMINARY EXAMINATION

NAME: _____ ()

CLASS: 24 / _____

CHEMISTRY

Paper 3 Free Response Questions

9729/03

13 September 2024

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and register 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 additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A

Answer **all** questions

Section B

Answer **one** question

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

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	A1	/ 21	Paper 1 (15%)	/ 30
	A2	/ 16	Paper 2 (30%)	/ 75
	A3	/ 23	Paper 3 (35%)	/ 80
	B4*	/ 20	Paper 4 (20%)	/ 55
	B5*	/ 20	Percentage	
	*Circle the question you have attempted			Grade

This document consists of **28** printed pages.

Section A

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

1 (a) (i) State the full electronic configuration of an Fe²⁺ ion. [1]

(ii) Explain why Fe²⁺(aq) ions are green, whereas aqueous Group 2 metal ions are not coloured. [4]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

(b) Iron(II) carbonate can be prepared by reacting solutions of the two ions, Fe²⁺(aq) and CO₃²⁻(aq). Explain why the same method cannot be used to prepare solid iron(III) carbonate. [2]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

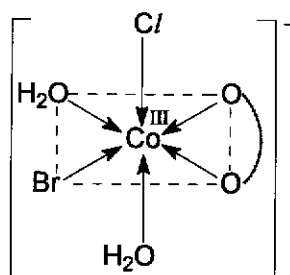
(e) The ethanedioate ion, $C_2O_4^{2-}$, can act as a bidentate ligand.

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

(ii) The complex $[Co(H_2O)_2(C_2O_4)BrCl]^-$ exists as stereoisomers.

Isomer L has the following structure.

The $C_2O_4^{2-}$ ligand is represented using .



Isomer L

Draw an isomer that has an equal and opposite effect on plane polarised light compared to isomer L. [1]

.....

.....

.....

.....

.....

.....

.....

.....

.....

[Total: 21]

- 2 (a) A sample of sulfur contains four stable isotopes as shown in Table 2.1.

Table 2.1

relative isotopic mass of S	percentage abundances / %
31.97	94.99
32.97	0.75
<i>w</i>	4.25
35.97	0.01

The relative atomic mass of sulfur in this sample is 32.06.

Use the data in Table 2.1 to calculate a value for *w* to 2 decimal places.

[1]

.....

.....

.....

.....

.....

.....

.....

.....

- (b) Table 2.2 lists the boiling points of different sulfur containing compounds.

Table 2.2

compound	formula	M_r	boiling point / °C
thiourea	$\begin{array}{c} \text{S} \\ \\ \text{H}_2\text{N}-\text{C}-\text{NH}_2 \end{array}$	76.1	150
thionyl fluoride	$\begin{array}{c} \text{O} \\ \\ \text{F}-\text{S}-\text{F} \end{array}$	86.1	-44
thionyl chloride	$\begin{array}{c} \text{O} \\ \\ \text{Cl}-\text{S}-\text{Cl} \end{array}$	119.1	79

- (i) Explain the difference in the boiling points between thionyl chloride and thionyl fluoride. [1]
- (ii) Explain why the boiling point of thiourea is much higher than thionyl fluoride with similar molecular mass. [1]

.....

.....

.....

.....

.....

.....

.....

.....

- (d) Sulfur combines with oxygen atom to form four sulfur oxoanions. Table 2.3 shows the average oxidation number of sulfur (S) and number of oxygen atoms in the oxoanions.

Table 2.3

oxoanion	average oxidation number of S	number of oxygen atoms
D	+2	3
E	+3	4
F	x	6
G	+6	y

All four sulfur oxoanions have two sulfur atoms and an overall negative charge of 2.

Only **D** has one central atom.

In **D**, **E** and **F** only,

- the sulfur atoms are bonded directly to each other and
- no oxygen atom is attached to another oxygen atom.

- (i) Suggest a value for x and y in the table. [2]
- (ii) Suggest the structural formulae showing the bonding in **D** and **E**. [2]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

[Total: 16]

3 Many important chemical compounds are derived from benzene.

- (a) X-ray diffraction studies show that all the carbon-carbon bonds in benzene are identical and equal in length.

Explain, in terms of hybridisation and orbital overlap, the identical and equal C–C bond length in benzene. [2]

.....

.....

.....

.....

.....

.....

.....

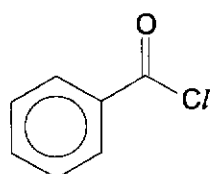
.....

.....

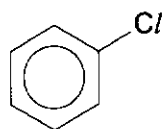
.....

.....

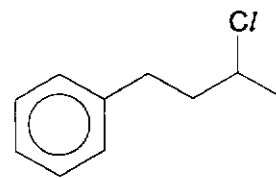
- (b) The three compounds below differ in their rate of hydrolysis when each compound is added separately to water at 25°C.



benzoyl chloride



chlorobenzene



3-chloro-1-phenylbutane

Arrange the three compounds in the order of increasing relative rate of hydrolysis. Explain your answer. [4]

.....

.....

.....

.....

.....

.....

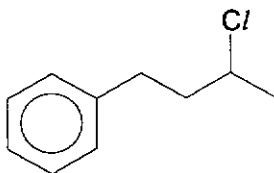
.....

.....

.....

.....

- (c) 3-chloro-1-phenylbutane undergoes a reaction to form three different organic products **L**, **M** and **N**.



3-chloro-1-phenylbutane

L, **M** and **N** decolourises aqueous bromine. **L** and **M** are cis-trans isomers of each other.

- State the type of reaction and the reagents and conditions to form **L**, **M** and **N** from 3-chloro-1-phenylbutane. [2]
- Draw the structures of **L**, **M** and **N**. Label the structures clearly as **L**, **M** and **N**. [2]
- Explain how molecules **L** and **M** are cis-trans isomers of each other. [1]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

- (d) Tulobuterol is a drug that is used in the management of asthma. It can be synthesised from benzene in four steps as shown in Fig. 3.1.

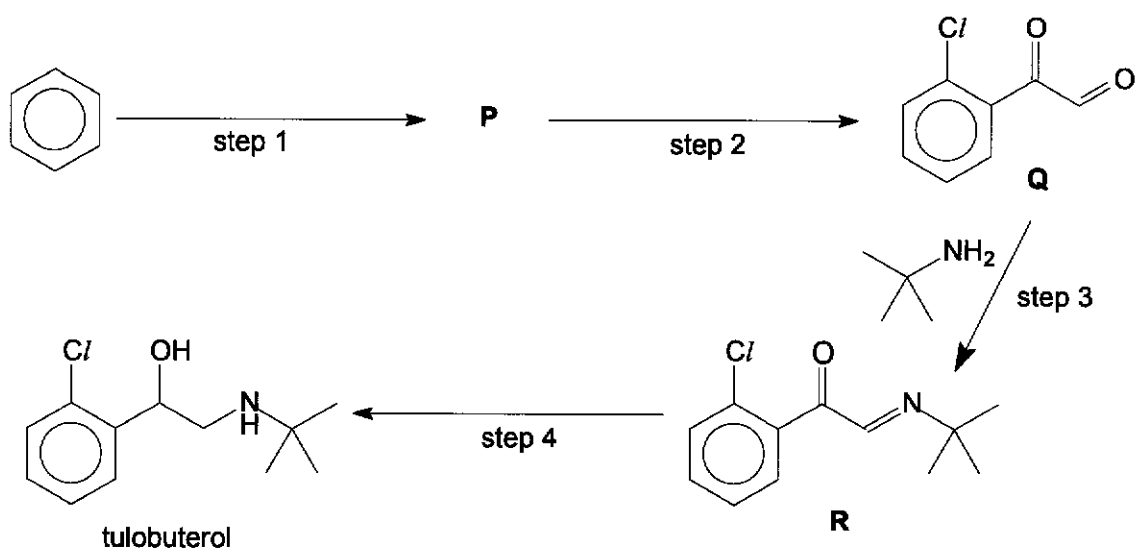


Fig. 3.1

- (i) Using information from the *Data Booklet*, suggest the structure for compound **P**, and reagents and conditions for each of the steps 1 and 2. [3]

- (ii) Suggest the type of reaction that occurred in step 3. [1]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

- (e) Benzoyl chloride readily undergoes a nucleophilic acyl substitution reaction with phenol to form phenyl benzoate.

Fig. 3.2 shows an incomplete mechanism for steps 1 and 2 of the reaction.

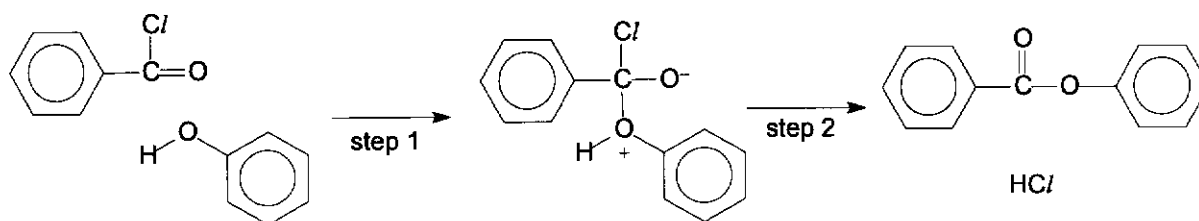
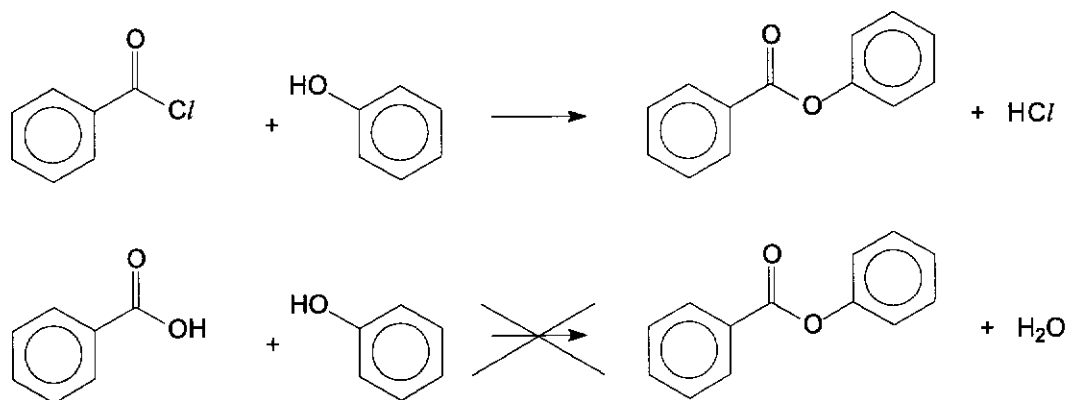


Fig. 3.2

- (i) On Fig. 3.2, draw curly arrows to show the mechanism for these two steps. Show all relevant lone pairs of electrons and dipoles. [3]
- (ii) Unlike benzoyl chloride, benzoic acid cannot undergo nucleophilic acyl substitution with phenol to form phenyl benzoate.



In terms of delocalisation of electrons, suggest why benzoyl chloride is more reactive towards phenol as compared to benzoic acid. [1]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

- (f) In non-polar solvents, benzoic acid, $C_6H_5CO_2H$, can form a dimer containing two hydrogen bonds.

Draw the structure of the dimer formed. Include lone pairs and dipoles and label the hydrogen bonds. [1]

.....

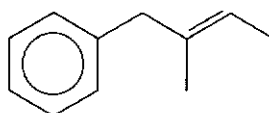
.....

.....

.....

.....

- (g) Compound **S** undergoes an addition reaction with $ICl(g)$.



S

- (i) Draw the structures of the two possible constitutional isomers that could be formed. [1]
- (ii) Draw the structure of the intermediate that forms the major product in the reaction. Give a reason for the structure drawn. [2]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

[Total: 23]

Section B

Answer **one** question from this section.

- 4 (a) With reference to *Data Booklet*, describe and explain the trend in the thermal stability of HCl, HBr and HI. [3]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

- (b) Butan-2-ol is formed from the nucleophilic substitution reaction of 2-bromobutane, $\text{CH}_3\text{CH}_2\text{CHBrCH}_3$ with 1 mol dm^{-3} aqueous NaOH.

The concentration of $\text{CH}_3\text{CH}_2\text{CHBrCH}_3$ was monitored over a period and the results were recorded in Table 4.1.

Table 4.1

time/s	$[\text{CH}_3\text{CH}_2\text{CHBrCH}_3] / \text{mol dm}^{-3}$
0	0.02100
100	0.01800
200	0.01600
300	0.01400
400	0.01200
500	0.01050
600	0.00900
700	0.00800
800	0.00700
900	0.00600
1000	0.00525
1100	0.00450

- (c) Compound **V**, $C_{11}H_{14}O_2$ forms compounds **W** and **X** with aqueous acidified potassium manganate(VII) in the presence of heat. **W**, $C_7H_6O_2$ gives effervescence with sodium carbonate.

Samples of compound **X** are reacted separately with

- alkaline aqueous iodine forming a yellow precipitate
- Fehling's reagent and no change is observed
- an excess of $LiAlH_4$ to form a chiral organic compound **Y**

Y is also formed when **V** is heated with aqueous H_2SO_4 .

Suggest possible structures for **V**, **W**, **X** and **Y**.

For each reaction described, state the type of reaction and explain what the information tells you about the functional groups present in each compound. [7]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

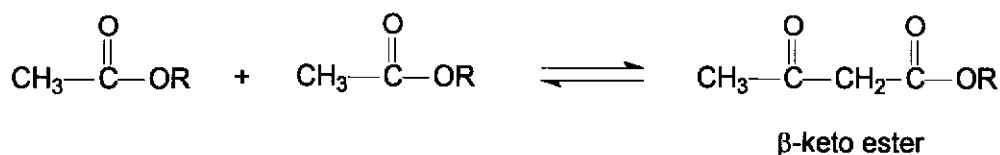
.....

.....

.....

.....

- (d) Claisen condensation reaction is a reversible reaction between two esters to yield a β -keto ester.



In the synthesis of ethyl 3-oxobutanoate, the α -hydrogen of ethyl ethanoate is removed by the addition of one equivalent of ethoxide ion as shown in equation 4.1. The carbanion formed reacts with another molecule of ethyl ethanoate to form ethyl 3-oxobutanoate in equation 4.2.

equation 4.1



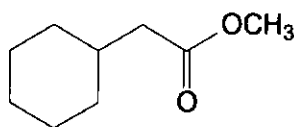
equation 4.2



- (i) Ethyl ethanoate behaves as an acid in equation 4.1 and equation 4.2.

Identify the type of acid behaviour shown by ethyl ethanoate in each of these equations. Explain your answers. [2]

- (ii) Suggest the structure of the final product formed from the Claisen condensation of compound Z.



Z

[1]

.....

.....

.....

.....

.....

.....

.....

.....

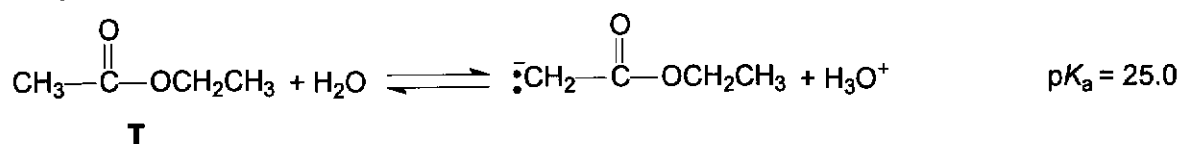
.....

.....

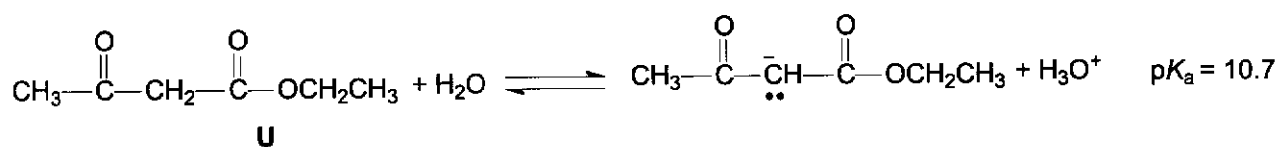
.....

- (e) The dissociation equilibrium of two compounds, **T** and **U**, are shown in equation 4.3 and equation 4.4 respectively.

equation 4.3



equation 4.4



Suggest why $\text{p}K_{\text{a}}$ of **U** is lower than that of **T**.

[2]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

[Total: 20]

- 5 (a) When solid NaCl and $AlCl_3$ are separately added to water, solutions with different pH values are produced.

Explain why the two chlorides differ in their reaction with water. State the pH of the resulting solutions and write appropriate equations to illustrate your answers. [3]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

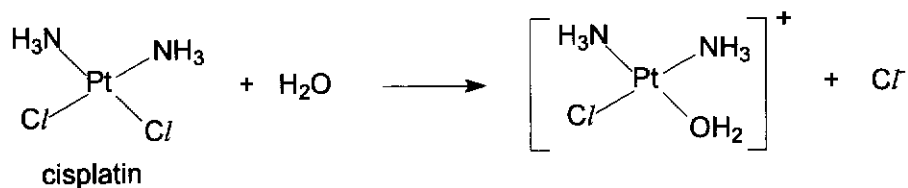
.....

.....

.....

.....

- (b) The rate of hydrolysis of the anticancer drug cisplatin can be investigated by monitoring the concentration of the chloride ion formed.



Complete hydrolysis of cisplatin takes more than 24 hours.

A solution of $0.010 \text{ mol dm}^{-3}$ cisplatin was allowed to undergo hydrolysis at pH 7 and 25°C with excess water. At suitable time intervals, an aliquot of the cisplatin mixture was pipetted into a conical flask and quenched.

The amount of chloride ion is titrated against aqueous AgNO_3 using potassium chromate indicator.

Fig. 5.1 shows the concentration of chloride ions formed on hydrolysis of cisplatin against time for this experiment.

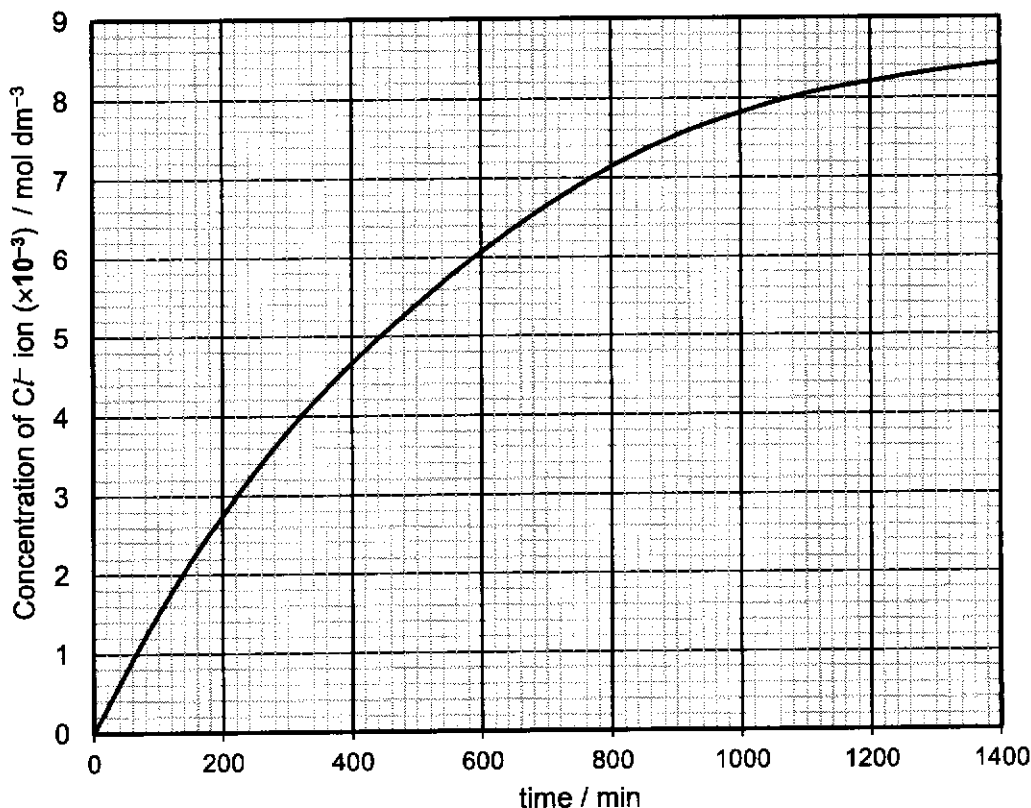
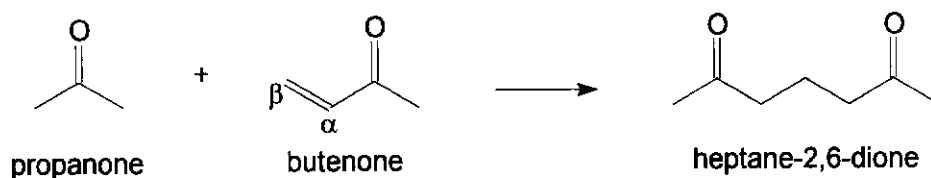


Fig. 5.1

- (i) Considering the total concentration of chloride that will be obtained upon complete hydrolysis of cisplatin, use Fig. 5.1 to show that the reaction is first order with respect to cisplatin. [2]

- (c) The formation of heptane-2,6-dione via a *Michael Addition reaction* involves the formation of a carbon-carbon bond between propanone and butenone (an α,β -unsaturated ketone).



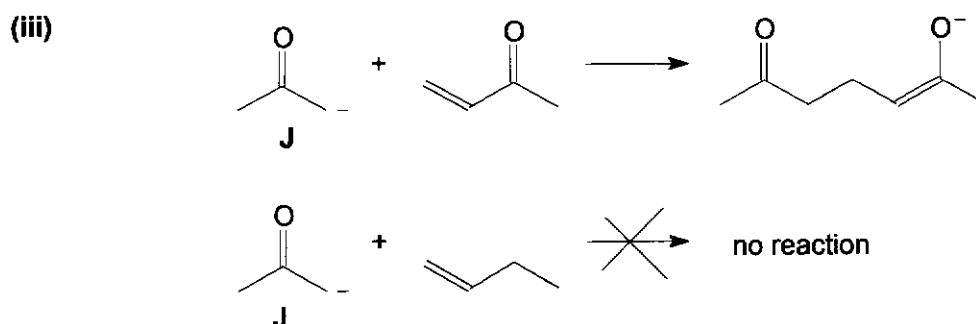
The three steps of the reaction are described in Table 5.1.

Table 5.1

step	equation
1	<chem>CC(=O)C.[OH-]>>CC([O-])C.O</chem>
2	<chem>CC([O-])C.C=CC(=O)C>>CC(=O)CCC([O-])=C</chem>
3	<chem>CC(=O)CCC([O-])=C.O>>CC(=O)CCCC(=O)C.[OH-]</chem>

- (i) State the type of reaction in step 1. [1]

- (ii) Complete the nucleophilic addition mechanism for step 2 in Table 5.1 by adding a lone pair and three curly arrows. [1]

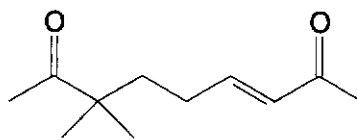


No reaction occurs when but-1-ene is used in place of butenone to react with J in step 2.

Using the concept of electronegativity and electronic effect, explain why butenone reacts with J while but-1-ene does not. [2]

25

- (iv) Compound **K** undergoes an intramolecular *Michael Addition* reaction to form a product, C₁₁H₁₈O₂.



K

Suggest a structure for the product formed.

[1]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

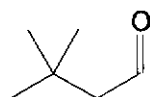
.....

.....

.....

.....

- (d) A carbon-carbon bond can also be formed between two molecules of compound **H** using suitable reagents and conditions.

**H**

Give the systematic name of compound **H**. [1]

.....

- (e) **L**, C_6H_9ClO , is a non-aromatic compound.

L reacts with 2,4-dinitrophenylhydrazine to form an orange precipitate but does not react with Tollen's reagent.

1 mole of **L** reacts with 2 moles of hydrogen gas in the presence of solid platinum.

When **L** is heated with potassium manganate(VII) in aqueous sodium hydroxide, then followed by adding sulfuric acid to the resultant mixture, **M** and **N** are formed.

M, $C_2H_4O_2$, liberates carbon dioxide gas upon addition of aqueous sodium carbonate solution.

N, $C_4H_4O_5$, reacts with 2,4-dinitrophenylhydrazine to form an orange precipitate.

1 mole of **N** reacts with 2 moles of aqueous sodium hydroxide.

Suggest possible structures for **L**, **M** and **N**.

For each reaction described, state the type of reaction and explain what the information tells you about the functional groups present in each compound. [7]

.....

.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....

[Total: 20]



ANDERSON SERANGOON JUNIOR COLLEGE
2024 JC 2 PRELIMINARY EXAMINATION

NAME: _____ () CLASS: 24 / _____

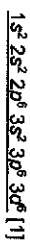
CHEMISTRY

9729/03

Paper 3 Free Response Questions

SUGGESTED SOLUTIONS

1 (a) (i) State the full electronic configuration of an Fe^{2+} ion. [1]



(ii) Explain why $Fe^{2+}(aq)$ ions are green, whereas aqueous Group 2 metal ions are not coloured. [4]

In the presence of water ligands, the partially filled 3d orbitals of Fe^{2+} are split into two levels with a small energy gap, ΔE (d orbital splitting).

When a 3d electron absorbs energy from the visible light region corresponding to ΔE , this electron is promoted from the d orbital of a lower energy level to a d orbital of a higher energy level (d-d transition).

The green colour of $Fe^{2+}(aq)$ is the complement of the red colour absorbed.

Aqueous Group 2 metal ions do not have electrons in the d subshell for d-d transition to occur.

[1]: partially filled 3d-orbital for $Fe^{2+}(aq)$; small energy gap

[1]: d-d transition

[1]: green colour of $Fe^{2+}(aq)$ is the complement of the red colour absorbed

[1]: no electron in 3d-orbital for group 2 metal ions and no d-d transition

(b) Iron(II) carbonate can be prepared by reacting solutions of the two ions, $Fe^{2+}(aq)$ and $CO_3^{2-}(aq)$. Explain why the same method cannot be used to prepare solid iron(II) carbonate. [2]

Due to the smaller cation size and a larger positive charge than Fe^{2+} , Fe^{3+} has a higher charge density (high polarising power). Fe^{3+} is able to draw electrons to itself from the oxygen atoms of the neighbouring water molecules, which further polarises the O-H bonds, thereby producing H^+ in the solution. [1]

H^+ in the solution undergoes acid-base reaction with the carbonate ions and produce CO_2 instead. [1]

(c) The minimum temperature to decompose some Group 2 carbonates increases down the group as shown in Table 1.1.

Table 1.1

Group 2 carbonate	Minimum temperature of decomposition / °C
$MgCO_3$	350
$CaCO_3$	840
$SiCO_3$	1289
$BaCO_3$	1360

When heated, solid copper(II) carbonate behaves in a similar way to the Group 2 carbonates.

(i) Write an equation for the thermal decomposition of copper(II) carbonate. [1]



(ii) Use data from the Data Booklet and Table 1.1 to suggest a minimum temperature at which pure copper(II) carbonate decomposes. Explain your reasoning. [3]

Cu^{2+} has an ionic radius of 0.073 nm, which is an intermediate between that of Mg^{2+} (0.065) and Ca^{2+} (0.099). [1]

Minimum decomposition temperature of $CuCO_3$ could be 450 °C. (accept value between 360 – 820). [1]

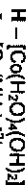
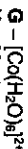
Cu^{2+} has a charge density between that of Mg^{2+} and Ca^{2+} . Hence, it has and weaker polarising power than Mg^{2+} but stronger than that of Ca^{2+} . The electron cloud of the carbonate is distorted and the C-O bond is weakened to a smaller extent than by Mg^{2+} but greater extent than by Ca^{2+} . Hence, a temperature higher than 350 °C but lower than 840 °C is required. [1]

(d) The chemistry and coordination of cobalt(II) compounds are similar to those of copper(II) compounds with similar ligands.

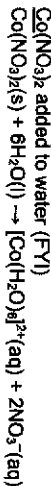
(i) When cobalt(II) nitrate, $Co(NO_3)_2$, is added to water, a pink solution of G is formed.

When aqueous sodium hydroxide is added to solution G, a blue precipitate H is observed. Precipitate H dissolves when excess aqueous ammonia is added to form a brown solution I. Nitrogen and hydrogen are the only other elements in the octahedral cobalt-containing complex in I.

Identify the complex species in G, H and I. For each of the reactions to form H and I, identify the type of reaction and give relevant chemical equations. [4]



[2] All three species correctly identified



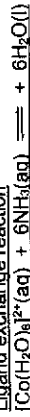
Aqueous sodium hydroxide added to G:

Acid-base reaction



Aqueous ammonia added to precipitate H:

Ligand exchange reaction



[2] for types of reaction and equations

- (ii) Addition of concentrated hydrochloric acid to pink solution G forms a blue solution J. Solution J turns pink again when water is added to it. [2]

With the aid of a balanced equation, explain these observations.



There's an equilibrium between G and J.

Addition of HCl causes concentration of Cl^- to increase and position of equilibrium shifts to the right and form J. $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ undergoes ligand exchange reaction with Cl^- ligands to form the blue complex, $[\text{CoCl}_4]^{2-}(\text{aq})$. [1] for equation and explanation.

When water is added, concentration of ions decreases, and position of equilibrium shifts to the left to form more ions and forms the pink $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. [1]

- (iii) Salt K has the molecular formula $\text{CoN}_5\text{H}_{17}\text{OCl}_3$ ($M_r = 268.4$). It has one or more ligands which is similar to those found in complex species G, H and J.

When 1.00 g of salt K is dissolved in water, the resulting solution required 22.40 cm^3 of 0.50 mol dm^{-3} silver nitrate solution for complete reaction.

Calculate the number of moles of free chloride ions per mole of K and give the structural formula of the complex ion in K. [2]

Number of moles of $\text{AgNO}_3 = 22.4/1000 \times 0.50 = 0.0112$ mol

Number of moles of free $\text{Cl}^- = 0.0112$ mol

Number of moles of K = $1/268.4 = 0.00372$ mol

Number of moles of free Cl^- per mole of K = $0.0112/0.00372 = 3$ [1]

Since there are 3 free Cl^- ion, there is no Cl^- coordinated to the Co center.

Structure of the complex ion in K is $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$. [1]

- (e) The ethanedioate ion, $\text{C}_2\text{O}_4^{2-}$, can act as a bidentate ligand.

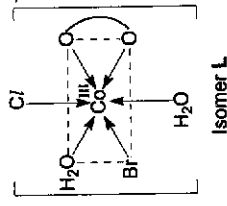
(i) Explain what is meant by a ligand. [1]

A ligand is a neutral molecule or an anion that has at least one lone pair of electrons to be used in forming a dative bond to the central metal atom or ion.

- (ii) The complex $[\text{Co}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]\text{BrCl}$ exists as stereoisomers.

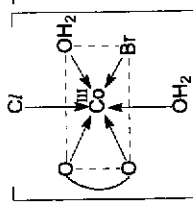
Isomer L has the following structure.

The $\text{C}_2\text{O}_4^{2-}$ ligand is represented using O and C .



Isomer L

Draw an isomer that has an equal and opposite effect on plane polarised light compared to isomer L. [1]



Mirror image of isomer L [1]

[Total: 21]

- 2 (a) A sample of sulfur contains four stable isotopes as shown in Table 2.1.

Table 2.1

relative isotopic mass of S	percentage abundances / %
31.97	94.99
32.97	0.75
w	4.25
35.97	0.01

The relative atomic mass of sulfur in this sample is 32.06.

Use the data in Table 2.1 to calculate a value for w to 2 decimal places.

[1]

$$32.06 = \frac{(31.97 \times 94.99) + (32.97 \times 0.75) + (w \times 4.25) + (35.97 \times 0.01)}{100}$$

$$3206 = 3205.9303 + 4.25w$$

$$w = 33.90$$

[1] answer to 2 dp and no units.

- (b) Table 2.2 lists the boiling points of different sulfur containing compounds.

Table 2.2

compound	formula	M_r	boiling point / °C
thiourea	<chem>NC(=S)N</chem>	76.1	150
thionyl fluoride	<chem>OS(=F)F</chem>	86.1	-44
thionyl chloride	<chem>OS(=Cl)Cl</chem>	119.1	79

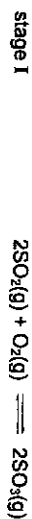
- (i) Explain the difference in the boiling points between thionyl chloride and thionyl fluoride. [1]

As SOCl2 has more electrons / bigger electron cloud than that of SOF2, the electron cloud of SOCl2 is more easily polarised. Hence, more energy is required to overcome the stronger instantaneous dipole-induced dipole attractions between SOCl2 molecules. [1]

- (ii) Explain why the boiling point of thiourea is much higher than thionyl fluoride with similar molecular mass. [1]

More energy is required to overcome the stronger hydrogen bonding between CS(NH2)2 molecules than weaker instantaneous dipole-induced dipole attraction (permanent dipole-permanent dipole attraction) between SOF2 molecules. [1]

- (c) The Contact process used to produce sulfuric acid involves three stages. Using V2O5 as a catalyst, stage I achieves 99.5% conversion of sulfur dioxide to sulfur trioxide.



- (i) Write an expression each for K_c and K_p of reaction in stage I. [2]

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$$

$$K_p = \frac{(p_{\text{SO}_3})^2}{(p_{\text{SO}_2})^2(p_{\text{O}_2})}$$

[1] for each expression

- (ii) Using the ideal gas equation, show that $K_p = K_c \left(\frac{1}{RT}\right)$. [1]

$$\begin{aligned} \text{Using } pV &= nRT \\ p &= (n/V)RT \\ &= cRT \end{aligned}$$

$$K_p = \frac{([\text{SO}_3]RT)^2}{([\text{SO}_2]RT)^2([\text{O}_2]RT)}$$

$$\begin{aligned} &= \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]RT} \\ &= \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} \left(\frac{1}{RT}\right) \\ &= K_c \left(\frac{1}{RT}\right) \text{ (shown)} \end{aligned}$$

[1]

- (iii) At 723 K, the equilibrium partial pressures of SO2, O2 and SO3 are 600 Pa, 3300 Pa and 11400 Pa respectively.

Calculate the value of K_p for the reaction in stage I. State the units. [2]

$$K_p = (11400)^2 / (600)^2(3300) = 0.109 \text{ Pa}^{-1}$$

[1] for correct final answer
[1] for unit

- (iv) When the temperature increases from 723 K to 1000 K, the partial pressure of SO2 increases. Deduce the sign of ΔH for the forward reaction in stage I. [2]

ΔH is negative. [1] with reasoning

When T increases, $p(\text{SO}_2)$ increases. This shows that position of equilibrium has shifted to the left to favour the backward endothermic reaction. [1]

Since endothermic reaction is favoured when T increases, we can conclude that the backward reaction is endothermic and forward reaction is exothermic.



- (v) State and explain the effect of the presence of a catalyst on the equilibrium position and the value of the equilibrium constant. [2]

A catalyst has no effect on the equilibrium position and the value of K_c . [1]

The presence of catalyst increases the rate of the forward and backward reaction to the same extent. [1]

$$(K_c = k_f / k_b \Rightarrow K_c \text{ constant})$$

- (d) Sulfur combines with oxygen atom to form four sulfur oxoanions. Table 2.3 shows the average oxidation number of sulfur (S) and number of oxygen atoms in the oxoanions. [2]

Table 2.3

oxoanion	average oxidation number of S	number of oxygen atoms
D	+2	3
E	+3	4
F	x	6
G	+6	y

All four sulfur oxoanions have two sulfur atoms and an overall negative charge of 2.

Only D has one central atom.

In D, E and F only,

- the sulfur atoms are bonded directly to each other and
- no oxygen atom is attached to another oxygen atom.

- (i) Suggest a value for x and y in the table. [2]

For F:

$$2x + 6(-2) = -2$$

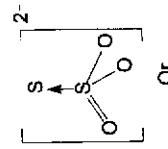
$$x = \mathbf{+5}$$

For G:

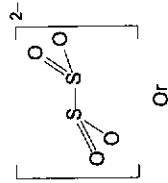
$$2(+6) + y(-2) = -2$$

$$y = \mathbf{7}$$

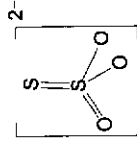
- (ii) Suggest the structural formulae showing the bonding in D and E. [2]



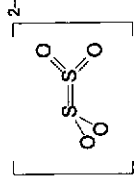
Or



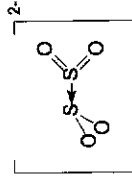
Or



structural formula of D



Or



structural formula of E

[1] for each correct structure

[Total: 16]

3 Many important chemical compounds are derived from benzene.

- (a) X-ray diffraction studies show that all the carbon-carbon bonds in benzene are identical and equal in length.

Explain, in terms of hybridisation and orbital overlap, the identical and equal C-C bond length in benzene.

The carbon atoms in benzene are sp² hybridised.

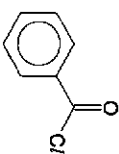
[2]

Each C atom uses two sp² hybrid orbitals to overlap head-on with the sp² hybrid orbitals of two adjacent C atoms to form two C-C σ bonds. [1]

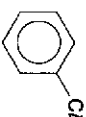
The unhybridised p orbitals of each carbon atom overlaps sideways with its adjacent p orbitals of carbon atoms on either side above and below the plane of the ring to form a π electron cloud. The six electrons in the π electron cloud are delocalised. [1]

Hence each C-C bond has the same electron density and bond strength making them equal and intermediate in length between single and double carbon-carbon bonds.

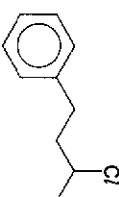
- (b) The three compounds below differ in their rate of hydrolysis when each compound is added separately to water at 25°C.



benzoyl chloride



chlorobenzene



3-chloro-1-phenylbutane

Arrange the three compounds in the order of increasing relative rate of hydrolysis.

Explain your answer.

[4]

Increasing rate of hydrolysis:

chlorobenzene, 1-chloro-2-phenylethane, benzoyl chloride [1]

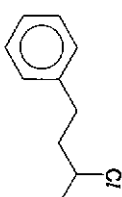
Hydrolysis is the fastest for benzoyl chloride. This is because the C atom of the acyl group is bonded to two highly electronegative atoms, O and Cl. This makes the C highly electron-deficient and very susceptible to reaction even with weak nucleophiles such as H₂O. [1]

Hydrolysis is slower for 3-chloro-1-phenylbutane. This is because the C atom bonded to Cl is bonded to only one electronegative atom, Cl. This makes the C less electron-deficient and less susceptible to reaction with nucleophiles. [1]

No hydrolysis takes place for chlorobenzene. This is because the p-orbital of the Cl atom overlaps with the π-electron cloud of the benzene ring. The lone pair of electrons in the p-orbital of the Cl atom can delocalise into the benzene ring creating partial double bond character, resulting in the strong C-Cl bond that is very difficult to break in chlorobenzene. Furthermore, there is also reduced electron deficiency on the C atom. [1]

The π electron cloud of the benzene also sterically hinders the attack by the nucleophile on the carbon bonded to chlorine.

- (c) 3-chloro-1-phenylbutane undergoes a reaction to form three different organic products L, M and N.



3-chloro-1-phenylbutane

L, M and N decolourises aqueous bromine. L and M are cis-trans isomers of each other.

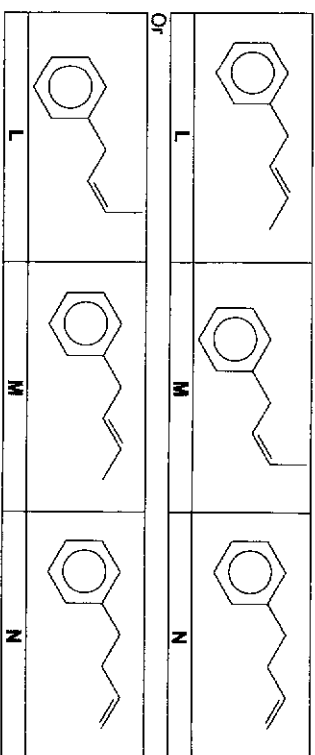
- (i) State the type of reaction and the reagents and conditions to form L, M and N from 3-chloro-1-phenylbutane.

[2]

Type of reaction: Elimination [1]

Reagents and condition: NaOH in ethanol, heat under reflux [1]

- (ii) Draw the structures of L, M and N. Label the structures clearly as L, M and N. [2]



[1] for N

[1] for L and M (cis and trans clearly shown in the structures)

- (iii) Explain how molecules L and M are cis-trans isomers of each other. [1]

Both L and M have a C=C bond, with both carbon atoms of the C=C bonded to two different groups (an alkyl group and a H atom), allowing for different spatial arrangements of these two groups on each of the carbon atoms due to restricted rotation around the C=C bond. [1]

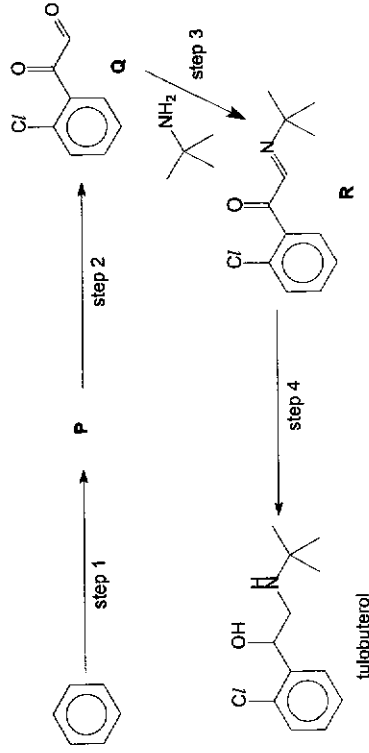
In L, the H atoms are on the opposite sides of the C=C bond, so L is the trans isomer, whereas in M, the two-H groups are on the same side of the C=C bond, so M is the cis isomer

OR

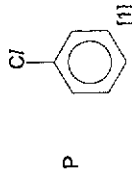
Both L and M have a C=C bond, with both carbon atoms of the C=C bonded to two different groups (an alkyl group and a H atom), allowing for different spatial arrangements of these two groups on each of the carbon atoms due to restricted rotation around the C=C bond. [1]

In **M**, the H atoms are on the opposite sides of the C=C bond, so **M** is the trans isomer, whereas in **L**, the two-H groups are on the same side of the C=C bond, so **L** is the cis isomer.

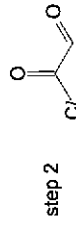
- (d) Tulobuterol is a drug that is used in the management of asthma. It can be synthesised from benzene in four steps as shown in Fig. 3.1.



- (i) Using information from the Data Booklet, suggest the structure for compound **P**, and reagents and conditions for each of the steps 1 and 2. [3]



step 1 $\text{Cl}_2, \text{AlCl}_3$, anhydrous, room temperature [1]



- (ii) Suggest the type of reaction that occurred in step 3. [1]

Condensation or addition-elimination [1]

- (e) Benzoyl chloride readily undergoes a nucleophilic acyl substitution reaction with phenol to form phenyl benzoate.

Fig. 3.2 shows an incomplete mechanism for steps 1 and 2 of the reaction.

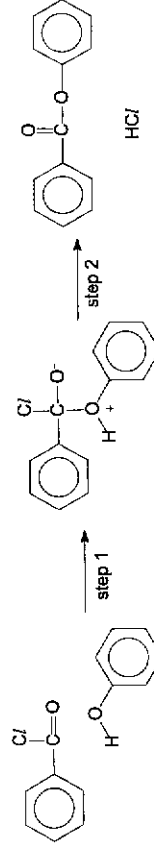
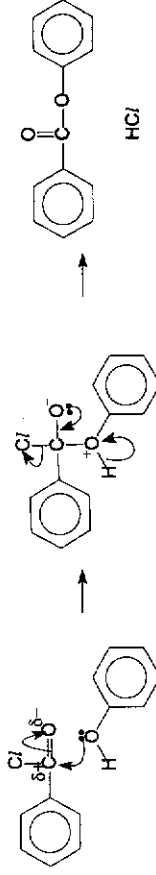


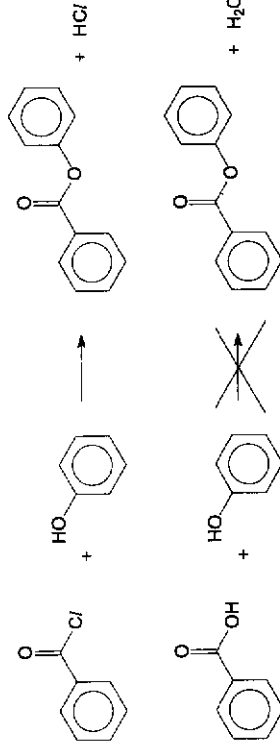
Fig. 3.2

- (i) On Fig. 3.2, draw curly arrows to show the mechanism for these two steps. Show all relevant lone pairs of electrons and dipoles. [3]



[3]

- (ii) Unlike benzoyl chloride, benzoic acid cannot undergo nucleophilic acyl substitution with phenol to form phenyl benzoate.



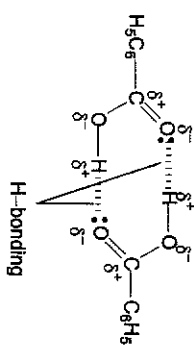
In terms of delocalisation of electrons, suggest why benzoyl chloride is more reactive towards phenol as compared to benzoic acid. [1]

There is a smaller extent of delocalisation of lone pair of electrons from Cl atom to the π electron cloud of the C=O in benzoyl chloride as compared to delocalisation of lone pair of electrons from O atom to the π electron cloud of the C=O in benzoic acid. This makes the C atom of C=O more electron deficient in benzoyl chloride than that in benzoic acid. [1] This makes benzoyl chloride more susceptible to a reaction with phenol.

Why is there a smaller extent of delocalisation in benzoyl chloride? Overlap of 2p orbital of the C atom of C=O with the 3p orbital of the Cl atom is less effective in benzoyl chloride as compared to the overlap of 2p orbital of the C atom of the C=O with the 2p orbital of the O atom of the OH group in benzoic acid.

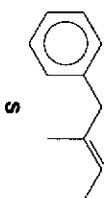
- (f) In non-polar solvents, benzoic acid, $C_6H_5CO_2H$, can form a dimer containing two hydrogen bonds.

Draw the structure of the dimer formed. Include lone pairs and dipoles and label the hydrogen bonds. [1]

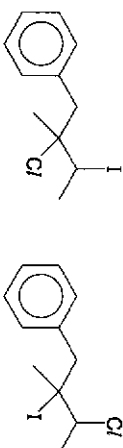


[1]

- (g) Compound **S** undergoes an addition reaction with $ICl(g)$.

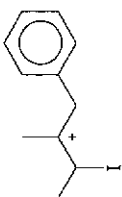


- (i) Draw the structures of the two possible constitutional isomers that could be formed. [1]



[1] for both structures

- (ii) Draw the structure of the intermediate that forms the major product in the reaction. Give a reason for the structure drawn. [2]



[1]

Intermediate that forms the major product

This intermediate is preferably formed compared to the other intermediate as there are more electron-donating alkyl groups bonded to the electron deficient C atom (C^+). This disperses the positive charge on the C to a greater extent and stabilise the intermediate to a greater extent. [1]

[Total: 23]

- 4 (a) With reference to *Data Booklet*, describe and explain the trend in the thermal stability of HCl , HBr and HI . [3]

HCl does not decompose.

HBr decomposes slightly to give some brown fumes of Br_2 .

HI decomposes readily to give purple fumes of I_2 on gentle heating. [1] describing the trend

- Thermal stability decreases from HCl to HBr to HI .
 - This is because the size of valence orbitals increases and become more diffused from Cl to Br and to I . This causes less effective overlap between the (valence) orbital of halogen and (s) orbital of hydrogen.
 - $H-X$ bond becomes weaker from HCl to HBr to HI and bond energy $H-X$ decreases.
 - Bond energy: $H-Cl$ (431 kJ mol^{-1}) > $H-Br$ (366 kJ mol^{-1}) > $H-I$ (298 kJ mol^{-1}).
- Hence ease of decomposition increases from HCl to HBr to HI . [2]

- (b) Butan-2-ol is formed from the nucleophilic substitution reaction of 2-bromobutane, $CH_3CH_2CHBrCH_3$ with 1 mol dm^{-3} aqueous $NaOH$.

The concentration of $CH_3CH_2CHBrCH_3$ was monitored over a period and the results were recorded in Table 4.1.

Table 4.1

time/s	$[CH_3CH_2CHBrCH_3] / \text{mol dm}^{-3}$
0	0.02100
100	0.01800
200	0.01600
300	0.01400
400	0.01200
500	0.01050
600	0.00900
700	0.00800
800	0.00700
900	0.00600
1000	0.00525
1100	0.00450

- (i) Use the data to prove that reaction is first order with respect to $CH_3CH_2CHBrCH_3$. [1]

$[CH_3CH_2CHBrCH_3]$ took 500 s to decrease from 0.02100 mol dm⁻³ to 0.0105 mol dm⁻³ and another 500 s from 0.0105 mol dm⁻³ to 0.00525 mol dm⁻³ (can also use 0.01800 to 0.00900 to 0.0045)

Since 1/2 is constant at 500 s, order of reaction with respect to $CH_3CH_2CHBrCH_3 = 1$

[1] show and conclude that two $t_{1/2}$ is constant

- (ii) The rate of reaction is also found to be first order with respect to OH^- . Write the rate equation for the nucleophilic substitution of $CH_3CH_2CHBrCH_3$ with aqueous $NaOH$. Include the units for the rate constant. [1]

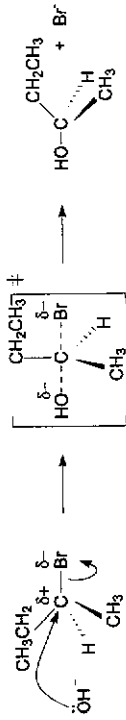
rate = $k[CH_3CH_2CHBrCH_3][OH^-]$

Unit for k : $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$

[1] for both rate equation and unit.

- (iii) Describe the nucleophilic substitution mechanism of a single enantiomer of $\text{CH}_3\text{CH}_2\text{CHBrCH}_3$ with aqueous NaOH . Show the stereochemistry of the reactant and product clearly in your answer. [3]

Nucleophilic substitution ($\text{S}_{\text{N}}2$)



- ✓ dipole on C-Br
- ✓ lone pair on OH^-
- ✓ arrow from lone pair on OH^- to C
- ✓ show attack of OH^- from 180° away from the leaving group
- ✓ arrow from C-Br bond to Br
- ✓ transition state (partial negative charges on O and Br and symbol)
- ✓ transition state (partial bonds)
- ✓ Br formed
- ✓ stereochemistry shown in reactant
- ✓ inverted stereochemistry shown in the product

[3]

- (c) Compound **V**, $\text{C}_{11}\text{H}_{14}\text{O}_2$ forms compounds **W** and **X** with aqueous acidified potassium manganate(VII) in the presence of heat. **W**, $\text{C}_7\text{H}_6\text{O}_2$ gives effervescence with sodium carbonate.

Samples of compound **X** are reacted separately with

- alkaline aqueous iodine forming a yellow precipitate
- Fehling's reagent and no change is observed
- an excess of LiAlH_4 to form a chiral organic compound **Y**

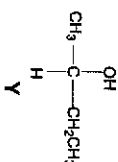
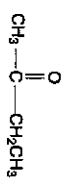
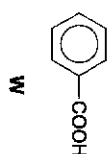
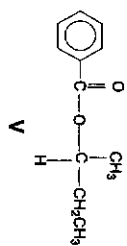
Y is also formed when **V** is heated with aqueous H_2SO_4 .

Suggest possible structures for **V**, **W**, **X** and **Y**.

For each reaction described, state the type of reaction and explain what the information tells you about the functional groups present in each compound. [7]

- **V** undergoes hydrolysis and oxidation with aqueous acidified potassium manganate(VII) to form **W** and **X**.
→ **V** is an ester.
- **W** has C:H ratio \equiv 1: 1 and no. of C \geq 6.
→ **W** contains a benzene ring.
- **W** undergoes acid-base reaction with sodium carbonate.
→ **W** is a carboxylic acid.
- **X** undergoes oxidation with aqueous alkaline iodine.
→ **X** has the structure $\text{CH}_3-\text{C}(=\text{O})-\text{R}$
- **X** does not undergo oxidation with Fehling's reagent.
→ **X** is not an aldehyde.
- **X** undergoes reduction with LiAlH_4 to form **Y**.
→ **Y** is a secondary alcohol.
- **V** undergoes hydrolysis when heated with aqueous H_2SO_4 . **Y** is an alcohol.

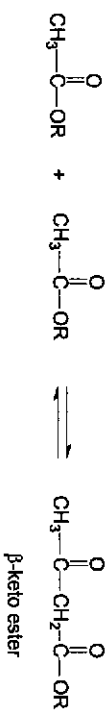
	Info from Qn	Type of Reaction	Deduction
1	Compound V , $\text{C}_{11}\text{H}_{14}\text{O}_2$ forms compounds W and X with aqueous acidified potassium manganate(VII) in the presence of heat. W has molecular formula $\text{C}_7\text{H}_6\text{O}_2$.	<u>Hydrolysis</u> ✓ <u>Oxidation</u> ✓	V is an <u>ester</u> . ✓
2			<ul style="list-style-type: none"> • W has <u>C:H ratio</u> \equiv 1: 1 and <u>no. of C</u> \geq 6. → W contains a <u>benzene ring</u>. ✓ • X contains 4 C
3	W , $\text{C}_7\text{H}_6\text{O}_2$ gives effervescence with sodium carbonate.	<u>acid-base reaction</u> ✓	W is a <u>carboxylic acid</u> . ✓
4	X reacts with alkaline aqueous iodine forming a yellow precipitate.	<u>oxidation</u> ✓	X has the structure $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$. ✓
5	X has no change with Fehling's reagent.	No <u>oxidation</u> ✓	X is <u>not an aldehyde</u> or X is a <u>ketone</u> . ✓
6	X reacts with an excess of LiAlH_4 to form a chiral organic compound Y .	<u>reduction</u> ✓	Y is a <u>secondary alcohol</u> . ✓
7	Y is also formed when V is heated with aqueous H_2SO_4 .	<u>hydrolysis</u> ✓	Y is an <u>alcohol</u> . ✓ (credit this if this is not credited in 6)



[1] for each structure of V, W, X and Y

[3] for types of reaction and deductions

(d) Claisen condensation reaction is a reversible reaction between two esters to yield a β -keto ester.



In the synthesis of ethyl 3-oxobutanoate, the α -hydrogen of ethyl ethanoate is removed by the addition of one equivalent of ethoxide ion as shown in equation 4.1. The carbanion formed reacts with another molecule of ethyl ethanoate to form ethyl 3-oxobutanoate in equation 4.2.

equation 4.1



equation 4.2



(i) Ethyl ethanoate behaves as an acid in equation 4.1 and equation 4.2.

Identify the type of acid behaviour shown by ethyl ethanoate in each of these equations. Explain your answers. [2]

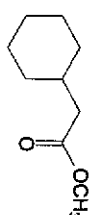
Equation 4.1:

Brønsted Lowry acid. It donated a H⁺ to the ethoxide ion to form the carbanion and ethanol. [1]

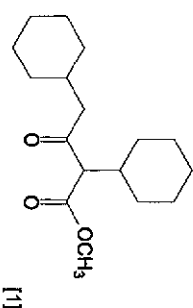
Equation 4.2:

Lewis acid. It accepted a pair of electrons from the carbanion to form ethyl 3-oxobutanoate. [1]

(ii) Suggest the structure of the final product formed from the Claisen condensation of compound Z.

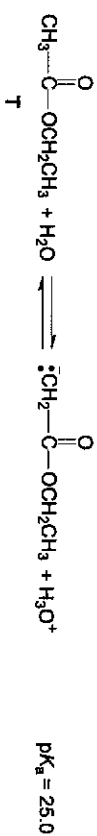


[1]

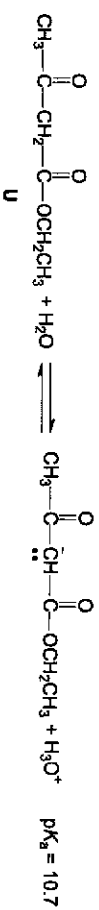


(e) The dissociation equilibrium of two compounds, T and U, are shown in equation 4.3 and equation 4.4 respectively.

equation 4.3



equation 4.4



Suggest why pK_a of U is lower than that of T. [2]

In the anion of U, there are two electron withdrawing C=O groups as compared to one electron-withdrawing C=O group in the anion of T. [1]

This disperses the negative charge on the anion of U and stabilises the anion to a greater extent. Hence, the dissociation of the U to release H⁺ is more favoured. It is more acidic than T and has a lower pK_a value than T. [1]

Or

In the anion of U, the lone pair of electrons on C⁻ can be delocalised to the π electron clouds of two C=O groups as compared to one C=O group in the anion of T. [1]

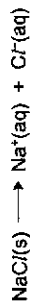
This disperses the negative charge on the anion of U and stabilises the anion to a greater extent. Hence, the dissociation of the U to release H⁺ is more favoured. It is more acidic than T and has a lower pK_a value than T. [1]

[Total: 20]

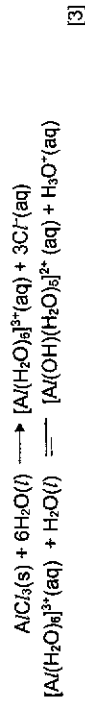
- 5 (a) When the NaCl and AlCl₃ are separately added to water, solutions with different pH values are produced.

Explain why the two chlorides differ in their reaction with water. State the pH of the resulting solutions and write appropriate equations to illustrate your answers. [3]

NaCl(s) undergoes hydration only. Na⁺ has low charge density and does not hydrolyse in water. Hence pH is 7.



AlCl₃(s) undergoes hydration and appreciable hydrolysis. Since Al³⁺ has a higher charge density than Na⁺, it can further polarise the O-H bond in the neighboring water molecules, producing H⁺ in the solution to form an acidic solution of pH 3.



- (b) The rate of hydrolysis of the anticancer drug cisplatin can be investigated by monitoring of the concentration of the chloride ion formed.



Complete hydrolysis of cisplatin takes more than 24 hours.

A solution of 0.010 mol dm⁻³ cisplatin was allowed to undergo hydrolysis at pH 7 and 25 °C with excess water. At suitable time intervals, an aliquot of the cisplatin mixture was pipetted into a conical flask and quenched.

The amount of chloride ion is titrated against aqueous AgNO₃ using potassium chromate indicator.

Fig. 5.1 shows the concentration of chloride ions formed on hydrolysis of cisplatin against time for this experiment.

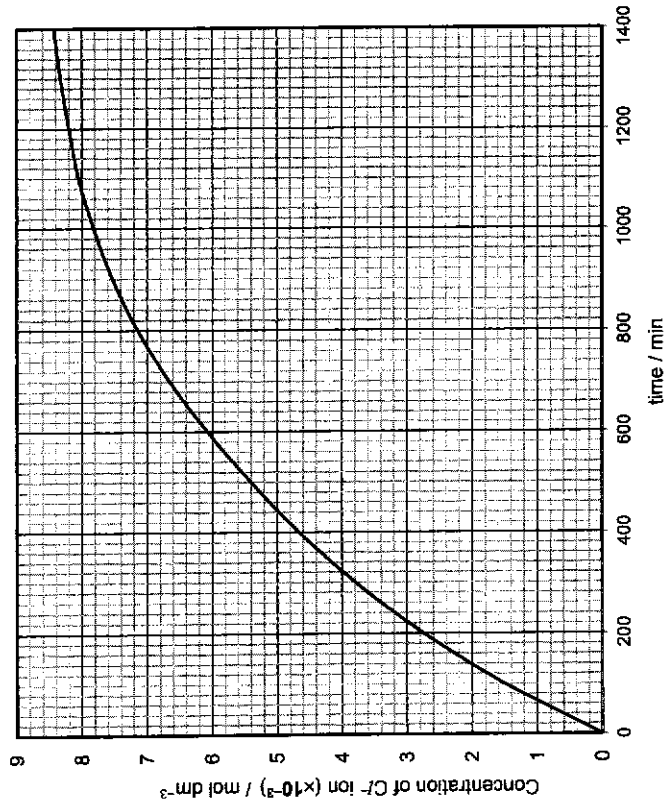
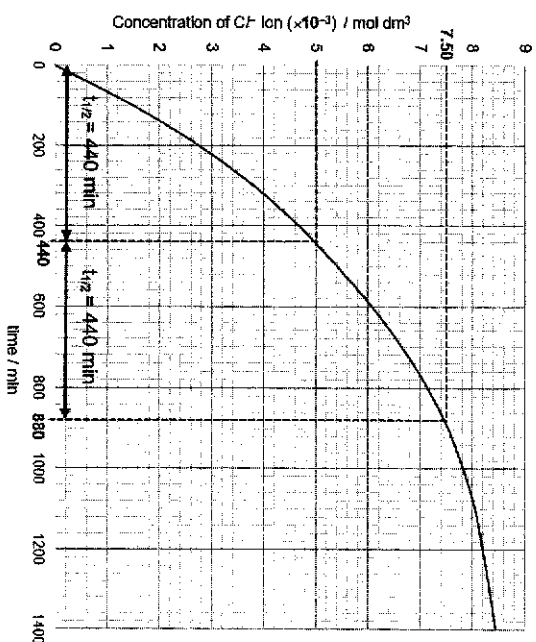


Fig. 5.1

- (i) Considering the total concentration of chloride that will be obtained upon complete hydrolysis of cisplatin, use Fig. 5.1 to show that the reaction is first order with respect to cisplatin. [2]



Since the 1 mol cisplatin produces 1 mol Cr^{3+} upon hydrolysis
 $\text{max} [\text{Cr}^{3+}] \text{ formed} = 0.010 \text{ mol dm}^{-3}$
 $= 10.0 \times 10^{-3} \text{ mol dm}^{-3}$

$[\text{Cr}^{3+}]$ ($\times 10^{-3}$)	$t_{1/2}$	$t_{1/2}$	$t_{1/2}$
10.0	\rightarrow	5.0	\rightarrow
5.0	\rightarrow	2.5	\rightarrow
2.5	\rightarrow	0
0	\rightarrow	5.0	\rightarrow
.....	\rightarrow	7.5	\rightarrow
.....	\rightarrow	10.0

From the graph, $t_{1/2}$ is constant at ≈ 440 min

\therefore Reaction is first order with respect to cisplatin

[1] state $\text{max} [\text{Cr}^{3+}] = 0.010 \text{ mol dm}^{-3}$, construction lines, show at least 2 $t_{1/2}$
 [1] conclude constant $t_{1/2}$

(ii) The concentration of cisplatin is halved and a new series of experiments was carried out at the same temperature.

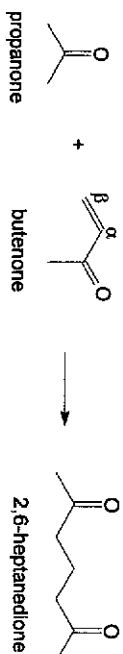
Suggest how the gradient at each point will change when a similar graph like the one in Fig. 5.1 was plotted. [1]

When concentration is halved, the rate of the hydrolysis reaction is halved. Hence the gradient of each point will be halved. [1]

(iii) Suggest why the unit for the rate constant for this reaction is s^{-1} despite its rate-determining step being a bimolecular reaction. [1]

Since water is in excess, its concentration of H_2O remains relatively constant throughout the reaction. The rate of reaction can be approximated to be rate = $k[\text{cisplatin}]$ (pseudo first order reaction). [1]

(c) The formation of 2,6-heptanedione via a Michael Addition reaction involves the formation of a carbon-carbon bond between propanone and butenone (an α,β -unsaturated ketone).



The three steps of the reaction are described in Table 5.1.

Table 5.1

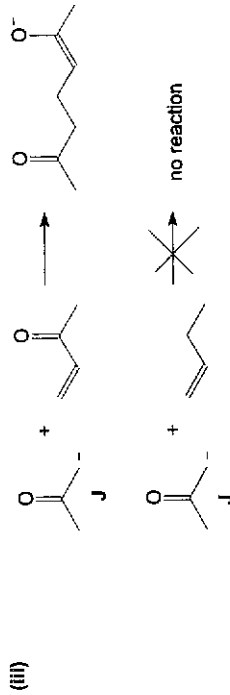
step	equation
1	<chem>CC(=O)C + OH- >> CC(O)C + H2O</chem>
2	<chem>CC(O)C + CC=CC(=O)C >> CC(O)CC(C)CC(=O)C</chem>
3	<chem>CC(O)CC(C)CC(=O)C + H2O >> CC(O)CC(C)CC(=O)C + OH-</chem>

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

step 1: acid-base reaction [1]

(ii) Complete the nucleophilic addition mechanism in step 2 in Table 5.1 by adding a lone pair and three curly arrows. [1]





No reaction occurs when but-1-ene is used in place of butene to react with **J** in step 2.

Using the concept of electronegativity and electronic effect, explain why buteneone reacts with **J** while but-1-ene does not. [2]

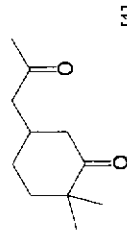
In $\text{CH}_3\text{COCH}=\text{CH}_2$, the electronegative oxygen of the carbonyl group exerts an electron-withdrawing effect and polarises the $\text{C}=\text{C}$ bond. Hence, the $\text{C}=\text{C}$ becomes electron deficient and becomes susceptible to a reaction with the nucleophile J. [1]

In $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$, the C atoms in $\text{C}=\text{C}$ have the same electronegativity. Thus, the C atoms do not have δ^+ / not electron-deficient and will not be susceptible to a reaction with a nucleophile. [1]

(iv) Compound **K** undergoes an intramolecular *Michael Addition* reaction to form a product, $\text{C}_{11}\text{H}_{18}\text{O}_2$.

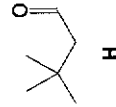
**K**

Suggest a structure for the product formed. [1]



[1]

(d) A carbon-carbon bond can also be formed between two molecules of compound **H** using suitable reagents and conditions.

**H**

Give the systematic name of compound **H**. [1]

3,3-dimethylbutanal [1]

(e) **L**, $\text{C}_6\text{H}_9\text{ClO}$, is a non-aromatic compound.

L reacts with 2,4-dinitrophenylhydrazine to form an orange precipitate but does not react with Tollen's reagent.

1 mole of **L** reacts with 2 moles of hydrogen gas in the presence of solid platinum.

When **L** is heated with potassium manganate(VII) in aqueous sodium hydroxide, then followed by adding sulfuric acid to the resultant mixture, **M** and **N** are formed.

M, $\text{C}_2\text{H}_4\text{O}_2$, liberates carbon dioxide gas upon addition of aqueous sodium carbonate solution.

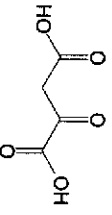
N, $\text{C}_4\text{H}_8\text{O}_3$, reacts with 2,4-dinitrophenylhydrazine to form an orange precipitate.

1 mole of **N** reacts with 2 moles of aqueous sodium hydroxide.

Suggest possible structures for **L**, **M** and **N**.

For each reaction described, state the type of reaction and explain what the information tells you about the functional groups present in each compound. [7]

	Information	Type of reaction	Deduction
1	L reacts with 2,4-DNPH to form an orange precipitate	<ul style="list-style-type: none"> condensation [✓] 	<ul style="list-style-type: none"> L is a ketone and not an aldehyde [✓]
2	L but does not react with Tollen's reagent.	<ul style="list-style-type: none"> No oxidation [✓] 	
3	1 mole of L reacts with 2 moles of hydrogen gas in the presence of solid platinum.	<ul style="list-style-type: none"> reduction [✓] 	<ul style="list-style-type: none"> Since L contains 1 $\text{C}=\text{O}$, L contains 1 $\text{C}=\text{C}$ group [✓] $\text{C}=\text{O}$ and $\text{C}=\text{C}$ reduce to 2° alcohol and alkane
4	When L is heated with potassium manganate(VII) in aqueous sodium hydroxide, then followed by adding sulfuric acid to the resultant mixture, M and N are formed.	<ul style="list-style-type: none"> oxidative cleavage [✓] Nucleophilic substitution [✓] when heated with $\text{NaOH}(\text{aq})$ 	<ul style="list-style-type: none"> Absence of Cl in M and N, chloroalkane group in K hydrolyses to form an alcohol [✓]
5	M , $\text{C}_2\text{H}_4\text{O}_2$, liberates carbon dioxide gas upon addition of aqueous sodium carbonate solution.	<ul style="list-style-type: none"> acid-base [✓] 	<ul style="list-style-type: none"> M is a carboxylic acid M is $\text{CH}_3\text{CO}_2\text{H}$ / ethanoic acid
6	N , $\text{C}_4\text{H}_8\text{O}_3$, reacts with 2,4-dinitrophenylhydrazine to form an orange precipitate	<ul style="list-style-type: none"> condensation 	<ul style="list-style-type: none"> N is a ketone [✓] (cannot accept 'aldehyde' as N is an oxidation product)


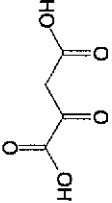
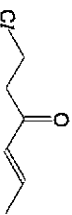
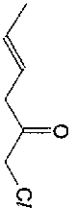
10	1 mole of N reacts with 2 moles of aqueous sodium hydroxide.	• acid-base [1]	• N is a dibasic acid [1]
			
			<ul style="list-style-type: none"> Chloroalkane group in K hydrolyses to form an primary alcohol in (4) which oxidises to a carboxylic acid in N with KMnO_4 in (4)

Heated with KMnO_4 in NaOH

[Total: 20]

[3] 1 mark for each correct structure

[4] for types of reactions and deductions

M		N		L	 Or 
					No need to show cis-trans

