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**JURONG PIONEER JUNIOR COLLEGE**  
**JC2 PRELIMINARY EXAMINATION 2024**

**CHEMISTRY**

**9729/01**

**Higher 2**

**16 September 2024**

Paper 1 Multiple Choice Questions

**1 hour**

Candidates answer on the Question paper.

Additional Materials:      Multiple Choice Answer Sheet  
                                  Data Booklet

**READ THESE INSTRUCTIONS FIRST**

Write in soft pencil.

Do not use staples, paper clips, glue or correction fluid.

Write your name, class and exam index number on the Answer Sheet in the spaces provided unless this has been done for you.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A, B, C or D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

**Read the instructions on the Answer Sheet very carefully.**

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

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

This document consists of **12** printed pages.

- 1 Which statement about relative atomic mass is correct?
- A It is the average of the masses of all the isotopes of that element.
  - B It is the sum of the relative masses of the neutrons and protons in each atom.
  - C It is the ratio of the average mass of one atom of an element to the mass of one  $^1\text{H}$  atom.
  - D It is the ratio of the mass of one mole of atoms of an element to one-twelfth the mass of one mole of  $^{12}\text{C}$  atoms.
- 2 The ionisation energies, IE, in  $\text{kJ mol}^{-1}$ , of five elements are given in the table.

element	$2^{\text{nd}}$ ionisation energy / $\text{kJ mol}^{-1}$	$3^{\text{rd}}$ ionisation energy / $\text{kJ mol}^{-1}$	$4^{\text{th}}$ ionisation energy / $\text{kJ mol}^{-1}$
F	3370	6040	8410
Ne	3950	6150	9290
Na	4560	6940	9540
Mg	1450	7740	10500
Al	1820	2740	11600

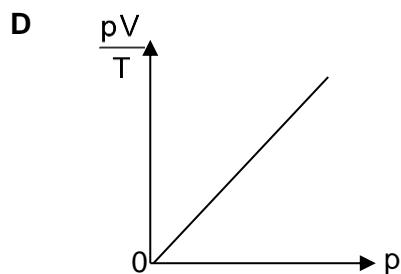
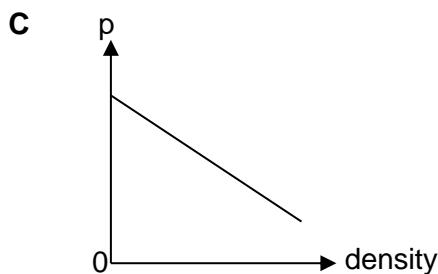
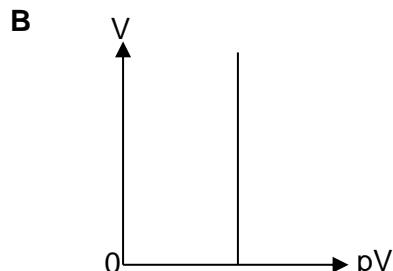
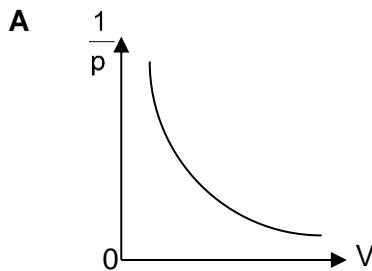
Which statement about these ionisation energies is correct?

- A The  $2^{\text{nd}}$  IE of F is greater than the  $3^{\text{rd}}$  IE of Al because  $\text{Al}^{2+}$  ions have more outer shell electrons than  $\text{F}^+$  ions.
  - B The  $3^{\text{rd}}$  IE of all the elements in the table involves the removal of an electron from the same shell.
  - C The  $4^{\text{th}}$  ionisation energy of Na is greater than the  $3^{\text{rd}}$  IE of Ne because the nuclear charge of Na is greater than that of Ne.
  - D The successive ionisation energies of these elements increase as these electrons are being taken from the same shell.
- 3 Why is the molecule of  $\text{BCl}_3$  planar, whereas the molecule of  $\text{PH}_3$  is pyramidal?
- A The boron atom has no d-orbitals available for bonding.
  - B The covalent radius of chlorine is greater than that of hydrogen.
  - C The repulsion between chlorine atoms is greater than that between hydrogen atoms.
  - D The boron atom in  $\text{BCl}_3$  has six electrons in its valence shell, whereas the phosphorus atom in  $\text{PH}_3$  has eight.

- 4 After an oil spillage at sea, a liquid hydrocarbon layer floats on the surface of the water. Which statements help to explain this observation?

- 1 Hydrocarbon molecules are not solvated by water.
  - 2 There are only instantaneous dipole–induced dipole interactions between hydrocarbon molecules.
  - 3 Hydrogen bonding between water molecules causes water molecules to be packed closely together.
- A** 2 only                                   **B** 1 and 2 only  
**C** 2 and 3 only                           **D** 1, 2 and 3

- 5 Which diagram correctly describes the behavior of a fixed mass of an ideal gas at constant  $T$  (measure in K)?



- 6 A mixture of the three gases, oxygen, nitrogen and argon, is at a total pressure of 500 kPa. There is a total of 1.2 moles of gases in the mixture.

If the oxygen gas alone occupied the entire volume of the mixture, it would exert a pressure of 150 kPa.

At room conditions, the amount of nitrogen gas in the mixture would occupy a volume of 5.76 dm<sup>3</sup>.

Using the data from above, what is the partial pressure of the argon gas in the mixture?

- A** 150 kPa                                   **B** 200 kPa  
**C** 250 kPa                                   **D** 300 kPa

- 7 When aqueous ammonia is added to a solution containing hexaaquairon(III) ions,  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ , a red-brown precipitate is formed which does not dissolve when excess ammonia is added.

Which of the following states the role of ammonia in this reaction?

- 1 Brønsted-Lowry base
  - 2 Ligand
  - 3 Lewis acid
  - 4 Reducing agent
- A** 1 only  
**B** 4 only  
**C** 1 and 2 only  
**D** 2 and 3 only

- 8 Use of the Data Booklet is relevant to this question.

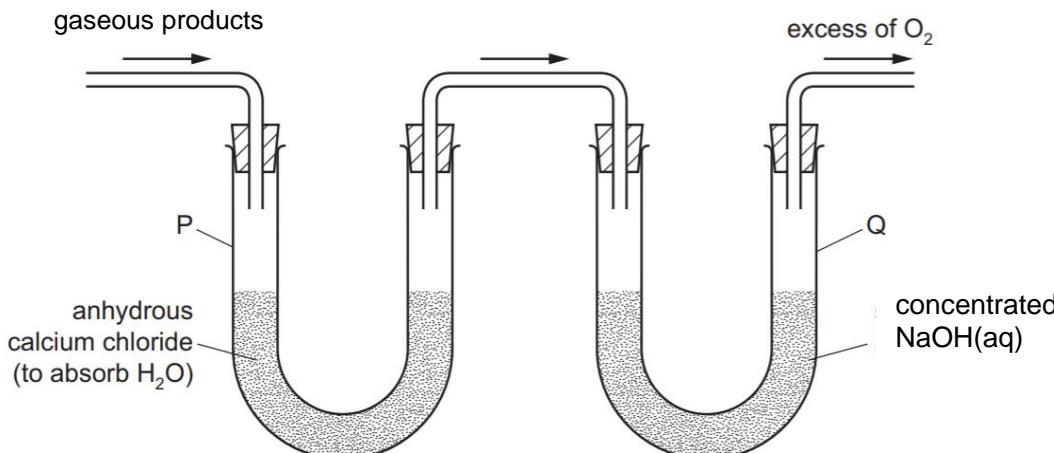
An element **M** can exist in a few oxidation states.

15.00 cm<sup>3</sup> of an aqueous solution of 0.100 mol dm<sup>-3</sup> of **M**<sup>n+</sup> required 20.00 cm<sup>3</sup> of 0.0250 mol dm<sup>-3</sup> of acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution for a complete reaction.

What is the change in oxidation state of **M**?

- A** 2      **B** 3      **C** 4      **D** 5

- 9 A sample of the hydrocarbon C<sub>6</sub>H<sub>12</sub> is completely burned in excess dry oxygen and the gaseous products collected as shown.



The increases in mass of the collecting vessels P and Q are  $M_P$  and  $M_Q$  respectively.

What is the ratio of  $M_P / M_Q$ ?

- A** 0.41      **B** 0.82      **C** 1.2      **D** 2.4

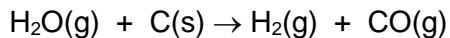
**10** Use of the Data Booklet is relevant to this question.

A butane burner is used to heat water. The  $M_r$  of butane is 58.

- $\Delta H_c$  of butane is  $-2877 \text{ kJ mol}^{-1}$ .
- 250 g of water is heated from  $12^\circ\text{C}$  to  $100^\circ\text{C}$ .
- The burner transfers 47% of the heat released from the burning fuel to the water.

Assume that the butane undergoes complete combustion and none of the water evaporates.  
What is the minimum mass of butane that must be burnt?

- A** 0.071 g      **B** 1.85 g      **C** 3.94 g      **D** 4.48 g

**11** Hydrogen can be made from steam.

The Gibbs free energy change of reaction at two different temperatures are shown.

$$\Delta G_1 = +78 \text{ kJ mol}^{-1} \text{ at } 378\text{K}$$

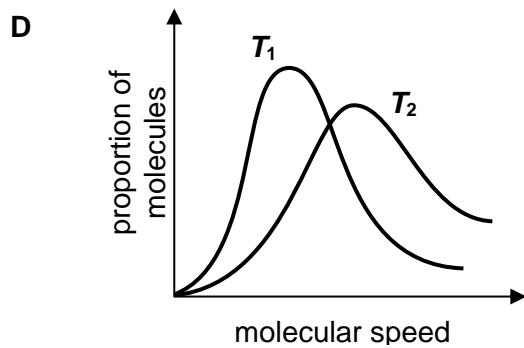
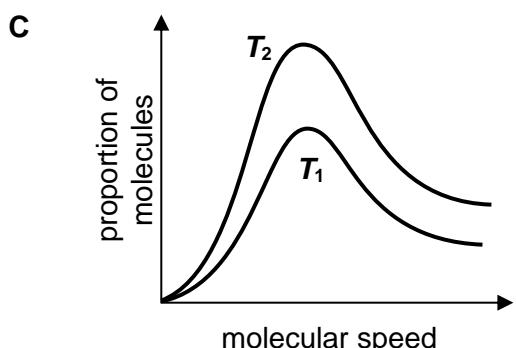
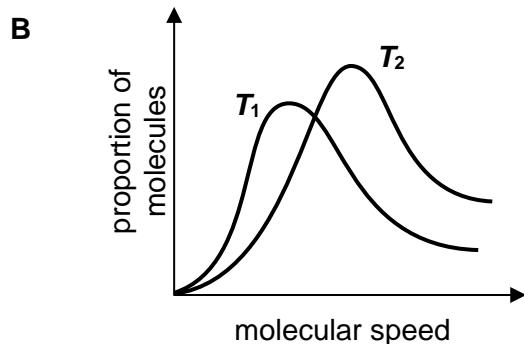
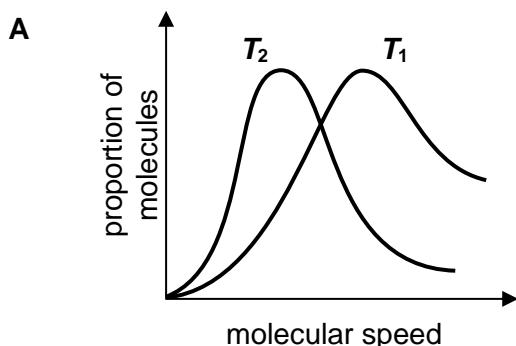
$$\Delta G_2 = -58 \text{ kJ mol}^{-1} \text{ at } 1300\text{K}$$

Which row of the table gives the correct signs of  $\Delta H$  and  $\Delta S$  for this reaction?

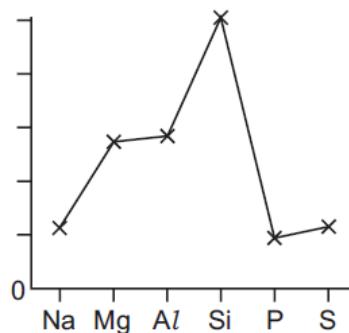
	$\Delta H$	$\Delta S$
<b>A</b>	—	—
<b>B</b>	—	+
<b>C</b>	+	—
<b>D</b>	+	+

- 12 One mol of neon gas at temperature  $T_1$  was added to another one mol of neon and the temperature was increased to  $T_2$ .

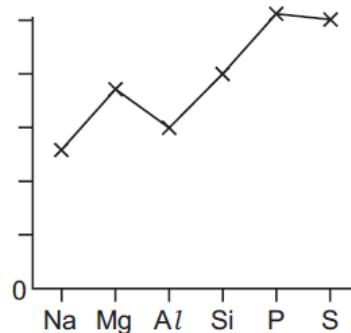
Which of the following diagrams correctly represents the Boltzmann distribution of molecular speeds before and after the changes were made?



- 13 The trends in two physical properties of the elements Na, Mg, Al, Si, P and S are shown in the following graphs.



Graph 1



Graph 2

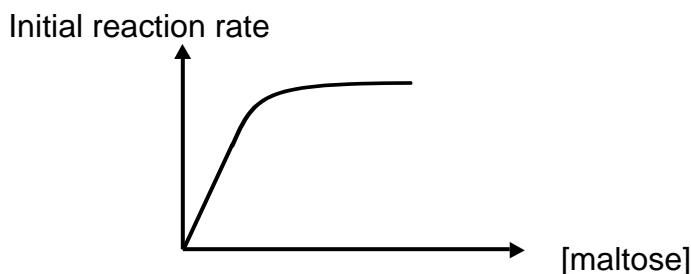
Which of the following illustrates the correct physical property for the corresponding graphs above?

	Graph 1	Graph 2
<b>A</b>	melting point	1 <sup>st</sup> ionisation energy
<b>B</b>	melting point	electrical conductivity
<b>C</b>	1 <sup>st</sup> ionisation energy	electrical conductivity
<b>D</b>	1 <sup>st</sup> ionisation energy	melting point

14 Which of the following statements are correct for a system at dynamic equilibrium?

- 1 The rate of both forward and backward reaction is the same.
  - 2 The concentration of reactants is equal to the concentration of products.
  - 3 The rate constant of forward reaction is equal to the rate constant of the backward reaction.
- A 1 only  
B 1 and 2 only  
C 1 and 3 only  
D 1, 2 and 3 only

15 The graph shows the result of an investigation of the initial rate of hydrolysis of maltose by the enzyme amylase. In the experiments, the initial concentration of maltose was varied, but that of amylase was kept constant.



Which conclusions can be deduced from these results?

- A When [maltose] is low, the rate is zero order with respect to [maltose].  
B When [maltose] is high, the rate is independent of [maltose].  
C When [maltose] is low, the rate is independent of [amylase].  
D When [maltose] is high, the rate is first order with respect to [amylase].

16 A saturated solution of  $\text{Ca}(\text{OH})_2$  is found to have a pH of 12.3 at 25 °C.

Which of the following statements is **incorrect**?

- A The pH of the solution would increase when  $\text{Ca}(\text{NO}_3)_2$  is added  
B The solubility of  $\text{Ca}(\text{OH})_2$  would increase when temperature is raised to 35 °C.  
C The solubility of  $\text{Ca}(\text{OH})_2$  will decrease when solid  $\text{Na}_2\text{O}$  is added.  
D The  $K_{\text{sp}}$  of  $\text{Ca}(\text{OH})_2$  is  $4 \times 10^{-6} \text{ mol}^3 \text{ dm}^{-9}$ .

## 17 Use of the Data Booklet is relevant to this question.

Which of the following solutions would result in a colour change when left to stand in the atmosphere?

- A an acidified solution of tin(II) chloride
- B an acidified solution of cobalt(II) nitrate
- C a solution of potassium manganate(VII)
- D an acidified solution of vanadium(II) sulfate

18 Adding concentrated HCl(aq) to CuSO<sub>4</sub>(aq) causes the colour of the solution to change from blue to green.

Which of the following row correctly shows the number of d-electrons and the energy gap between the d-orbitals, before and after the reaction?

	number of d-electrons	energy gap between the d-orbitals
A	changes	changes
B	remains the same	changes
C	changes	remains the same
D	remains the same	remains the same

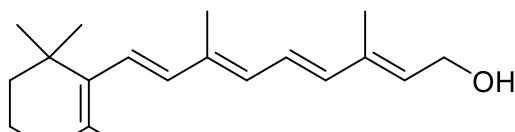
19 How many structurally isomeric secondary alcohols are there with the molecular formula C<sub>5</sub>H<sub>12</sub>O?

A 1

B 2

C 3

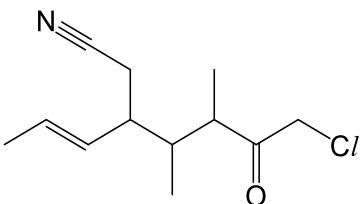
D 4

20 When retinol reacts completely with cold alkaline KMnO<sub>4</sub>, it forms product E. How many stereoisomers do retinol and E have?

retinol

	retinol	E
A	2 <sup>4</sup>	2 <sup>8</sup>
B	2 <sup>5</sup>	2 <sup>8</sup>
C	2 <sup>4</sup>	2 <sup>10</sup>
D	2 <sup>5</sup>	2 <sup>10</sup>

- 21 Which of the following options about the structure below is correct?

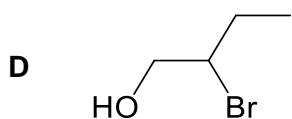
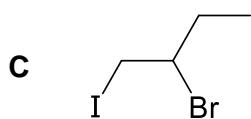
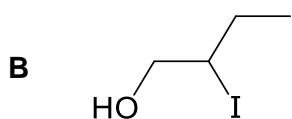
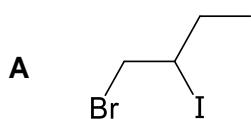


	Number of <i>sp</i> hybridised C	Number of <i>sp</i> <sup>2</sup> hybridised C	Number of <i>sp</i> <sup>3</sup> hybridised C
A	1	3	8
B	1	3	6
C	0	4	8
D	0	4	6

- 22 Which list contains all compounds that are made during the free radical substitution of chloromethane with chlorine?

- A  $\text{C}_2\text{H}_6$ ,  $\text{CCl}_4$ ,  $\text{CH}_2\text{Cl}_2$
- B  $\text{CH}_2\text{CCl}_2$ ,  $\text{CCl}_4$ ,  $\text{CHCl}_3$
- C  $\text{HCl}$ ,  $\text{CH}_3\text{CH}_2\text{Cl}$ ,  $\text{CHCl}_3$
- D  $\text{CH}_2\text{C}/\text{CH}_2\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$

- 23 Which of the following **cannot** be formed as one of the products, when but-1-ene reacts with  $\text{IBr}(\text{aq})$ ?



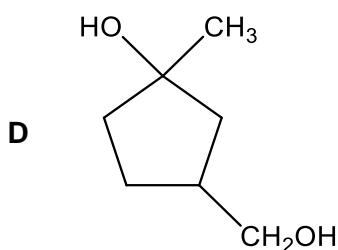
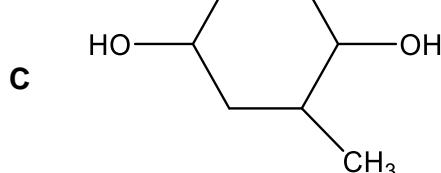
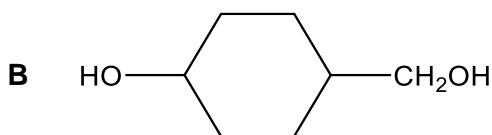
- 24 Which pair of reagents reacts to form a product with a chiral carbon atom?

- A  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{NaOH}$  in ethanol
- B  $(\text{CH}_3)_2\text{C}=\text{O} + \text{NaBH}_4$
- C  $\text{CH}_3\text{CH}_2\text{CHO} + \text{HCN}$
- D  $\text{CH}_3\text{COCl} + \text{CH}_3\text{NH}_2$

- 25 Heating compound **F**,  $C_7H_{14}O_2$ , under reflux with an excess of acidified potassium manganate(VII) produces compound **G**.

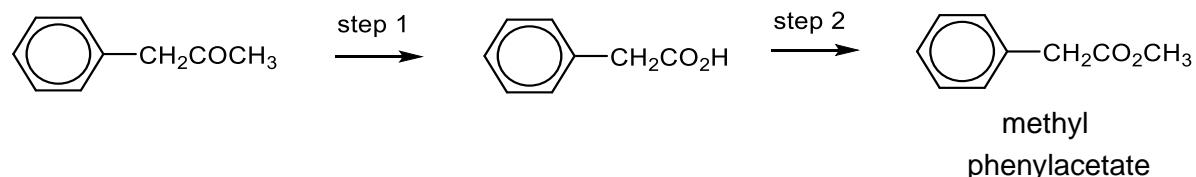
Compound **G** produces hydrogen gas with sodium metal and forms orange crystals with 2,4-DNPH reagent.

What could **F** be?



- 26 Methyl phenylacetate has a strong odour similar to honey. It is used in the flavour industry and in perfumes to impart honey scents.

The following pathway shows the synthesis of methyl phenylacetate via a 2-step pathway.

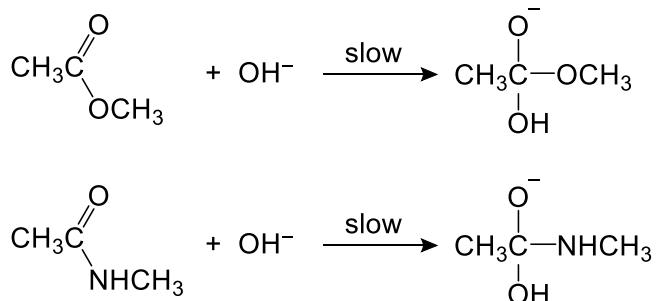


Which reagents can be used for step 1 and step 2?

	step 1	step 2
<b>A</b>	acidified $\text{KMnO}_4$	$\text{CH}_3\text{OH}$ , concentrated $\text{H}_2\text{SO}_4$
<b>B</b>	$\text{H}_2\text{SO}_4$ (aq)	$\text{CH}_3\text{COOH}$ , concentrated $\text{H}_2\text{SO}_4$
<b>C</b>	$\text{NaOH}$ (aq), $\text{I}_2$	$\text{CH}_3\text{OH}$ , concentrated $\text{H}_2\text{SO}_4$
<b>D</b>	acidified $\text{K}_2\text{Cr}_2\text{O}_7$	$\text{CH}_3\text{COOH}$ , concentrated $\text{H}_2\text{SO}_4$

- 27 1 mol of an ester ( $\text{CH}_3\text{CO}_2\text{CH}_3$ ) and 1 mol of an amide ( $\text{CH}_3\text{CONHCH}_3$ ) underwent base hydrolysis separately and the initial rate of reaction was measured. It was found that the ester undergoes hydrolysis approximately three times faster than the amide.

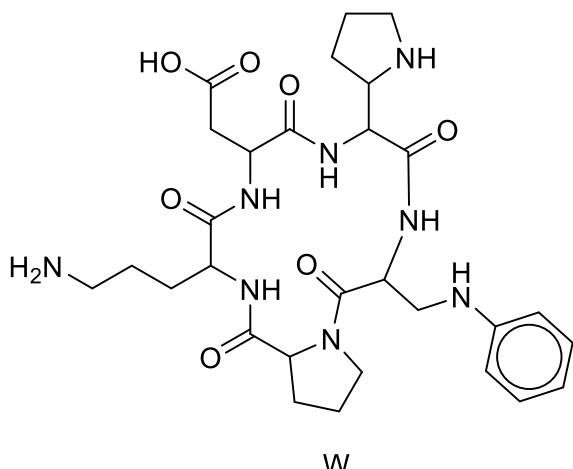
The slow step of the base hydrolysis of the ester and amide is the same and shown below.



Which statements help to explain the faster rate of base hydrolysis of the ester?

- 1 Oxygen is more electronegative than nitrogen.
  - 2 The lone pair of electrons on the nitrogen atom in the amide interacts more with the carbonyl group.
  - 3 There are two lone pairs of electrons on the oxygen atom in the ester and only one lone pair of electrons on the nitrogen atom in the amide.
- A** 1, 2 and 3  
**B** 1 and 2 only  
**C** 1 and 3 only  
**D** 2 and 3 only

- 28 Compound **W** is a cyclic oligopeptide.



How many amide linkages exist in compound **W**?

- A** 5      **B** 6      **C** 7      **D** 8

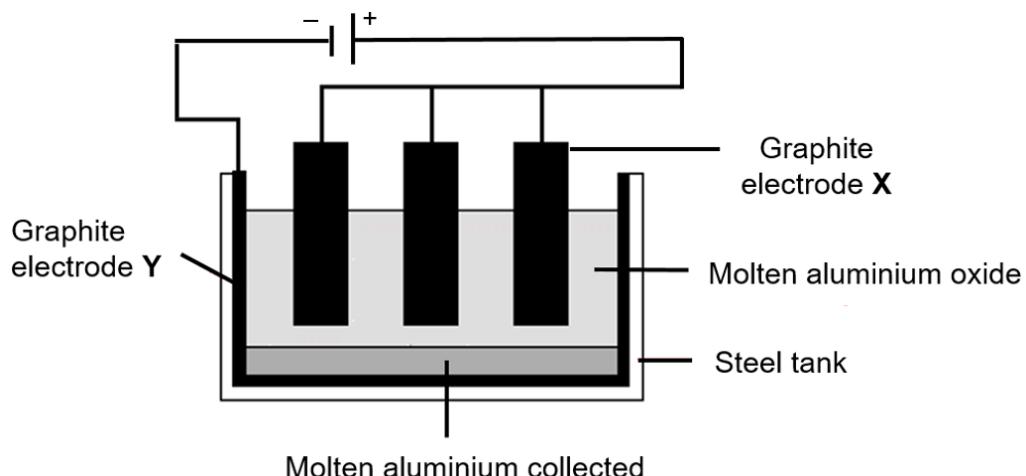
- 29 An octapeptide was analysed in the chemistry laboratory by treating it with enzymes. The following fragments were obtained after the partial hydrolysis that is catalysed by the enzymes.

ser-arg-pro  
cys-pro  
pro-ser  
pro-ala-phe-gly

Which of the following is the correct sequence of the octapeptide?

- A ser-arg-pro-ala-phe-gly-cys-pro
- B pro-ser-arg-pro-ala-phe-gly-cys
- C cys-pro-ser-arg-pro-ala-phe-gly
- D cys-pro-ala-phe-gly-ser-arg-pro

- 30 Aluminium is extracted from its ore by electrolysis.



Which of the following statements is correct?

- 1 Oxygen gas is produced.
  - 2 Aluminum ions migrate to electrode X.
  - 3 Electrons move from electrode X to electrode Y via the external circuit.
- |                       |                       |
|-----------------------|-----------------------|
| <b>A</b> 1 and 2 only | <b>B</b> 1 and 3 only |
| <b>C</b> 2 and 3 only | <b>D</b> 1 only       |

**Jurong Pioneer Junior College**  
**2024 H2 Chemistry**  
**Paper 1 Worked Solutions**

1	D	The definition for atomic mass is the ratio of the average mass of one atom of an element to one-twelfth the mass of one atom of $^{12}\text{C}$ . In option D, the mass of one mole of atoms of an element has already considered all the isotopes and their relative abundances.
2	C	<p>✗A <math>\text{Al}^{2+}</math> ions <math>1\text{s}^22\text{s}^22\text{p}^63\text{s}^1</math>; <math>\text{F}^+</math> ions. <math>1\text{s}^22\text{s}^22\text{p}^4</math>  Incorrect as <math>\text{Al}^{3+}</math> has 1 outer shell electron vs <math>\text{F}^+</math> 6 outer shell electron. 2nd IE of F is greater than the 3rd IE of Al as 3s electron is <math>\text{Al}^{2+}</math> is higher in energy and further away from the nucleus (hence lower nuclear attraction) than the 2p electron in <math>\text{F}^+</math>.</p> <p>✗B Incorrect as the 3<sup>rd</sup> IE involves the removal of 3<sup>rd</sup> electron from Al is from 3<sup>rd</sup> principal quantum shell as compared to the removal of 3<sup>rd</sup> electrons from the 2<sup>nd</sup> PQM for the remaining 4 species.</p> <p>✓C <math>\text{Na}^{3+} 1\text{s}^22\text{s}^22\text{p}^{4+}</math> vs <math>\text{Ne}^{2+} 1\text{s}^22\text{s}^22\text{p}^4</math>  Same no of electrons but as <math>\text{Na}^{3+}</math> has more protons than Ne, hence higher nuclear charge, thus nuclear attraction of outermost electrons in <math>\text{Na}^{3+}</math> is higher, thus higher 4<sup>th</sup> IE for Na compared to 3<sup>rd</sup> IE for Ne .</p> <p>✗D Incorrect as the removal of electrons are removed from different PQM.</p>
3		 <p>Due to the no of bond pairs and lone pairs of electrons in each molecule –  <math>\text{BCl}_3</math>: 3 Bond Pairs ;      <math>\text{PH}_3</math>: 3 Bond Pairs &amp; 1 Lone pair  The shape of <math>\text{BCl}_3</math> and <math>\text{PH}_3</math> are trigonal planar and trigonal pyramidal respectively</p>
4	D	<p>(1, 2 and 3)</p> <p>✓1: Only id–id attraction can be formed between hydrocarbon molecules and <math>\text{H}_2\text{O}</math> molecules which is weaker than the hydrogen bonds between <math>\text{H}_2\text{O}</math> molecules. Hence, the energy released upon forming the less favourable interaction is not sufficient to compensate the energy required to break the stronger hydrogen bonds. Hence, hydrocarbon molecules are not solvated by water and hence the two layers are immiscible.</p> <p>✓2: See (1).</p> <p>✓3: The stronger hydrogen bonds between <math>\text{H}_2\text{O}</math> molecules pulls the molecules closer to each other and hence, the volume of water is smaller. Given similar mass, the density of water is higher and hence, it will be below the hydrocarbon layer.</p>

5	B	<p>Under constant n and T, the ideal gas equation is simplified to <math>pV = k</math> (where <math>k</math> is a constant and <math>k = nRT</math>).</p> <ul style="list-style-type: none"> <li>* A Rearranging <math>pV = k</math> such that <math>y = \frac{1}{p}</math> and <math>x = V</math> (i.e. <math>\frac{1}{p} = kV</math>) , a graph of <math>y = mx</math> is obtained (i.e. <u>straight line passing through origin</u>).</li> <li>✓ B Since <math>pV</math> is a constant and <math>x = pV</math>, a graph of <math>x = c</math> is obtained (i.e. <u>vertical line</u>)</li> <li>* C Rearranging <math>pV = nRT</math> such that <math>y = p</math> and <math>x = \rho</math> (i.e. <math>p = \frac{\rho RT}{M_r}</math>), a graph of <math>y = mx</math> is obtained (i.e. <u>straight line passing through origin</u>).</li> <li>* D Rearranging <math>pV = nRT</math> such that <math>y = \frac{pV}{T}</math> and <math>x = p</math> (i.e. <math>\frac{pV}{T} = nR = \text{constant}</math>), a graph of <math>y = c</math> is obtained (i.e. <u>horizontal line</u>)</li> </ul>																								
6	C	<p>Mol ratio of <math>O_2 = \frac{150}{500} = 0.3</math>  Hence amt of <math>O_2 = 0.3 \times 1.2 = 0.36 \text{ mol}</math>  Amt of <math>N_2 = \frac{5.76}{24} = 0.24 \text{ mol}</math>  Hence amt of <math>Ar = 1.2 - 0.36 - 0.24 = 0.6 \text{ mol}</math>  Thus <math>p_{Ar} = \frac{0.6}{1.2} \times 500 = \underline{\underline{250 \text{ kPa}}}</math></p>																								
7	A	<p>1 only</p> <p>When aqueous ammonia is added to a solution containing hexaaquairon(III) ions, <math>[Fe(H_2O)_6]^{3+}</math>, a red-brown precipitate is formed.</p> $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ <p>where <math>NH_3</math> is <b>Brønsted-Lowry base</b> where it accepts proton to release <math>OH^-</math> which will then ppt with <math>Fe^{3+}</math> to form red-brown ppt, <math>Fe(OH)_3</math>.</p> $Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3$ <p>Ppt does not dissolve when excess ammonia is added, indicates that there is <b>no further reaction or no ligand exchange</b> to form a soluble complex.</p>																								
8	A	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ $n(M^{n+}) \text{ used} = 0.100 \times \frac{15.00}{1000} = 0.0015 \text{ mol}$ $n(Cr_2O_7^{2-}) \text{ used} = 0.0250 \times \frac{20.00}{1000} = 0.0005 \text{ mol}$ <table style="margin-left: auto; margin-right: auto;"> <tr> <td style="padding-right: 20px;">ratio</td> <td><math>Cr_2O_7^{2-}</math></td> <td>:</td> <td><math>e^-</math></td> <td>:</td> <td><math>M^{n+}</math></td> </tr> <tr> <td></td> <td>0.0005</td> <td></td> <td><math>6(0.0005) = 0.003</math></td> <td></td> <td></td> </tr> <tr> <td></td> <td></td> <td></td> <td>0.003</td> <td></td> <td>0.0015</td> </tr> <tr> <td></td> <td></td> <td></td> <td>2</td> <td>:</td> <td>1</td> </tr> </table> <p>Hence, <b>1 <math>M^{n+}</math> loses 2 electrons and the oxidation state of M changes by 2.</b></p>	ratio	$Cr_2O_7^{2-}$	:	$e^-$	:	$M^{n+}$		0.0005		$6(0.0005) = 0.003$						0.003		0.0015				2	:	1
ratio	$Cr_2O_7^{2-}$	:	$e^-$	:	$M^{n+}$																					
	0.0005		$6(0.0005) = 0.003$																							
			0.003		0.0015																					
			2	:	1																					

9	A	$C_6H_{12} + 9O_2 \rightarrow 6CO_2 + 6H_2O$ Since $6CO_2 \equiv 6H_2O \equiv 1C_6H_{12}$ , $n(CO_2)$ formed = $n(H_2O)$ formed = $x$ mol $\frac{M_p}{M_Q} = \frac{\text{mass of } H_2O}{\text{mass of } CO_2} = \frac{(x) \times 18.0}{(x) \times 44.0} = \underline{\underline{0.41}}$
10	C	$\text{Energy absorbed by water} = 250 \times 4.18 \times (100 - 12) \times 10^{-3}$ $= 91.96 \text{ kJ}$ $\text{Energy evolved by combustion of butane} = 91.96 \times \frac{100}{47} = 195.6 \text{ kJ}$ $195.6 = 2877 \times \frac{m(\text{butane})}{58}$ $m(\text{butane}) = 3.944 \approx 3.94 \text{ g}$
11	D	$H_2O(g) + C(s) \rightarrow H_2(g) + CO(g)$ $\Delta S > 0$ as there is an increase in disorderliness from 1 to 2 mol of gas particles. $\Delta G = \Delta H - T \Delta S$ $\begin{array}{c} -ve \\ \underbrace{+ve}_{-ve} \end{array}$ <p>If <math>\Delta H &lt; 0</math>, <math>\Delta G &lt; 0</math> at all temperatures.</p> <p>However, <math>\Delta G_1</math> becomes more negative as temperature increases; hence</p> $\Delta G = \Delta H - T \Delta S$ $\begin{array}{c} +ve \\ \underbrace{+ve}_{-ve} \end{array}$ <p>When temperature increases, <math>-T\Delta S</math> becomes more negative.</p> <p>At <u>high enough temperatures</u>, <math>\Delta G &lt; 0</math> since <math>  -T\Delta S   &gt;  \Delta H </math>.</p> <p>Reaction is <u>spontaneous at high enough temperatures</u>. when temperature increases</p>
12	B	With the addition of another mole of gas, the area under the graph increases. When the temperature increased, the Maxwell Boltzmann graph peak will be shifted to the right.
13	A	<p>Graph 1:</p> <p>The melting point increases from Na to Al as the metallic bonding is stronger. Si has the highest melting point as it is a giant covalent lattice which requires the largest amount of energy to overcome the strong network of Si-Si bond. <math>S_8</math> and <math>P_4</math> are simple covalent molecule. As the number of electrons for <math>S_8</math> increases, the id-id increases, hence, the melting point increases.</p> <p>Graph 2:</p> <p>Across the period, nuclear charge increases while the increase in shielding effect is insignificant as electrons are added to the same shell. The effective nuclear charge increases, hence, the 1<sup>st</sup> ionisation energy increases. However, the first ionisation energy for Al is lower than expected because less energy is needed to remove the 3p electron which is further away from nucleus and experience additional shielding from 3s electrons.</p>

14	A	<p>1 only</p> <p>When a system is at a state of dynamic equilibrium,</p> <ul style="list-style-type: none"> <li>the concentration of all reactants and products <b>remains constant</b> and an equilibrium mixture is obtained.</li> <li>the rate of forward reaction = the rate of the backward reaction.</li> <li>Equilibrium can only be achieved in a <b>closed system</b>, where there is no loss or gain of substances to and from the surroundings.</li> </ul>
15	B	<p>When <b>[maltose] is very low</b> as compared to [enzyme], <b>many empty active sites of the enzyme molecules available for binding</b> so the reaction is approximately <b>1<sup>st</sup> order w.r.t. maltose</b>.</p> <p>As <b>[maltose] increases, more active sites of enzymes</b> are occupied by maltose molecules so reaction is <b>no longer 1<sup>st</sup> order w.r.t maltose</b></p> <p>At <b>high enough [maltose], all active sites are occupied by maltose molecules</b> (i.e. saturated) so any further increase in [CO<sub>2</sub>] will not increase the rate. Hence, the reaction becomes <b>zero order w.r.t maltose</b>.</p>
16	A	<p>Ca(OH)<sub>2</sub> (s) ⇌ Ca<sup>2+</sup> (aq) + 2OH<sup>-</sup>(aq) ... (1)</p> <p>✗A INCORRECT. When common ion Ca<sup>2+</sup> is added, [Ca<sup>2+</sup>] increases, hence POE in (1) shifts to the left, [OH<sup>-</sup>] decreases, hence pH increases</p> <p>✓B CORRECT. Increasing temperature increases solubility of solids</p> <p>✓C CORRECT. When Na<sub>2</sub>O is added into the solution, NaOH is formed. When common ion OH<sup>-</sup> is added, [OH<sup>-</sup>] increases, hence POE in (1) shifts to the left, solubility of Ca(OH)<sub>2</sub> decreases.</p> <p>✓D CORRECT.      [OH<sup>-</sup>] = 10<sup>-1.7</sup> = 0.0200 mol dm<sup>-3</sup>  [Ca<sup>2+</sup>] = 0.0100 mol dm<sup>-3</sup>  K<sub>sp</sub> = [Ca<sup>2+</sup>][OH<sup>-</sup>]<sup>2</sup> = 0.01 × 0.02<sup>2</sup> = 4 × 10<sup>-6</sup> mol<sup>3</sup> dm<sup>-9</sup></p>
17	D	<p>O<sub>2</sub> + 4H<sup>+</sup> + 4e ⇌ 2H<sub>2</sub>O      E<sup>o</sup> = +1.23V  O<sub>2</sub> + 2H<sub>2</sub>O + 4e ⇌ 4OH<sup>-</sup>      E<sup>o</sup> = +0.40V  Sn<sup>4+</sup> + 2e ⇌ Sn<sup>2+</sup>      E<sup>o</sup> = +0.15V  Co<sup>3+</sup> + e ⇌ CO<sup>2+</sup>      E<sup>o</sup> = +1.89V  MnO<sub>4</sub><sup>-</sup> + 8H<sup>+</sup> + 5e ⇌ Mn<sup>2+</sup> + 4H<sub>2</sub>O      E<sup>o</sup> = +1.52V  V<sup>3+</sup> + e ⇌ V<sup>2+</sup>      E<sup>o</sup> = -0.26V</p> <p>✗A INCORRECT. Sn will not show any colour change even though there is a reaction between 2Sn<sup>2+</sup> + O<sub>2</sub> + 4H<sup>+</sup> → 2H<sub>2</sub>O + 2Sn<sup>4+</sup> (E<sup>o</sup><sub>cell</sub> = +1.08V &gt; 0) as Sn ions have no colour</p> <p>✗B INCORRECT. E<sup>o</sup><sub>cell</sub> = +1.23 – 1.89 &lt; 0; not energetically feasible</p> <p>✗C INCORRECT. No reaction as both will undergo reduction reactions.</p> <p>✓D CORRECT E<sup>o</sup><sub>cell</sub> = +1.23 – (-0.26) &gt; 0; energetically feasible 4V<sup>2+</sup> + O<sub>2</sub> + 4H<sup>+</sup> → 2H<sub>2</sub>O + V<sup>3+</sup></p>



23	D	<p>Type of reaction: <u>electrophilic addition</u></p> <p>Since iodine is less electronegative than Br, iodine will bear the <math>\delta+</math> charge and functions as the electrophile.</p> <p>The product must contain I atom. (reject D)</p> <p>Br<sup>-</sup> and H<sub>2</sub>O can function as nucleophile to attack either carbocation to give the products in Option A to C.</p>
24	C	<p>✗A <math>\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{NaOH}</math> in ethanol <math>\rightarrow \text{CH}_3\text{CH}=\text{CH}_2</math> (no C*) + HCl</p> <p>✗B <math>(\text{CH}_3)_2\text{C}=\text{O} + \text{NaBH}_4 \rightarrow (\text{CH}_3)_2\text{CH(OH)}</math> (no C*)</p> <p>✓C <math>\text{CH}_3\text{CH}_2\text{CHO} + \text{HCN} \rightarrow \text{CH}_3\text{CH}_2\text{C}^*\text{H}(\text{CN})\text{OH}</math></p> <p>✗D <math>\text{CH}_3\text{COCl} + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{CONHCH}_3 + \text{HCl}</math></p>
25	B	<p>✗A</p> <p><math>(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}</math> <math>\xrightarrow[\text{reflux}]{\text{acidified KMnO}_4}</math> <math>(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}</math></p> <p style="text-align: center;">F <span style="margin-left: 10em;">G</span></p> <p>H<sub>2</sub> produced with Na no orange crystals with 2,4-DNPH</p> <p>✓ B</p> <p></p> <p><math>\xrightarrow[\text{reflux}]{\text{acidified KMnO}_4}</math> </p> <p>H<sub>2</sub> produced with Na orange crystals with 2,4-DNPH</p> <p>✗C</p> <p></p> <p><math>\xrightarrow[\text{reflux}]{\text{acidified KMnO}_4}</math> </p> <p>no H<sub>2</sub> produced with Na orange crystals with 2,4-DNPH</p>

		<p><b>xD</b>      F      CH<sub>2</sub>OH</p> <p>acidified KMnO<sub>4</sub> reflux</p> <p><b>G</b>      CO<sub>2</sub>H</p> <p>H<sub>2</sub> produced with Na no orange crystals with 2,4-DNPH</p>
26	C	<p>Step 1: positive iodoform test as it involves the removal of 1 -CH<sub>3</sub> group. Cannot perform strong oxidation otherwise benzoic acid will be formed.</p> <p>Step 2: Nucleophilic acyl substitution (formation of ester)</p>
27	B	<p><b>(1 and 2 only)</b></p> <p> <b>✓1:</b> Since O is more electronegative, O of CH<sub>3</sub>O<sup>-</sup> can bear the negative charge better than N of CH<sub>3</sub>NH<sup>-</sup>.     </p> <p> <b>✓2:</b> The orbital of N is closer in size to that of C and hence, the overlap of orbitals between the C of C=O and N is more effective than that between C of C=O and O.     </p> <p> <b>x3:</b> Only one lone pair can be delocalised into the adjacent C=O. Hence, the number of lone pair on O does not affect the rate of hydrolysis.     </p>

28	A	<p>Identify the alpha-carbons in the backbone of the oligopeptide (in *). You can then easily identify the amide linkages in compound W (circled below).</p> <p>* alpha carbon</p>
29	C	<p>cis-pro pro-ser ser-arg-pro pro-ala-phe-gly  cys-pro-ser-arg-pro-ala-phe-gly</p>
30	B	<p>1 and 3 only Option 1 is correct. Electrode <b>X</b> is the positive electrode i.e. the anode, anions (i.e. <math>O^{2-}</math>) migrate here and oxidation takes place. <math>O^{2-}</math> is oxidised to <math>O_2(g)</math>.  Option <b>2</b> is incorrect. Electrode <b>Y</b> is the negative electrode i.e. the cathode, cations (i.e. <math>A^{\beta+}</math>) migrate here and reduction takes place.  Option <b>3</b> is correct Electrons move from negative terminal of the battery to electrode <b>Y</b>, and electrode <b>X</b> to the positive terminal of the battery. Thus, electrons move from electrode <b>X</b> to electrode <b>Y</b>.</p>

NAME \_\_\_\_\_

CLASS **23S**



**JURONG PIONEER JUNIOR COLLEGE**  
**JC2 PRELIMINARY EXAMINATION 2024**

**CHEMISTRY**

Paper 2 Structured Questions

**9729/02**

**10 September 2024**

**2 hours**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

**READ THESE INSTRUCTIONS FIRST**

Write your name, class and index number in the spaces at the top of this page.

Write in dark blue or black pen.

You may use a HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

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

A Data Booklet is provided.

The number of marks is given in brackets [ ] at the end of each question or part question.

<b>For Examiner's Use</b>	
1	7
2	11
3	13
4	14
5	12
6	18
<b>Penalty</b> (delete accordingly)	
Lack 3 sf in final answer	-1 / NA
Missing/wrong units in final ans	-1 / NA
Bond linkages	-1 / NA
<b>Total</b>	<b>75</b>

This document consists of **22** printed pages and **2** blank pages.

Answer **ALL** the questions in the spaces provided.

**1 Use of the Data Booklet is relevant to this question.**

The most recent updates to the Periodic Table occurred in 2016, when IUPAC officially recognised the discovery of four new elements: Nihonium (Nh), Moscovium (Mc), Tennessine (Ts), and Oganesson (Og), completing the seventh row of the table.

Table 1.1 lists the number of protons, neutrons and electrons in four particles, each from one of the elements mentioned above.

Each particle may be an atom, an anion or a cation.

**Table 1.1**

element	particle	atomic no.	nucleon no.	no. of protons	no. of neutrons	no. of electrons
Nihonium (Nh)	<b>Nh</b>	113	286	113	173	113
Moscovium (Mc)	<b>Mc<sup>3-</sup></b>	115	290		175	118
Tennessine (Ts)	<b>Ts<sup>-</sup></b>	117			177	
Oganesson (Og)	<b>Og</b>		294	118		118

- (a)** Based on the positions of the four new elements in the Periodic Table, state the Group that each of the elements belong to.

Nh .....

Mc .....

Ts .....

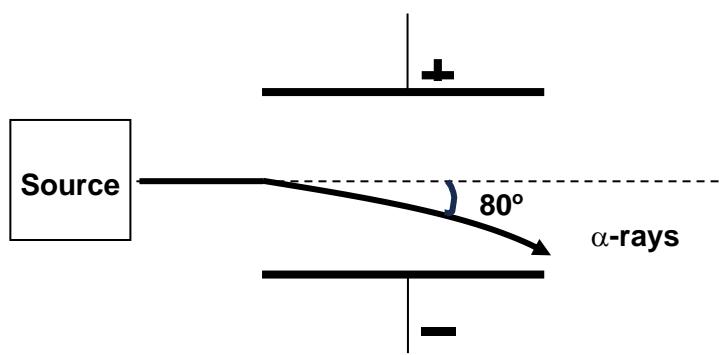
Og .....

[1]

- (b)** Fill in the empty spaces in Table 1.1.

[2]

- (c)** A stream consisting of  $\alpha$ -particles ( $\text{He}^{2+}$ ) is subjected to an electric field as shown in Fig. 1.1 below.

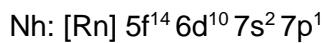


**Fig. 1.1**

Determine, by calculation, the angle of deflection for a second stream consisting of  $\text{Mc}^{3-}$  that is passed through the same electric field.

[1]

- (d) The simplified electronic configuration of Nihonium is given below.



- (i) Using information from Table 1.1, give the simplified electronic configuration of Moscovium (Mc).

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[1]

- (ii) Predict if Nh or Mc would have a higher first ionisation energy. Briefly explain your answer.

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[2]

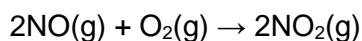
[Total: 7]

- 2 (a) Catalytic converters containing platinum solid convert over 90% of carbon monoxide and gaseous nitrogen oxides into harmless gases such as  $\text{CO}_2$  and  $\text{N}_2$ . Outline the mode of action of the platinum catalyst.

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[2]

One reaction in which air can be polluted with nitrogen oxides is shown below.



0.05 mol dm<sup>-3</sup> of NO and 0.005 mol dm<sup>-3</sup> of O<sub>2</sub> were mixed and the rate of reaction was followed by measuring the concentration of oxygen remaining after various time intervals.

The following graph was obtained in Fig. 2.1.

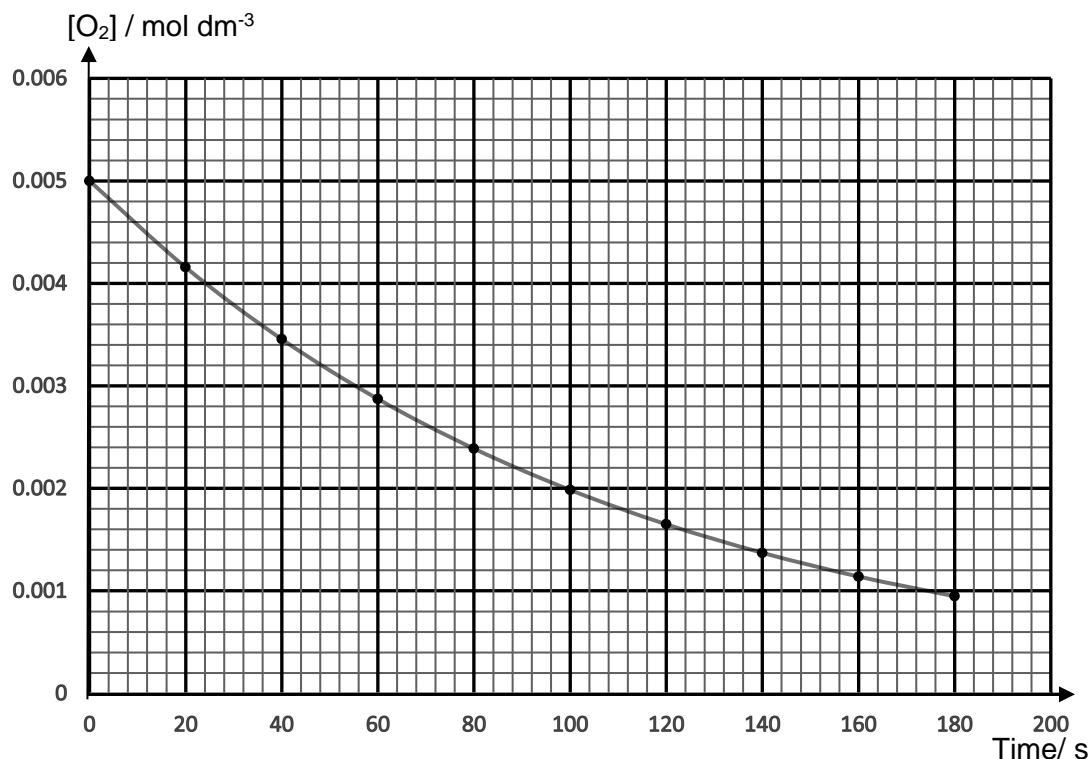


Fig. 2.1

- (b) (i) Define the term *half-life* of a reaction.

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[1]

- (ii) Show all your working and draw clearly any construction lines on Fig. 2.1 to determine the order of reaction with respect to O<sub>2</sub>.

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[2]

- (iii) Show all your working and clearly draw any construction lines on Fig. 2.1 to determine the initial rate of reaction. State its units.

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[2]

- (c) Further experiments were carried out changing the [NO] but keeping the initial [O<sub>2</sub>] constant at 0.10 mol dm<sup>-3</sup>. The following results were obtained.

**Table 2.1**

Experiment	Initial [NO] / mol dm <sup>-3</sup>	Initial rate / mol dm <sup>-3</sup> min <sup>-1</sup>
1	0.01	3.75 × 10 <sup>-5</sup>
2	0.02	1.50 × 10 <sup>-4</sup>

- (i) Using the data from Table 2.1, deduce the order of reaction with respect to NO.

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[1]

- (ii) Write the rate equation for this reaction.

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[1]

- (iii) Using Table 2.1, calculate a value for the rate constant. Include units of the rate constant in your answer.

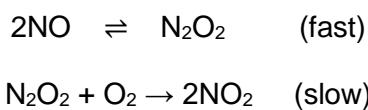
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[1]

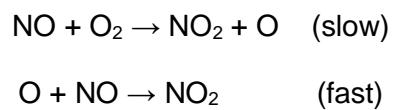
- (d) Two possible mechanisms for this reaction are given below.

State the mechanism which is consistent with the rate equation you have written in (c)(ii) and explain your answer.

Mechanism 1



Mechanism 2

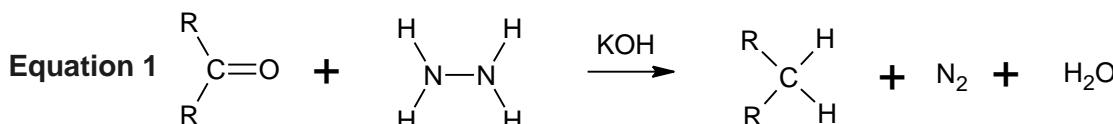


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[1]

[Total: 11]

- 3 The Wolff-Kishner reaction transforms ketones or aldehydes into alkanes by using hydrazine,  $\text{N}_2\text{H}_4$  and potassium hydroxide, KOH, as illustrated in equation 1 below.

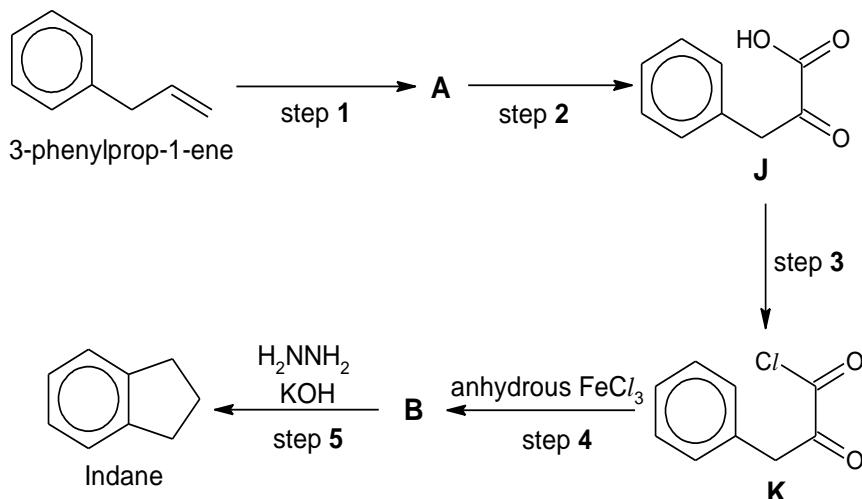


- (a) State the type of reaction in equation 1.

..... [1]

- (b) Indane,  $\text{C}_9\text{H}_{10}$ , is an ortho-fused bicyclic hydrocarbon consisting of a benzene ring fused to a cyclopentane ring. It is used as an anti-vibration agent for aviation fuel.

Indane can be synthesised from 3-phenylprop-1-ene by the following route, incorporating Wolff-Kishner reaction.



- (i) Draw the structures of **A** and **B**.

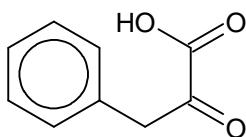
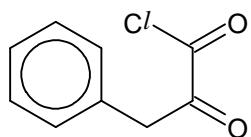
[2]

- (ii) State the reagents and conditions for steps 1, 2 and 3.

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 .....  
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[3]

- (iii) By means of a simple chemical test, distinguish compounds **J** and **K**.  
State the observations for each compound clearly.

**J****K**

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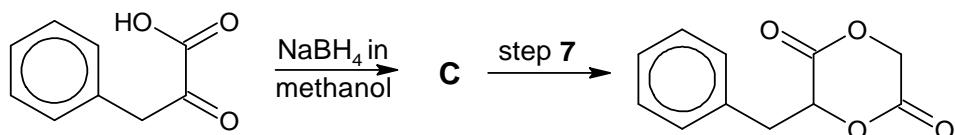
[2]

- (c) Nitration of 3-phenylprop-1-ene can be achieved by reacting it with concentrated  $\text{H}_2\text{SO}_4$  and concentrated  $\text{HNO}_3$ .

Name and draw the reaction mechanism for the nitration of 3-phenylprop-1-ene.

[3]

- (d) Compound **J** can be used as a starting material to produce a cyclic diester as shown below.



- (i) Draw the structure of **C**.

[1]

- (ii) Suggest the reagents and conditions for step 7.

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[1]

[Total: 13]

- 4 (a) Compound **D** is a sweet-smelling organic compound with the molecular formula  $C_5H_9BrO_2$ . It is known that each molecule of **D** contains two functional groups. A student from JPJC was tasked to determine the structure of compound **D**. Table 4.1 below shows the chemical reactions that the student carried out for compound **D**.

**Table 4.1**

expt	reagent	Result
1	$AgNO_3(aq)$ , warm	cream precipitate formed which was soluble in an excess of $NH_3(aq)$ .
2	$NaOH(aq)$ , heat	two products were formed; <b>E</b> ( $C_3H_5O_3Na$ ) and <b>F</b> ( $C_2H_6O$ ).

- (i) State the identity of the cream precipitate formed in experiment 1.

Hence or otherwise, name the functional group, shown by experiment 1, that is present in compound **D**.

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.....

[1]

- (ii) State the type of reaction undergone in reaction 2 and identify the other functional group in **D**.

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[1]

The student conducted further chemical tests on compounds **E** and **F** separately. The results of the tests are given in Table 4.2.

**Table 4.2**

experiment	reagent	Result
3	$PCl_5(s)$	misty fumes were formed for both <b>E</b> and <b>F</b> .
4	$I_2$ , $NaOH(aq)$ , warm	pale yellow precipitate formed for both <b>E</b> and <b>F</b> .

- (iii) Based on both experiments 3 and 4, what is the common functional group that could be present in both compounds **E** and **F**? Explain your answer, giving the type of reaction undergone.

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.....

[1]

- (iv) Using your answers in (a)(i), (a)(ii) and (a)(iii), draw the structures of compounds **E** and **F**.

[2]

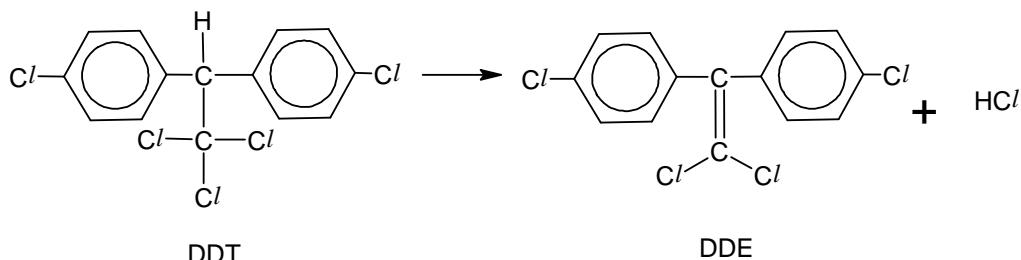
- (v) The student now has enough information to determine the structural formula of **D**.

Draw the fully displayed structure of **D**.

[1]

- (b)** Dichlorodiphenyltrichloroethane (DDT) is an organochlorine pesticide that was widely used during the 20th century for controlling insect-borne diseases like malaria.

The equation below shows the environmental degradation of DDT to dichlorodiphenyl dichloroethylene (DDE).



- (i) State the type of reaction for the conversion of DDT to DDE.

.....

[1]

Table 4.3 below shows the results when aqueous silver nitrate is heated with 0.5 mol of DDT and 0.5 mol of DDE separately.

**Table 4.3**

	Time taken for precipitate (ppt) to appear	No. of moles of ppt formed per mole of compound reacted
DDT	5 min	$x$ mol
DDE	no ppt	0 mol

- (ii) State the value of  $x$  in Table 4.3.

.....

[1]

- (iii) Explain why no precipitate was observed for the reaction with DDE.

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[2]

- (iv) In organic chemistry, a geminal compound is a molecule in which 2 or more identical or similar functional groups are attached to the same carbon atom.

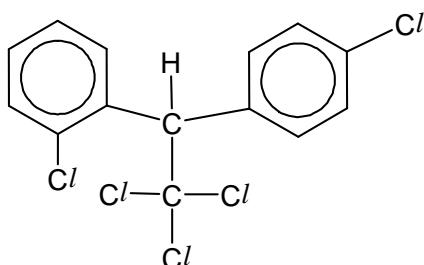
When DDT reacts with hot aqueous NaOH, a gem-triol, is formed as an intermediate. A gem-triol contains three -OH groups bonded to the same carbon atom. The gem-triol formed is unstable and it readily converts to the final product, **S**.

**S** reacts with aqueous  $\text{Na}_2\text{CO}_3(\text{aq})$  to liberate a colourless gas.

Draw the structure of the organic compound **S**.

[1]

- (c) (i) 1,1,1-trichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane, or o,p'-DDT, is an constitutional isomer of DDT. The structure of o,p'-DDT is given below.



o,p'-DDT

State the type of stereoisomerism exhibited by o,p'-DDT.

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[1]

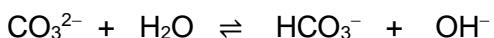
- (ii) Draw the stereoisomers of o,p'-DDT.

[2]

[Total: 14]

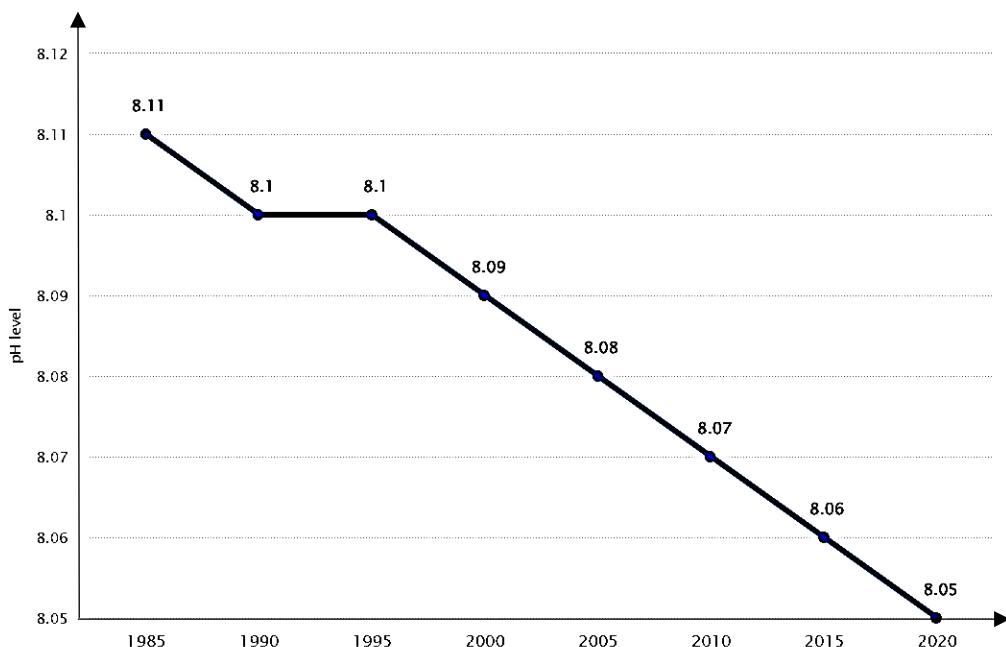
- 5 The pH of the seawater in the ocean is regulated by the carbonate - bicarbonate ( $\text{CO}_3^{2-}$  /  $\text{HCO}_3^-$ ) buffer system.

Main buffering system:



Recently, changes in the pH of the oceans by ocean acidification has been a concern. Ocean acidification, primarily caused by the absorption of carbon dioxide,  $\text{CO}_2$ , from the atmosphere, poses a significant threat to marine ecosystems worldwide.

The increased concentration of  $\text{CO}_2$  in seawater leads to changes in the pH as shown in Fig. 5.1 below which shows the average ocean pH level worldwide from 1985 to 2020.



**Fig. 5.1**

- (a) (i) Using Fig. 5.1, state and explain the trend of the pH of the seawater of the ocean.

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[1]

- (ii) With the aid of equations show how the carbonate - bicarbonate buffer system in seawater maintains the pH when there is an increase in amounts of  $\text{H}^+$  or  $\text{OH}^-$  in the seawater.

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[2]

- (iii) Use the pH value from Fig. 5.1, show that the molar ratio of bicarbonate to carbonate ion of a sample of seawater from 2020 is 89:1.

Given that the  $K_b$  of  $\text{CO}_3^{2-}$  is  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ .

[2]

The total  $\text{CO}_3^{2-} + \text{HCO}_3^-$  content of the seawater can be found by boiling a seawater sample with an excess of dilute sulfuric acid and absorbing the  $\text{CO}_2$  evolved in a solution of barium hydroxide,  $\text{Ba}(\text{OH})_2$ .

The precipitated barium carbonate,  $\text{BaCO}_3$  can be filtered off, dried and weighed.

When a  $100 \text{ cm}^3$  seawater sample was treated in the above-mentioned process, 0.281 g of  $\text{BaCO}_3$  was produced.

*[Assume that the seawater sample is from the year 2020]*

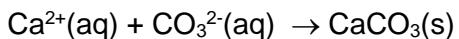
- (iv) Show that the total amount of  $\text{CO}_3^{2-} + \text{HCO}_3^-$  content in the seawater sample is  $1.42 \times 10^{-3} \text{ mol}$ .

[1]

- (v) Hence, using the information in (a)(iii) & (a)(iv) calculate  $[\text{CO}_3^{2-}]$  in the  $100 \text{ cm}^3$  seawater sample from 2020.

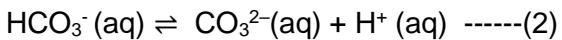
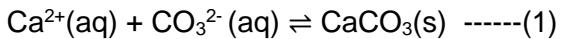
[2]

- (b) Organisms with calcium carbonate shells produce their shells according to the equation shown.



Changes in the pH alters the chemical balance of the oceans and affects marine life, particularly organisms with calcium carbonate shells.

- (i) Using the equations below and the concept of Le Chatelier's principle and solubility product, explain why marine organisms will not be able to build shells if pH of the seawater decreases.



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[2]

- (ii) The concentration of  $\text{Ca}^{2+}$  ions in the seawater sample from 2020 is  $3.99 \times 10^{-4} \text{ mol dm}^{-3}$ .

Given that  $K_{\text{sp}}$   $\text{CaCO}_3$  is  $3.30 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$ , calculate the minimum  $[\text{CO}_3^{2-}]$  for the organisms to form their shells in 2020.

[1]

- (iii) Using your answer in (a)(v) and (b)(ii), explain whether the organisms will be able to form their shells in the seawater in 2020?

[1]

[Total: 12]

- 6 (a) Haemoglobin and hemocyanin are two oxygen-transporting proteins found in living organisms. Both proteins are coloured due to the presence of transition metals, such as iron in haemoglobin and copper in hemocyanin, that form complexes essential for their oxygen-binding properties.

- (i) Why are transition metal complexes coloured?

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[3]

- (ii) Non-transition metal compounds, in contrast, tend to be colourless.

Explain why a solution containing  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  is colourless.

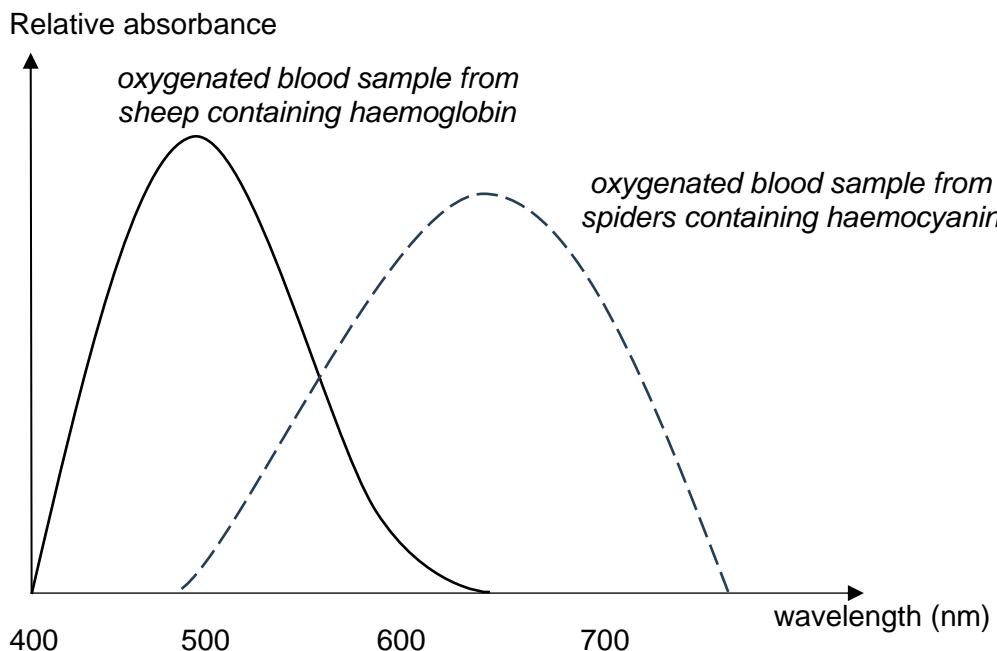
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[1]

Absorption spectra, an analytical method in chemistry, show the wavelengths of light absorbed by substances.

Chemists use this technique to analyse the oxygenated blood samples from sheep (haemoglobin) and spiders (haemocyanin) to compare their absorption characteristics.

The result of the analysis is shown in Fig. 6.1.



*Fig. 6.1: Graph showing Absorption Spectra*

The wavelengths associated with each colour of visible light are given below in Table 6.1. Light of a longer wavelength is lower in energy than light of a shorter wavelength.

**Table 6.1**

colour of visible light	wavelength (nm)
Red	620 – 750
Orange	590 – 620
Yellow	570 – 590
Green	495 – 570
Blue	450 – 495
Violet	380 – 450

- (iii) The oxygenated blood of sheep, which contains haemoglobin, is red.

Using this information and the data provided, predict the colour of the oxygenated blood of spiders, which contains haemocyanin.

[1]

- (iv) What deduction can be made from the absorption spectra in Fig. 6.1, about the size of the d-orbital splitting in the two samples of oxygenated blood, containing different complexes of haemoglobin and haemocyanin?  
Explain your answer.

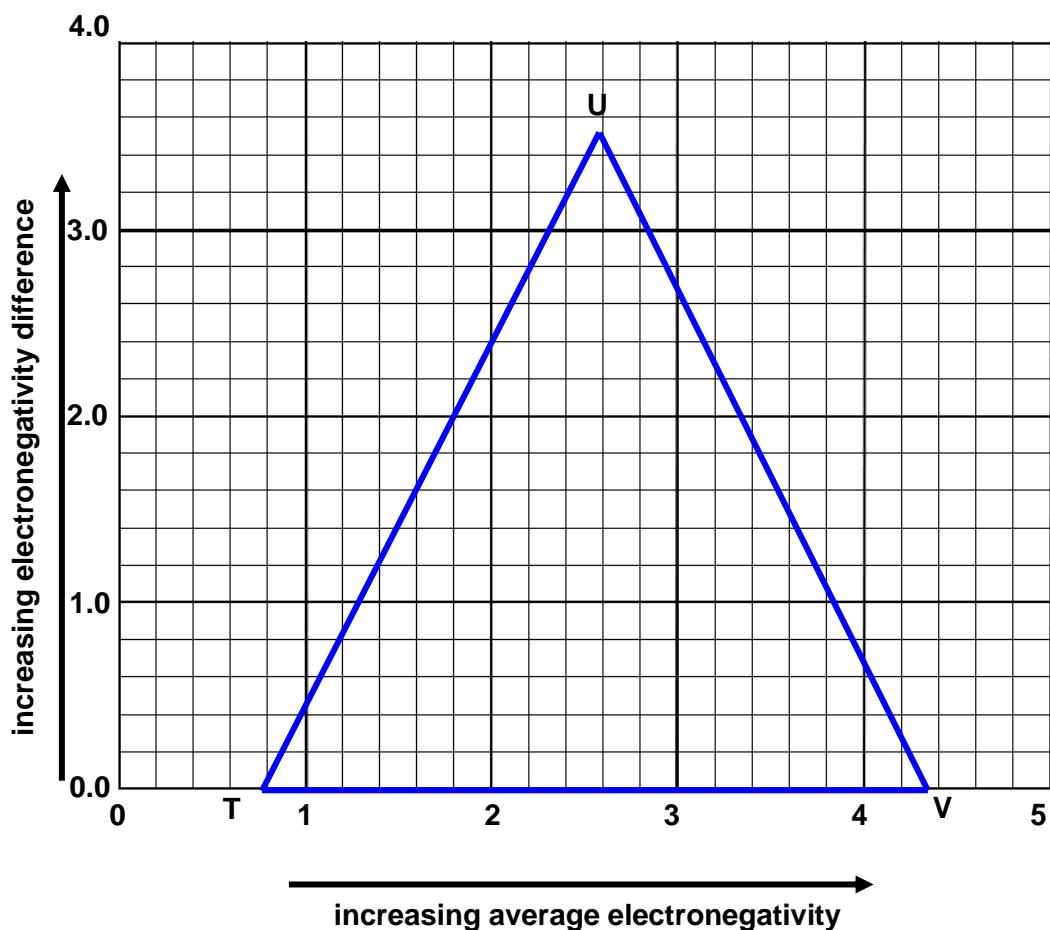
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[2]

- (b) The van Arkel triangle, invented by Dutch chemist Anton Eduard van Arkel, is a tool used to classify the bonding in compounds as ionic, covalent, or metallic.

Fig. 6.2 shows an example of a van Arkel triangle.

The y-axis represents the difference in electronegativity between two elements, while the x-axis shows the average electronegativity of the two elements.



**Fig. 6.2**

Table 6.2 provides the electronegativity values of some of elements from Period 3 of the Periodic Table, based on Pauling's Scale. The average electronegativity is calculated based on the sum of the electronegativities of the two elements in the compound, divided by two.

**Table 6.2**

Element	Electronegativity
Na	0.9
Mg	1.2
Al	1.5
Si	1.8
P	2.1
S	2.5
Cl	3.0

- (i) Plot the position of  $\text{Cl}_2$  and  $\text{AlCl}_3$  on the diagram. Label your points clearly in Fig. 6.2.

[2]

- (ii) The three extremes on the van Arkel triangle, namely **T**, **U** and **V**, represent the three types of chemical bonding, metallic, ionic and covalent.

State the correct type of bonding present at each of the bonding extremes.

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[2]

- (c) (i) In the liquid state,  $\text{AlCl}_3$  exists as a compound with a molar mass of 267 g mol<sup>-1</sup>.

Draw the structure of this compound.

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[1]

- (ii) The boiling points of  $\text{Al}_2\text{O}_3$  and  $\text{AlCl}_3$  in the liquid state are 2977 °C and 180 °C respectively.

Explain, in terms of structure and bonding, the difference in their boiling points.

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[2]

- (iii) The pH values of the solutions of two Period 3 chlorides are given below in Table 6.3.

**Table 6.3**

compound	pH of 1.0 mol dm <sup>-3</sup> solution
MgCl <sub>2</sub>	X
AlCl <sub>3</sub>	Y

Write equations for the reaction of AlCl<sub>3</sub> with water.

State the values of x and y in Table 6.3 above. Briefly explain the different pH values of the two chloride solutions.

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[3]

- (iv) The lattice energy of magnesium chloride is  $-2582 \text{ kJ mol}^{-1}$ . Some enthalpy changes of hydration are listed in Table 6.4.

**Table 6.4**

Ions	$\Delta H_{\text{hyd}}$ / kJ mol <sup>-1</sup>
Mg <sup>2+</sup>	-1980
Cl <sup>-</sup>	-381

Using the data provided, calculate the enthalpy change of solution of magnesium chloride.

[1]

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**JURONG PIONEER JUNIOR COLLEGE**  
**JC2 PRELIMINARY EXAMINATION 2024**

**CHEMISTRY**

**9729/02**

Paper 2 Structured Questions

**10 September 2024**

**2 hours**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

**READ THESE INSTRUCTIONS FIRST**

Write your name, class and index number in the spaces at the top of this page.

Write in dark blue or black pen.

You may use a HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

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

A Data Booklet is provided.

The number of marks is given in brackets [ ] at the end of each question or part question.

<b>For Examiner's Use</b>	
1	7
2	11
3	13
4	14
5	12
6	18
<b>Penalty</b> (delete accordingly)	
Lack 3sf in final answer	-1 / NA
Missing/wrong units in final ans	-1 / NA
Bond linkages	-1 / NA
<b>Total</b>	<b>75</b>

This document consists of **19** printed pages and **1** blank page.

Answer **ALL** the questions in the spaces provided.

**1 Use of the Data Booklet is relevant to this question.**

The most recent updates to the Periodic Table occurred in 2016, when IUPAC officially recognised the discovery of four new elements: Nihonium (Nh), Moscovium (Mc), Tennessine (Ts), and Oganesson (Og), completing the seventh row of the table.

Table 1.1 lists the number of protons, neutrons and electrons in four particles, each from one of the elements mentioned above. Each particle may be an atom, an anion or a cation.

**Table 1.1**

element	particle	atomic no.	nucleon no.	no. of protons	no. of neutrons	no. of electrons
Nihonium (Nh)	<b>Nh</b>	113	286	113	173	113
Moscovium (Mc)	<b>Mc<sup>3-</sup></b>	115	290		175	118
Tennessine (Ts)	<b>Ts<sup>-</sup></b>	117			177	
Oganesson (Og)	<b>Og</b>		294	118		118

- (a) Based on the positions of the four new elements in the Periodic Table, state the Group that each of the elements belong to.

Nh .....

Mc .....

Ts .....

Og .....

Nh: Group 13

Mc: Group 15

Ts: Group 17

Og: Group 18

All groups correct. Do not accept Group 3, 5, 7, 0. [1]

[1]

Examiner's comments:

Students would need to recall that elements in the periodic table are arranged according to their atomic number / proton number.

By referring to the Data Booklet, it is clear that the 4 missing elements belong to Group 13, 15, 17 and 18 respectively.

	13	14	15	16	17	18
						2 He helium 4.0
5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2	
13 Al aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 Cl chlorine 35.5	18 Ar argon 39.9	
31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8	
49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3	
81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –	
✓	114 Fl flerovium –	✓	116 Lv livermorium –	✓	✓	

Common mistakes that are not accepted:

- Group 3, 5, 7, 8, 0
- Group III, V, VII, VIII, VIII

(b) Fill in the empty spaces in Table 1.1.

element	parti -cle	atomic no.	nucleon no.	no. of protons	no. of neutrons	no. of electrons
Nihonium (Nh)	Nh	113	286	113	173	113
Moscovium (Mc)	Mc <sup>3-</sup>	115	290	115	175	118
Tennessee (Ts)	Ts <sup>-</sup>	117	294	117	177	118
Oganesson (Og)	Og	118	294	118	176	118

[2]

Examiner's comments:

Generally, quite well done. A few careless mistakes.

Students need to understand the following:

- Atomic no. = no. of protons
- Nucleon no. = no. of protons + no. of neutrons
- To find no. of electrons:
  - o For cations: take away the relevant no. of electrons
  - o For anions: add the relevant no. of electrons

- (c) A stream consisting of  $\alpha$ -particles ( $\text{He}^{2+}$ ) is subjected to an electric field as shown in Fig. 1.1 below.

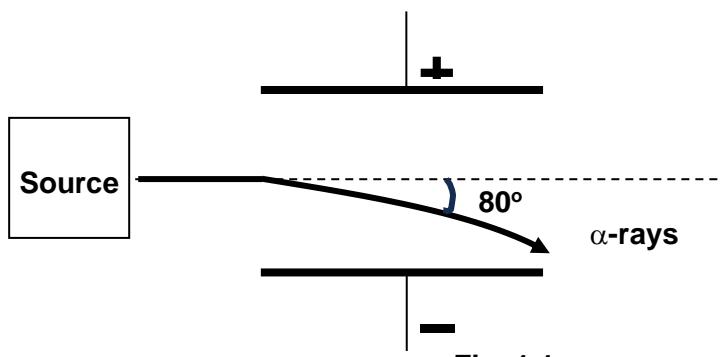


Fig. 1.1

Determine, by calculation, the angle of deflection for a second stream consisting of  $\text{Mc}^{3-}$  that is passed through the same electric field.

Since **angle of deflection  $\propto$  charge/mass**,

[1]

$$\frac{\text{angle of deflection of } \alpha\text{-particles}}{\text{angle of deflection of } \text{Mc}^{3-}} = \frac{2/4}{3/290}$$

Solving, angle of deflection of  $\text{Mc}^{3-} = -1.6551 \approx -1.66^\circ$

Examiner's comments:

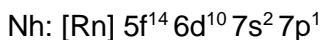
Not so well done.

Key concept here is that the **angle of deflection  $\propto$  charge/mass**.

Common mistakes:

- did not apply the correct formula;
- did not indicate – or state towards the positive plate to show direction (did not penalise this time round);
- did not round off to 3 s.f.

- (d) The simplified electronic configuration of Nihonium is given below.



- (i) Using information from Table 1.1, give the simplified electronic configuration of Moscovium (Mc).



[1]

Examiner's comments:

This was meant to be quite a doable part of the question but there were quite a number of mistakes. Looking at the atomic/proton numbers, Mc should have 2 more electrons than Nh.

Common mistakes that are not given credit:

- 5f<sup>14</sup> 6d<sup>10</sup> 7s<sup>2</sup> 7p<sup>3</sup>
- [Rn] 5f<sup>14</sup> 6d<sup>10</sup> 7s<sup>2</sup> 7p<sup>6</sup>

- (ii) Predict if Nh or Mc would have a higher first ionisation energy. Briefly explain your answer.

Mc would have a higher first ionisation energy than Nh.

Across the period, nuclear charge increases while shielding effect remains constant, leading to an increase in effective nuclear charge OR strong nuclear attractions on the valence electrons

[2]

Examiner's comments:

This part was generally well done.

A common mistake was to use the explanation of increasing IE down a group, i.e. increase in shielding effect outweighs increase in nuclear charge, rather than across a period.

Another point that students tend to miss out is the increase in nuclear charge which is due to an increase in proton number. Please take note that nuclear charge is NOT equivalent to effective nuclear charge.

[Total: 7]

- 2 (a) Catalytic converters containing platinum solid convert over 90% of carbon monoxide and gaseous nitrogen oxides into harmless gases such as CO<sub>2</sub> and N<sub>2</sub>.

Outline the mode of action of the platinum catalyst.

The catalyst in the catalytic converter is a heterogeneous catalyst.

The reactant molecules adsorb(\*) onto the surface of the metal catalyst (Pd & Pt) via formation of weak (temporary) bonds.

This weakens the bonds in the reactant molecules and thus provides an alternative reaction mechanism of lower activation energy. The surface concentration of the reactants also increases.

The product molecules desorbs from the catalyst surface, making the surface available for adsorption of new reactant molecules.

[2]

Examiner's comments:

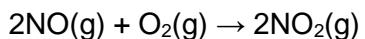
This part was not so well done.

Students need to understand and apply the mode of action for heterogeneous catalyst. Some wrote as homogenous/heterozygous/heterolytic etc, which were all incorrect.

The key mode of actions would include:

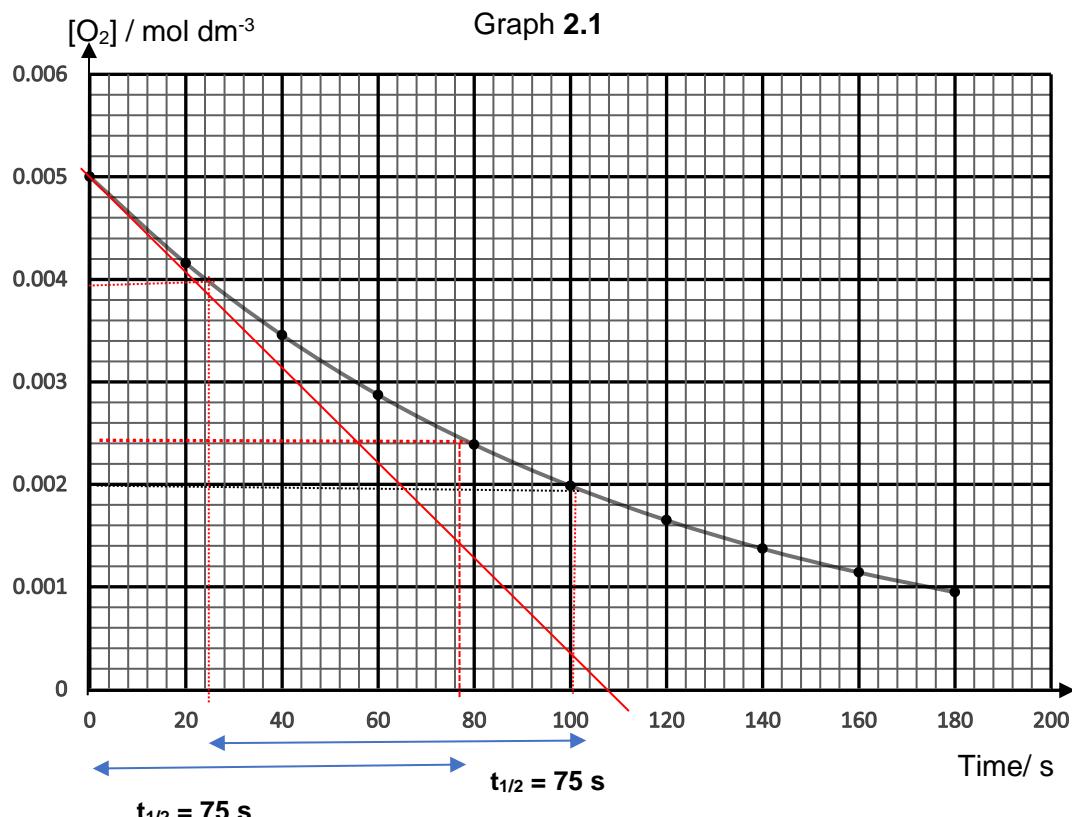
- Adsorption (not absorption)
- Reaction (weakening of bonds and forming of new bonds)
- Desorption

One reaction in which air can be polluted with nitrogen oxides is shown below.



0.05 mol dm<sup>-3</sup> of NO and 0.005 mol dm<sup>-3</sup> of O<sub>2</sub> were mixed and the rate of reaction was followed by measuring the concentration of oxygen remaining after various time intervals.

The following graph was obtained.



- (b) (i) Define the term *half-life* of a reaction.

**Half-life**,  $t_{1/2}$ , is the time taken for the reactant concentration to decrease to half of its original/ initial value.

[1]

Examiner's comments:

This part was well done.

But there were a few mistakes made by candidates:

- “product concentration” or not stating that it refers to reactant concentration/amount.
- concentration of reactants: Please take note that half-life is in reference to only 1 reactant. (did not penalise)
- “decrease by 2”.

- (ii) Show all your working and draw clearly any construction lines on the Graph 2.1 to determine the order of reaction with respect to O<sub>2</sub>.

(✓) construction lines for two  $t_{1/2}$  + labelled as  $t_{1/2}$  or values on graph  
 (✓) two correctly read  $t_{1/2}$  values either stated or indicated on graph

Using graph of [NO] = 0.10 mol dm<sup>-3</sup>,

When concentration of [O<sub>2</sub>] decreases from 0.0050 mol dm<sup>-3</sup> to 0.0025 mol dm<sup>-3</sup>, half life = 75 s

When [O<sub>2</sub>] decreases from 0.0040 mol dm<sup>-3</sup> to 0.0020 mol dm<sup>-3</sup> (halved), half-life = 75 s (can be average or either half-life)

Since half-lives are constant (✓), the order of reaction with respect to O<sub>2</sub> is 1. (✓)

[2]

Examiner's comments:

This part was generally well done.

A few things to take note:

- do indicate clearly on the graph where are the half-lives and the values for the examiners;
- it is important to use "consecutive half-lives". (not penalised this time round);
- some students read off the graphs wrongly for half-life.  
Eg. 0.005 to 0.002; 0.0025 to 0.001 [incorrect examples]

- (iii) Show all your working and clearly draw any construction lines on the Graph 2.1 to determine the initial rate of reaction. Include its units.

Initial Rate Method – draw a gradient at t = 0 min

$$\text{Gradient} = (0.005 - 0) / (0 - 108) = -4.63 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$$

Take modulus and ignore the negative sign;

hence rate is  $4.63 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$

[2]

Examiner's comments:

The part was generally well done.

The few things to take note:

- rate is ALWAYS positive. No such thing as a negative rate of reaction.  
As such, initial rate = | gradient |
- Quite a handful of students did not know how to construct the tangent to the curve at t = 0s properly. Consequently, the value of their rate is either too high or too low.  
The range that was accepted was ±20%.  
 $3.70 \times 10^{-5}$  to  $5.56 \times 10^{-5}$

Students are strongly encouraged to purchase a curved ruler and learn how to use it to draw a tangent to the curve at any point.

- (c) Further experiments were carried out changing the [NO] but keeping the initial  $[O_2]$  constant at  $0.10 \text{ mol dm}^{-3}$ . The following results were obtained.

**Table 2.1**

Experiment	Initial [NO] / mol dm <sup>-3</sup>	Initial rate / mol dm <sup>-3</sup> min <sup>-1</sup>
1	0.01	$3.75 \times 10^{-5}$
2	0.02	$1.50 \times 10^{-4}$

- (i) Using the data from the Table 2.1, deduce the order of reaction with respect to NO.

Let  $\text{rate} \propto [\text{NO}]^a$ .

$$\frac{(\text{rate})_2}{(\text{rate})_1} = \frac{1.50 \times 10^{-4}}{3.75 \times 10^{-5}} = \frac{(0.02)^b}{(0.01)^b}$$

$$4 = 2^b \quad \therefore b = 2$$

OR, When [NO] is x2 or doubled while keeping  $[O_2]$  constant, initial rate is x4 or quadrupled.

$\therefore$  the order of reaction with respect to [NO] is **2**.

[1]

Examiner's comments:

- This was well answered.
- Students should avoid using “increases” or “decreases” as some incorrectly stated that “the initial rate is decreased/reduced to  $4x$ ” instead of “to  $\frac{1}{4}x$ ”.

- (ii) Write the rate equation for this reaction.

$$\text{rate} = k[\text{NO}]^2[\text{O}_2]$$

[1]

Examiner's comments:

- This was well answered.
- Some forgot to include  $[O_2]$ .

- (iii) Using **Table 2.1**, calculate a value for the rate constant. Include units of rate constant in your answer.

$$3.75 \times 10^{-5} = k(0.01)^2(0.1)$$

$$\text{OR, } 1.50 \times 10^{-4} = k(0.02)^2(0.1)$$

$$k = 3.75 \text{ mol}^{-2} \text{ dm}^6 \text{ min}^{-1}$$

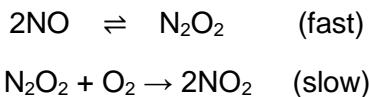
[1]

Examiner's comments:

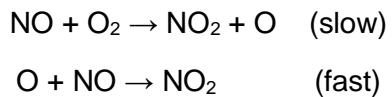
- Many could not derive the correct units for  $k$ .
- Many stated ‘ $s^{-1}$ ’ instead of ‘ $\text{min}^{-1}$ ’.
- Some did not use the data in **Table 2.1**.

(d) Two possible mechanisms for this reaction are given below.

Mechanism 1



Mechanism 1



State the mechanism which is consistent with the rate equation you have written in (c)(ii) and explain your answer.

Mechanism 1 (✓)

$$\text{From step 1, } K_c = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} \quad \text{or} \quad k_f[\text{NO}]^2 = k_b[\text{N}_2\text{O}_2]$$

$$[\text{N}_2\text{O}_2] = K_c [\text{NO}]^2 \quad [\text{N}_2\text{O}_2] = \frac{k_f}{k_b} [\text{NO}]^2$$

From the slow step which is the rate-determining step,

$$\text{rate} = k' [\text{N}_2\text{O}_2] [\text{O}_2] \quad (\checkmark)$$

$$= k' K_c [\text{NO}]^2 [\text{O}_2] \quad (\text{or } k' \frac{k_f}{k_b} [\text{NO}]^2 [\text{O}_2])$$

$$\Rightarrow \text{rate} = k [\text{NO}]^2 [\text{O}_2], \quad (\checkmark) \text{ where } k = k' K_c \quad (\text{or } k = k' \frac{k_f}{k_b}) = \text{constant.}$$

OR,

Since the rate-determining step (slow step) involves one N<sub>2</sub>O<sub>2</sub> molecule and one O<sub>2</sub> molecule (✓) colliding together, rate  $\propto$  [N<sub>2</sub>O<sub>2</sub>][O<sub>2</sub>].

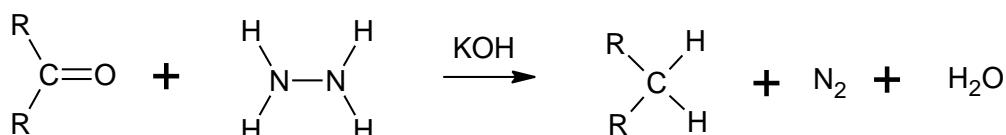
Since N<sub>2</sub>O<sub>2</sub> is the intermediate and one N<sub>2</sub>O<sub>2</sub> molecule is formed from two NO molecules (✓) in step 1 i.e.  $[\text{N}_2\text{O}_2] \propto [\text{NO}]^2$ , the overall rate  $\propto [\text{NO}]^2[\text{O}_2]$ . [1]

Examiner's comments:

- A small proportion of students could explain their choice of mechanism at molecular level with reference to the slow step.
- Common mistakes were to state "one mole" of reactant colliding with "one mole" of another reactant or did not state the number of particles involved in the rate-determining step.

[Total: 11]

- 3 The Wolff-Kishner reaction transforms ketones or aldehydes into alkanes by using hydrazine,  $N_2H_4$  and potassium hydroxide, KOH. An example of such a reaction is shown in equation 1 below.

Equation 1

- (a) State the type of reaction in equation 1.

*When ketone/aldehyde is transformed to alkane, an O atom is lost and two H atoms are gained.*

Reduction

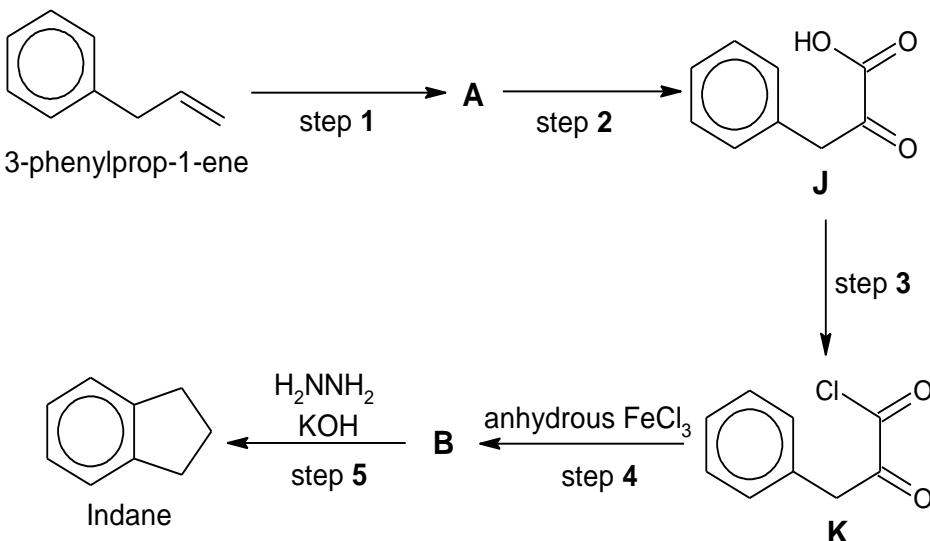
[1]

Examiner's comments:

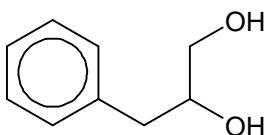
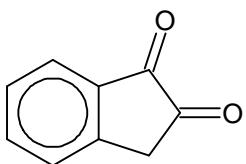
- Only a small proportion of students stated the type of reaction correctly.
- Students should name the reaction w.r.t to the organic reagent undergoing the reaction. For example, when an aldehyde is oxidised to a carboxylic acid with acidified  $KMnO_4$ , we name this reaction "oxidation" rather than "redox".
- Common responses are "redox", "nucleophilic addition" & "condensation".

- (b) Indane,  $C_9H_{10}$ , is an ortho-fused bicyclic hydrocarbon consisting of a benzene ring fused to a cyclopentane ring. It is used as an anti-vibration agent for aviation fuel.

Indane can be synthesised from 3-phenylprop-1-ene by the following route, incorporating Wolff-Kishner reaction.



- (i) Draw the structures of **A** and **B**.

**A****B**

[2]

Examiner's comments:

- This was generally not well answered.
- More students could give structure **A** correctly than **B**.

- (ii) State the reagents and conditions for steps 1, 2 and 3.

step 1: cold, KMnO<sub>4</sub>(aq), NaOH(aq) (or H<sub>2</sub>SO<sub>4</sub>(aq))  
**must state “aqueous” or “dilute”.**

step 2: K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>(aq), H<sub>2</sub>SO<sub>4</sub>(aq), heat under reflux  
**must state “aqueous” once.**

step 3: PCl<sub>5</sub>, r.t. or PCl<sub>3</sub>, heat or SOCl<sub>2</sub>, heat  
**reject “aq”. BOD for “PCl<sub>5</sub>, heat”**

[3]

Examiner's comments:

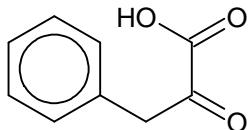
- For **step 1**: this was generally not well answered.  
“cold and aqueous/dilute KMnO<sub>4</sub>” must be stated to earn the credit.
- For **step 2**: Only a small proportion of students gave the correct answer.  
Common mistakes were stating “KMnO<sub>4</sub>”, “heat” without reflux or “heat with immediate distillation”.  
Students should recognise that benzylic H atoms are present in **A** and that it would be converted to benzoic acid if “KMnO<sub>4</sub>(aq) in H<sub>2</sub>SO<sub>4</sub>(aq), heat” was used.
- For **step 3**: students often gave the correct answer.  
BOD was given for “PCl<sub>5</sub>, heat” or “PCl<sub>5</sub>(g)/PCl<sub>3</sub>(g)/SOCl<sub>2</sub>(g)”.  
Students should know the physical states of these reagents: PCl<sub>5</sub>(s), PCl<sub>3</sub>(l) & SOCl<sub>2</sub>(l)”. As such, students are advised not to give state symbol.  
As PCl<sub>5</sub>, PCl<sub>3</sub> and SOCl<sub>2</sub> can undergo hydrolysis readily in the presence of water, these reagents must be dry/anhydrous. Hence, those who stated “aq” were marked down.

- (iii) By means of a simple chemical test, distinguish compounds **J** and **K**.

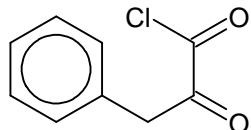
**Identify the difference in functional group:**

Carboxylic acid

acyl chloride



**J**



**K**

Reagent & conditions: aqueous AgNO<sub>3</sub> **reject with heating** (acyl chloride is very reactive and does not need heat, rtp suffices)

Observations: White ppt. of AgCl will be seen **immediately for K**.

No white ppt. will be formed **for J**.

**OR**

Reagent & conditions: PCl<sub>5</sub> or heat with SOCl<sub>2</sub>

Observations: White fumes of HCl will be seen **for J**.

No white fumes will be seen **for K**.

**OR**

Reagent & conditions: Na(s) or Mg(s)

Observations: For J, effervescence is seen and H<sub>2</sub> gas evolved pops with a lighted splint.

No effervescence of H<sub>2</sub> gas will be seen **for K**.

**OR**

Reagent & conditions: A few drops of water (given in 2019 P2 Q4(a)) [1]

Observations: For K, gas of HCl which turns damp blue litmus paper red will be formed.

No gas of HCl will be formed **for J**.

[2]

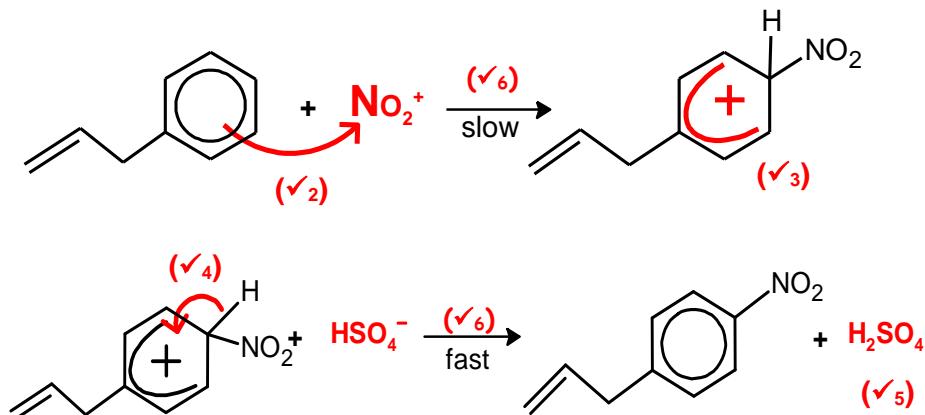
#### Examiner's comments:

- A significant number of students used “Na<sub>2</sub>CO<sub>3</sub>(aq)/NaHCO<sub>3</sub>(aq)” test which was rejected.  
Students must know that without water, RCOOH would not give H<sup>+</sup> to undergo acid-base reaction with Na<sub>2</sub>CO<sub>3</sub>(s)/NaHCO<sub>3</sub>(s). Hence, to test for RCOOH, the reagent must be Na<sub>2</sub>CO<sub>3</sub>(aq) or NaHCO<sub>3</sub>(aq).  
With the presence of water from the aqueous reagent, acyl chloride **K** would undergo hydrolysis readily to give a carboxylic acid and a strong HCl(aq) acid. Hence both **J** and **K** would undergo acid-base reaction in this test to give effervescence of CO<sub>2</sub>.
- Some students used “water” and stated that **K** would give white fumes of HCl. This test was rejected as with (excess) water, HCl(aq) would be formed readily and white fumes might not be seen. However, credit was given to students who stated “add a few drops of water” but “white fumes” would not earn the credit for observation.

- (c) Nitration of 3-phenylprop-1-ene can be achieved by reacting it with conc H<sub>2</sub>SO<sub>4</sub> and conc HNO<sub>3</sub>.

Name and draw the reaction mechanism for the nitration of 3-phenylprop-1-ene.

**Electrophilic substitution correct spelling**



(✓<sub>1</sub>) - balanced equation for the generation of NO<sub>2</sub><sup>+</sup> electrophile.

(✓<sub>2</sub>) - full arrow from π electron cloud of benzene ring to N of NO<sub>2</sub><sup>+</sup>.

(✓<sub>3</sub>) - arenium ion with delocalisation of +ve charge over 5 sp<sup>2</sup> C (not at the sp<sup>3</sup> C) and NO<sub>2</sub><sup>+</sup> directed to 2- or 4-position w.r.t. the alkyl side chain.

(✓<sub>4</sub>) - full arrow from C–H bond (not from H) to the +ve charge of arenium ion

(✓<sub>5</sub>) - correct product with regeneration of H<sub>2</sub>SO<sub>4</sub> catalyst & balanced eqn.

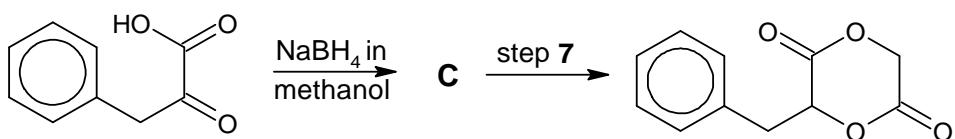
(✓<sub>6</sub>) - correctly labelled the “slow” and “fast” steps

[3]

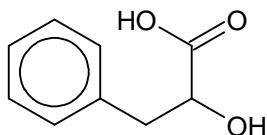
Examiner's comments:

- This was generally well answered.
- Some students forgot to name the mechanism.
- Some students gave product with —NO<sub>2</sub> substituted at 3-position w.r.t. the side-chain. Students should recognise that the C of the hydrocarbon side-chain directly bonded to the benzene ring is sp<sup>3</sup> hybridised and so this side-chain is considered as an alkyl group which is ring-activating and 2,4-directing.
- Students should be more precise in drawing the two curly arrows and the delocalised curve of +ve charge (the +ve charge should be placed ‘inside’ the delocalised curve and not at the sp<sup>3</sup> carbon with —NO<sub>2</sub>). As such, students are advised to draw bigger arenium ion.

- (d) Compound **J** can be used as a starting material to produce a cyclic diester as shown below.



- (i) Draw the structure of **C**.



[1]

Examiner's comments:

- This was generally not well answered.

- (ii) Suggest the reagent and conditions for step 7.

HOCH<sub>2</sub>COOH, concentrated H<sub>2</sub>SO<sub>4</sub>, heat

[1]

Examiner's comments:

- This proved difficult for many students.
- For those who could figure out the organic reagent tend to get the conditions wrong. They omitted "heat" or used "H<sub>2</sub>SO<sub>4</sub>(aq)".
- BOD was given to "conc. H<sub>2</sub>SO<sub>4</sub>(aq)" although "aq" was a wrong state symbol for concentrated H<sub>2</sub>SO<sub>4</sub>. Students are advised not to give state symbol for conc. H<sub>2</sub>SO<sub>4</sub>. Just state "concentrated H<sub>2</sub>SO<sub>4</sub>".

[Total: 14]

- 4 (a) Compound **D** is a sweet-smelling organic compound with the molecular formula  $C_5H_9BrO_2$ . It is known that each molecule of **D** contains two functional groups.

A student from JPJC was tasked to determine the structure of compound **D**.

Table 4.1 below shows the chemical reactions that the student carried out for compound **D**.

**Table 4.1**

expt	reagent	Result
1	$AgNO_3(aq)$ , warm	cream precipitate formed which was soluble in an excess of $NH_3(aq)$ .
2	$NaOH(aq)$ , heat	two products were formed; compound <b>E</b> ( $C_3H_5O_3Na$ ) and compound <b>F</b> ( $C_2H_6O$ ).

- (i) State the identity of the cream precipitate formed in experiment 1.

Hence or otherwise, name the functional group, shown by experiment 1, that is present in compound **D**.

silver bromide/  $AgBr$  (✓)  
alkyl bromide / bromoalkane / halogenoalkane (✓)

[1]

Examiner's comments:

- This was generally well answered.

- (ii) State the type of reaction undergone in reaction 2 and identify the other functional group in **D**.

Alkaline hydrolysis (✓) of ester (✓)

Examiner's comments:

- This was generally well answered.

The student conducted further chemical tests on compounds **E** and **F** separately. The results of the tests are given in Table 4.2

**Table 4.2**

Expt	reagent	Result
3	$PCl_5(s)$	misty fumes were produced for both compounds <b>E</b> and <b>F</b> .
4	$I_2$ , $NaOH(aq)$ , warm	pale yellow precipitate observed for both compounds <b>E</b> and <b>F</b> .

- (iii) Based on experiments 3 and 4, what is the common functional group that could be present in both compounds **E** and **F**? Explain your answer, giving the type of reaction.

Both are alcohols. (✓)

They undergo nucleophilic substitution in Expt 3 and undergo oxidation / positive iodoform test in Expt 4. (✓)

OR

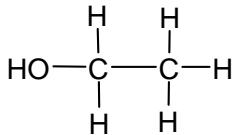
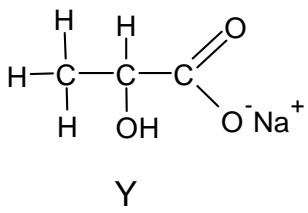
[1]

Both contain the following group,  $\text{RCH}(\text{OH})\text{CH}_3$  or  $-\text{CH}(\text{OH})\text{CH}_3$  (✓), and hence undergo oxidation / positive iodoform test (✓) with  $\text{I}_2$ ,  $\text{NaOH(a)}$ , warm.

Examiner's comments:

- This was generally not well answered.
- Common mistakes were stating wrong type of reactions e.g. "nucleophilic acyl substitution", "condensation" and giving wrong spelling e.g. "nucleophilic", "substituition".
- Some students concluded both E & F are alcohols based on Expt 3 alone and left out Expt 4 in their answer.

(iv) Using your answers in (a)(i) and (a)(ii), draw the structure of compounds **E** and **F**.



Z

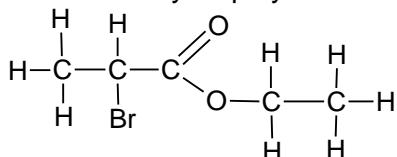
[2]

Examiner's comments:

- Most students are able to get the correct structure for compound F, but not E.
- Common mistakes for compound E were drawing a bond between O and Na, drawing a carboxylic acid, wrong position of the -OH group.

(v) The student now has enough information to determine the structural formula of **D**.

Draw the fully displayed structure of **D**.



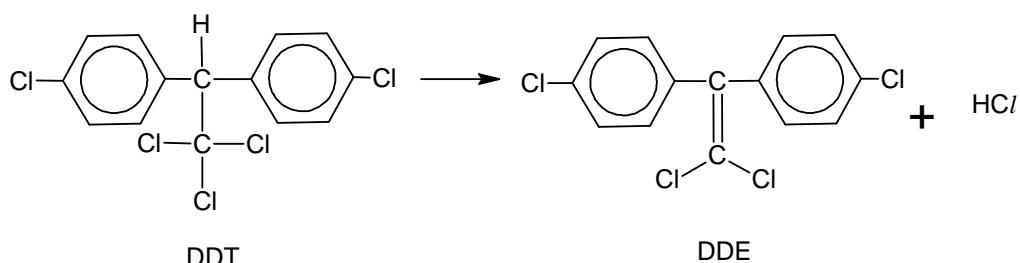
[1]

Examiner's comments:

- This proved difficult for many students. There is a significant number who left this part blank.
- Some students forgot about the alkyl bromide that is present in D (from a(i)). Students must learn to recognise that upon alkaline hydrolysis of ester D, the alkyl bromide present in the structure is also converted to alcohol (see Structure E).
- For those who could figure out the structure of D, some forgot to draw the displayed structure and hence got 0 mark.
- Some were not sure about the acid component and alcohol component of the ester and got them mixed up.

- (b) Dichlorodiphenyltrichloroethane (DDT) is a well-known organochlorine pesticide that was widely used during the 20th century for controlling insect-borne diseases like malaria.

The equation below shows the environmental degradation of DDT to dichlorodiphenyldichloroethylene (DDE).



- (i) State the type of reaction for the conversion of DDT to DDE.

elimination

[1]

Examiner's comments:

- This was generally well-answered.

Table 4.3 below shows the results when aqueous silver nitrate is heated with 0.5 mol of DDT and 0.5 mol of DDE separately.

	Time taken for ppt to appear	No. of moles of ppt formed per mole of compound reacted
DDT	5 min	$x$ mol
DDE	no ppt	0 mol

Table 4.3

- (ii) What would be the value of  $x$  in Table 4.3?

1.5 mol

[1]

Examiner's comments:

- Only a small proportion of students answered this part correctly. Common mistake is "3 mol".
- Students should read the question carefully and note that 3 C-Cl bonds are present in DDT.
- Since 0.5 mol of DDT is used, hence  $0.5 \times 3 = 1.5$  mol of AgCl ppt was formed.

- (iii) Explain why no precipitate was observed for the reaction with DDE.

DDE contains 2 chlorobenzene (Cl bonded to benzene C) functional groups and two chloroalkene functional groups (Cl bonded to alkene C). All these 4 Cl groups are resistant towards nucleophilic substitution reactions.

Reason:

p-p orbital overlap (✓) between the chlorine and the 6 C atoms in benzene / 2 C atoms in C=C bond, results in the delocalisation of lone pair of electrons on Cl (✓) into the  $\pi$ -electron system of the adjacent benzene and C=C bond (✓), forming partial double bond character (✓\*) in C-Cl. This strengthens the C-Cl bond, and hence does not undergo nucleophilic substitution.

[2]

Examiner's comments:

- This was generally not well answered.
- Common wrong responses were “availability of lone pair on Cl for substitution” or “delocalise and disperse the charge to stabilise the C-Cl bonds”.
- A significant number missed out “p-p orbital overlap” or “partial double bond character” or “C=C bond”.

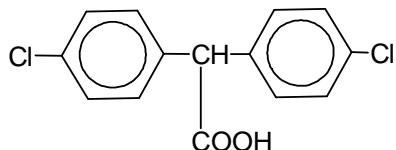
- (iv)** In organic chemistry, a geminal compound is a molecule in which two or more identical or similar functional groups are attached to the same carbon atom.

When DDT reacts with hot aqueous NaOH, a gem-triol, is formed as an intermediate. A gem-triol contains three hydroxyl -OH groups bonded to the same carbon atom. The gem-triol formed is unstable and it readily converts to the final product, **S**.

**S** reacts with aqueous Na<sub>2</sub>CO<sub>3</sub>(aq) to liberate a colourless gas.

Draw the structure of the organic compound **S**.

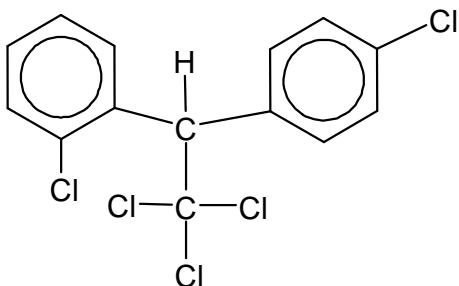
[1]

**S:**Examiner's comments:

- This part was generally well answered.
- Common wrong response was drawing the gem-triol.

- (c) (i)** 1,1,1-trichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane, or o,p'-DDT, is an constitutional isomer of DDT.

The structure of o,p'-DDT is given below.



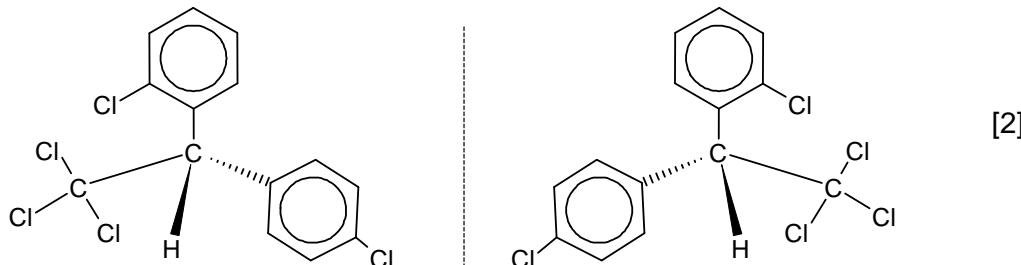
o,p'-DDT

State the type of stereoisomerism exhibited by o,p'-DDT.  
**Enantiomerism**

Examiner's comments:

- This part was generally well answered.
- Common mistakes were wrong spelling “enantioomerism”, gave “cis-trans isomerism” and “positional isomerism” as the answer.

(ii) Draw its isomers.

Examiner's comments:

- This was generally not well answered.
- Common wrong responses were not drawing 3D (tetrahedral shape), writing condensed formula for the 2 benzene groups, drawing the shaded wedge and dash on opposite sides (should draw next to each other).

[Total: 14]

5 The pH of the seawater in the ocean is regulated by the carbonate - bicarbonate ( $\text{CO}_3^{2-}$  /  $\text{HCO}_3^-$ ) buffer system.



Recently, changes in the pH of the oceans by ocean acidification has been a concern. Ocean acidification is caused by the absorption of carbon dioxide ( $\text{CO}_2$ ) from the atmosphere, and poses a significant threat to marine ecosystems worldwide.

The increased concentration of  $\text{CO}_2$  in seawater leads to changes in the pH as shown by the graph below which shows the average ocean pH level worldwide from 1985 to 2020.

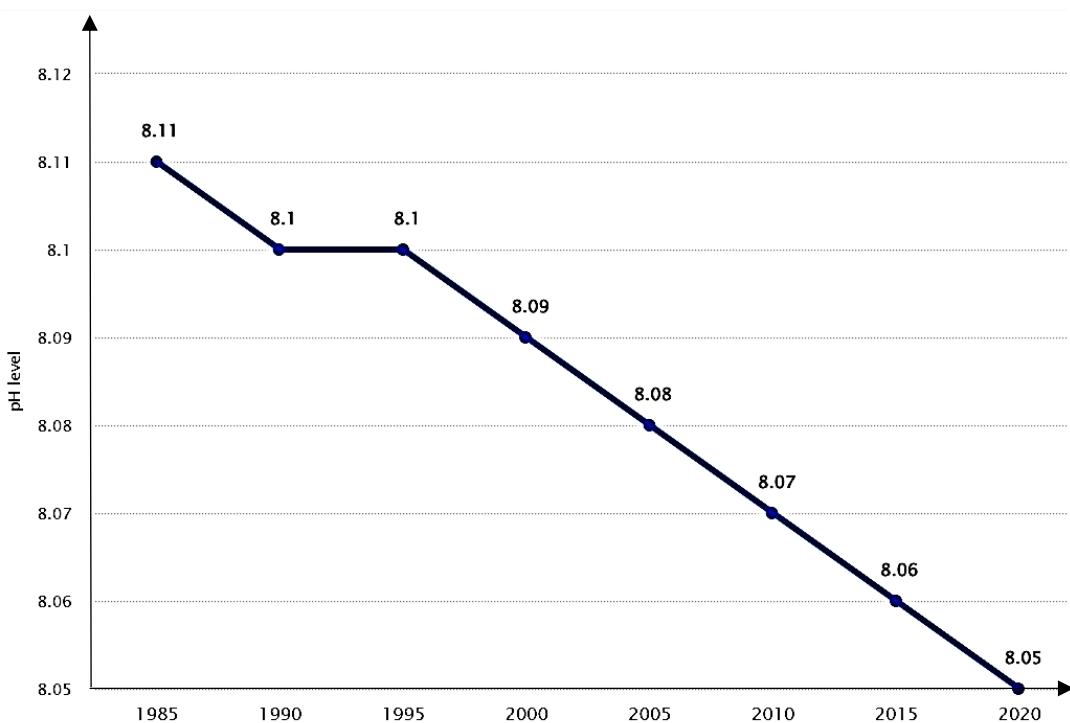


Fig. 5.1

- (a) (i) Using the Fig 5.1, state and explain the trend of pH of the seawater of the ocean.

pH of seawater decreased. (✓)

CO<sub>2</sub> from the atmosphere dissolves in the seawater to produce H<sub>2</sub>CO<sub>3</sub> which produces H<sup>+</sup>. This increases the [H<sup>+</sup>] which cause the pH to decrease. (✓)

[1]

Examiner's comments:

This question was badly done as students merely state the trend but did not explain why the pH decreased. Just stating that there is an increased absorption of CO<sub>2</sub> do not warrant any credit as this was already written in the question. Some write about the equilibrium shift of  $\text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{OH}^-$  which fails to explain why H<sup>+</sup> is increasing.

- (ii) With the aid of equations show how the carbonate - bicarbonate buffer system in seawater maintains the pH when there is an increase in amounts of H<sup>+</sup> or OH<sup>-</sup> in the seawater.

upon addition of OH<sup>-</sup>,  
 $\text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$

\*full arrow must be used

upon addition of H<sup>+</sup>,  
 $\text{CO}_3^{2-}(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{HCO}_3^-$

[2]

- (iii) Use the pH value from Fig 5.1, show that the molar ratio of bicarbonate to carbonate ion of a sample of seawater from 2020 is 89:1.

Given that the  $K_b$  of  $\text{CO}_3^{2-}$  is  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ .

Alkaline buffer:



$$\text{pOH} = \text{p}K_b + \lg \frac{[\text{salt}]}{[\text{base}]}$$

$$14 - 8.05 = -\lg (1.0 \times 10^{-4}) + \lg \frac{[\text{HCO}_3^-]}{[\text{CO}_3^{2-}]}$$

$$\frac{[\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} = \frac{89}{1} \text{ (as shown)}$$

[2]

Examiner's comments:

(ii) This part was not well done as students only explained but did not write equations to show how the seawater maintains the pH. Some did not write the equation with irreversible arrow. So 1 mark was penalised overall if both equations are written with reversible arrow. Students must read the question carefully and answer it properly instead of writing in essay form when the qn only asked for equations.

(ii) This question proves to be difficult as may did not see this as an alkaline buffer. From Fi 5.1, they can get the pH of the seawater but need to change to pOH if using the formula for finding the ratio using buffer equation. If using pH value (8.05), the students must use the correct salt

and acid which is  $8.05 = -\lg (1.0 \times 10^{-10}) + \lg \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$ .

The total  $\text{CO}_3^{2-} + \text{HCO}_3^-$  content of the seawater can be found by boiling a seawater sample with an excess of dilute sulfuric acid and absorbing the  $\text{CO}_2$  evolved in a solution of barium hydroxide,  $\text{Ba}(\text{OH})_2$ .

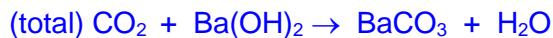
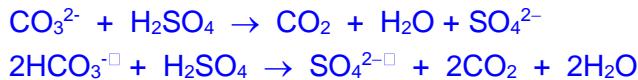
The precipitated barium carbonate,  $\text{BaCO}_3$  can be filtered off, dried and weighed.

When a  $100 \text{ cm}^3$  seawater was treated in the above-mentioned process, 0.281 g of  $\text{BaCO}_3$  was produced.

*[Assume that the seawater sample is from the year 2020]*

- (iv) Show that the total amount of  $\text{CO}_3^{2-} + \text{HCO}_3^-$  content in the seawater sample is  $1.42 \times 10^{-3}$  mol.

After boiling with excess  $\text{H}_2\text{SO}_4$ , all  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  will be converted to  $\text{CO}_2$ .



$$\text{Amount of BaCO}_3 \text{ formed} = \frac{0.281}{137.3 + 12.0 + 3(16.0)} = \underline{\underline{1.42 \times 10^{-3} \text{ mol}}}$$

Total amount of  $\{\text{CO}_3^{2-} + \text{HCO}_3^-\}$  in sample

= Total amount of  $\text{CO}_2$  reacted with  $\text{Ba}(\text{OH})_2$

= Amount of  $\text{BaCO}_3$  formed

=  $1.42 \times 10^{-3}$  mol

[1]

Examiner's comments:

Most just found the amount but may not know that  $(\text{total}) \text{CO}_2 + \text{Ba}(\text{OH})_2 \rightarrow \text{BaCO}_3 + \text{H}_2\text{O}$ . However, credit was given as long as working is shown how the amount was found.

- (v) Hence, using the information in (a)(iii) & (a)(iv) calculate  $[\text{CO}_3^{2-}]$  in the  $100 \text{ cm}^3$  seawater from 2020.

Let  $x$  be the original amount of  $\text{CO}_3^{2-}$  present in the seawater.

Since  $\frac{[\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} = 89$ , amount of  $\text{HCO}_3^-$  in seawater =  $89x$

Total amount of  $\{\text{CO}_2 + \text{HCO}_3^-\} = x + 89x = 90x = 1.424 \times 10^{-3}$  mol

Amount of  $\text{CO}_3^{2-}$  in  $100 \text{ cm}^3$  seawater,

$$x = \frac{1.424 \times 10^{-3}}{90} = 1.582 \times 10^{-5} \text{ mol} \quad (\text{ecf from iv answer})$$

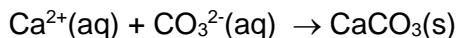
$$[\text{CO}_3^{2-}(\text{aq})] \text{ in seawater} = 1.582 \times 10^{-5} \times \frac{1000}{100} = 1.58 \times 10^{-4} \text{ mol dm}^{-3}$$

[2]

Examiner's comments:

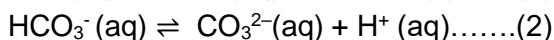
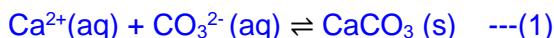
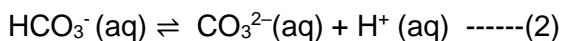
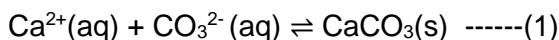
Since the question was guided, majority could do this question. Some forgot to calculate the concentration and left the answer as amount of  $\text{CO}_3^{2-}$ .

- (b) Organisms with calcium carbonate shells produce their shells according to the equation shown.



Changes in the pH alters the chemical balance of the oceans and affecting marine life, particularly organisms with calcium carbonate shells.

- (i) Using the equations below and the concept of Le Chatelier's principle and solubility product, explain why marine organisms will not be able to build shells if pH of the seawater decreases.



When pH decreases,  $[\text{H}^+]$  increases, (✓) hence the following happens:

- By LCP, the position of equilibrium (2) shifts to the left (✓) to decrease  $[\text{H}^+]$ , hence  $[\text{CO}_3^{2-}]$  decreases. (✓)
- Eqm (1) shifts to left (✓) to increase  $[\text{CO}_3^{2-}]$  so  $\text{CaCO}_3$  dissolves
- Ionic product of  $\text{CaCO}_3$  drops to  $< K_{\text{sp}}(\text{CaCO}_3)$ , (✓) hence
- precipitation of  $\text{CaCO}_3$  is not possible. Therefore, marine organisms will not be able to build shells if pH of the seawater decreases.

[2]

Examiner's comments:

Most could answer well about equilibrium shift and were able to state which eqm equation was affected by the decrease in pH. However, majority of the students were not able to write that ionic product of  $\text{CaCO}_3$  drops to  $< K_{\text{sp}}(\text{CaCO}_3)$  due to the eqm shift. The qn has specially state that there is a need to use solubility product concept so students must read the qn carefully before answering.

- (ii) The concentration of  $\text{Ca}^{2+}$  ions in the seawater sample from 2020 is  $3.99 \times 10^{-4} \text{ mol dm}^{-3}$ .

Given that  $K_{\text{sp}}$   $\text{CaCO}_3$  is  $3.30 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$ , calculate the minimum  $[\text{CO}_3^{2-}]$  for the organisms to form their shells in 2020.

For precipitation, ionic product  $\geq K_{\text{sp}}$ .

At first trace of precipitation,  $[\text{Ca}^{2+}] [\text{CO}_3^{2-}] \geq 3.30 \times 10^{-9}$

$$(3.99 \times 10^{-4}) [\text{CO}_3^{2-}] \geq 3.30 \times 10^{-9}$$

$$[\text{CO}_3^{2-}] \geq 8.27 \times 10^{-6} \text{ mol dm}^{-3}$$

[1]

Examiner's comments:

This was well done however some students did not state the minimum  $[\text{CO}_3^{2-}]$  and left it as  $[\text{CO}_3^{2-}] > 8.27 \times 10^{-6} \text{ mol dm}^{-3}$  which is a range.

- (iii) Using your answer in (a)(v) and (b)(ii), explain whether the organisms will be able to form their shells in the seawater in 2020?

It will form the shell as  $[CO_3^{2-}]$  in the seawater > the minimum  $[CO_3^{2-}] = 8.27 \times 10^{-6} \text{ mol dm}^{-3}$

$[IP > K_{sp}]$ .

[1]

**[allow ecf as long as concept is correct]**

Examiner's comments:

This was well done but some found IP of  $CaCO_3$  when the qn specifically stated that to use answer in (a)(v) and (b)(ii) so just need to compare the concentration of  $CaCO_3$  in seawater and the minimum concentration of  $CaCO_3$  needed for precipitation.

[Total: 12]

- 6 (a) Haemoglobin and hemocyanin are two oxygen-transporting proteins found in living organisms. Both proteins are coloured due to the presence of transition metals, such as iron in haemoglobin and copper in hemocyanin, that form complexes essential for their oxygen-binding properties.

- (i) Why are transition metal complexes coloured?

In complexes, lone pairs on the approaching ligands cause a splitting of the energy of d-orbitals into 2 groups with an energy gap,  $\Delta E$ , between them. [3]

When a d-electron from lower energy group is promoted to the higher energy group (d-d transition), wavelengths of visible light that corresponding to  $\Delta E$  is absorbed.

Colour of the complex will be complementary to the wavelengths of the light absorbed.

Examiner's comments:

Students who use their own words to write answers usually missed out the key points. Some explanation was vague and hence credit was not given. It is advisable for students to memorise the key points.

- (ii) Non-transition metal compounds, in contrast, tend to be colourless. Explain why a solution containing  $[Mg(H_2O)_6]^{2+}$  is colourless.

$Mg^{2+}: 1s^2 2s^2 2p^6$

Since  $Mg^{2+}$  has no d electron (✓), hence d-d transition is not possible (✓), visible light is not absorbed thus  $[Mg(H_2O)_6]^{2+}$  is colourless.

OR

The energy gap from highest occupied orbitals to the next empty orbital is too large (✓), which requires absorption of radiation outside of visible region. (✓)

[2]

Examiners' comments:

What examiners are looking out for

- 1) **no d electron**
- 2) hence, **no d to d electronic transition** thus no visible light is absorbed

Misconceptions including below:

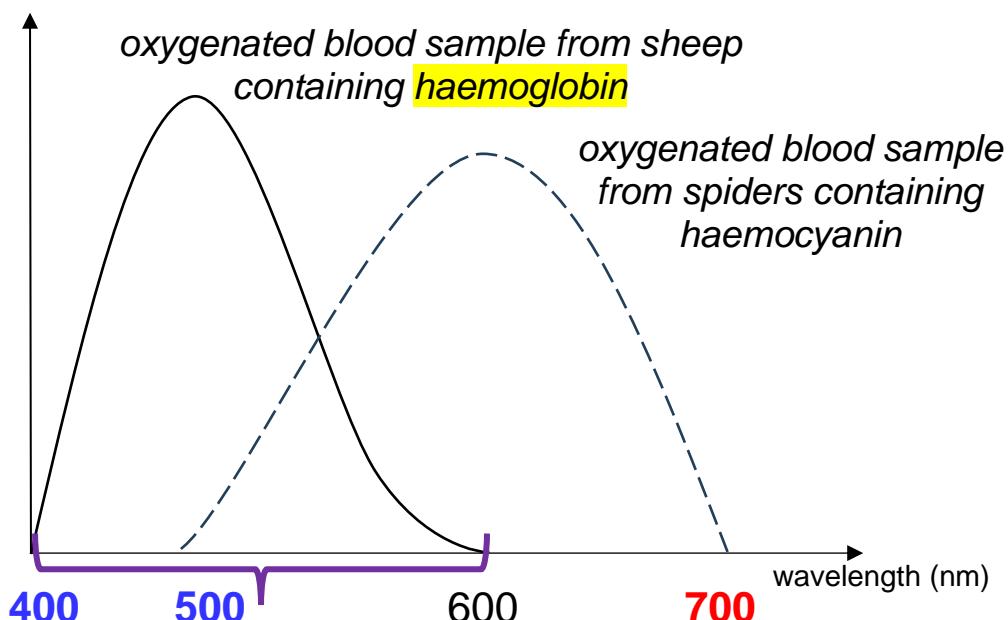
- Some said  $Mg^{2+}$  has fully filled d subshell which is wrong it has empty d subshell
- Some wrote about ligand exchange that has nothing to do with this

Absorption spectra, an analytical method in chemistry, show the wavelengths of light absorbed by substances.

Chemists use this technique to analyse the oxygenated blood samples from sheep (haemoglobin) and spiders (haemocyanin) to compare their absorption characteristics.

The result of the analysis is shown in Fig. 6.1.

Relative absorbance



**Haemoglobin absorb shorter wavelength  
=> absorb higher frequency =>higher  $\Delta E$**

The wavelengths associated with each colour of visible light are given below. Light of a longer wavelength is lower in energy than light of a shorter wavelength.

colour of visible light	wavelength (nm)
red	620 – 750
orange	590 – 620
yellow	570 – 590
green	495 – 570
blue	450 – 495
violet	380 – 450

- (iii) The oxygenated blood of sheep, which contains haemoglobin, is red. Using this information and the data provided, predict the colour of the oxygenated blood of spiders, which contains haemocyanin.

Blue / Violet

[accept blue-violet]

Examiner's comments

Analyse the absorbance curve given: qn states blood of sheep, which contains haemoglobin, is red.

Look carefully at the graph, haemoglobin DID not absorb red light energy – thus it appears red.

(Because the colour observed/ something appears as is COMPLEMENTARY to what is absorbed!)

Look at graph, haemocyanin did not absorb 400-500nm which is violet or blue thus it appears violet/ blue.

- (iv) What deduction can be made from the absorption spectra in Fig. 6.1, about the size of the d-orbital splitting in the two samples of oxygenated blood, containing different complexes of haemoglobin & haemocyanin? Explain your answer.  
 The d-orbital splitting/energy gap in the complex of haemoglobin is larger than haemocyanin.

This is because shorter wavelength of light (higher frequency of light) is absorbed, indicating that  $\Delta E$  is larger ie. electron in lower d-orbitals absorbs more energy to be promoted to the higher d-orbitals.

[2]

where **h** is Planck's constant

**c** is the speed of light

**$\lambda$**  is the wavelength of radiation absorbed

**f** is the frequency of radiation absorbed

**$c = f\lambda$  (c = constant, when  $f \uparrow, \lambda \downarrow$ )**

$$\Delta E = hf = \frac{hc}{\lambda}$$

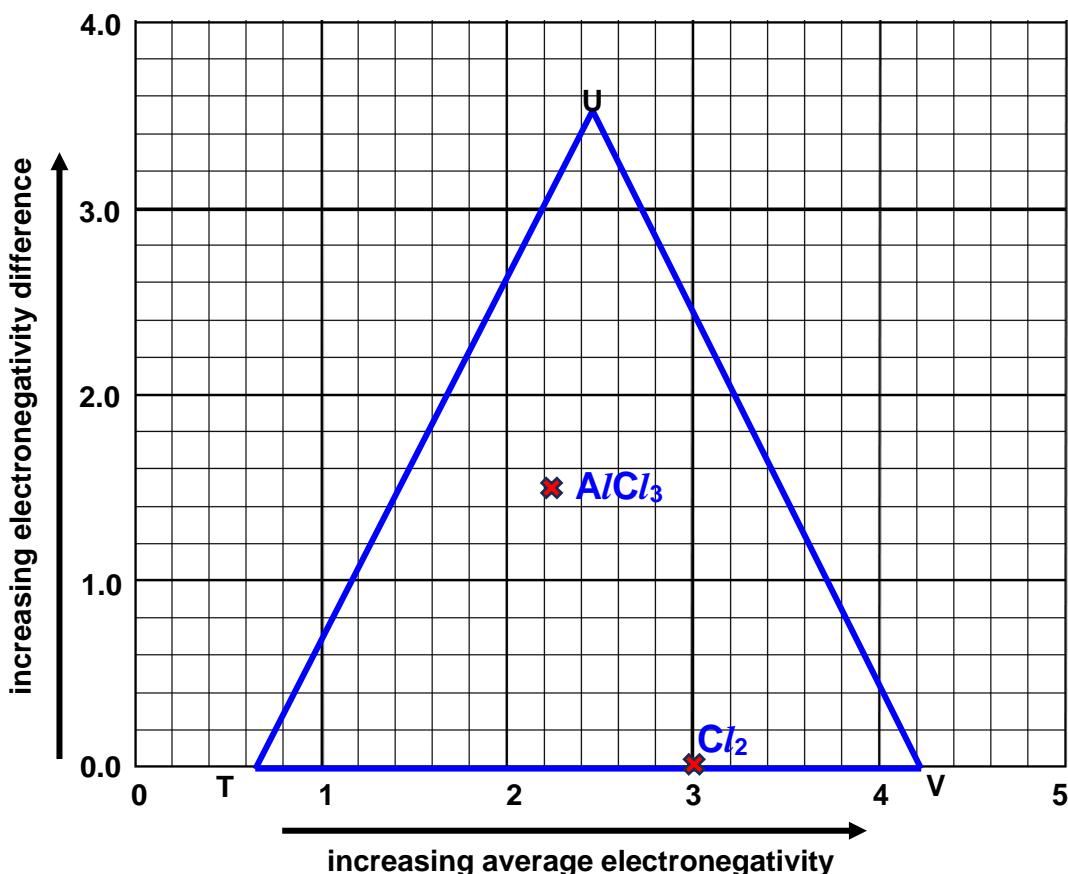
Hence  $\frac{c}{\lambda} = f$

[Total:7]

- (b) The van Arkel triangle, invented by Dutch chemist Anton Eduard van Arkel, is a tool used to classify the bonding in compounds as ionic, covalent, or metallic.

Fig. 6.2 shows an example of a van Arkel triangle.

The **y-axis represents the difference in electronegativity between two elements**, while the **x-axis shows the average electronegativity**.



**Fig. 6.2**

Table 6.1 provides the electronegativity values of some of elements from Period 3 of the Periodic Table, based on Pauling's Scale. The average electronegativity is calculated based on the sum of the electronegativities of the two elements in the compound, divided by two.

**Table 6.1**

Element	Electronegativity
Na	0.9
Mg	1.2
Al	1.5
Si	1.8
P	2.1
S	2.5
Cl	3.0

- (i) Plot the position of Cl<sub>2</sub> and AlCl<sub>3</sub> on the diagram. Label your points clearly in Fig. 6.2. [2]

- (ii) The three extremes on the van Arkel triangle, namely **T**, **U** and **V**, represent the three types of chemical bonding, metallic, ionic and covalent.

State the correct type of bonding present at each of the bonding extremes.

Pls know definition of electronegativity: **Electronegativity** is a measure of the tendency of an atom to attract a bonding pair of electrons.

**T: metallic**

(metals are low in electronegativity, don't want to attract electrons to itself, want to lose electrons)

**U: ionic** (big difference in electronegativity => tends to be ionic)

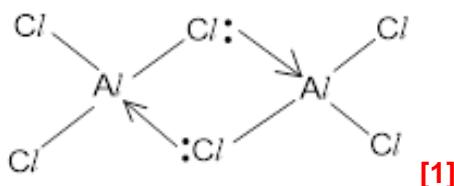
**V: covalent** (higher in electronegativity. Cl-Cl bond has zero difference in electronegativity as both Cl has same electronegativity) [2]

Examiner: Quite well done, most get at least 1 or 2 marks.

- (c) (i) In the liquid state,  $\text{AlCl}_3$  exists as a compound with a molar mass of 267 g mol<sup>-1</sup>.

Draw the structure of this compound.

Molar mass of 267 g mol<sup>-1</sup> is twice mass of  $\text{AlCl}_3$ , showing 2 molecules of  $\text{AlCl}_3$  dimerised.



Examiner: Pls show lone pair and dative bonds

- (ii) The boiling points of  $\text{Al}_2\text{O}_3$  and  $\text{AlCl}_3$  in the liquid state are 2977 °C and 180 °C respectively.

Explain, in terms of structure and bonding, the difference in their boiling points.

$\text{Al}_2\text{O}_3$  has a giant ionic lattice (✓) structure while  $\text{AlCl}_3/\text{Al}_2\text{Cl}_6$  has a simple molecular (✓) structure.

More energy is required to overcome the stronger ionic bonds / electrostatic forces of attractions between  $\text{Al}^{3+}$  and  $\text{O}^{2-}$  ions (✓) than the weaker id-id interactions between  $\text{AlCl}_3/\text{Al}_2\text{Cl}_6$  molecules (✓).

[2]

Examiner: Huge misconceptions:

A significant number wrongly think  $\text{Al}_2\text{O}_3$  is giant covalent or simple covalent structure.

Note Al is metal, O is non metal. Metal and non-metal combine to form IONIC compounds – O level knowledge, with exception of  $\text{AlCl}_3$  which is simple covalent – that you can infer from low boiling point of 180 °C!

Common mistakes: Miss out structures: giant ionic lattice structure or  $\text{AlCl}_3/\text{Al}_2\text{Cl}_6$  has a simple molecular or simple covalent structure.

Some thought  $\text{AlCl}_3$  is polar with pd-pd attraction between molecules – this is wrong because  $\text{AlCl}_3$  is non-polar no net dipole moment

- (iii) The pH values of the solutions of two Period 3 chlorides are given below.

compound	pH of 1.0 mol dm <sup>-3</sup> solution
MgCl <sub>2</sub>	X
AlCl <sub>3</sub>	Y

[3]

Write equations for the reaction of AlCl<sub>3</sub> with water.

State the values of x and y in the table above. Briefly explain the different pH values of the two chloride solutions.



$$x = 6.5 \quad (\checkmark)$$

$$y = 3 \quad (\checkmark)$$

Since Al<sup>3+</sup> has higher charge density(✓) than Mg<sup>2+</sup>, it has a greater degree/ extent of hydrolysis(✓) in aq solution, resulting in lower pH.

Examiner comments: Most common confusion was mixing up period 3 chlorides with oxides pls revise! Key concept for Period chlorides = hydrolysis

Key concept for oxides = acid base behaviour of oxides

Charge density is for ION eg. Al<sup>3+</sup> not for AlCl<sub>3</sub>

- (iv) The lattice energy of magnesium chloride is -2582 kJ mol<sup>-1</sup>. Some enthalpy changes of hydration are listed in Table 6.4.

Table 6.4

Ions	$\Delta H_{\text{hyd}}$ / kJ mol <sup>-1</sup>
Mg <sup>2+</sup>	-1980
Cl <sup>-</sup>	-381

Using the data provided, calculate the enthalpy change of solution of magnesium chloride.

$$\begin{aligned}\Delta H_{\text{soln}}(\text{MgCl}_2) &= - \text{LE} + \sum \Delta H_{\text{hyd}}(\text{ions}) \\ &= -(-2582) + (-1980) + 2(-381) \\ &= \underline{-160.0 \text{ kJ mol}^{-1} \quad (3sf + sign + units)} \quad [1]\end{aligned}$$

[1]

Examiner comments: Forgot the equation

$\Delta H_{\text{soln}}(\text{ionic compound}) = - \text{LE} + \sum \Delta H_{\text{hyd}}(\text{ions})$

**and forgot to substitute coefficient of Cl<sup>-</sup> ie. 2**

[Total:18]



**JURONG PIONEER JUNIOR COLLEGE**  
**JC2 PRELIMINARY EXAMINATION 2024**

**CHEMISTRY**

**9729/03**

**Higher 2**

**12 September 2024**

**2 hour**

Paper 3 Free Response

Candidates answer on the Question paper.

Additional Materials: Data Booklet

**READ THESE INSTRUCTIONS FIRST**

Write your name, class and index number in the spaces at the top of this page.

Write in dark blue or black pen.

You may use a 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.

Write the Question number of the Question you have attempted, in the box provided below.

A Data Booklet is provided.

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

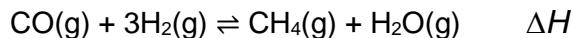
The number of marks is given in brackets [ ] at the end of each question or part question.

<b>For Examiner's Use</b>	
1	/
2	/
3	/
4 or 5	/
<b>Penalty</b> (delete accordingly)	
Lack 3sf in final answer	<b>-1 / NA</b>
Missing/wrong units in final ans	<b>-1 / NA</b>
Bond linkages	<b>-1 / NA</b>
<b>Total</b>	<b>80</b>

This document consists of **32** printed pages inclusive of 1 blank page.

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

- 1 (a) One version of the Fischer-Tropsch process for manufacturing methane is the reaction of carbon monoxide with hydrogen.



A mixture of CO and H<sub>2</sub> in a 1:3 molar ratio was added into a sealed vessel and heated to 1200K. At equilibrium, 40% of the CO had reacted. The total pressure in the vessel was 12 atm at equilibrium.

- (i) Write the expression for the equilibrium constant,  $K_p$ , for this reaction. [1]
- (ii) Use your expression to calculate the value of  $K_p$  for the reaction at 1200K. Include its units. [3]
- (iii) Given that the value of  $K_p$  decreases with increasing temperature, deduce the sign for the enthalpy change,  $\Delta H$  of the forward reaction. Explain your reasoning. [1]

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**(b)** Describe and explain how the entropy of each of the following systems will change during the stated process.

- 1 mol of  $N_2(g)$  at 298K is added to 1 mol of  $CH_4(g)$  at 298K.
- 1 mol of  $Cl_2(g)$  at 298 K is heated to 373 K.

Assume the pressure of each gas remains at 1 atm throughout and no reaction occurs between  $N_2$  and  $CH_4$ .

[2]

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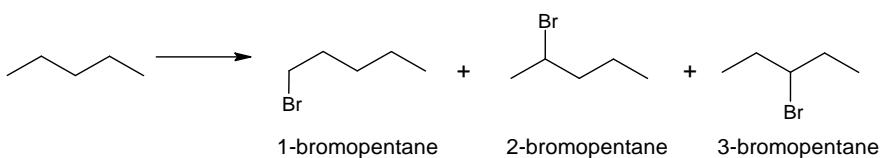
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- (c) (i) During the monobromination of pentane, three different bromoalkanes are formed as shown in Fig. 1.1.



**Fig. 1.1**

Predict the expected theoretical ratio in which these three products would form if the monobromination of pentane occurs randomly.

Explain your answer.

[2]

- (ii) When the monobromination was practically carried out in an experiment, the percentage of 1-bromopentane was obtained in the lowest proportion.

Suggest an explanation for the difference between this experimental result and what you predicted in (c)(i).

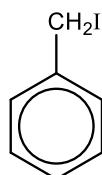
[1]

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- (d) The *Wurtz* reaction below shows two iodoalkanes react with Na in dry ether, to form a new carbon–carbon bond, resulting in the formation of a new alkane.



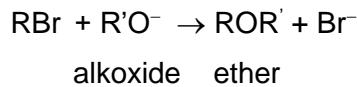
Reaction of a single iodoalkane, RI, with Na metal in dry ether via *Wurtz* reaction will give a good yield of symmetrical alkane product. Draw the organic product formed when (iodomethyl)benzene reacts with Na metal in dry ether.



(iodomethyl)benzene

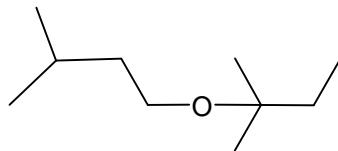
[1]

- (e) Bromoalkanes and alkoxides react in the Williamson ether synthesis to form the ether functional group containing C-O-C, an example of which is shown below.



It is known that S<sub>N</sub>2 mechanism is usually undergone in Williamson ether synthesis.

Suggest the structures of the halogenoalkane and alkoxide ion RO<sup>-</sup> you would use to synthesise the ether below, using the Williamson synthesis method.



[1]

- (f) (i)  $\text{CH}_3\text{OCH}_3$ , methoxymethane is the simplest ether which is used as aerosol propellants. Given that  $\text{CH}_3\text{OCH}_3$ , contains C-O-C bond, draw the 'dot-and-cross' diagram for  $\text{CH}_3\text{OCH}_3$ .

Use VSEPR (valence shell electron pair repulsion) theory to describe and explain the shape about the oxygen and suggest the C-O-C bond angle of a  $\text{CH}_3\text{OCH}_3$  molecule.

[3]

- (ii) By considering the polarity of each of the bonds it contains, and the shape about the oxygen of the  $\text{CH}_3\text{OCH}_3$  molecule, deduce the overall polarity of the  $\text{CH}_3\text{OCH}_3$  molecule.

[1]

- (iii) Boiling points of some compounds with similar  $M_r$  as methoxymethane such as propane, ethanol and ethylamine are given below in Table 1.1.

Suggest explanations for these differences.

**Table 1.1**

compound	$M_r$	formula	boiling point / °C
ethylamine	45	$\text{CH}_3\text{CH}_2\text{NH}_2$	17
ethanol	46	$\text{CH}_3\text{CH}_2\text{OH}$	78
propane	44	$\text{CH}_3\text{CH}_2\text{CH}_3$	-42

[3]

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[Total:19]

- 2 (a) (i)** Halogens can behave as Lewis acids or Lewis bases. The reaction of benzene and  $Cl_2$  requires the use of  $AlCl_3$ , to generate the electrophile.
- Define what is meant by a Lewis acid.
  - Using the reaction of  $Cl_2$  with  $AlCl_3$ , state which species is behaving as Lewis acid and which is behaving as Lewis base.
- [2]

- (ii)** Benzene and phenol both undergo electrophilic substitution with halogens under different conditions.

Explain why the reaction of phenol with halogens occurs more readily and does not require the use of halogen carrier catalyst,  $AlCl_3$ , like benzene does.

[1]

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- (b) The standard reduction potential for 1,4-benzoquinone /benzene-1,4-diol is shown in Fig. 2.1.

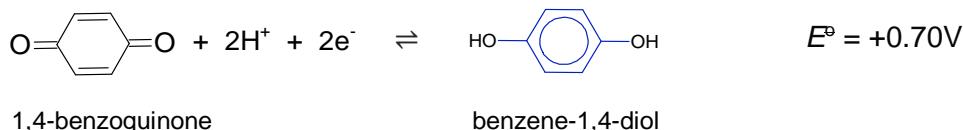
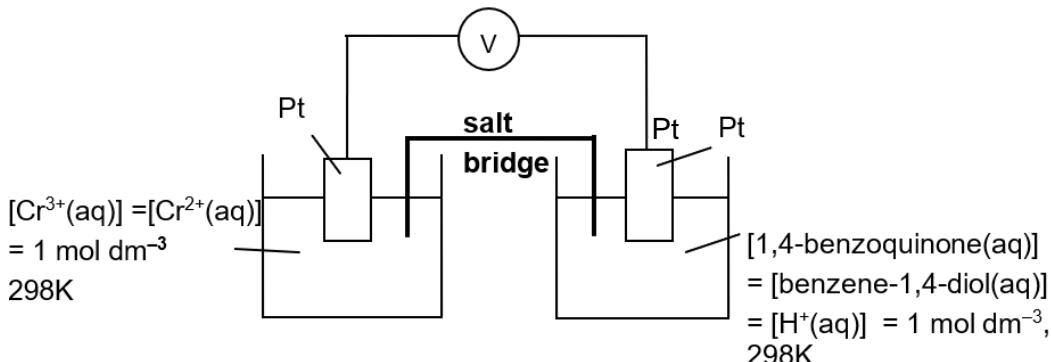
**Fig. 2.1**

Fig. 2.2 below shows how the standard cell potential between the  $\text{Cr}^{3+}/\text{Cr}^{2+}$  half-cell and the 1,4-benzoquinone /benzene-1,4-diol half-cell is measured.

**Fig. 2.2**

- (i) Using data from the *Data Booklet* and the above information, calculate  $E^\ominus_{\text{cell}}$  for the cell in Fig. 2.2 and state which is the negative electrode. [2]
- (ii) Construct the overall equation for the reaction that occurred in the cell. [1]
- (iii) Calculate  $\Delta G^\ominus$  for the reaction you wrote in (b)(ii). [1]

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- (c) State and explain what happens to the  $E_{\text{cell}}$  when pH of the 1,4-benzoquinone /benzene-1,4-diol half-cell decreased.

[2]

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- (d) Another experiment is set up using the same electrochemical cell. In this experiment, the  $\text{Cr}^{2+}$  concentration is changed to  $0.15 \text{ mol dm}^{-3}$ . All other concentrations remain at their standard values.

The Nernst equation is shown.

$$E = E^{\circ} + \frac{0.059}{n} \log \frac{\text{[oxidised species]}}{\text{[reduced species]}}$$

$n$  = number of electrons transferred

$E^{\circ}$  is the standard reduction potential for the  $\text{Cr}^{3+}/\text{Cr}^{2+}$  electrode system.

- (i) Use the Nernst equation and the *Data Booklet* to calculate the electrode potential for the  $\text{Cr}^{3+}/\text{Cr}^{2+}$  half cell in this experiment.

[1]

- (ii) Using your answer in (d)(i) and data given in (b), calculate  $E_{\text{cell}}$  for this electrochemical cell.

[1]

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- (e) The aldol reaction is a useful method to make new carbon–carbon bonds in organic chemistry. It involves combining 2 molecules of the same aldehyde or ketone to form a product which contains both a carbonyl functional group (aldehyde or ketone) and alcohol functional group.

The aldol **A** is made by reacting ethanal with a small amount of NaOH(aq) at room temperature. The 3 stages of the reaction are given in Table 2.1.

Stage	Equation
1	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{CHO} \\   \\ \text{H} \end{array} + :\text{OH}^- \rightleftharpoons \begin{array}{c} -\text{:CH}_2\text{CHO} \\   \\ \text{B} \end{array} + \text{H}_2\text{O}$
2	$\begin{array}{c} \text{O} \\    \\ \text{H}-\text{C}-\text{CH}_3 \end{array} + \begin{array}{c} -\text{:CH}_2\text{CHO} \\   \\ \text{B} \end{array} \rightleftharpoons \begin{array}{c} \text{O}^- \\    \\ \text{H}-\text{C}-\text{CH}_2\text{CHO} \\   \\ \text{CH}_3 \end{array}$
3	$\begin{array}{c} \text{O}^- \\    \\ \text{H}-\text{C}-\text{CH}_2\text{CHO} \\   \\ \text{CH}_3 \\ \text{C} \end{array} + \text{H}-\ddot{\text{O}}\text{H} \rightleftharpoons \begin{array}{c} \text{OH} \\   \\ \text{H}-\text{C}-\text{CH}_2\text{CHO} \\   \\ \text{CH}_3 \\ \text{A} \end{array} + :\text{OH}^-$

Table 2.1

- (i) Suggest the type of reaction in stage 1. [1]
- (ii) 1,4-cyclohexanedione can be formed from 1,4-benzoquinone.



1,4-cyclohexanedione

1,4-cyclohexanedione reacts with the presence of NaOH at room temperature via the 3 stages shown in Table 2.1. A product with 12 carbons, **D** was formed. Draw the structure of **D**.

[1]

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- (f) Aluminium objects have a thin insoluble oxide layer,  $Al_2O_3$ , on their surfaces. This oxide can be removed by adding NaOH(aq) to the aluminium object.

(i) Explain why  $Al_2O_3$  is insoluble in water. [1]

(ii) Write an equation which describes the reaction occurring when NaOH(aq) is added to the aluminium oxide. [1]

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- (g) Compound **E**, C<sub>10</sub>H<sub>18</sub>O is optically active and decolourises orange aqueous Br<sub>2</sub>. **E** reacts with sodium, Na to form H<sub>2</sub> gas.

**E** reacts with an excess hot acidified concentrated KMnO<sub>4</sub> to produce three different organic molecules, **F**, C<sub>3</sub>H<sub>6</sub>O, **H**, (CO<sub>2</sub>H)<sub>2</sub>, and **G**, C<sub>5</sub>H<sub>8</sub>O<sub>3</sub>. One of these organic molecules is further oxidised to CO<sub>2</sub>.

**F** and **G** both react with 2,4-dinitrophenylhydrazine. **E**, **F** and **G** react with aqueous alkaline iodine forming a yellow precipitate. **G** reacts with aqueous Na<sub>2</sub>CO<sub>3</sub>(aq) giving off effervescence of a colourless gas.

Suggest the structures of **E**, **F** and **G**. For each reaction, state the *type of reaction* and explain what the information tells you about the functional groups present in each compound.

[6]

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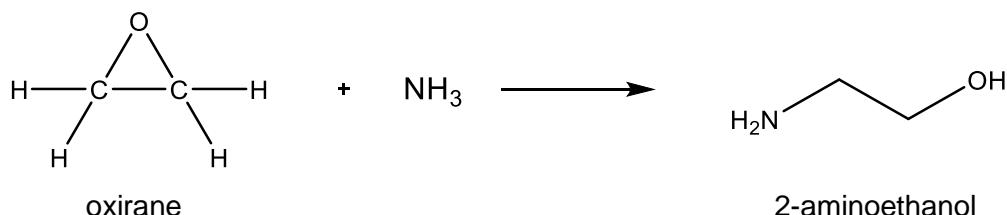
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- 3 Epoxides such as oxirane are 3-membered ring cyclic ethers, which can undergo ring-opening reactions.

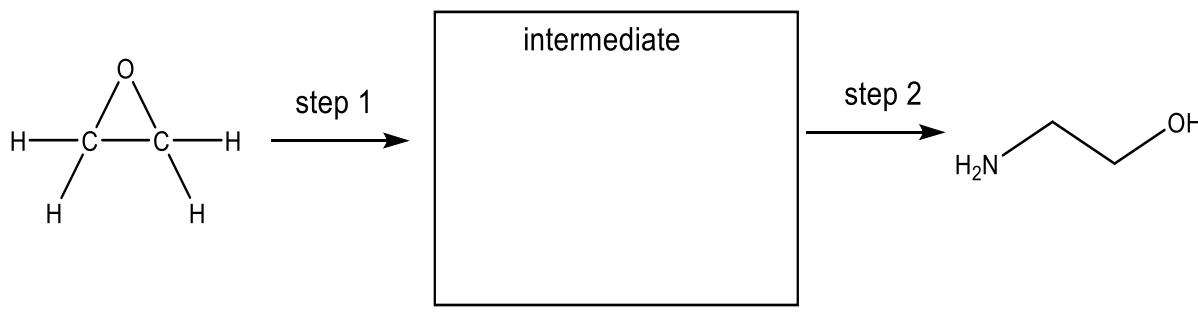
An example of an epoxide ring-opening reaction involves nucleophilic attack by  $\text{NH}_3$  on oxirane in Fig. 3.1 as shown below.

(a)

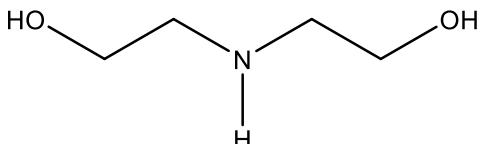
**Fig. 3.1**

- (i) Complete the mechanism of step 1 on Fig. 3.2 by adding all relevant curly arrows, lone pairs of electrons, charges and partial charges; and draw the structure of the organic intermediate.

[2]

 $\text{NH}_3$ **Fig. 3.2**

- (ii) A small amount of by-product, shown below, is produced during the reaction shown in Fig. 3.1.

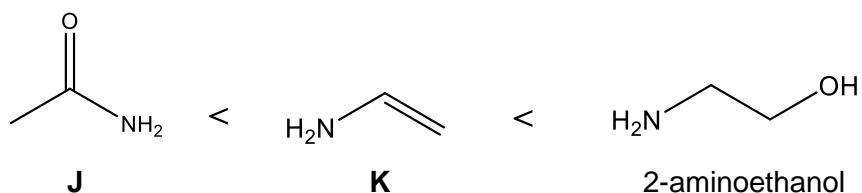


Suggest how the formation of the by-product can be minimised.

[1]

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- (b) By considering the structure of **each** compound **J**, **K** and 2-aminoethanol, explain the order of basicity of these 3 compounds, which are arranged in order of increasing basicity.



[3]

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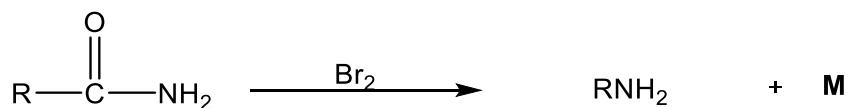
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- (c) A method to synthesise amines directly from primary amides is the Hofmann rearrangement reaction, which was discovered by August Hofmann in 1881.

When a primary amide is treated with bromine,  $\text{Br}_2$ , under suitable conditions, a gaseous primary amine and an unknown gas, **M**, are formed, as exemplified by the following equation.



When a primary amide, **L**, was reacted with  $\text{Br}_2$  under suitable conditions, 0.586g of a mixture of two gases: a gaseous primary amine and gas **M** were produced.

The gas mixture occupies a volume of  $326 \text{ cm}^3$  (measured at 298 K and  $1.00 \times 10^5 \text{ Pa}$ ). The addition of excess  $\text{NaOH(aq)}$  to the gaseous mixture caused its volume to decrease by  $163 \text{ cm}^3$ .

- (i) Prove that the average  $M_r$  for the gaseous mixture is 44.5. [1]
- (ii) Suggest the identity of the gas that reacted with  $\text{NaOH (aq)}$ . [1]
- (iii) Hence calculate the  $M_r$  of the other gas in the gaseous mixture and suggest its identity. [2]
- (iv) Suggest the structure formula for primary amide **L**. [1]

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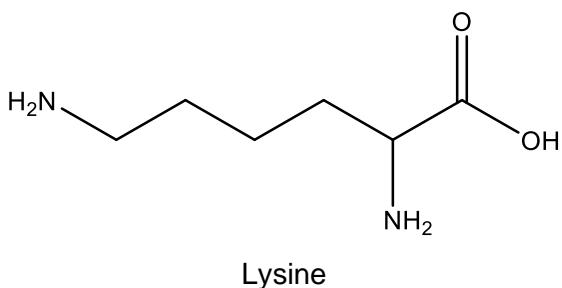
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- (d) Lysine is an essential  $\alpha$ -amino acid that is a precursor to many proteins. Due to its importance in biological processes, a lack of lysine can lead to several illnesses including anaemia.



There are three  $pK_a$  values associated with lysine: 2.2, 9.0 and 10.5.

- (i) At room temperature, lysine exists as a white crystalline solid while 2-aminoethanol is a liquid. Explain the above. [2]

- (ii) Make use of the above  $pK_a$  values to suggest the major species present in solutions of lysine at the following pH values.

- pH 3.0
- pH 9.7

[2]

Solution **N**, a  $10 \text{ cm}^3$  sample containing  $0.200 \text{ mol dm}^{-3}$  of a **fully protonated** lysine, was titrated against  $0.200 \text{ mol dm}^{-3}$   $\text{NaOH}$  (aq).

- (iii) What is the initial pH of solution **N**? (ignore the effect of  $pK_2$  and  $pK_3$  on the pH). [2]

- (iv) Sketch the pH-volume added curve you would expect to obtain when  $40 \text{ cm}^3$  of  $0.200 \text{ mol dm}^{-3}$   $\text{NaOH}$ (aq) is added to  $10 \text{ cm}^3$  sample of solution **N**. Mark clearly the initial pH and the point(s) of maximum buffering capacity. [3]

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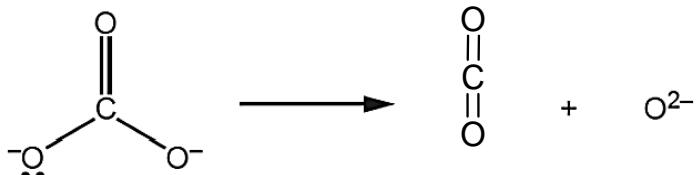
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**Section B**Answer **one** question from this section.

- 4 (a) Group 2 carbonates decompose when heated to form the metal oxide and carbon dioxide.

- (i) Suggest a mechanism for the decomposition of the carbonate ion by adding two curly arrows on Fig. 4.1.

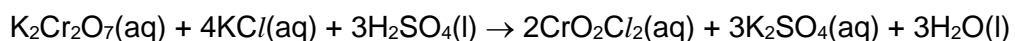
**Fig. 4.1**

[1]

Nickel carbonate,  $\text{NiCO}_3$ , and lithium carbonate,  $\text{Li}_2\text{CO}_3$ , decompose on heating in a similar manner to the Group 2 carbonates.

- (ii) Suggest why  $\text{NiCO}_3$  decomposes more readily than  $\text{CaCO}_3$ . [2]
- (iii) Suggest why the Group 1 carbonates, other than  $\text{Li}_2\text{CO}_3$ , do not decompose when heated. [1]
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- (b) Chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ , can be prepared by heating a mixture of potassium dichromate(VI) and potassium chloride with concentrated sulfuric acid.



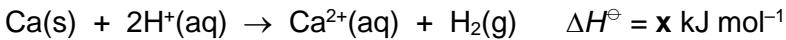
Use the data in Table 4.1 to calculate the enthalpy change of the reaction,  $\Delta H_r$ .

**Table 4.1**

compound	enthalpy change of formation, $\Delta H_f^\ominus$ / kJ mol <sup>-1</sup>
$\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$	-2061
$\text{KCl}(\text{aq})$	-437
$\text{H}_2\text{SO}_4(\text{l})$	-814
$\text{CrO}_2\text{Cl}_2(\text{aq})$	-580
$\text{K}_2\text{SO}_4(\text{aq})$	-1438
$\text{H}_2\text{O}(\text{l})$	-286

[2]

- (c) (i) Define what is meant by the standard enthalpy change of atomisation of calcium.
- (ii) The ionic equation for the reaction of calcium with HCl acid is shown below.



By constructing an energy cycle using the data in Table 4.2, and data from the *Data Booklet*, calculate a value for **x**.

**Table 4.2**

standard enthalpy change of atomisation of Ca(s)	+178 kJ mol <sup>-1</sup>
standard enthalpy change of hydration of Ca <sup>2+</sup> (g)	-1576 kJ mol <sup>-1</sup>
standard enthalpy change of hydration of H <sup>+</sup> (g)	-1090 kJ mol <sup>-1</sup>

[3]

- (iii) The standard enthalpy change for the reaction between Ca(s) and CH<sub>3</sub>CO<sub>2</sub>H(aq) is less negative than **x**.

Suggest an explanation for this.

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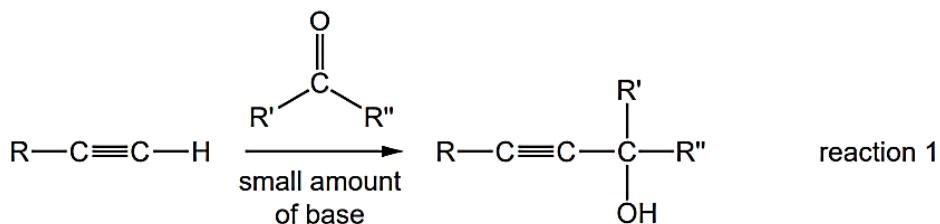
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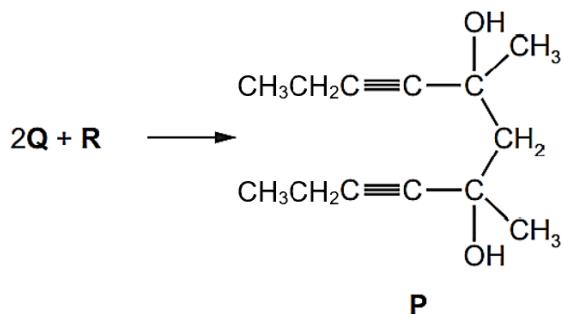
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- (d) Alkynes, compounds containing a C≡C, can react with carbonyl compounds under basic conditions as shown in reaction 1 in Fig. 4.2.

**Fig. 4.2**

An alkyne, **Q**, and a carbonyl compound, **R**, react together to form compound **P** as shown in Fig. 4.3.

**Fig. 4.3**

Use reaction 1 to suggest the structures of alkyne **Q** and carbonyl compound **R**. [1]

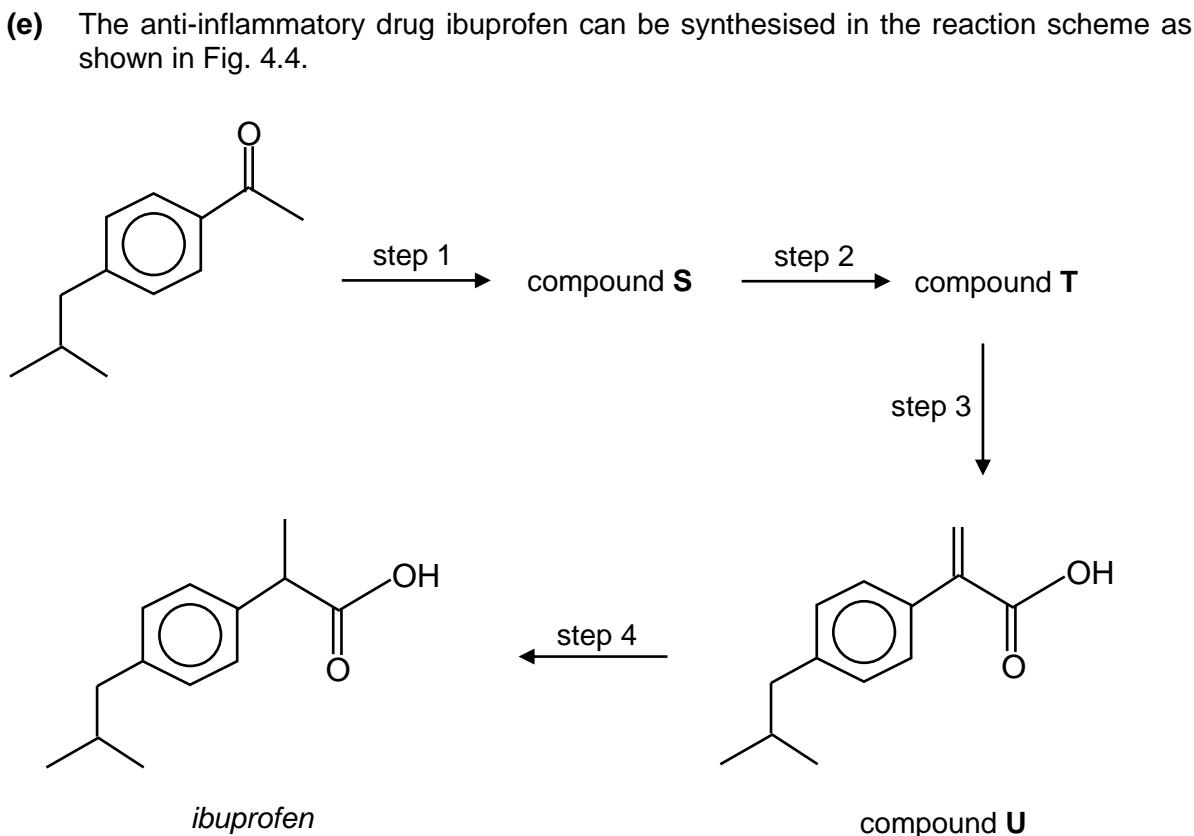


Fig. 4.4

- (i) Identify compounds **S** and **T**. [2]
- (ii) State the reagents and conditions for steps 1 to 4. [4]
- (iii) Compound **U** reacts with  $\text{Br}_2(\text{aq})$  to give two isomers as shown in Fig. 4.5.

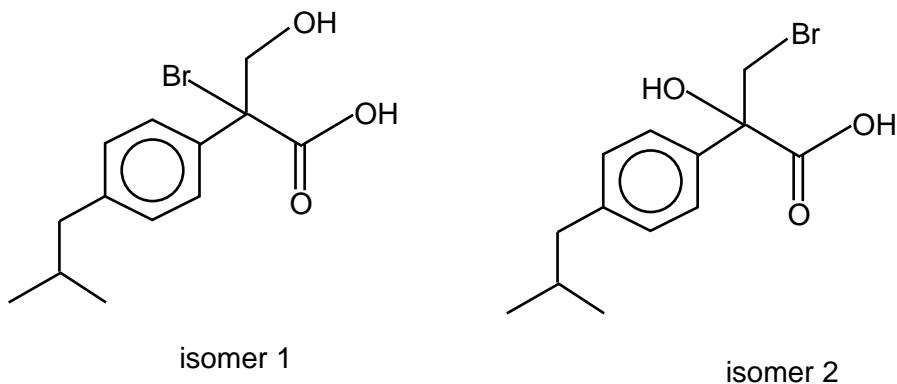


Fig. 4.5

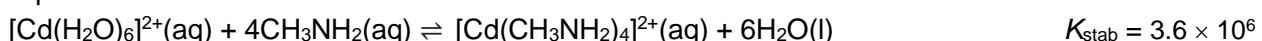
State which isomer is formed at higher proportion. Explain your answer.

[2]

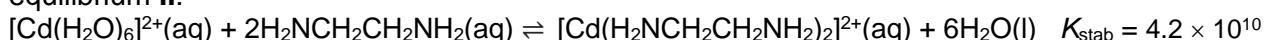


- 5 (a) Cadmium ions form complexes with primary amines and with 1,2-diaminoethane.

equilibrium I:



equilibrium II:



- (i) Write an expression for the stability constant,  $K_{\text{stab}}$ , for equilibrium I, and state its units.

[1]

Cadmium ions are toxic and need to be removed from some water supplies. This is often done by adding a complexing agent such as  $\text{CH}_3\text{NH}_2(\text{aq})$ .

- (ii) A sample of ground water contains  $1.00 \times 10^{-4}$  mol  $\text{dm}^{-3}$  of  $\text{Cd}^{2+}(\text{aq})$ . Calculate the concentration of  $\text{CH}_3\text{NH}_2(\text{aq})$  needed to reduce the concentration of  $\text{Cd}^{2+}(\text{aq})$  in the sample of ground water to  $\frac{1}{1000}$  of its original concentration.

[2]

- (iii) 1,2-diaminoethane is a bidentate ligand. State the coordination number and the geometry of  $[\text{Cd}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]^{2+}$  complex ion.

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- (b) The structure of picolinic acid is shown in Fig. 5.1 below.

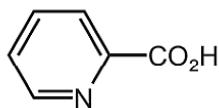


Fig. 5.1

When picolinic acid is placed in basic solution, a bidentate ligand, V, is formed.

- (i) Draw the structure of V and on this structure, draw the lone pairs of electrons on the atoms that could form coordinate bonds to a transition metal ion.

[1]

- (ii) V reacts with aqueous chromium(III) ions,  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ , in a 3 : 1 ratio to form a new neutral complex.

State the type of reaction that has occurred.

Draw a diagram of the structure of the new complex formed, showing the **3-dimensional** arrangement around the Cr(III) ion.

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- (c) A 0.155 g of impure sample of ammonium vanadate(V),  $\text{NH}_4\text{VO}_3$ , is dissolved in an excess of dilute acid.

In this solution all vanadium is present as  $\text{VO}_2^+$  ions. An excess of zinc powder is added to the solution and all the  $\text{VO}_2^+$  ions are reduced to  $\text{V}^{2+}$  ions. The mixture is filtered to remove any remaining zinc powder.

When the resulting solution is titrated, 21.10  $\text{cm}^3$  of 0.0250 mol  $\text{dm}^{-3}$  acidified  $\text{MnO}_4^-$  oxidises all  $\text{V}^{2+}$  ions back to  $\text{VO}_2^+$  ions.

- (i) Construct an ionic equation for the reaction between  $\text{V}^{2+}$  and acidified  $\text{MnO}_4^-$ .

[1]

- (ii) Calculate the percentage by mass of  $\text{NH}_4\text{VO}_3$  in the 0.155 g impure sample of  $\text{NH}_4\text{VO}_3$ .

[2]

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- (d) When a particular copper ore was reduced, an alloy was produced which was composed mainly of copper, but with minor nickel and silver impurities.

In order to purify it, this alloy was made the anode of an electrolytic cell similar to the one shown in Fig. 5.2.

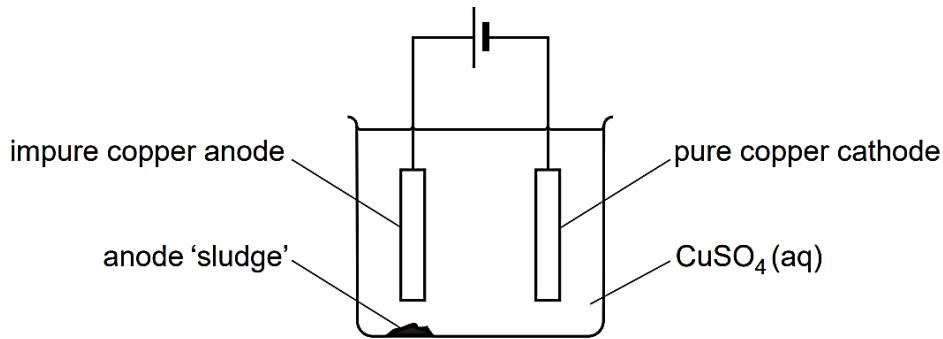


Fig. 5.2

At the impure copper anode, Cu is oxidised to  $\text{Cu}^{2+}$  which goes into the solution. At the pure copper cathode,  $\text{Cu}^{2+}$  is reduced to Cu which deposits on the cathode.

- (i) Explain, with reference to relevant  $E^\ominus$  values from the *Data Booklet*, what happens to the nickel and silver impurities during this purification procedure. [2]
- (ii) Calculate the expected increase in mass of the cathode when a current of 15.0 A was passed through the cell for 5.0 hours. [2]

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- (e) When yellow-brown anhydrous  $\text{CuCl}_2$  is dissolved in water, it gives a blue solution.
- (i) When the blue solution is boiled with copper metal and aqueous hydrochloric acid, a colourless solution **W**, which contains complex ion of copper and chlorine, is formed.

After filtering off the excess copper metal and diluting the colourless solution with water, a white solid **X**, containing copper and chlorine only, is formed. The oxidation number of copper in **W** and **X** are the same.

Identify the complex ion in **W** and the solid compound **X**.

[2]

- (ii) When concentrated hydrochloric acid is added to the blue solution, the colour changes to yellow-green. When water is added to the resulting yellow-green solution, the colour changes back to blue.

Suggest an explanation of these observations with an aid of a balanced equation.

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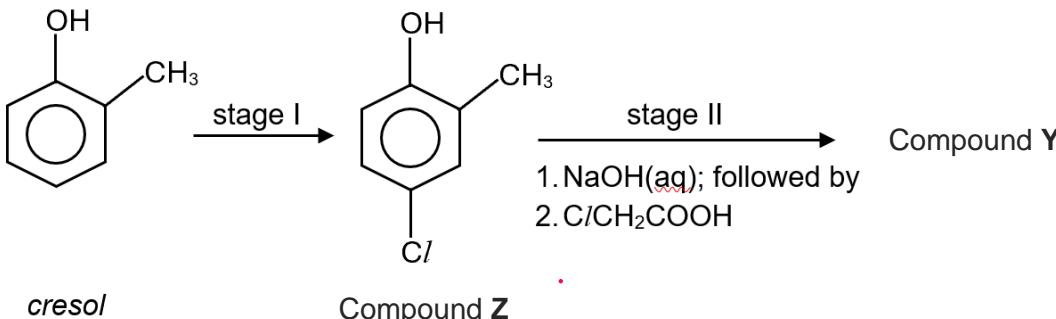
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- (f) Cresols are precursors or synthetic intermediate to other compounds and materials, including plastics, pesticides, pharmaceuticals, and dyes.

An organic compound **Y**, a selective herbicide, can be synthesised from cresol by the following route in Fig. 5.3.



**Fig. 5.3**

- (i) Give the structure of compound **Y**. [1]
- (ii) Suggest why NaOH(aq) is added to compound **Z** in stage II before C/CH<sub>2</sub>COOH is added. [1]

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**Additional answer space**

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**JURONG PIONEER JUNIOR COLLEGE**  
**JC2 PRELIMINARY EXAMINATION 2024**

**CHEMISTRY**

**9729/03**

**Higher 2**

**12 September 2024**

**2 hours**

Paper 3 Free Response Questions

Candidates answer on the Question paper.

Additional Materials: Data Booklet

**READ THESE INSTRUCTIONS FIRST**

Write your name and class on all the work you hand in.

Write in dark blue or black pen on both sides of the paper.

You may use a HB pencil for any diagrams, 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.

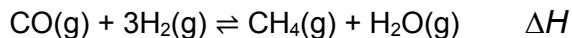
<b>For Examiner's Use</b>	
1	/
2	/
3	/
4 or 5	/
<b>Penalty</b> (delete accordingly)	
Lack 3sf in final answer	-1 / NA
Missing/wrong units in final ans	-1 / NA
Bond linkages	-1 / NA
<b>Total</b>	<b>80</b>

This document consists of **32** printed pages.

## Section A

Answer all the questions in this section.

- 1 (a)** One version of the Fischer-Tropsch process for manufacturing methane is the reaction of carbon monoxide with hydrogen.



A mixture of CO and H<sub>2</sub> in a 1:3 molar ratio was introduced into a sealed vessel and heated to 1200K. At equilibrium, 40% of the CO had reacted. The total pressure in the vessel was 12 atm at equilibrium.

- (i)** Write an expression for the equilibrium constant, K<sub>p</sub> for this reaction.

$$K_p = \frac{P_{\text{H}_2\text{O}} \times P_{\text{CH}_4}}{P_{\text{CO}} \times (P_{\text{H}_2})^3}$$

[1]

Examiner's comments:

This was generally well answered. Common mistakes:

- Excluding partial pressure of water in the expression.
- Using [ ]

- (ii)** Use your expression to calculate the value of K<sub>p</sub> for the reaction at 1200K. Include its units.

	3H <sub>2</sub> (g)	+ CO(g)	↔	CH <sub>4</sub> (g)	+ H <sub>2</sub> O(g)
<b>Initial amount/mol</b>	3x	x	-	-	-
<b>Change/mol</b>	-3(0.4)x	-0.4x	+ (0.4)x	+ (0.4)x	
<b>Equilibrium amount/mol</b>	1.8x	0.6x	0.4x	0.4x	

$$\text{Total amount at equilibrium} = 1.8x + 0.6x + 0.8x = 3.2x$$

$$P_{\text{H}_2} = \frac{1.8x}{3.2x} \times 12 = 6.75 \text{ atm}$$

$$P_{\text{CO}} = \frac{0.6x}{3.2x} \times 12 = 2.25 \text{ atm}$$

$$P_{\text{CH}_4} = P_{\text{H}_2\text{O}} = \frac{0.4x}{3.2x} \times 12 = 1.5 \text{ atm}$$

$$K_p = \frac{(1.50)^2}{(6.75)^3 (2.25)} = 0.00325 \text{ atm}^{-2}$$

[3]

Examiner's comments:

This was generally well answered. Most students were able to get some marks. Answers in kPa are accepted but students are advised to leave their answers in units given in question and not to spend time converting the units.

- (iii) Given that the value of  $K_p$  decreases with increasing temperature, deduce the sign for the enthalpy change,  $\Delta H$  of the forward reaction. Explain your reasoning.

Since  $K_p$  decreases with increasing temperature, it implies that the position of equilibrium has shifted left to favour endothermic reaction or absorb some heat. Hence, the forward reaction is exothermic and the sign of  $\Delta H$  of the forward reaction is negative.

[1]

Examiner's comments:

This was generally well answered. Some of the students failed to read the question carefully and just state that the forward reaction is exothermic without giving the sign.

- (b) Describe and explain how the entropy of each of the following systems will change during the stated process.

- 1 mol of N<sub>2</sub>(g) at 298K is added to 1 mol of CH<sub>4</sub>(g) at 298K.
- 1 mol of Cl<sub>2</sub>(g) at 298 K is heated to 373 K.

Assume the pressure of each gas remains at 1 atm throughout and no reaction occurs between N<sub>2</sub> and CH<sub>4</sub>.

- 1 mol of N<sub>2</sub>(g) at 298K is added to 1 mol of CH<sub>4</sub>(g) at 298K.  
 $\Delta S^\ominus > 0$  as there is an increase in disorder of system since there is more ways of arranging the particles OR distributing the energy among the particles due to mixing.
- 1 mol of Cl<sub>2</sub>(g) at 298 K is heated to 373 K.  
 $\Delta S^\ominus > 0$  as there is an increase in disorder of system since an increase in temperature increases the (average) kinetic energy of gas molecules causing a broadening of the Boltzmann energy distribution (emphasise in debrief), resulting in more ways of arranging the energy quanta among the particles in the hotter system.

[2]

Examiner's comments:

This was generally well answered. Most students missed out "mixing" to explain for the increase in disorderliness in the first part. Students are reminded to be careful in their answers. The correct answer should be "Increase in entropy, S" or "change in entropy,  $\Delta S^\ominus$ , is positive".

- (c) (i) During the monobromination of pentane, three different bromoalkanes are formed as shown in Fig. 1.1.

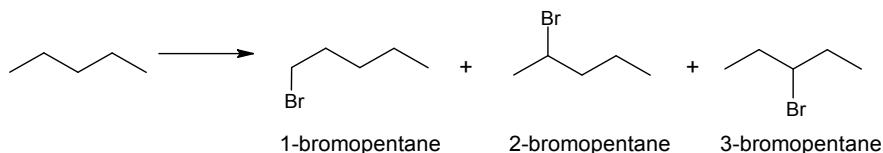


Fig. 1.1

Predict the expected theoretical ratio in which these three products would form if the monobromination of pentane occurs randomly.

Explain your answer.

[2]

1-bromopentane: 2-bromopentane: 3-bromopentane = 6:4:2 = 3:2:1

The substitution reaction is random.

There are 6 chemically equivalent H atoms that can be substituted to form 1-bromopentane, 4 chemically equivalent H atoms that can be substituted to form 2-bromopentane, 2 chemically equivalent H atoms that can be substituted to form 3-bromopentane.

[2]

Examiner's comments:

- This was generally well answered.

- (ii) When the monobromination was practically carried out in an experiment, the percentage of 1-bromopentane was obtained in the lowest proportion.

Suggest an explanation for the difference between this experimental result and what you predicted in (c)(i).

The intermediate formed in free radical substitution to form 1-bromopentane is a primary radical which is most electron deficient and least stable, as it has least electron-donating alkyl groups bonded to it.

Thus it is less favourably formed and is the minor product.

[1]

Examiner's comments:

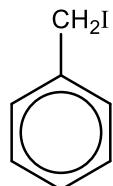
- This was generally not well answered.
- Common wrong responses were “the intermediate is a primary carbocation” or “less electron donating alkyl groups to disperse the charge”.
- A significant number missed out “least stable” or “electron-donating”.

- (d) The *Wurtz* reaction below shows two iodoalkanes react with sodium metal in dry ether, to form a new carbon–carbon bond, resulting in the formation of a new alkane.



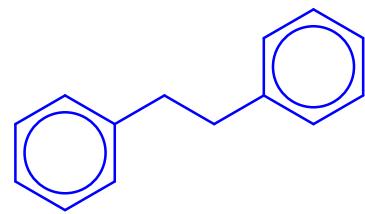
Reaction of a single iodoalkane with sodium metal in dry ether via *Wurtz* reaction will give a good yield of symmetrical alkane product.

Draw the organic product formed when (iodomethyl)benzene reacts with sodium metal in dry ether.



(iodomethyl)benzene

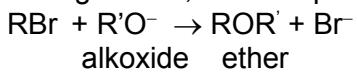
[1]



Examiner's comments:

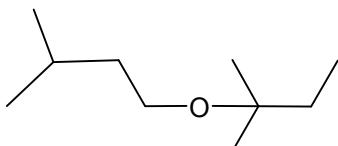
- This was generally well answered.

- (e) Bromoalkanes and alkoxides react in the Williamson ether synthesis to form the ether functional group containing C-O-C, an example of which is shown below.

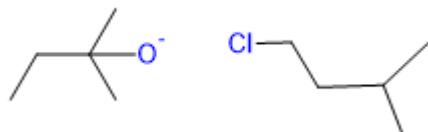


It is known that S<sub>N</sub>2 mechanism is usually undergone in Williamson ether synthesis.

Suggest the structures of the halogenoalkane and alkoxide ion RO<sup>-</sup> you would use to synthesise the ether below, using the Williamson synthesis method.



[1]



Should be primary halogenoalkane as S<sub>N</sub>2 mechanism is undergone.

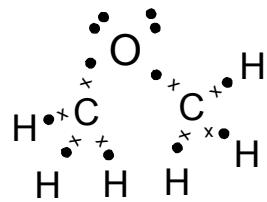
Examiner's comments:

- This part was generally well answered.
- Common wrong response was drawing a tertiary halogenoalkane.
- Students must learn to recognise that since the question is about S<sub>N</sub>2, it should be a primary halogenoalkane.

- (f) (i) CH<sub>3</sub>OCH<sub>3</sub>, methoxymethane is the simplest ether which is used as aerosol propellants. Given that CH<sub>3</sub>OCH<sub>3</sub>, contains C-O-C bond, draw the 'dot-and-cross' diagram for CH<sub>3</sub>OCH<sub>3</sub>.

Use VSEPR (valence shell electron pair repulsion) theory to describe and explain the shape about the oxygen and suggest the C-O-C bond angle of a CH<sub>3</sub>OCH<sub>3</sub> molecule.

[3]



Lone pair -lone pair repulsion> lone pair-bond pair repulsion> bond-pair-bond pair repulsion.

The O in CH<sub>3</sub>OCH<sub>3</sub> has 2 bond pairs and 2 lone pairs of electrons. Shape is bent about O and C-O-C bond angle is 104.5 or 105°.

Examiner's comments:

- Only a small proportion of students scored full marks for this part.
- Students should read the question carefully and note that they should use VSEPR theory to explain the shape. A significant number of students left out the explanation, and stated only shape and bond angle.

- (ii) By considering the polarity of each of the bonds it contains, and the shape about the oxygen of the  $\text{CH}_3\text{OCH}_3$  molecule, deduce the overall polarity of the  $\text{CH}_3\text{OCH}_3$  molecule.
- C-O bonds are polar
  - Thus dipole moments do not cancel out or overall molecule is polar or has net dipole moment

[1]

Examiner's comments:

- This proved difficult for many students.
- A large number of students did not consider the polar C-O bonds caused by the difference in electronegativity, which results in dipole moments.
- For those who used drawings, they failed to indicate the dipole moment and partial charges on the C-O bonds, resulting in no marks being awarded.

- (iii) Boiling points of some compounds with similar  $M_r$  as methoxymethane such as propane, ethanol and ethylamine are given below in Table 1.1. Suggest explanations for these differences.

**Table 1.1**

Compound	$M_r$	Formula	boiling point / °C
Ethylamine	45	$\text{CH}_3\text{CH}_2\text{NH}_2$	17
Ethanol	46	$\text{CH}_3\text{CH}_2\text{OH}$	78
Propane	44	$\text{CH}_3\text{CH}_2\text{CH}_3$	-42

[3]

Comparing boiling point propane < ethylamine<ethanol:

All have simple molecular or simple covalent structures.

Comparing why boiling point of propane < ethylamine:

Larger amount of energy is required to overcome the stronger hydrogen bonding between  $\text{C}_2\text{H}_5\text{NH}_2$  molecules than that required for the weaker instantaneous dipole-induced dipole attractions between propane molecules

Comparing why boiling point of ethylamine < ethanol:

Since O is more electronegative than N, hence O-H bond is more polar than N-H bond, more energy is required to overcome the stronger hydrogen bonds between ethanol molecules than that between ethylamine molecules.

#### Examiner's comments:

This was generally well answered, with most candidates scoring 2 marks on average, but few candidates were able to gain full credit of 3 marks.

Common mistakes include:

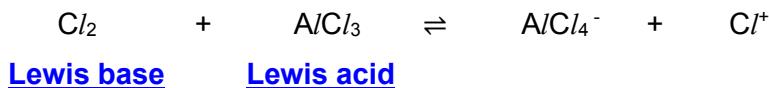
- Did not state "simple molecular structure / simple covalent compounds / simple covalent molecules".
- Wrote that ethylamine or ethanol molecules have pd-pd between molecules rather than hydrogen bonds.
- Discussed polarity of C-O bond vs C-H bond, rather than O-H bond vs N-H bond.
- Did not mention energy required to overcome the IMFs.

[Total:19]

- 2 (a) (i) Halogens can behave as Lewis acids or Lewis bases. The reaction of benzene and chlorine,  $\text{Cl}_2$  requires the use of halogen carrier,  $\text{AlCl}_3$ , to generate the electrophile.

- Define what is meant by a Lewis acid.
- Using the reaction of  $\text{Cl}_2$  with  $\text{AlCl}_3$ , state which species is behaving as Lewis acid and which is behaving as Lewis base. [2]

Lewis acid is an electron pair / lone pair acceptor.



Examiner's comments:

Performance for this part of the question was average.

Common mistakes for the definition include:

- did not state electron "pair" or lone "pair".
- wrongly stated "donor" rather than "acceptor".

- (ii) Benzene and phenol both undergo electrophilic substitution with halogens under different conditions.

Explain why the reaction of phenol with halogens occurs more readily and does not require the use of halogen carrier catalyst, like benzene does.

[1]

The lone pair of electrons on oxygen is delocalised into the pi-system of the benzene ring through p-p orbital overlap between O and pi electron cloud of the benzene ring) makes benzene ring more electron-rich, causing phenol to be more readily attacked by electrophiles.

Thus phenol do not require the need for a stronger electrophile created by reaction between  $\text{Cl}_2$  with  $\text{AlCl}_3$ .

Examiner's comments:

This part of the question was not well done. Answers were often incomplete.

Please note that "increasing the -ve charge in benzene" is not accepted as benzene is a neutral molecule.

Correct phrases would be "increase the electron density in the benzene ring" or "making benzene more electron rich".

- (b) The standard reduction potential for 1,4-benzoquinone /benzene-1,4-diol is shown in Fig. 2.1.

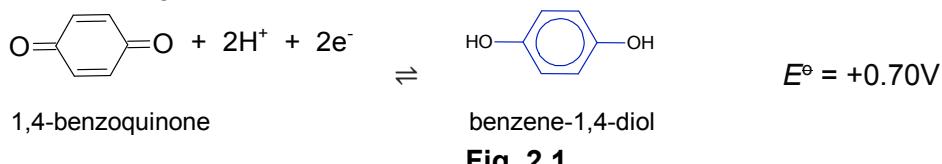
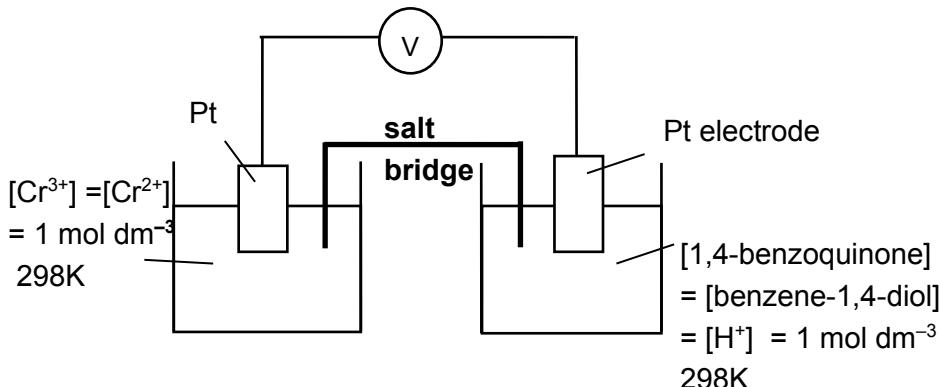


Fig. 2.2 below shows how the standard cell potential between the  $\text{Cr}^{3+}/\text{Cr}^{2+}$  half-cell and the 1,4-benzoquinone /benzene-1,4-diol half-cell is measured.

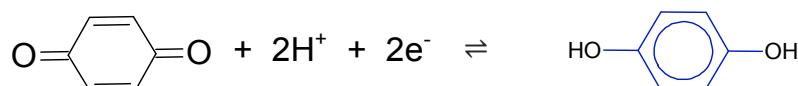


**Fig. 2.2**

- (i) Using data from the *Data Booklet* and the above information, calculate  $E^\ominus_{\text{cell}}$  for the cell in Fig. 2.2 and state which is the negative electrode. [2]



$$E^\ominus = -0.41\text{ V (oxidation)}$$



$$E^\ominus = +0.70\text{ V (reduction)}$$

$$E^\ominus_{\text{cell}} = +0.70 - (-0.41) = +1.11\text{ V} > 0, \text{ energetically feasible.}$$

Negative electrode is the anode undergoing oxidation (producing electrons), is the  $\text{Cr}^{3+}/\text{Cr}^{2+}$ .

Examiner's comments:

Generally, well done.

Most students were able to calculate  $E_{\text{cell}}$  correctly. However, many omitted the +ve sign and the units.

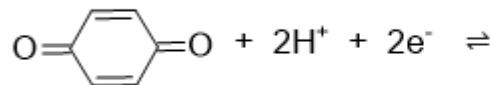
Quite a handful of students did not answer the second part of the question, which is to state which is the negative electrode

- (ii) Construct the overall equation for the reaction that has taken place in the cell.

[1]



$E^\circ = -0.41 \text{ V}$  (oxidation)

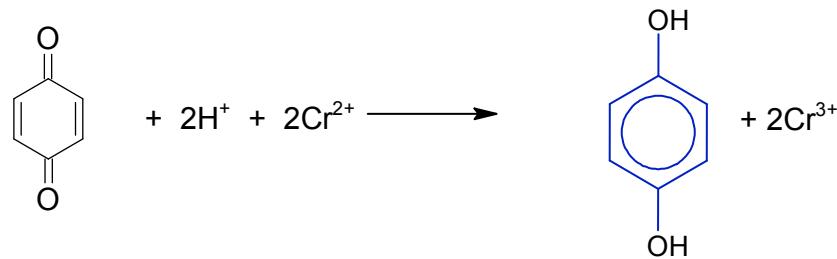


1,4-benzoquinone



benzene-1,4-diol

$E^\circ = +0.70 \text{ V}$  (reduction)

**Overall:****Examiner's comments:**

Performance for this part of the question was average.

Common mistakes include:

- species on the wrong side of the question. Eg.  $\text{Cr}^{3+}$  to  $\text{Cr}^{2+}$ .
- equations not balanced.
- using a reversible arrow instead of an irreversible arrow.

- (iii) Calculate  $\Delta G^\circ$  for the reaction you wrote in (b)(ii).

[1]

$$\Delta G^\circ = -nFE^\circ$$

$$n = 2$$

$$\Delta G^\circ = -2 \times 96500 \times (+1.11) = -214 \text{ kJ mol}^{-1}$$

Examiner's comments:

Simple question but many mistakes

Most common mistake in units in  $\Delta G^\circ$ . Wrong units, zero mark for this qn

Units for  $\Delta G^\circ = -nFE^\circ$  is  $\text{J mol}^{-1}$  pls take note!

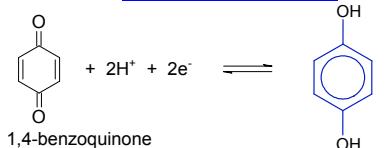
Another common mistake: missing out -ve sign. Pls memorise eqn!

When  $E^\circ$  is positive,  $\Delta G^\circ$  is negative => Both mean reaction is energetically feasible.

- (c) State and explain what happens to the  $E_{\text{cell}}$  when pH of the 1,4-benzoquinone /benzene-1,4-diol half-cell decreased.

[2]

When  $[\text{H}^+]$  increased this causes the position of equilibrium



$E(1,4\text{-benzoquinone}/\text{benzene-1,4-diol})$  or  $E_{\text{cathode}}$  more positive.  
 $\therefore E_{\text{cell}}$  becomes more positive.

Examiner's comments:

Major misconception

At least 20% mistakenly wrong  $[\text{H}^+]$  drop when pH drop – wrong!

$$\text{pH} = -\log[\text{H}^+]$$

$[\text{H}^+]$  and pH are inversely related!

Another common mistake: Forgetting to write out the exact eqm that you are referring to. Pls write out the exact eqm in the A level exam (or you can make reference to eqm in Fig. 2.1 eg. in this question)

- (d) Another experiment is set up using the same electrochemical cell. In this experiment, the  $\text{Cr}^{2+}$  concentration is changed to  $0.15 \text{ mol dm}^{-3}$ . All other concentrations remain at their standard values.

The Nernst equation is shown.

$$E = E^\circ + \frac{0.059}{n} \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

n = number of electrons transferred

$E^\circ$  is the standard reduction potential for the  $\text{Cr}^{3+}/\text{Cr}^{2+}$  electrode system.

- (i) Use the Nernst equation and the *Data Booklet* to calculate the electrode potential for the  $\text{Cr}^{3+}/\text{Cr}^{2+}$  half cell in this experiment.

[1]

$$E = -0.41 + \frac{0.059}{1} \log \frac{[1]}{[0.15]} \text{ use of } n = 1$$

$$E = -0.41 + 0.05 = -0.36 \text{ V}$$

Application qn, badly done. 10% got this correct.

**Read carefully  $n_e$  transferred = 1 in the  $\text{Cr}^{3+} + \text{e}^- \rightleftharpoons \text{Cr}^{2+}$**

- (ii) Using your answer in (d)(i) and data given in (b), calculate  $E_{\text{cell}}$  for this electrochemical cell.

[1]

$$E_{\text{cell}} = +0.70 - (-0.36) = +1.06 \text{ V} > 0$$

**Do not forget to write + sign for  $E_{\text{cell}}$ .**

- (e) The aldol reaction is a useful method to make new carbon–carbon bonds in organic chemistry. It involves combining two molecules of the same aldehyde or ketone to form a product which contains both a carbonyl functional group (aldehyde or ketone) and alcohol functional group.

The aldol **A** is made by reacting ethanal with a small amount of  $\text{NaOH(aq)}$  at room temperature. The three stages of the reaction are described in Table 2.1.

Stage	Equation
1	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{CHO} \\   \\ \text{H} \end{array} + :\text{OH}^- \rightleftharpoons \begin{array}{c} \text{:CH}_2\text{CHO} \\   \\ \text{B} \end{array} + \text{H}_2\text{O}$
2	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{CH}_3 \end{array} + \begin{array}{c} \text{:CH}_2\text{CHO} \\   \\ \text{B} \end{array} \rightleftharpoons \begin{array}{c} \text{O:} \\   \\ \text{H}-\text{C}-\text{CH}_2\text{CHO} \\   \\ \text{CH}_3 \end{array}$
3	$\begin{array}{c} \text{O:} \\   \\ \text{H}-\text{C}-\text{CH}_2\text{CHO} \\   \\ \text{CH}_3 \end{array} + \text{H}-\text{OH} \rightleftharpoons \begin{array}{c} \text{OH} \\   \\ \text{H}-\text{C}-\text{CH}_2\text{CHO} \\   \\ \text{CH}_3 \end{array} + :\text{OH}^-$

**Table 2.1**

- (i) Suggest the type of reaction in stage 1.

[1]

**Acid base**

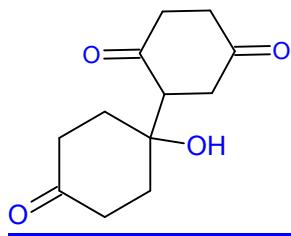
- (ii) 1,4-cyclohexanedione can be formed from 1,4-benzoquinone.



1,4-cyclohexanedione

1,4-cyclohexanedione reacts with the presence of  $\text{NaOH}$  at room temperature via the 3 stages shown in Table 2.1. A product with 12 carbons, **D** was formed. Draw the structure of **D**.

[1]



Application qn, badly done. Pls revise aldol condensation mechanism in the carbonyl tutorial challenging question make sure you know it. Alpha C is C bonded to C=O directly and alpha H is acidic, lost H<sup>+</sup> to form nucleophile lone pair on alpha C, this nucleophile attack delta positive C.

- (f) Aluminium objects have a thin insoluble oxide, Al<sub>2</sub>O<sub>3</sub>, layer on their surfaces. This oxide can be removed by adding NaOH(aq) to the aluminium object.

- (i) Explain why Al<sub>2</sub>O<sub>3</sub> is insoluble in water.

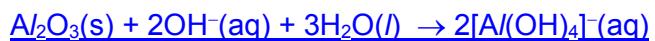
[1]

The hydration energy released upon forming ion–dipole interactions between the ions and water molecules is insufficient to compensate the energy required to overcome the strong ionic bonds between Al<sup>3+</sup> and O<sup>2-</sup> ions.

Hence, Al<sub>2</sub>O<sub>3</sub> is insoluble in water.

- (ii) Write an equation which describes the reaction occurring when NaOH(aq) is added to the aluminium oxide.

[1]



or



- (g) Compound E, C<sub>10</sub>H<sub>18</sub>O is optically active and decolourises orange aqueous Br<sub>2</sub>. E reacts with sodium, Na to form H<sub>2</sub> gas.

E reacts with an excess hot acidified concentrated KMnO<sub>4</sub> to produce three different organic molecules, F, C<sub>3</sub>H<sub>6</sub>O, H, (CO<sub>2</sub>H)<sub>2</sub>, and G, C<sub>5</sub>H<sub>8</sub>O<sub>3</sub>. One of these organic molecules is further oxidised to CO<sub>2</sub>.

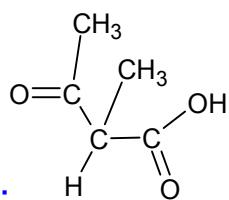
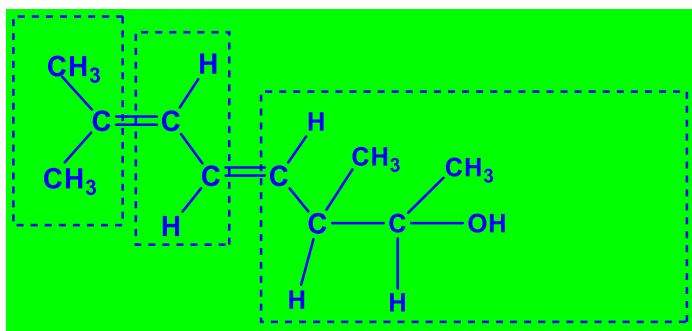
F and G both react with 2,4-dinitrophenylhydrazine. E, F and G react with aqueous alkaline iodine forming a yellow precipitate. G reacts with aqueous Na<sub>2</sub>CO<sub>3</sub>(aq) giving off effervescence of a colourless gas.

Suggest the structures of E, F and G. For each reaction, state the *type of reaction* and explain what the information tells you about the functional groups present in each compound.

[6]

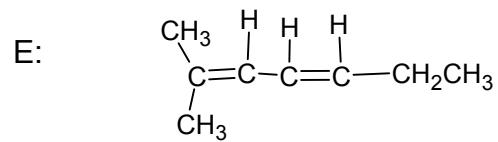
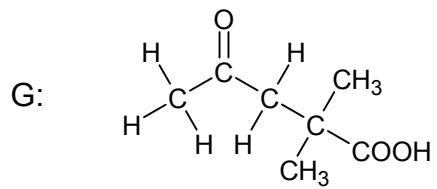
Information	Type of reaction	Deduction (of functional group)
E rotates plane-polarised light.		E contain a chiral carbon

<b>Ratio of C:H in E is not 1:1</b>	-	<b>No benzene in E</b>
<b>E reacts with aqueous Br<sub>2</sub>.</b>	<b>Electrophilic addition</b>	<b>Alkene in E</b>
<b>E reacts with sodium, Na, to produce H<sub>2</sub>(g).</b>	<b>E undergoes redox reject acid-metal</b>	<b>E contains alcohol Reject phenol/ carboxylic acid</b>
<b>E reacts with an excess hot concentrated KMnO<sub>4</sub> to produce three different organic molecules, F, C<sub>3</sub>H<sub>6</sub>O, H, (CO<sub>2</sub>H)<sub>2</sub>, and G, C<sub>6</sub>H<sub>10</sub>O</b>	<b>Oxidative cleavage/ oxidation</b>	<b>E contains alkene or C=C</b>
<b>G reacts with aqueous Na<sub>2</sub>CO<sub>3</sub>(aq) giving off effervescence of a colourless gas.</b>	<b>Acid base reaction Reject acid carbonate</b>	<b>G has carboxylic acid (✓)</b>
<b>F and G both react with 2,4-dinitrophenylhydrazine</b>	<b>Condensation</b>	<b>F and G are ketone</b>
<b>F and G react with aqueous alkaline iodine forming a yellow precipitate.</b>	<b>Oxidation/ positive iodoform test</b>	<b>G contains -COCH<sub>3</sub></b>
<b>E react with aqueous alkaline iodine forming a yellow precipitate.</b>	<b>Oxidation/ positive iodoform test</b>	<b>E contains -CH(OH)(CH<sub>3</sub>)</b>

**Compound E:**

**F: CH<sub>3</sub>COCH<sub>3</sub>    G: \_\_\_\_\_**

**Alternative answers:**



[Total:2]

- 3 2-aminoethanol molecules are a component in the formation of cellular membranes and are thus a molecular building block for life. Basic in nature, 2-aminoethanol is often used for alkalization of water in steam cycles of power plants.

(a) A synthesis of 2-aminoethanol is shown in Fig 3.1.

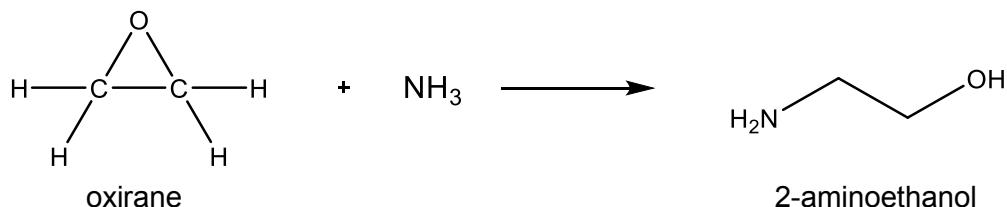


Fig. 3.1

- (i) Complete the mechanism of step 1 on Fig. 3.2 by adding all relevant curly arrows, lone pairs of electrons, charges and partial charges; and draw the structure of the organic intermediate.

[2]

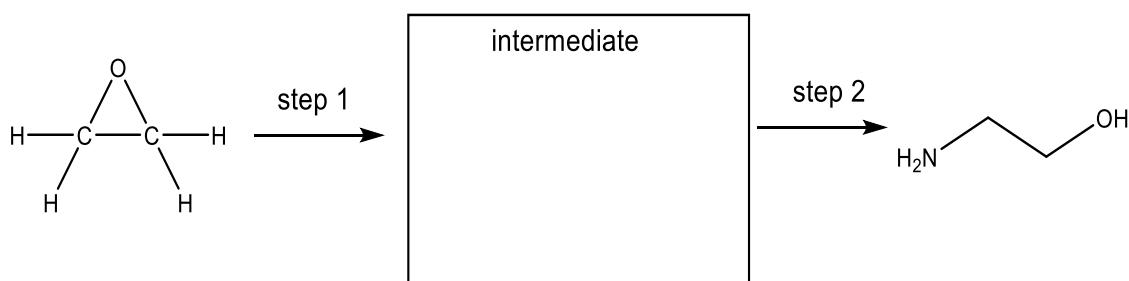
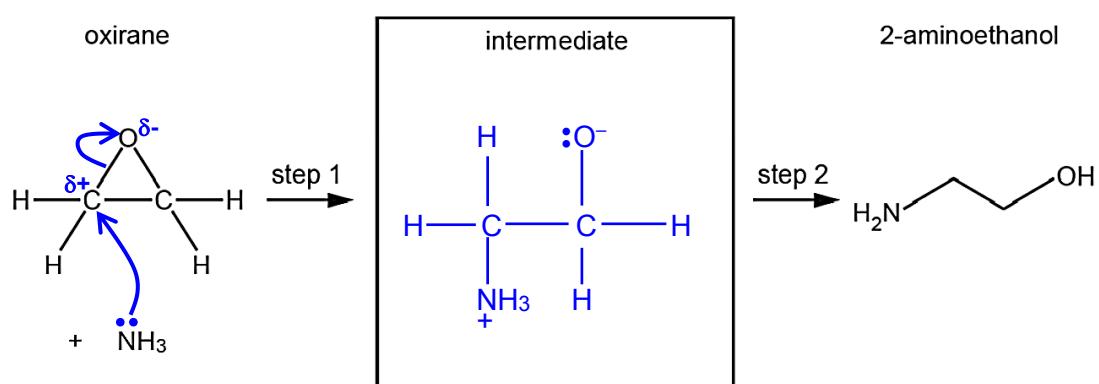
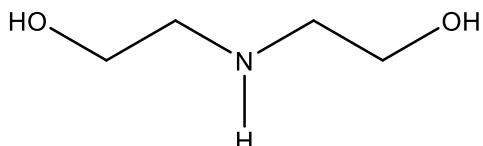


Fig. 3.2



- (ii) A small amount of by-product, shown below, is produced during the reaction shown in Fig 3.1.

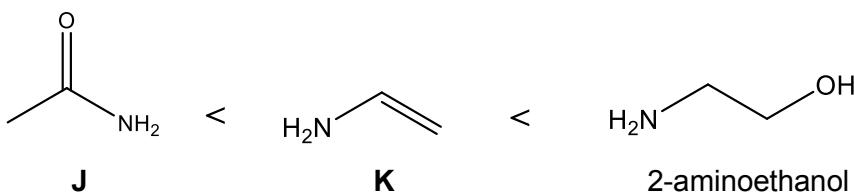


Suggest how the formation of the by-product can be minimised.

[1]

Use an excess of ammonia or limiting amount of oxirane

- (b) By considering the structure of **each** compound **J**, **K** and 2-aminoethanol, explain the order of basicity of these 3 compounds, which are arranged in order of increasing basicity.



[3]

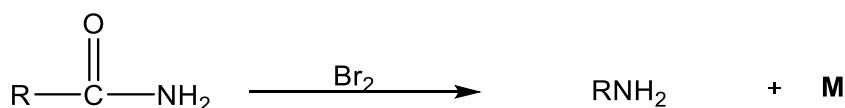
**2-aminoethanol** contains an electron-donating group, making the lone pair on N atom more available to accept a proton or donate to H<sup>+</sup>/ acid, hence it is the most basic among the 3 compounds.

For amide **J**, the p-p orbital overlap results in delocalisation of lone pair of electrons on N atom into C=O and since C=O is a strong electron-withdrawing group, the lone pair of electrons on N atom is NOT available for protonation. Hence, **J** is neutral.

For **K**, the p-p orbital overlap results in delocalisation of lone pair of electrons on N atom into adjacent C=C and hence, making the lone pair of electrons on N atom less available to accept a proton.

- (c) A method to synthesise amines directly from primary amides is the Hofmann rearrangement reaction, which was discovered by August Hofmann in 1881.

When a primary amide is treated with bromine, Br<sub>2</sub>, under suitable conditions, a gaseous primary amine and an unknown gas, **M**, are formed, as exemplified by the following equation.



When a primary amide, **L**, was reacted with Br<sub>2</sub> under suitable conditions, 0.586g of a mixture of two gases: a gaseous primary amine and gas **M** were produced.

The gas mixture occupies a volume of 326 cm<sup>3</sup> (measured at 298 K and 1.00 × 10<sup>5</sup> Pa). The addition of excess NaOH(aq) to the gaseous mixture caused its volume to decrease by 163 cm<sup>3</sup>.

- (i) Prove that the average  $M_r$  for the gaseous mixture is 44.5.

[1]

Assuming that the gaseous mixture behaves like ideal gas (i.e.  $pV = nRT$ ),

$$pV = \frac{mRT}{M_r}$$

$$\Rightarrow M_r \text{ of gaseous mixture} = \frac{(0.586)(8.31)(298)}{(1.00 \times 10^5)(326 \times 10^{-6})}$$

$$= 44.5 \text{ (no unit)}$$

- (ii) Suggest the identity of the gas that reacted with NaOH (aq).

[1]

CO<sub>2</sub>

- (iii) Hence calculate the  $M_r$  of the other gas in the gaseous mixture and suggest its identity.

[2]

$$\text{Volume of CO}_2 = 163 \text{ cm}^3$$

$$\text{Volume of other gas} = 326 - 163 = 163 \text{ cm}^3$$

For gases measured at the same p and T, **volume ratio = mole ratio**.

$$\begin{array}{c:c:c} \text{volume of CO}_2 & : & \text{volume of other gas} \\ 163 & : & 163 \\ 1 & : & 1 \end{array}$$

$$\text{Average } M_r \text{ of mixture} = \sum (\text{relative abundance}) \times (M_r \text{ of individual gas})$$

$$44.5 = \left( \frac{1}{2} \times 44.0 \right) + \frac{1}{2} \times M_r \text{ of other gas}$$

$$M_r \text{ of other gas} = \underline{\underline{45.0}}$$

The other gas is needs to a primary amine,  $\text{RNH}_2$

$$\text{Hence } 45 - (14+2) = 29;$$

$$\text{Hence R} = \text{C}_2\text{H}_5$$

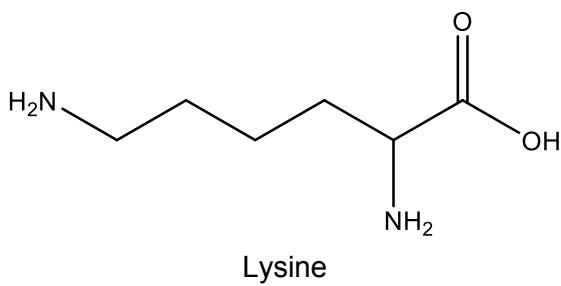


- (iv) Suggest the structure formula for amide L.

[1]



- (d) Lysine is an essential  $\alpha$ -amino acid that is a precursor to many proteins. Due to its importance in several biological processes, a lack of lysine can lead to several illnesses including anaemia.



There are three  $pK_a$  values associated with lysine, 2.2, 9.0 and 10.5

- (i) At room temperature, lysine exists as a white crystalline solid while 2-aminoethanol is a liquid. Explain the above.

[2]

In the solid state, lysine exists in the zwitterionic form.

There exists stronger electrostatic forces of attraction / ionic bonds between the positive  $-\text{NH}_3^+$  and the negative  $-\text{COO}^-$ , compared to ethanolamine, where there are weaker hydrogen bonds between the 2-aminoethanol molecules.

A larger amount of energy is required to overcome these forces of attraction between the zwitterions, hence the melting point of lysine is much higher than that of ethanolamine.

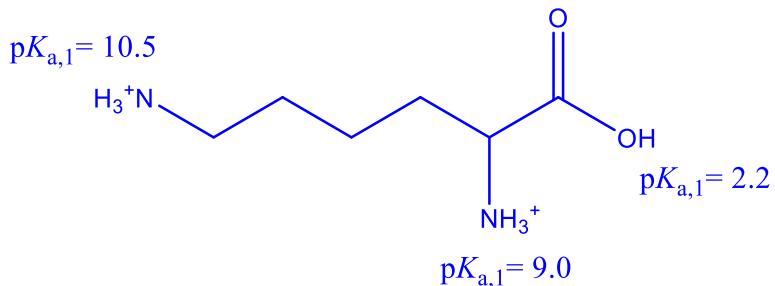
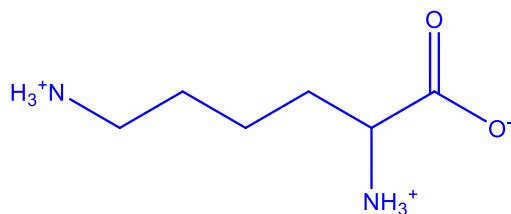
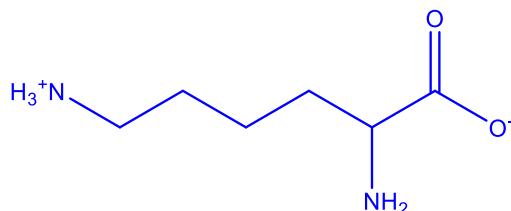
Examiner's Comments:

Many only scored one mark for this question as they did not identify the amino acid as zwitterions and also did not state that there is ionic bonds between the oppositely charged ions. Students should always state the attraction between the particles (ions, molecules etc) clearly. Many wrongly stated that the amino acids have hydrogen bonds between the molecules. Some did not even state the intermolecular forces of attractions for 2-aminoethanol when the questions clearly demand the explanation for physical states of both the compounds

- (ii) Make use of the above  $pK_a$  values to suggest the major species present in solutions of lysine at the following pH values.

- pH 3.0
- pH 9.7

[2]

**At pH 3.0****At pH 9.7**Examiner's Comments:

Very poorly done. This could be due to the wrong assigning of  $pK_a$  values to the groups in lysine. Students must revise this topic on how to assign the  $pK_a$  values for the protonated form of the amino acids. The details on how to do this is given below.

Determining the overall charge on an Amino Acid

Step 1: Draw the structure of amino acid at low pH (protonated form)

- 1) all -COOH remains as -COOH
- 2) all -NH<sub>2</sub> are protonated to -NH<sub>3</sub><sup>+</sup>

Step 2: Assign  $pK_a$  values to all acidic groups for protonated form of amino acid.

- 1) as -COOH is more acidic than -NH<sub>3</sub><sup>+</sup>, thus  $pK_a(-\text{COOH}) < pK_a(-\text{NH}_3^+)$
- 2)  $\alpha$ -COOH more acidic than side chain -COOH group
- 3)  $\alpha$ -NH<sub>2</sub> less basic than side chain -NH<sub>2</sub> group

**Step 3: Compare pH of the solution to the  $pK_a$  value of each acidic group to determine if the dominant form is the protonated or deprotonated form.**

- 1) If  $\text{pH} < pK_a$ , protonated form remains ( $\text{H}^+$  is added)
- 2) If  $\text{pH} > pK_a$ , deprotonation takes place ( $\text{H}^+$  is removed)

Solution N, a  $10 \text{ cm}^3$  sample containing  $0.200 \text{ mol dm}^{-3}$  of a **fully protonated** lysine, was titrated against  $0.200 \text{ mol dm}^{-3}$  NaOH (aq).

- (iii) What is the initial pH of solution N? [2]

*Ignore the effect of  $pK_{a2}$  and  $pK_{a3}$*

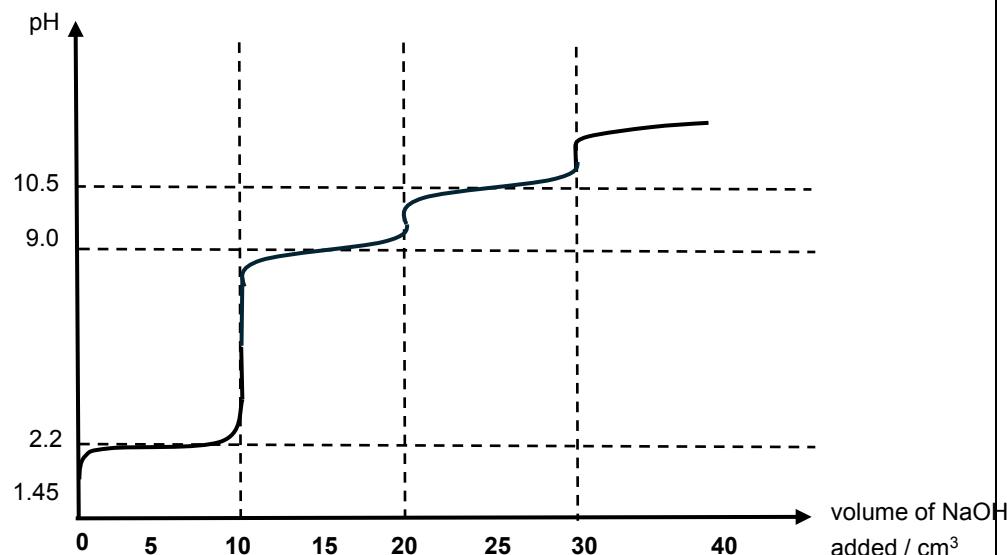
Use  $pK_{a,1}$  to find pH

$$\begin{aligned} [\text{H}^+] &= \sqrt{c \times K_{a,1}} \\ &= \sqrt{0.200 \times 10^{-2.2}} = \underline{\underline{0.0355 \text{ mol dm}^{-3}}} \\ \text{pH} &= -\lg(0.0355) = \underline{\underline{1.45}} \end{aligned}$$

Examiner's Comments:

Students clearly did not take into account of the statement on ignoring  $pK_2$  and  $pK_3$  and calculated the pH when  $3\text{H}^+$  is liberated which is wrong.

- (iv) Sketch the pH-volume added curve you would expect to obtain when  $40 \text{ cm}^3$  of  $0.200 \text{ mol dm}^{-3}$  NaOH(aq) is added to  $10 \text{ cm}^3$  sample of solution N. Mark clearly the initial pH and the point(s) of maximum buffering capacity. [3]



Examiner's Comments:

Generally was poorly done. Since there are 3  $pK_a$  values, there should be 3 equivalence points (3 vertical segments in the graph) and 3 buffers shown by the max buffering capacity values at 2.2, 9.0 and 10.5 at  $5 \text{ cm}^3$ ,  $15 \text{ cm}^3$  and  $25 \text{ cm}^3$  respectively. Many did not state the volumes and only state the pH values of the buffers and so lost 1 mk for that. Must also calculate the volume of NaOH needed at the respective equivalence pts \*( $10 \text{ cm}^3$ ,  $20 \text{ cm}^3$  and  $30 \text{ cm}^3$ ) and shown clearly on the graph.

[Total: 20]

- 4 (a) Group 2 carbonates decompose when heated to form the metal oxide and carbon dioxide

- (i) Suggest a mechanism for the decomposition of the carbonate ion by adding two curly arrows on Fig. 4.1.

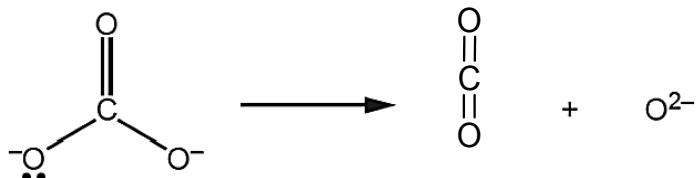


Fig. 4.1

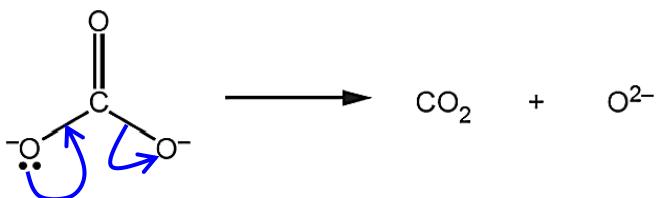
[1]

Nickel carbonate,  $\text{NiCO}_3$ , and lithium carbonate,  $\text{Li}_2\text{CO}_3$ , decompose on heating in a similar manner to the Group 2 carbonates.

- (ii) Suggest why  $\text{NiCO}_3$  decomposes more readily than  $\text{CaCO}_3$ . [2]

- (iii) Suggest why the Group 1 carbonates, other than  $\text{Li}_2\text{CO}_3$ , do not decompose when heated. [1]

(i)



- (ii)  $\text{Ni}^{2+}$  has a higher charge density than  $\text{Ca}^{2+}$  since the radius/size of  $\text{Ni}^{2+}$  is smaller.

Hence  $\text{Ni}^{2+}$  has a greater ability to polarise the large  $\text{CO}_3^{2-}$  anion (or greater polarising power) than  $\text{Ca}^{2+}$  and the C—O bond in  $\text{CO}_3^{2-}$  is weakened to a larger extent for  $\text{NiCO}_3$ .

Since it is easier to break the C—O bond in  $\text{NiCO}_3$ ,  $\text{NiCO}_3$  is thermally less stable and it decomposes more readily than  $\text{CaCO}_3$ .

- (iii) Other Group 1 cations have low/lower charge density due to their large/larger radius/size and hence they cannot polarise the large  $\text{CO}_3^{2-}$  anion (or they have low polarising power).

∴ other Group 1 carbonates do not decompose when heated.

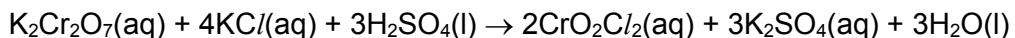
#### Examiner's Comments:

(i) Many didn't get the credit due to the first curly arrow. The first curly arrow should point from the lone pair (given) to the bond. Many pointed the arrow to the carbon instead.

(ii) This part was generally quite well done. Some discussed charge density and polarising power of Ni vs Ca instead of  $\text{Ni}^{2+}$  vs  $\text{Ca}^{2+}$ . Some compared ionic bond strength.

(iii) Many did not discuss the radii of  $\text{M}^+$  as compared to  $\text{Li}^+$ .

- (b) Chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ , can be prepared by heating a mixture of potassium dichromate(VI) and potassium chloride with concentrated sulfuric acid.

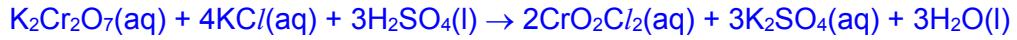


Use the data in Table 4.1 to calculate the enthalpy change of the reaction,  $\Delta H_r$ .

**Table 4.1**

compound	enthalpy change of formation, $\Delta H_f^\ominus$ / kJ mol $^{-1}$
$\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$	-2061
$\text{KCl}(\text{aq})$	-437
$\text{H}_2\text{SO}_4(\text{l})$	-814
$\text{CrO}_2\text{Cl}_2(\text{aq})$	-580
$\text{K}_2\text{SO}_4(\text{aq})$	-1438
$\text{H}_2\text{O}(\text{l})$	-286

[2]



$$(-2061) \quad 4(-437) \quad 3(-814) \quad 2(-580) \quad 3(-1438) \quad 3(-286)$$

$$\begin{aligned}\Delta H_r^\ominus &= \sum m \Delta H_f^\ominus (\text{products}) - \sum n \Delta H_f^\ominus (\text{reactants}) \\ &= 2(-580) + 3(-1438) + 3(-286) - (-2061) - 4(-437) - 3(-814) \\ &= \underline{\underline{-81.0}} \text{ (or } \underline{\underline{81}} \text{)} \text{ kJ mol}^{-1}\end{aligned}$$

Examiner's Comments:

This was quite well done. Those who solved by energy cycle were less successful in getting the correct answer. Some used the wrong formula and ended with a +ve sign in their answer.

- (c) (i) Define what is meant by the standard enthalpy change of atomisation of calcium.

[1]

It is the heat energy absorbed when 1 mole of calcium gaseous atoms,  $\text{Ca(g)}$ , is formed from its element at standard state,  $\text{Ca(s)}$ , at 298 K and 1 bar.

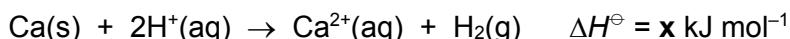
[1]

Examiner's Comments:

This was not well done.

Many did not state "1 mole", the standard conditions "298 K & 1 bar" or make reference to Ca. It is inappropriate to state "solid Ca atoms" even though the chemical symbol ( $\text{Ca(s)}$ ) may seem to imply this as Ca element in its standard state is a metal with strong electrostatic attractions between the metal cations and the delocalised valence electrons.

- (ii) The ionic equation for the reaction of calcium with hydrochloric acid is shown below.



By constructing an energy cycle using the data in Table 4.2, and data from the *Data Booklet*, calculate a value for  $\mathbf{x}$ .

**Table 4.2**

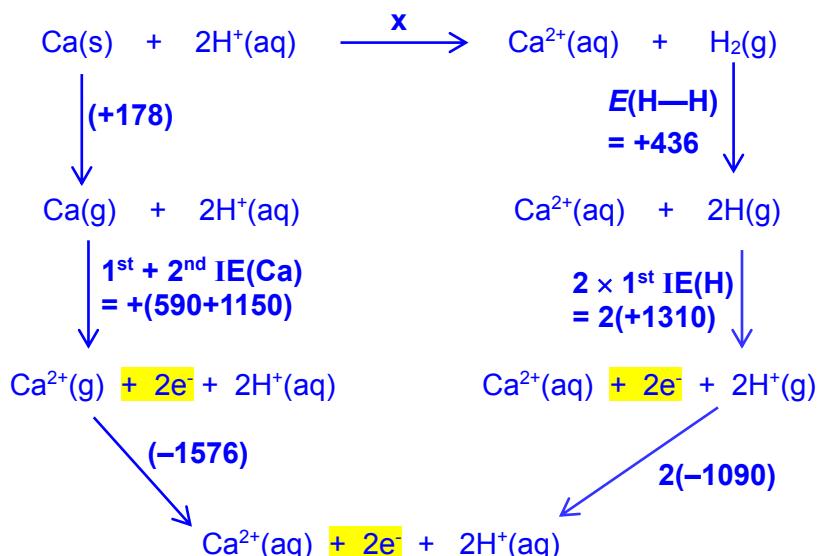
standard enthalpy change of atomisation of Ca(s)	+178 kJ mol <sup>-1</sup>
standard enthalpy change of hydration of Ca <sup>2+</sup> (g)	-1576 kJ mol <sup>-1</sup>
standard enthalpy change of hydration of H <sup>+</sup> (g)	-1090 kJ mol <sup>-1</sup>

[3]

- (iii) The standard enthalpy change for the reaction between Ca(s) and CH<sub>3</sub>COOH(aq) is less negative than  $\mathbf{x}$ .

Suggest an explanation for this.

(i)



By *Hess' Law*,

$$\begin{aligned} \mathbf{x} &= +(+178) + (590 + 1150) + (-1576) - 2(-1090) - 2(+1310) - (+436) \\ &= \underline{-534} \end{aligned}$$

Examiner's Comments:

This was generally not well done.

Some students did not close their energy cycles and hence were not successful in getting the correct final answer.

BOD was given to those who left out '2e<sup>-</sup>' in their IE eqn.

- (ii)  $\text{HCl}$  is a strong acid which ionises/dissociates completely in water while  $\text{CH}_3\text{COOH}$  is a weak acid which ionises/dissociates partially in water. Some heat energy is absorbed to fully/completely ionise/dissociate the  $\text{CH}_3\text{COOH}$ .

Hence  $\Delta H^\ominus$  is less exothermic than  $x$ .

Examiner's Comments:

This was generally not well done.

Common mistakes are “heat was lost to the surroundings” and “the bond energy was an average value”.

- (d) Alkynes, compounds containing a  $\text{C}\equiv\text{C}$ , can react with carbonyl compounds under basic conditions as shown in reaction 1 in Fig.4.2.

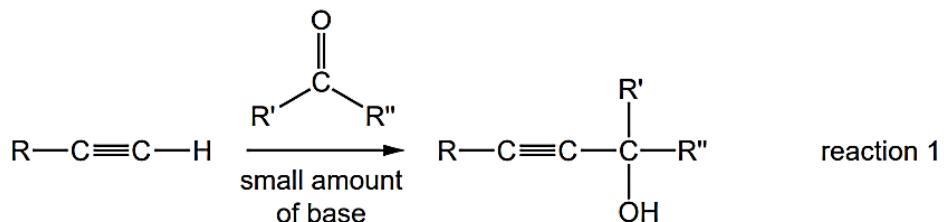


Fig. 4.2

An alkyne, **Q**, and a carbonyl compound, **R**, react together to form compound **P** as shown in Fig. 4.1.

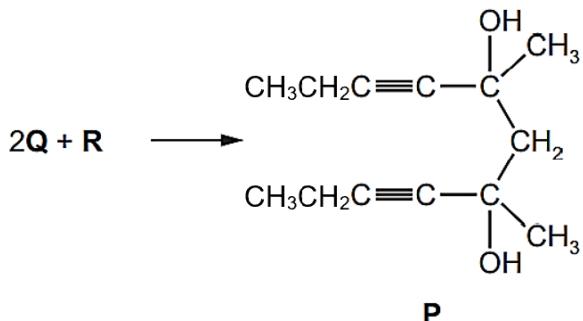
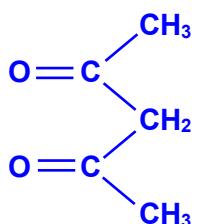


Fig. 4.3

Use reaction 1 to suggest the structures of **Q** and **R**.

[1]



Examiner's Comments:

A significant number of students did not attempt this question.

Some students have difficulty deducing the structure of R.

- (e) The anti-inflammatory drug ibuprofen can be synthesised in the reaction scheme as shown in Fig. 4.4.

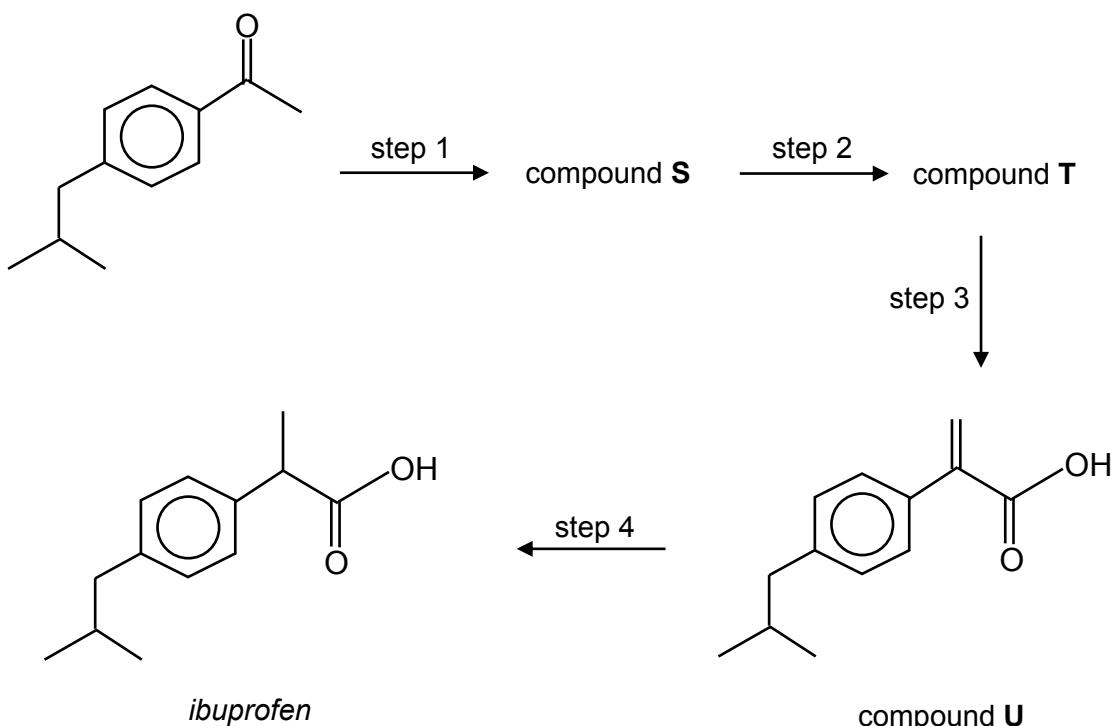
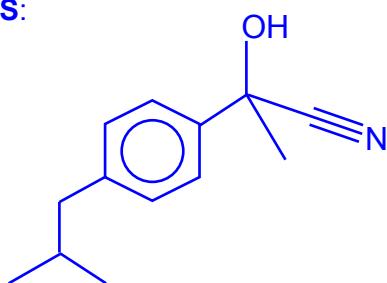
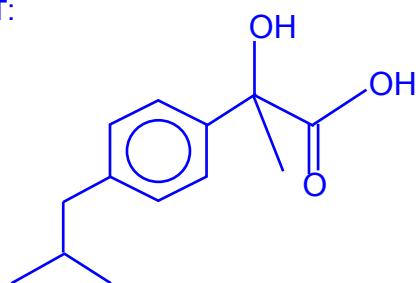


Fig. 4.4

- (i) Identify compounds **S** and **T**.

[2]

**S:****T:**

- (ii) State the reagents and conditions for steps 1 to 4.

[4]

step 1: HCN, trace amount of NaCN (or NaOH), cold

step 2: H<sub>2</sub>SO<sub>4</sub>(aq) (or HCl(aq)), heat

step 3: excess concentrated H<sub>2</sub>SO<sub>4</sub>, heat  
OR Al<sub>2</sub>O<sub>3</sub>, heat (or high temperature)

step 4: H<sub>2</sub>, Ni, heat OR H<sub>2</sub>, Pt, r.t (emphasise Pt no heat).

<p>(i) OR S:</p> <p>[1]</p>	<p>T:</p> <p>[1]</p>
<p>(ii)</p> <p>step 1: HCN, trace amount of NaCN (or NaOH), cold [1] reject 'heat'</p> <p>step 2: excess concentrated <math>H_2SO_4</math>, heat [1] reject '<math>H_2SO_4(aq)</math>' OR <math>Al_2O_3</math>, heat (or high temperature)</p> <p>step 3: <math>H_2SO_4(aq)</math> (or <math>HCl(aq)</math>), heat [1] must state "aq"</p> <p>step 4: <math>H_2</math>, Ni, heat OR <math>H_2</math>, Pt, r.t [1]</p>	

Examiner's Comments:

A significant number of students did not complete this part question.

- (i) Many students could get the structures of S and T. Some left out the methyl group.
- (ii) Many students could get step 1 and 4 correct. Step 2 and 3 proved to be challenging for students esp the elimination step.

- (iii) Compound **U** reacts with  $\text{Br}_2(\text{aq})$  to give two isomers as shown in Fig 4.5.

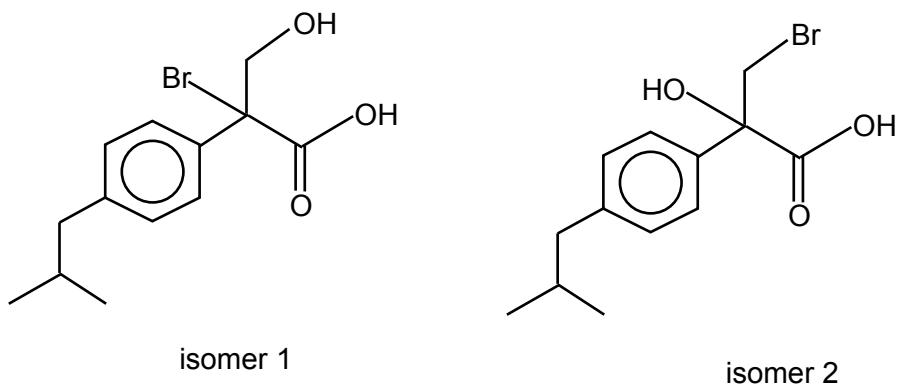
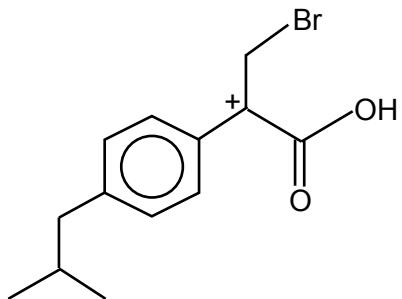


Fig. 4.5

State which isomer is formed at higher proportion. Explain your answer.

[2]

- (iii) Isomer 2.



The tertiary carbocation to form isomer 2 is more stable due to resonance effect as the positive charge on benzylic C can be delocalised into the benzene ring or the adjacent  $\text{C}=\text{O}$  through p-p orbital overlap, thereby dispersing the charge.

Examiner's Comments:

A significant number of students did not complete this part question.

This part proved to be challenging for students as nearly all students could not explain their answer.

The common mistake was to state that the reaction intermediate has "three/more electron-donating alkyl groups bonded to  $\text{C}^+$ ".

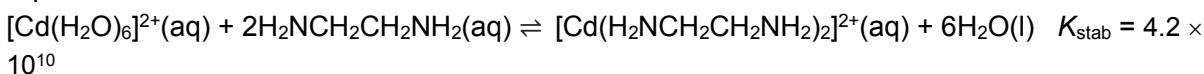
[Total: 20]

- 5 (a) Cadmium ions form complexes with primary amines and with 1,2-diaminoethane.

equilibrium I:



equilibrium II:



- (i) Write an expression for the stability constant,  $K_{\text{stab}}$ , for equilibrium I, and state its units.

[1]

(i)

$$K_{\text{stab}} = \frac{[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}}{[\text{Cd}(\text{H}_2\text{O})_6]^{2+} [\text{CH}_3\text{NH}_2]^4}; \quad \text{units : mol}^{-4} \text{ dm}^{12}$$

Examiner's comments:

This was not well answered. Common mistakes:

- Including water in the expression when it is an aqueous system
- Not including [ ] to represent concentration
- Units are often incorrect.

Cadmium ions are toxic and need to be removed from some water supplies. This is often done by adding a complexing agent such as  $\text{CH}_3\text{NH}_2(\text{aq})$ .

- (ii) A sample of ground water contains  $1.00 \times 10^{-4}$  mol  $\text{dm}^{-3}$  of  $\text{Cd}^{2+}(\text{aq})$ . Calculate the concentration of  $\text{CH}_3\text{NH}_2(\text{aq})$  needed to reduce the concentration of  $\text{Cd}^{2+}(\text{aq})$  in the sample of ground water to  $\frac{1}{1000}$  of its original concentration.

[2]

	$[\text{Cd}(\text{H}_2\text{O})_6]^{2+} + 4\text{CH}_3\text{NH}_2(\text{aq}) \rightleftharpoons [\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$			
Initial/mol $\text{dm}^{-3}$	: $1.00 \times 10^{-4}$	$y$	0	-
Change/mol $\text{dm}^{-3}$	: $-9.99 \times 10^{-5}$	$4(-9.99 \times 10^{-5})$	$+9.99 \times 10^{-5}$	-
Eqm/mol $\text{dm}^{-3}$	: $1.00 \times 10^{-7}$	$y - (3.996 \times 10^{-4})$	$9.99 \times 10^{-5}$	-
		$= z$		

$$K_{\text{stab}} = \frac{9.99 \times 10^{-5}}{(1 \times 10^{-7})(z)^4} = 3.6 \times 10^6$$

$$z^4 = 2.775 \times 10^{-4} \therefore z = 0.129$$

$$y - (3.996 \times 10^{-4}) = 0.129$$

$$\Rightarrow y = 0.129 \Rightarrow [\text{CH}_3\text{NH}_2] \text{ needed is } 0.129 \text{ mol dm}^{-3}$$

Examiner's comments:

This was not well answered. Most students are only able to calculate the concentration of  $[\text{Cd}(\text{H}_2\text{O})_6]^{2+}$  and unable to proceed further or they calculated the concentration of  $[\text{Cd}(\text{CH}_3\text{NH}_2)_4]^{2+}$  and presented that as concentration of  $\text{CH}_3\text{NH}_2$ .

- (iii) 1,2-diaminoethane is a bidentate ligand. State the coordination number and the geometry of  $[\text{Cd}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]^{2+}$  complex ion.

[1]

- (iii) Coordination no. is 4.

Geometry is tetrahedral or square planar.

Examiner's comments:

This was not well answered. Many students gave the coordination number as 2 and shape as linear by looking at the number of ligands bonded without considering that the ligand is bidentate.

- (b) The structure picolinic acid is shown.

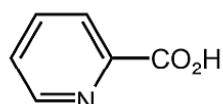


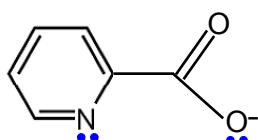
Fig. 5.1

When picolinic acid is placed in basic solution, a bidentate ligand, **V** in Fig. 5.1, is formed.

- (i) Draw the structure of **V** and on this structure, draw the lone pair of electrons on the atoms that could form coordinate bonds to a transition metal ion.

[1]

- (i)



Examiner's Comments:

A significant number of students did not complete this part question. The lone pair on N is often missing.

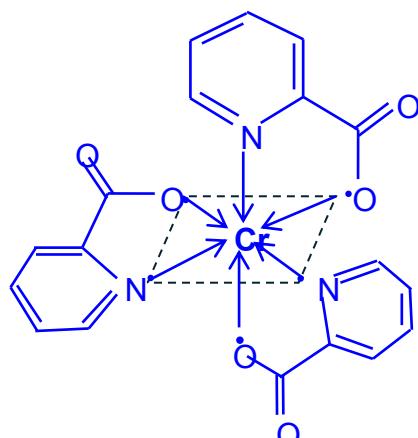
- (ii) **V** reacts with aqueous chromium(III) ions,  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ , in a 3 : 1 ratio to form a new neutral complex.

State the type of reaction that has occurred.

Draw a diagram of the structure of the new complex formed, showing the 3-dimensional arrangement around the Cr(III) ion.

[2]

- (ii) Ligand exchange reaction.



Examiner's Comments:

A significant number of students did not complete this part question.

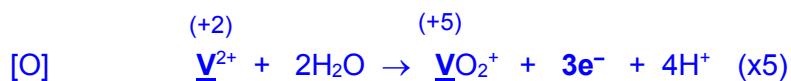
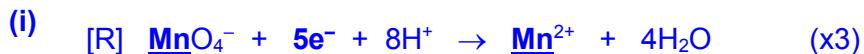
- (c) A 0.155 g of impure sample of ammonium vanadate(V),  $\text{NH}_4\text{VO}_3$ , is dissolved in an excess of dilute acid.

In this solution all vanadium is present as  $\text{VO}_2^+$  ions. An excess of zinc powder is added to the solution and all the  $\text{VO}_2^+$  ions are reduced to  $\text{V}^{2+}$  ions. The mixture is filtered to remove any remaining zinc powder.

When the resulting solution is titrated,  $21.10 \text{ cm}^3$  of  $0.0250 \text{ mol dm}^{-3}$  acidified  $\text{MnO}_4^-$  oxidises all  $\text{V}^{2+}$  ions back to  $\text{VO}_2^+$  ions.

- (i) Construct an ionic equation for the reaction between  $\text{V}^{2+}$  and acidified  $\text{MnO}_4^-$ .

[1]



Examiner's Comments:

This was not well answered. Many of the equation is not balanced correctly.

- (ii) Calculate the percentage by mass of  $\text{NH}_4\text{VO}_3$  in the 0.155 g impure sample of  $\text{NH}_4\text{VO}_3$ .

[2]

$$(ii) n(\text{MnO}_4^-) = \frac{21.10}{1000} \times 0.0250 = \underline{\underline{5.275 \times 10^{-4} \text{ mol}}}$$

$$n(\text{V}^{2+}) = \frac{5}{3} \times 5.275 \times 10^{-4} = \underline{\underline{8.792 \times 10^{-4} \text{ mol}}}$$

$= n(\text{VO}_2^+)$  present  $= n(\text{NH}_4\text{VO}_3)$  in 0.155 g impure sample.

$$\text{Mass of } \text{NH}_4\text{VO}_3 \text{ present} = 8.792 \times 10^{-4} \times \underline{\underline{116.9}} = \underline{\underline{0.1028 \text{ g}}}$$

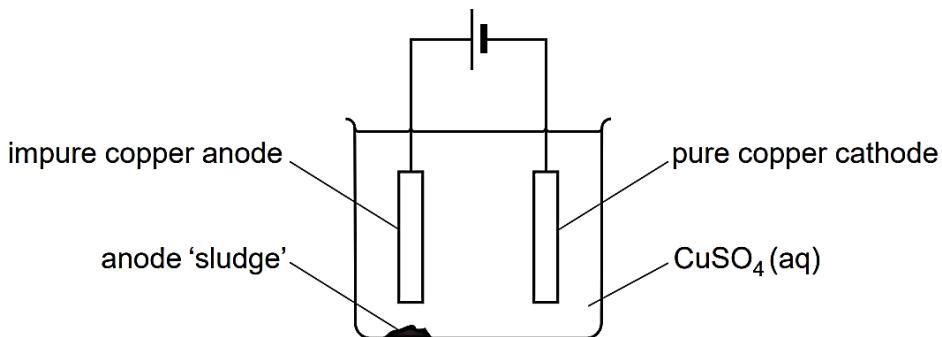
$$\therefore \% \text{ by mass of } \text{NH}_4\text{VO}_3 = \frac{0.1028}{0.155} \times 100 = \underline{\underline{66.3\%}}$$

Examiner's Comments:

This was not well answered. Many left this part blank. Some were able to gain some credit based on the equation given.

- (d) When a particular copper ore was reduced, an alloy was produced which was composed mainly of copper, but with minor nickel and silver impurities.

In order to purify it, this alloy was made the anode of an electrolytic cell similar to the one shown in Fig. 5.2.

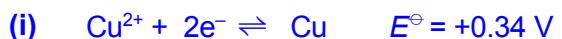


**Fig. 5.2**

At the impure copper anode, Cu is oxidised to  $\text{Cu}^{2+}$  which goes into the solution. At the pure copper cathode,  $\text{Cu}^{2+}$  is reduced to Cu which deposits on the cathode.

- (i) Explain, with reference to relevant  $E^\ominus$  values from the *Data Booklet*, what happens to the nickel and silver impurities during this purification procedure.

[2]



- Ni will be oxidised at the anode to  $\text{Ni}^{2+}$  as  $E^\ominus(\text{Ni}^{2+}/\text{Ni})$  is more negative than  $E^\ominus(\text{Cu}^{2+}/\text{Cu})$ .
- $\text{Ni}^{2+}$  will not be reduced to Ni at the cathode as  $E^\ominus(\text{Ni}^{2+}/\text{Ni})$  is less positive (or more negative) than  $E^\ominus(\text{Cu}^{2+}/\text{Cu})$ .  $\therefore \text{Ni}^{2+}$  will be remained in solution.
- Ag will not be oxidised at the anode to  $\text{Ag}^+$  as  $E^\ominus(\text{Ag}^+/\text{Ag})$  is less negative (or more positive) than  $E^\ominus(\text{Cu}^{2+}/\text{Cu})$
- It will be collected as ‘anode sludge’ at the base of the cell.

Examiner's Comments:

This was not well answered. Many left this part blank. Many students did not compare the electrode potential with  $E^\ominus(\text{Cu}^{2+}/\text{Cu})$  or state the electrode in which oxidation and reduction occur.

- (ii) Calculate the expected increase in mass of the cathode when a current of 15.0 A was passed through the cell for 5.0 hours.

[2]



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

$$n_e = \frac{15 \times (5 \times 60 \times 60)}{96500} = \underline{\underline{2.798 \text{ mol}}}$$

$$n(\text{Cu}) \text{ deposited} = \frac{1}{2} \times 2.798 \times 63.5 = \underline{\underline{88.8 \text{ g}}}$$

Examiner's Comments:

This was not well answered. Many left this part blank. Common mistake is to omit the mole ratio of Cu.

(e) When yellow-brown anhydrous  $\text{CuCl}_2$  is dissolved in water, it gives a blue solution.

- (i) When the blue solution is boiled with copper metal and aqueous hydrochloric acid, a colourless solution **W**, which contains complex ion of copper and chlorine, is formed.

After filtering off the excess copper metal and diluting the colourless solution with water, a white solid **X**, containing copper and chlorine only, is formed. The oxidation number of copper in **W** and **X** are the same.

Identify the complex ion in **W** and the solid compound **X**.

[2]

- (i) Complex ion in **W** :  $\text{CuCl}_2^-$  Solid compound **X** :  $\text{CuCl}$

Examiner's Comments:

This was not well answered. Many left this part blank.

- (ii) When concentrated hydrochloric acid is added to the blue solution, the colour changes to yellow-green. When water is added to the resulting yellow-green solution, the colour changes back to blue.

Suggest an explanation of these observations with an aid of a balanced equation.

[2]

- (ii) When concentrated HCl is added to  $\text{Cu}^{2+}(\text{aq})$ ,



high  $[\text{Cl}^-]$  causes the position of equilibrium of (1) to shift right, forming yellow  $[\text{CuCl}_4]^{2-}$ .

Solution appeared yellow-green due to mixture of pale blue  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  and yellow  $[\text{CuCl}_4]^{2-}$  presence in the solution.

Addition of water causes the concentrations of all aqueous ions to fall while  $[\text{H}_2\text{O}]$  remains relatively constant. This causes the position of equilibrium of (1) to shift left since there are more aqueous concentration terms on the left-hand side, forming back the original blue  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ .

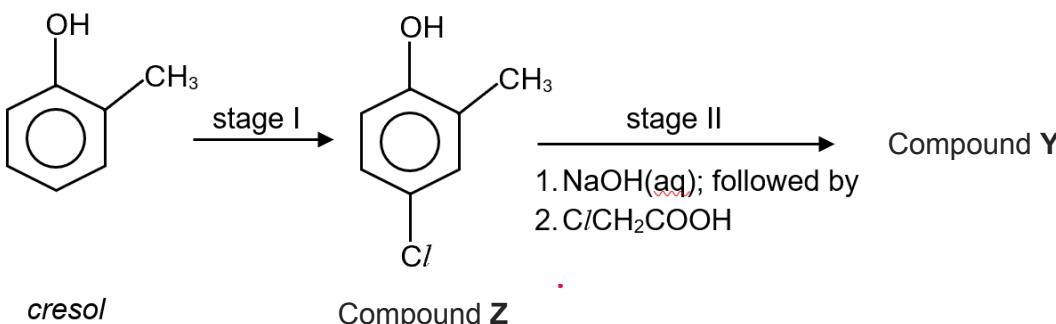
2(✓) [1]

Examiner's Comments:

This was not well answered. Many left this part blank.

- (f) Cresols are precursors or synthetic intermediate to other compounds and materials, including plastics, pesticides, pharmaceuticals, and dyes.

An organic compound **Y**, a selective herbicide, can be synthesised from cresol by the following route in Fig. 5.3.

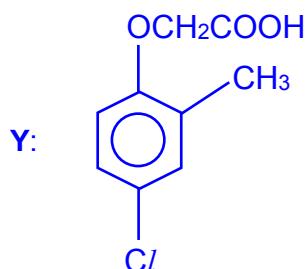


**Fig. 5.3**

- (i) Give the structure of compound **Y**.

[1]

(i)



Examiner's Comments:

This was not well answered. Many students thought that the product formed is an ester. They forgot that to form a phenyl ester, acyl chloride is required. Many did not consider nucleophilic substitution as the reaction that occurs.

- (ii) Suggest why NaOH(aq) is added to compound **Z** in stage II before C/CH<sub>2</sub>COOH is added.

[1]

- (ii) NaOH(aq) is added to convert Z to phenoxide which is a better/stronger nucleophile with a full negative charge.

Examiner's Comments:

This was not well answered. Many left this part blank. Credit were given for students who drew the structure of the phenoxide.

[Total: 20]

**Additional answer space**

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

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**JURONG PIONEER JUNIOR COLLEGE  
JC2 PRELIMINARY EXAMINATION 2024**

**CHEMISTRY**

**9729/04**

**Higher 2**

Paper 4 Practical

**13 August 2024**

**2 hours 30 minutes**

**Candidates answer on the Question paper.**

Additional Materials: As listed in the Confidential Instructions

**READ THESE INSTRUCTIONS FIRST**

Write your name, class and exam index number on all the work you hand in.

Give details of the practical shift and laboratory where appropriate, in the boxes provided.

Write in dark blue or black pen.

You may use a HB pencil for any diagrams, graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

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

You may lose marks if you do not show your working or if you do not use appropriate units.

Qualitative Analysis Notes are printed on pages 20 and 21.

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.

Shift	
Laboratory	

For Examiner's Use	
1	/ 14
2	/ 18
3	/ 11
4	/ 12
<b>Total</b>	<b>/ 55</b>

This document consists of **21** printed pages.

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

## 1 Investigation of some inorganic and organic reactions

You are provided with the following samples:

**FA 1** is an aqueous solution of an **organic compound, Y**.

**FA 2** is an aqueous solution of an **organic compound, Z**, which is an **isomer of Y**.

**FA 3** is a **solid sample** with molecular formula **XO<sub>n</sub>**, where **X** is a metal.

You will perform tests to identify:

- the structure of **Y** in **FA 1**
- the functional group of **Z** in **FA 2**
- the cation in **FA 3**

(a) (i) Perform the tests described in Table 1.1, and record your observations in the table.

Table 1.1

	tests	observations
1	To 1 cm depth of <b>FA 1</b> in a test-tube, add a small piece of sodium.  <b>Redox rxn. H<sub>2</sub>? Identify —OH in alcohol, phenol &amp; RCOOH.</b>	No observable change.  No —OH group ⇒ alcohol, phenol & RCOOH absent.
2	To 1 cm depth of aqueous $\text{AgNO}_3$ in a test-tube, add 1 cm depth of aqueous $\text{NaOH}$ . Then add aqueous $\text{NH}_3$ until the precipitate just dissolves.  <b>Preparing Tollens' reagent, <math>\text{Ag}(\text{NH}_3)_2^+(\text{aq})</math>.</b>  To this mixture, add 1 cm depth of <b>FA 1</b> . Heat the mixture in the <b>hot water-bath</b> .  <b>Oxidation. Silver mirror/grey ppt.? Identify aldehydes.</b>	<b>Brown ppt. (✓<sub>1</sub>)</b> dissolves to give a <b>colourless solution. (✓<sub>2</sub>)</b>  Brown $\text{Ag}_2\text{O}(\text{s})$ dissolves in $\text{NH}_3(\text{aq})$ to give colourless $\text{Ag}(\text{NH}_3)_2^+(\text{aq})$ Tollens' reagent.  Upon warming with FA 1, <b>no silver mirror (or no grey ppt.)</b> (or <b>no observable change</b> ). (✓ <sub>3*</sub> )  Aldehyde absent.
3	To 1 cm depth of <b>FA 1</b> in a test-tube, add 10 drops of aqueous sodium hydroxide.  Now add aqueous iodine dropwise, until a <b>permanent yellow/orange colour</b> is obtained.  Warm the mixture in the <b>hot water bath</b> for 2 minutes.  <b>Iodoform Test. Pale yellow ppt.? Identify ethanal &amp; ketones with <math>-\text{COCH}_3</math> and alcohols with <math>-\text{CH}(\text{OH})\text{CH}_3</math>.</b>	pale <b>yellow ppt. (✓<sub>4*</sub>)</b> formed.  <b><math>\text{CHI}_3</math> ppt. formed.</b> ⇒ ketone with $-\text{COCH}_3$ present.  4(✓) [2]; 1(✓*) [1] (✓ <sub>3*</sub> ) or (✓ <sub>4*</sub> )

[2]

- (ii) The molecular formula of Y is C<sub>3</sub>H<sub>6</sub>O and it has one functional group. Use your observations in Table 1.1 to deduce the structure of Y in FA 1.

FA 1 is a ketone with with –COCH<sub>3</sub>

Structure of Y in FA 1: CH<sub>3</sub>COCH<sub>3</sub>. [1]

[1]

- (iii) FA 2 contains an organic compound, Z, which is an isomer of Y. {M.F. C<sub>3</sub>H<sub>6</sub>O}

Z contains one functional group.

Devise one confirmatory test, other than those stated in Table 1.1, using the bench reagents provided to identify the functional group present in Z.

Carry out the test. Record details of the test performed and observations made in Table 1.2.

**Note:** Z is isomeric with Y  $\Rightarrow$  M.F. of Z is C<sub>3</sub>H<sub>6</sub>O.

An alkene or alcohol with C<sub>3</sub>H<sub>6</sub>O will have 2 functional groups, e.g. CH<sub>2</sub>=CHCH<sub>2</sub>OH.

Since Z contains only one functional group, Z is an aldehyde.

Table 1.2

Confirmatory Test	Observations
<p>To 1 cm depth of FA 2 in a test-tube, add 1 cm depth of *<u>dilute sulfuric acid</u> (or <u>dilute H<sub>2</sub>SO<sub>4</sub></u>) and a few drops of *<u>aqueous potassium manganate(VII)</u> (or <u>KMnO<sub>4</sub>(aq)</u>). <u>Heat</u> (or <u>Warm</u>) the mixture in the hot water-bath. [1]</p> <div style="border: 1px solid black; padding: 5px; margin-top: 10px;"> <p>*State the name or correct formula of the reagent used according to the label on the reagent bottle.</p> </div>	<p>Purple KMnO<sub>4</sub> decolourised [1] upon heating.</p>

The functional group present in Z: aldehyde [1] with correct test & observations

[3]

- (b) (i) Perform the tests described in Table 1.3, and record your observations in the table. Test and identify any gases evolved. If there is no observable change, write **no observable change**.

**FA 3 is a black solid.**

**Table 1.3**

tests		observations
<p>1 Place 1 cm depth of <b>sulfuric acid</b> in a test-tube. Add a spatula of <b>FA 3</b> to this test-tube, followed by another 2 cm depth of <b>aqueous potassium iodide</b>.</p> <p><b>Redox rxn? Brown I<sub>2</sub> soln? I<sup>-</sup> oxidises to I<sub>2</sub>? FA 3 is reduced?</b></p> <p>Filter the mixture into a clean test-tube and collect the filtrate.</p> <p><b>Filtrate colour? Residue colour?</b></p> <p>To the filtrate, add <b>aqueous sodium thiosulfate</b> dropwise, with shaking, until the solution first becomes colourless.</p> <p><b>I<sub>2</sub> + 2S<sub>2</sub>O<sub>3</sub><sup>2-</sup> → S<sub>4</sub>O<sub>6</sub><sup>2-</sup> + 2I<sup>-</sup> Brown I<sub>2</sub> reduces to colourless I<sup>-</sup>.</b></p> <p>Divide the resulting solution into two portions. These will be used in tests 2 and 3 respectively.</p>	<p><b>Brown/ orange / yellow solution obtained. (*✓<sub>1</sub>)</b></p> <p><b>I<sup>-</sup> oxidises to brown I<sub>2</sub> while FA 3 is reduced.</b></p> <p><b>Brown/orange/yellow filtrate (*✓<sub>1</sub>) Black/ dark brown residue. (✓<sub>2</sub>)</b></p>   <p><b>Brown/orange/yellow solution turns colourless.</b></p>	
<p>2 To the first portion, add <b>aqueous sodium hydroxide</b> slowly until no further change is seen.</p> <p>Leave the mixture on standing for 2 minutes.</p> <p><b>ppt? ppt sol. in xs? colour change of ppt. on standing?</b></p>	<p><b>Off-white/light brown ppt.</b></p>  <p><b>insoluble in excess NaOH. (✓<sub>3</sub>)</b></p>  <p><b>ppt. turned darker brown on standing. (*✓<sub>4</sub>)</b></p>  <p><b>Mn<sup>2+</sup> present in the filtrate.</b></p>	

[3]

3	<p>To the second portion, add aqueous ammonia slowly until no further change is seen.</p> <p><b>ppt? ppt sol. in xs?</b></p>	<p><u>Off-white/light brown ppt.</u> <u>insoluble in excess NH<sub>3</sub>.</u> (✓<sub>5</sub>)</p> <p><u>ppt. turned darker brown on standing.</u> (*✓<sub>4</sub>)</p>
4	<p>Place 3 cm depth of aqueous H<sub>2</sub>O<sub>2</sub> into a test-tube. Add a spatula of FA 3 to this test-tube.</p> <p><b>O<sub>2</sub> gas bubbles?</b> H<sub>2</sub>O<sub>2</sub> oxidises to O<sub>2</sub>? H<sub>2</sub>O<sub>2</sub> → O<sub>2</sub> + 2H<sup>+</sup> + 2e<sup>-</sup> or H<sub>2</sub>O<sub>2</sub> undergoes catalytic decomposition to give O<sub>2</sub>? 2H<sub>2</sub>O<sub>2</sub> → O<sub>2</sub> + 2H<sub>2</sub>O</p> <p><b>Note:</b> With H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub> gas will not form.</p>	<p><b>Brisk effervescence</b> noted. (✓<sub>6</sub>) <u>O<sub>2</sub> (✓<sub>7</sub>) gas relights a glowing splint.</u> (✓<sub>8</sub>)</p> 
		<p>No observable change to FA 3.</p> <p>7-8(✓) [3]; 4-6(✓) [2]; 2-3(✓) [1]</p>

(ii) Identify the metal ion in the filtrate.

metal ion: Mn<sup>2+</sup> [1]

In Test 1, KI(aq) reduces FA 3 to Mn<sup>2+</sup>(aq) which is collected in the filtrate.

Since FA 3 has M.F. of XOn (where X is a metal), X is Mn; and Mn in FA 3 should have higher oxidation state than +2.

⇒ FA 3 is MnO<sub>2</sub> or MnO<sub>3</sub> (not MnO).

[1]

(iii) Deduce the oxidation state of X in FA 3.

oxidation state of X in FA 3: +4 or +6. [1]

[1]

- (iv) Suggest the nature of FA 3 in the reaction occurring in Test 1. Give evidence from the observations in your experiment.

nature of FA 3: oxidising or oxidising agent [1]

evidence:

- FA 3/MnO<sub>n</sub> oxidises I<sup>-</sup>/KI to brown/orange/yellow I<sub>2</sub>(aq) after adding KI(aq). [1]

OR

- FA 3/MnO<sub>n</sub> is reduced to colourless Mn<sup>2+</sup>(aq) which gives a off-white/light brown Mn(OH)<sub>2</sub> ppt. insoluble in excess NaOH(aq)/NH<sub>3</sub>(aq). The ppt. darkened due to formation of brown Mn(OH)<sub>3</sub>(s) when contact in air on standing. [1]

[2]

- (v) Suggest the role of FA 3 in the reaction in Test 4.

role of FA 3: heterogeneous catalyst [1]

FA 3 is acting as a heterogeneous catalyst to increase the rate of decomposition of H<sub>2</sub>O<sub>2</sub>. Hence there is a rapid production of O<sub>2</sub> gas (brisk effervescence).



[1]

[Total: 14]

## 2 Determination of the molar enthalpy change of a reaction by an indirect method

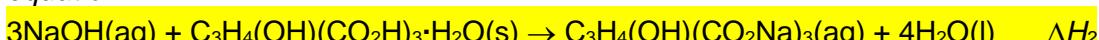
Sodium hydroxide and sulfuric acid react according to equation 1.

*equation 1*



Sodium hydroxide and citric acid crystals react according to equation 2.

*equation 2*



In this question, you will perform two experiments to determine the values for  $\Delta H_1$  and  $\Delta H_2$ . You will use your values of  $\Delta H_1$  and  $\Delta H_2$  to calculate a value for the enthalpy change shown in equation 3.

*equation 3*



In 2(d), you will use data provided to determine the concentration of sodium hydroxide in FA 4.

You are provided with:

FA 4 is aqueous sodium hydroxide, NaOH

FA 5 is 1.00 mol dm<sup>-3</sup> sulfuric acid, H<sub>2</sub>SO<sub>4</sub>

FA 6 is citric acid crystals, C<sub>3</sub>H<sub>4</sub>(OH)(CO<sub>2</sub>H)<sub>3</sub> · H<sub>2</sub>O

### (a) Experiment 1: Determination of the molar enthalpy change, $\Delta H_1$ , for the reaction in equation 1



You will follow the following instructions to perform the experiment.

Prepare a table in the space provided on the next page and record, to the appropriate level of precision: (**A single table!**)

- all temperatures measured,
- $T_{\text{ave}}$  and the change in temperature,  $\Delta T$  to 1 decimal place.

$\Delta T$  should be calculated using the following formula:

$$\Delta T = T_{\text{max}} - T_{\text{ave}}$$

$$T_{\text{ave}} = \frac{(\text{Volume of FA 4} \times T_{\text{FA4}}) + (\text{Volume of FA 5} \times T_{\text{FA5}})}{\text{Volume of FA 4} + \text{Volume of FA 5}}$$

#### (i) Method

1. Using a measuring cylinder, transfer 50.0 cm<sup>3</sup> of FA 4 (an excess) into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm<sup>3</sup> glass beaker.
2. Stir and measure the temperature of this FA 4,  $T_{\text{FA4}}$ .
3. Using another measuring cylinder, measure 20.0 cm<sup>3</sup> of FA 5.
4. Stir and measure the temperature of this FA 5,  $T_{\text{FA5}}$ .
5. Add the FA 5 from the measuring cylinder to the FA 4 in the Styrofoam cup.
6. Using the thermometer, stir the mixture continuously until it reaches its maximum temperature. Record this temperature,  $T_{\text{max}}$ .

## Results

$T_{FA4} / ^\circ C$	29.4	}
$T_{FA5} / ^\circ C$	29.6	
$T_{max} / ^\circ C$	38.2	
$T_{ave} / ^\circ C$	29.5	
$\Delta T / ^\circ C \text{ (or K)}$	8.7 (or +8.7)	

Using a 0.2 °C interval thermometer  
 ⇒ precision = 0.1 °C (half interval)  
 ⇒ all T readings to 1 d.p.

To 1 d.p. (following the instructions)

[1] Records all data in a single table with the required 5 correct headers and units + record all temp readings to the nearest 0.1 °C

[1] Calculates  $T_{ave}$  and  $\Delta T$  correctly to 1 d.p.

[1] Accuracy: student's  $\Delta T = \underline{8.3 \text{ to } 8.9}$

[3]

(ii) Calculate the heat change, q, for your experiment.

Assume that the specific heat capacity of the solution is  $4.18 \text{ J g}^{-1} \text{ K}^{-1}$  and that the density of the solution is  $1.00 \text{ g cm}^{-3}$ .  $\Rightarrow q = m \times c \times \Delta T$

$\Rightarrow m = \text{mass of final solution in the cup giving } \Delta T_{max}$   
 = total volume of final soln × density of final soln

$$\Delta T \text{ of } 1 ^\circ C = \Delta T \text{ of } 1 K$$

$$\Rightarrow \Delta T = 8.7 ^\circ C = 8.7 K$$

$$(38.2 + 273) - (29.5 + 273)$$

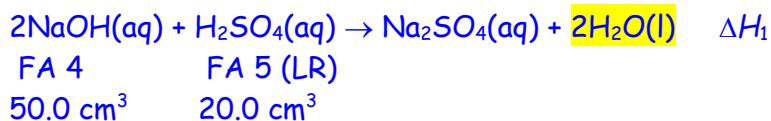
$$q = (50.0 + 20.0) \times 1.00 \times 4.18 \times \underline{8.7}$$

$$= \underline{2546 \text{ J}} = \underline{2.546 \text{ kJ}} \quad [1] \text{ ans. in J or kJ + ignore sign!}$$

$$q = \underline{2550 \text{ J or } 2.55 \text{ kJ}} \quad [1]$$

(iii) Determine the molar enthalpy change,  $\Delta H_1$ , for the reaction in equation 1. The sodium hydroxide is in excess.

Include the sign of  $\Delta H_1$  in your answer. heat evolved ⇒ exothermic,  $\Delta H_1 < 0$



$\Delta H_{neut}$  is the heat evolved when 1 mole of water is formed from the reaction of an acid and an alkali.

$\Rightarrow \Delta H_1$  is not  $\Delta H_{neut}$  since the eqn shows 2 mol of  $\text{H}_2\text{O}$  formed.  $\Delta H_1 = 2 \times \Delta H_{neut}$

$$\Rightarrow \Delta H_1 = - \left( \frac{q}{\text{amount of LR}} \right) \times \text{stoichiometric coefficient of LR}$$

$$n(\text{H}_2\text{SO}_4) \text{ reacted} = 1.00 \times \frac{20}{1000} = 0.0200 \text{ mol}$$

$$\Delta H_1 = - \left( \frac{2.546}{0.0200} \right) \times 1 = \underline{-127 \text{ kJ mol}^{-1}} \quad [1] \text{ ecf 'q' with correct sign}$$

$$\Delta H_1 = \underline{-127 \text{ kJ mol}^{-1}} \quad [1]$$

**(b) Experiment 2: Determination of the molar enthalpy change,  $\Delta H_2$ , for the reaction in equation 2**



You will follow the following instructions to perform the experiment.

In the space provided below, prepare tables (**2 tables**) in which to record for the experiment:

- all weighings and mass of **FA 6** added to an appropriate level of precision,
- all required temperature measurements and  $\Delta T$  to an appropriate level of precision.

**(i) Method**

1. Weigh the capped bottle containing **FA 6**.
2. Using a measuring cylinder, transfer  $50.0 \text{ cm}^3$  of **FA 4** into the other clean Styrofoam cup. Place this cup inside the used Styrofoam cup, which is placed in a  $250 \text{ cm}^3$  glass beaker.
3. Stir and measure the temperature of this **FA 4**,  $T_{\text{FA4}}$ .
4. Add all the **solid FA 6** to the **FA 4** in the Styrofoam cup.
5. Using the thermometer, stir the mixture continuously until it reaches its maximum temperature. Record this temperature,  $T_{\text{max}}$ .
6. Reweigh the empty bottle with its cap.

**Results**

$T_{\text{FA4}} / ^\circ\text{C}$	29.2
$T_{\text{max}} / ^\circ\text{C}$	35.0
$\Delta T / ^\circ\text{C (or K)}$	5.8 (or +5.8)

Mass of capped bottle with FA 6 / g	7.560
Mass of capped bottle with residual FA 6 / g	5.500
Mass of FA 6 added / g	2.060

[1] Tabulates all required mass readings in a single table with correct headers and units {reject "weight"} + records all mass readings to 3 d.p. + computes mass of FA 6 correctly.

[1] Records all temp data in a single table with the required 3 correct headers and units + records all temp. readings and  $\Delta T$  to the nearest  $0.1 ^\circ\text{C}$  + computes  $\Delta T$  correctly.

[1] Accuracy: student's  $(\Delta T/m) = 2.6$  to  $3.0$

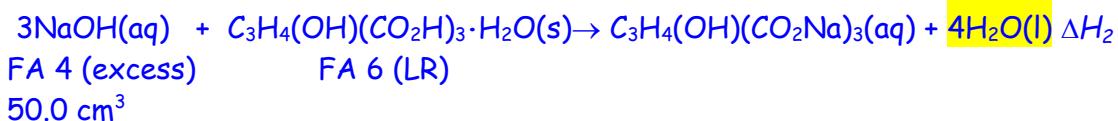
[3]

(ii) Given that:

- sodium hydroxide is used in excess;
- $M_r$  of  $C_3H_4(OH)(CO_2H)_3 \cdot H_2O$  is 210.0;
- specific heat capacity of the solution is  $4.18 \text{ J g}^{-1} \text{ K}^{-1}$ ;
- density of the solution is  $1.00 \text{ g cm}^{-3}$ ,

calculate the heat change,  $q$ , for your experiment and hence determine a value for the enthalpy change,  $\Delta H_2$ , for the reaction in equation 2.

Include the sign of  $\Delta H_2$  in your answer. {heat evolved  $\Rightarrow$  exothermic,  $\Delta H_2 < 0$ }



$$q = m \times c \times \Delta T$$

where  $m$  = mass of final solution in the cup absorbing the heat  
= total volume of final soln  $\times$  density of final solution

Assume that the added solids do not change the total volume of the final soln.  
 $\Rightarrow$  Do not include the mass of solid!

$$\begin{aligned} q &= 50.0 \times 1.00 \times 4.18 \times 5.8 \\ &= 1212 \text{ J} = 1.212 \text{ kJ} \quad [1] \text{ ans. in J or kJ + ignore sign} \end{aligned}$$

$\Delta H_2$  is not  $\Delta H_{\text{neut}}$  since the eqn shows 4 mol of  $H_2O$  formed.  $\Delta H_2 = 4 \times \Delta H_{\text{neut}}$   
 $\Rightarrow \Delta H_2 = -\left(\frac{q}{\text{amount of LR}}\right) \times \text{stoichiometric coefficient of LR}$

$$n(\text{citric acid reacted}) = \frac{2.060}{210.0} = 0.00981 \text{ mol}$$

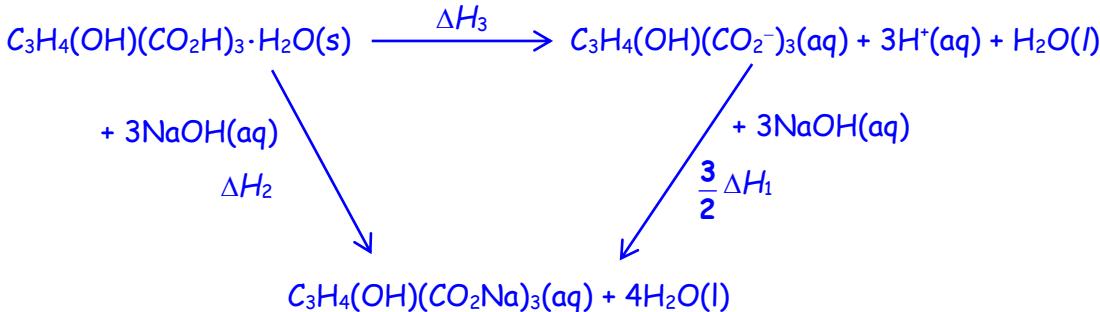
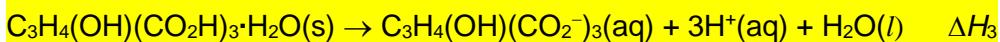
$$\Delta H_2 = -\left(\frac{1.212}{0.00981}\right) \times 1 = -124 \text{ kJ mol}^{-1} \quad [1] \text{ ecf 'q' with correct sign}$$

$$q = 1210 \text{ J or } 1.21 \text{ kJ}$$

$$\Delta H_2 = -124 \text{ kJ mol}^{-1} \quad [2]$$

- (c) Use your values of  $\Delta H_1$  and  $\Delta H_2$  to determine a value for the enthalpy change,  $\Delta H_3$ , for the reaction in equation 3.

Show your working clearly and include the sign of  $\Delta H_3$  in your answer.



$$\begin{aligned} \text{By Hess' Law, } \Delta H_3 &= \Delta H_2 - \frac{3}{2}\Delta H_1 \quad [1] \text{ with working} \\ &= -124 - \frac{3}{2}(-127) \\ &= \boxed{+66.5 \text{ kJ mol}^{-1}} \quad [1] \text{ with correct sign} \end{aligned}$$

$$\Delta H_3 = \boxed{+66.5 \text{ kJ mol}^{-1}}$$

[1] Shows working in all calculations + gives all final answers to 3 sf + gives correct units in all final ans: {for 2(a)(ii)(iii), (b)(ii)q,  $\Delta H_2$  & (c)}

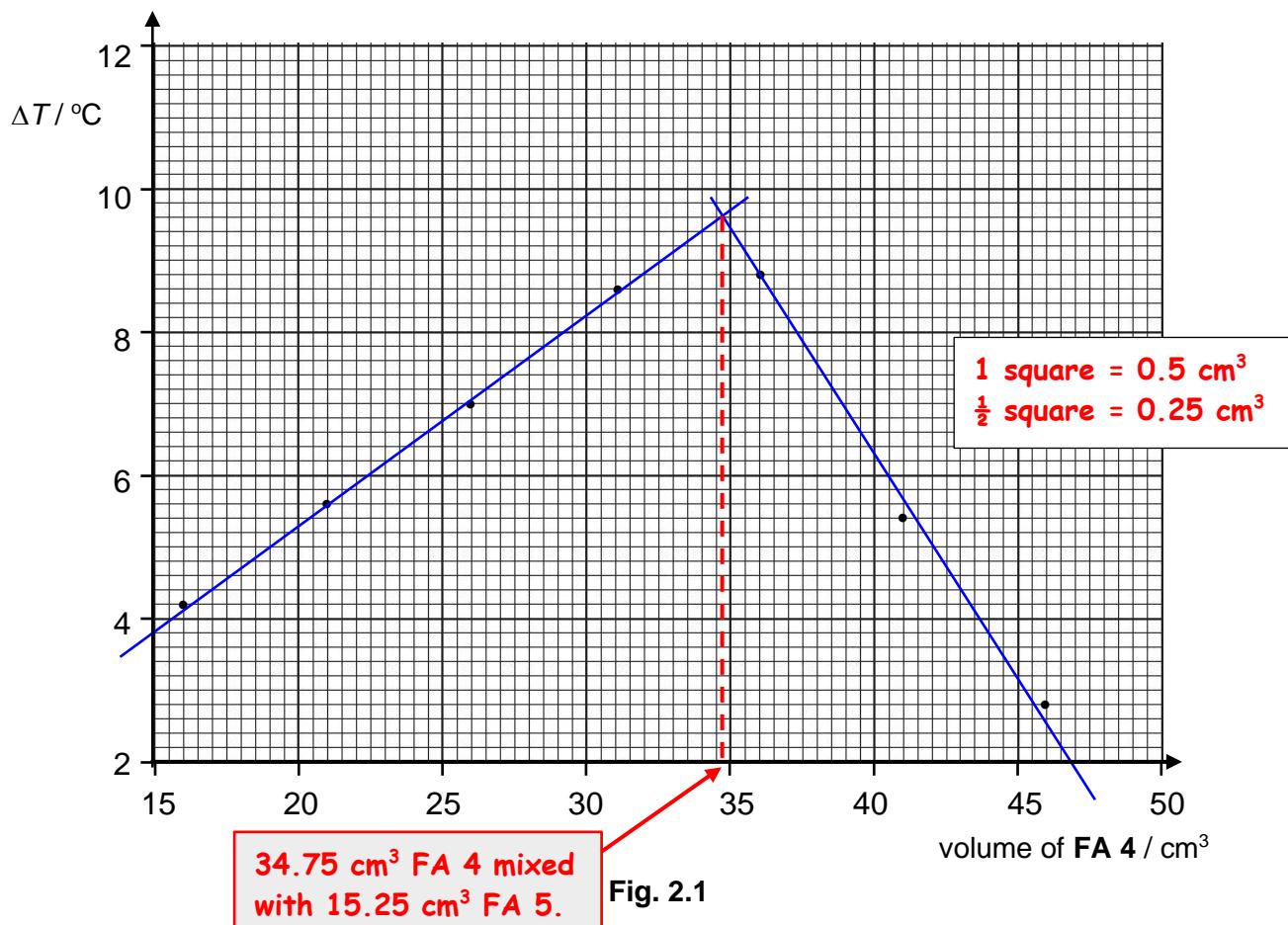
Any calculation not attempted loses this mark.

[3]

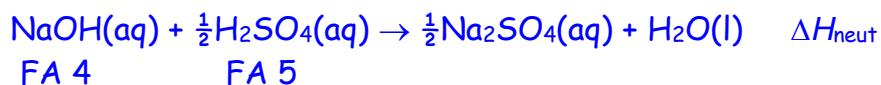
- (d) The procedure in experiment 1 can be used to determine the concentration of sodium hydroxide in FA 4.

A series of seven experiments were performed using different volumes of FA 4 and FA 5. In each experiment, the total volume of the two solutions was kept at  $50\text{ cm}^3$  and the change in temperature,  $\Delta T$ , was determined.

The results from the experiments were plotted on the grid in Fig. 2.1 below. By taking into account all of the points, two best-fit straight lines were drawn and the lines were extrapolated until they had crossed.



- (i) Explain, in terms of the reaction involved, the significance of the point of intersection of the two best-fit lines.



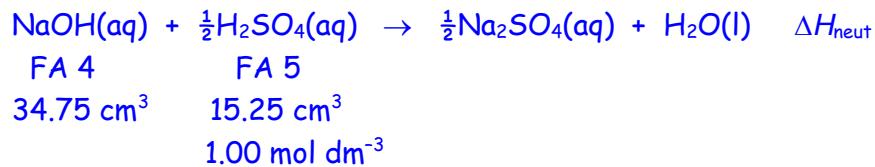
At this point, the equivalence point has reached where the acid/H<sub>2</sub>SO<sub>4</sub> exactly neutralises the base/NaOH present, [1] giving a salt solution.

It gives the maximum amount of water formed such that maximum amount of heat is evolved. [1]

[2]

Please refer to JC1 PC 1 and JC2 TP2 Q4 (planning) for further understanding.

- (ii) Using your graph, determine the volume of FA 4 at the point of intersection. Hence, determine the concentration, in mol dm<sup>-3</sup>, of sodium hydroxide in FA 4.



At the point of intersection,

Volume of NaOH = 34.75 cm<sup>3</sup> [1] read to the nearest half square

$$\text{Volume of H}_2\text{SO}_4 = \underline{\underline{50 - 34.75 = 15.25 \text{ cm}^3 (\checkmark)}}$$

$$\text{Amount of H}_2\text{SO}_4 = \underline{\underline{\frac{15.25}{1000} \times 1.00 = 0.01525 \text{ mol } (\checkmark)}}$$

$$\text{Amount of NaOH} = \underline{\underline{2 \times 0.01525 = 0.0305 \text{ mol } (\checkmark)}}$$

$$[\text{NaOH}] \text{ in FA 4} = \underline{\underline{\frac{1000}{34.75} \times 0.0305 = 0.878 \text{ mol dm}^{-3} (\checkmark)}}$$

**4(✓) [2], 2-3 (✓) [1]**

$$\text{Volume of NaOH} = \underline{\underline{34.75 \text{ cm}^3}}$$

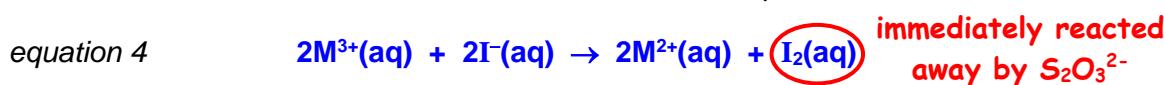
$$\text{Concentration of NaOH} = \underline{\underline{0.878 \text{ mol dm}^{-3}}} \quad [3]$$

[Total: 18]

### 3 Determination of the kinetics of a reaction between M<sup>3+</sup> ions and iodide ions, I<sup>-</sup>.

In this experiment, you will investigate how the rate of this reaction is affected by the concentration of M<sup>3+</sup> and I<sup>-</sup> ions.

M<sup>3+</sup> ions oxidise iodide ions, I<sup>-</sup>, to iodine, I<sub>2</sub> as shown in equation 4.



The rate equation is  $\text{rate} = k[\text{M}^{3+}]^a[\text{I}^-]^b$ , where a and b are either 0, 1 or 2.

When starch is added to the reaction mixture, a blue colour is immediately seen due to the formation of an iodine-starch complex.

If a small amount of thiosulfate ions, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, is also present in the reaction mixture, the formation of the blue colour is delayed as the iodine produced reacts immediately with thiosulfate ions, S<sub>2</sub>O<sub>3</sub><sup>2-</sup> as shown in equation 5.



When all the thiosulfate has been used, the iodine produced will turn starch indicator blue due to formation of iodine-starch complex.

FA 7 contains 0.0200 mol dm<sup>-3</sup> metal ions, M<sup>3+</sup>

FA 8 is 0.0080 mol dm<sup>-3</sup> aqueous potassium iodide, KI

FA 9 is 0.0060 mol dm<sup>-3</sup> sodium thiosulfate, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

Solution S is starch solution

You will perform a series of three experiments. You will add a fixed amount of sodium thiosulfate, FA 9, to each of your experiments. You will add an amount of deionised water so that the total volume is 55 cm<sup>3</sup>. The time taken for the blue colour to form allows the reaction rate to be determined.

(a) Fill Table 3.1 with the volume of deionised water needed in each experiment.

Table 3.1

experiment	volume of FA 7 / cm <sup>3</sup>	volume of FA 8 / cm <sup>3</sup>	volume of FA 9 / cm <sup>3</sup>	volume of solution S / cm <sup>3</sup>	volume of deionised water / cm <sup>3</sup>	time, t / s
1	20.0	10.0	15.0	10.0	0.0	16.6
2	10.0	10.0	15.0	10.0	10.0	31.3
3	25.0	5.0	15.0	10.0	0.0	53.1

To measure using a 10 cm<sup>3</sup> measuring cylinder.

1 interval = 0.2 cm<sup>3</sup>

½ interval = 0.1 cm<sup>3</sup> (∴ record all volumes of H<sub>2</sub>O to 1 d.p.)

To the nearest 0.1 s

[1] states correct volume of deionised water such that V<sub>total</sub> = 55 cm<sup>3</sup>

+ records volume of water to 1 d.p.

[1] record t to nearest 0.1 s

[1] correct trend ( $t_3 > t_2 > t_1$ )

[3]

## Experiment 1

The end-point of the reaction is the **first** appearance of a blue colour.

1. Use an appropriate measuring cylinder to transfer  $10.0 \text{ cm}^3$  of FA 8 into a  $100 \text{ cm}^3$  beaker. Place the beaker on the white tile.
2. Use appropriate measuring cylinders, transfer to the beaker.
  - $15.0 \text{ cm}^3$  of FA 9
  - $10.0 \text{ cm}^3$  of starch solution
  - appropriate volume of deionised water recorded in Table 3.1.
3. Use the measuring cylinder labelled FA 7 to transfer a  $20.0 \text{ cm}^3$  of FA 7 to the beaker and start the stopwatch at the instant of mixing.
4. Mix the contents in the beaker by **thoroughly** stirring.
5. Stop the stopwatch when the solution **first** turns blue.
6. Record the time taken,  $t$ , to nearest 0.1 s in Table 3.1.
7. Carefully wash out the beaker. Stand it upside down on a paper towel to drain.

## Experiment 2 and 3

Repeat experiment 1 using the volumes of FA 7, FA 8, FA 9, solution S and deionised water given in Table 3.1.

You should alternate the use of the two  $100 \text{ cm}^3$  beakers.

Record all values of  $t$  to nearest 0.1 s in Table 3.1.

- (b) Calculate the ratio of the time taken in experiment 2,  $t_{\text{expt } 2}$ , to the time taken in experiment 1,  $t_{\text{expt } 1}$ , using the expression shown.

Record your answer to **1 decimal place**.

$$\text{ratio 1} = \frac{t_{\text{expt } 2}}{t_{\text{expt } 1}} = \frac{31.3}{16.6} = \underline{1.9} \quad (\checkmark) \text{ with 1 dp}$$

Similarly, calculate and record the ratio of reaction time given below.

$$\text{ratio 2} = \frac{t_{\text{expt } 2}}{t_{\text{expt } 3}} = \frac{31.3}{53.1} = \underline{0.6} \quad (\checkmark) \text{ with 1 dp} \quad 2(\checkmark) [1]$$

**Accuracy:** ratio 1 = 1.8 - 2.0 \*[1]

**Accuracy:** ratio 2 = 0.5 - 0.6 \*[1]

\*Award [0] if the total volume of the two expts is not kept constant.

[3]

(c) The rate equation is  $\text{rate} = k[M^{3+}]^a[I^-]^b$

(i) Deduce the order, a, with respect to  $[M^{3+}]$ . Explain your deduction in terms of your experimental results.

- Since the total volume of the reaction mixture is kept constant, initial [reactant]  $\propto$  volume of reactant added.
- Since the same volume of  $\text{Na}_2\text{S}_2\text{O}_3$  is used, the same end-point is timed.  
 $\therefore \text{rate} \propto 1/t$ .

Comparing experiments 1 and 2,  $\text{rate} \propto [M^{3+}]^a$

$$\text{Since rate} \propto \frac{1}{t}, \frac{\text{rate}_{\text{expt1}}}{\text{rate}_{\text{expt2}}} = \frac{t_{\text{expt2}}}{t_{\text{expt1}}} = 1.9 = \frac{(20.0)^a}{(10.0)^a}$$

$$1.9 = 2^a \\ \Rightarrow a = 0.926 \approx 1$$

Or, When  $[M^{3+}]$  is  $\times 2$ ,  $t$  is  $\approx \frac{1}{2}$  and hence rate is  $\approx \times 2$ .

$\therefore$  the order of reaction w.r.t.  $[M^{3+}]$  is 1 or  $a = 1$ .

{ [1] with working }

[1]

(ii) Deduce the order, b, with respect to  $[I^-]$ . Explain your deduction in terms of your experimental results.

Hence, complete the expression for the rate equation.

Comparing Experiment 2 and 3,  $\text{rate} \propto [M^{3+}][I^-]^b$

$$\text{Since rate} \propto \frac{1}{t}, \frac{\text{rate}_{\text{expt3}}}{\text{rate}_{\text{expt2}}} = \frac{t_{\text{expt2}}}{t_{\text{expt3}}} \approx 0.6 = \frac{(25.0)(5.0)^b}{(10.0)(10.0)^b}$$

$$0.24 = 0.5^b \\ \Rightarrow b = \lg(0.24)/\lg(0.5) \\ = 2.06 \approx 2$$

{ [1] with working }

Or, Comparing Experiment 1 and 3,  $\text{rate} \propto [M^{3+}][I^-]^b$

$$\text{Since rate} \propto \frac{1}{t}, \frac{\text{rate}_{\text{expt1}}}{\text{rate}_{\text{expt3}}} = \frac{\frac{1}{16.6}}{\frac{1}{53.1}} = \frac{(20.0)(10.0)^b}{(25.0)(5.0)^b}$$

$$4.00 = 2^b \\ \Rightarrow b = 2$$

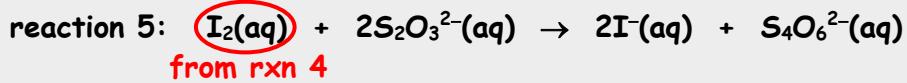
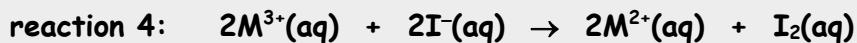
{ [1] with working }

$\therefore \text{rate} = k[M^{3+}][I^-]^2$  [1] ecf

[2]

- (d) (i) Instead of washing the beaker as required before performing the next experiment, a student simply just poured away the reaction mixture. There was some leftover reaction mixture in the beaker when he performed the subsequent experiment.

State, and explain, how the value of  $t$  would be affected.



For reaction 4,  $\text{rate} = k [M^{3+}][I^-]^2$

Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> is not the reactant for rxn 4 and hence the rate of qn 4 does not depend on [Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>].

However,  $t$  will change if the amount of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> added is changed since a fixed amount of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> is added as a "marker" to control the amount of I<sub>2</sub> that is needed to be produced for the appearance of blue-black colour.

The residual I<sub>2</sub> left (or I<sub>2</sub> produced from residual reactants) in the beaker will react with S<sub>2</sub>O<sub>3</sub><sup>2-</sup> added ( $\checkmark_1$ ) for the new experiment.

Since less S<sub>2</sub>O<sub>3</sub><sup>2-</sup> is left in the reaction mixture, less I<sub>2</sub> is needed to be produced ( $\checkmark_2$ ) for the appearance of blue colour.

Hence  $t$  will be smaller/shorter ( $\checkmark_3$ ). [1]

- (ii) Instead of adding 15.0 cm<sup>3</sup> of FA 9 in each experiment, a student used only 7.5 cm<sup>3</sup> of FA 9. (Total volume is still constant)

State, and explain, how the value of  $t$  would be affected.

Since amount of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> present in the reaction mixture is halved, half the amount of iodine is needed to be produced ( $\checkmark_4$ ) for the appearance of blue colour.

Hence  $t$  will be smaller/shorter ( $\checkmark_5$ ).

2-3( $\checkmark$ ) [1], 4-5( $\checkmark$ ) [2]

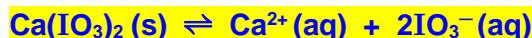
Reject 't becomes faster' as fast/slow is describing rate, not length of time. [1]

[Total: 11]

#### 4 Planning

The solubility of calcium iodate(V),  $\text{Ca}(\text{IO}_3)_2$ , at 20 °C, is approximately 2.4 g  $\text{dm}^{-3}$ .

When solid calcium iodate(V) is added to water, a small amount dissolves to form a saturated solution, establishing an equilibrium between the undissolved salt and its aqueous ions.

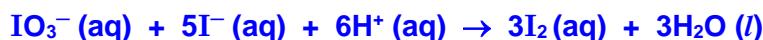


The equilibrium constant for the above solubility equilibrium,  $K_{\text{sp}}$ , is also known as the **solubility product of calcium iodate**.

$$K_{\text{sp}} = [\text{Ca}^{2+} (\text{aq})] [\text{IO}_3^- (\text{aq})]^2$$

This solubility product can be found by determining the equilibrium concentration of  $\text{IO}_3^-$  ions in a saturated solution of calcium iodate.

The exact concentration of  $\text{IO}_3^-$  ions is determined by titration. Excess aqueous KI and aqueous  $\text{H}^+$  is first added to a sample of saturated calcium iodate solution to liberate iodine.



The iodine liberated in the resulting mixture is then titrated with sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3$  of known concentration.



- (a) Using the information given above, you are required to write a plan to determine the solubility product,  $K_{\text{sp}}$ , of calcium iodate,  $\text{Ca}(\text{IO}_3)_2$ , at 20 °C.

You may assume that you are provided with:

- solid sodium thiosulfate crystals,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  ( $M_r = 248.2$ )
- solid calcium iodate,  $\text{Ca}(\text{IO}_3)_2$
- aqueous potassium iodide, KI, of about 0.2 mol  $\text{dm}^{-3}$
- aqueous hydrochloric acid, HCl, of about 1 mol  $\text{dm}^{-3}$
- starch indicator
- any other required apparatus normally found in a college laboratory.

Your plan should include details of, including quantities:

- the preparation of 250.0  $\text{cm}^3$  of 0.075 mol  $\text{dm}^{-3}$  aqueous  $\text{Na}_2\text{S}_2\text{O}_3$ ;
- the preparation of about 100  $\text{cm}^3$  of a saturated solution of calcium iodate,  $\text{Ca}(\text{IO}_3)_2$  at 20 °C;
- the essential details of the titration process.

To prepare 250.0 cm<sup>3</sup> of 0.075 mol dm<sup>-3</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>(aq):

$$\text{Mass of Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O required} = \frac{250}{1000} \times 0.075 \times 248.2 = *4.654 \text{ g}$$

1. Weigh accurately \*4.654/4.64 g of solid Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O into a weighing bottle using an electronic weighing balance.

(OR, Weigh accurately \*4.654/4.64 g of solid Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O into a small beaker using an electronic weighing balance.)

[1] step 1: accurately weigh the required mass of solid in 2-3 d.p.

2. Transfer all the weighed solid into a small beaker and dissolve the solid completely with about 60 cm<sup>3</sup> deionised water.

(OR, Add about 60 cm<sup>3</sup> of deionised water into the beaker to dissolve the solid completely.)

3. Using a filter funnel, carefully transfer the solution and all washings into a 250.0 cm<sup>3</sup> graduated/volumetric flask. Make up to the graduated mark with deionised water. Stopper and shake the flask well to obtain a homogeneous solution.

[1] step 2 & 3: accurately prepares 250 cm<sup>3</sup> of standard soln with complete transfer (no loss of S<sub>2</sub>O<sub>3</sub><sup>2-</sup>).

To prepare about 100 cm<sup>3</sup> of Ca(IO<sub>3</sub>)<sub>2</sub> saturated solution at 20 °C:

4. Use a 100 cm<sup>3</sup> measuring cylinder to transfer 100 cm<sup>3</sup> of deionised water into a 250 cm<sup>3</sup> conical flask.

5. Using a spatula, add a few tips of solid Ca(IO<sub>3</sub>)<sub>2</sub> into the conical flask. Stopper the flask and shake the flask for a few minutes. Keep adding more solid Ca(IO<sub>3</sub>)<sub>2</sub>, with shaking after each addition, until some Ca(IO<sub>3</sub>)<sub>2</sub> solids are left undissolved.

[1] step 4 & 5: correctly prepares a saturated soln of Ca(IO<sub>3</sub>)<sub>2</sub> {allow stirring using a glass rod or swirling in place of shaking; allow the use of a beaker or other appropriate apparatus.)

6. To ensure that the solution is saturated, shake the flask at intervals and leave the conical flask in a \*thermostat controlled water bath set at 20 °C for some time/30 min. There must be some solids left undissolved.

[1] step 6: ensures saturated soln reached eqm at 20 °C using a thermostat controlled water bath

7. To remove undissolved solids, filter the saturated solution into a dry conical flask using a dry filter funnel and a piece of dry filter paper.

[1] step 7: performs a dry filtration to remove undissolved solids and collect the filtrate in a dry flask.

Titration procedure:

8. Fill a burette with  $0.075 \text{ mol dm}^{-3}$   $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ .
9. Pipette \* $25.0 \text{ cm}^3$  of the saturated solution into a conical flask.
10. Use separate measuring cylinders to add to the conical flask  $10 \text{ cm}^3$  of  $\text{HCl}(\text{aq})$  and  $10 \text{ cm}^3$  of  $\text{KI}(\text{aq})$ .

[1] step 8-10: accurately prepares titrant and analyte in a conical flask with minimum  $10 \text{ cm}^3$  of  $\text{KI}$  & minimum  $5 \text{ cm}^3$  of  $\text{H}^+$ .

11. Titrate the liberated  $\text{I}_2$  in the mixture with  $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$  from the burette until the solution turns pale yellow. Then add about  $1 \text{ cm}^3$  of starch indicator and continue to titrate until the dark blue-black colour just disappears/turns colourless at the end-point.
12. Repeat the titration to obtain two consistent titres within  $0.10 \text{ cm}^3$  in difference.

[1] step 11: correct titration procedure using starch indicator with end-point colour change correctly stated.

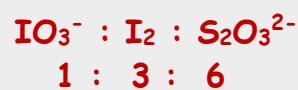
[7]

- (b) Outline how you would use your mean titre value to determine the solubility product of  $\text{Ca}(\text{IO}_3)_2$ .

In your calculations, you should let  $V \text{ cm}^3$  be your mean titre and express your final mathematical expression in terms of  $V$ .

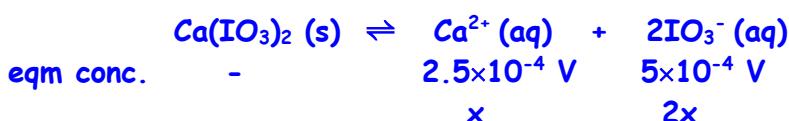
$$n(\text{S}_2\text{O}_3^{2-}) \text{ required} = \frac{V}{1000} \times 0.075 = 7.5 \times 10^{-5} V \text{ mol}$$

$$\begin{aligned} n(\text{IO}_3^-) \text{ in } *25.0 \text{ cm}^3 \text{ saturated soln} \\ = \frac{1}{6} \times 7.5 \times 10^{-5} V = 1.25 \times 10^{-5} V \text{ mol} [1] \end{aligned}$$



$[\text{IO}_3^-]$  in saturated solution

$$= \frac{1000}{*25.0} \times 1.25 \times 10^{-5} V = 5 \times 10^{-4} V \text{ mol dm}^{-3} [1] \quad * \text{volume of saturated soln used in titration.}$$



$$\begin{aligned} K_{\text{sp}} (\text{Ca}(\text{IO}_3)_2) &= [\text{Ca}^{2+}(\text{aq})] [\text{IO}_3^-(\text{aq})]^2 \\ &= (2.5 \times 10^{-4} V)(5 \times 10^{-4} V)^2 \\ &= 6.25 \times 10^{-11} V^3 \text{ mol}^3 \text{ dm}^{-9} \end{aligned}$$

$$(\text{OR} = 4x^3 = 4 \left( \frac{5 \times 10^{-4} V}{2} \right)^3 = \underline{6.25 \times 10^{-11} V^3 \text{ mol}^3 \text{ dm}^{-9}})$$

[1]

[3]

- (c) The experiment described in your plan in (a) is repeated using 0.1 mol dm<sup>-3</sup> aqueous Ca(NO<sub>3</sub>)<sub>2</sub> solution, instead of deionised water, to prepare a saturated solution of calcium iodate(V). {the solvent contain common Ca<sup>2+</sup> ions}

State and explain how, if at all, the titre values and calculated  $K_{sp}$  would be expected to differ from that obtained in (a).

Assume that both the experiments were carried out under the same conditions.

Presence of common ion Ca<sup>2+</sup> from Ca(NO<sub>3</sub>)<sub>2</sub>(aq) increases [Ca<sup>2+</sup>(aq)] and causes the position of equilibrium of Ca(IO<sub>3</sub>)<sub>2</sub>(s) ⇌ Ca<sup>2+</sup>(aq) + 2IO<sub>3</sub><sup>-</sup>(aq) to shift left. ∴ the solubility of Ca(IO<sub>3</sub>)<sub>2</sub> is reduced. [1]

With a lower [IO<sub>3</sub><sup>-</sup>] in saturated solution, the titre values will be smaller. However, since the temperature is kept constant, the calculated K<sub>sp</sub> value would remain the same/unchanged. [1] [2]

[Total: 12]

**Qualitative Analysis Notes**

[ppt. = precipitate]

**(a) Reactions of Aqueous Cations**

cation	Reaction with	
	NaOH(aq)	NH <sub>3</sub> (aq)
aluminium, Al <sup>3+</sup> (aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH <sub>4</sub> <sup>+</sup> (aq)	ammonia produced on heating	–
barium, Ba <sup>2+</sup> (aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca <sup>2+</sup> (aq)	white ppt. with high [Ca <sup>2+</sup> (aq)]	no. ppt.
chromium(III), Cr <sup>3+</sup> (aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu <sup>2+</sup> (aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe <sup>2+</sup> (aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe <sup>3+</sup> (aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg <sup>2+</sup> (aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn <sup>2+</sup> (aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn <sup>2+</sup> (aq)	white ppt. soluble in excess	white ppt. soluble in excess

**(b) Reactions of Anions**

<i>Anion</i>	<i>Reaction</i>
carbonate, $\text{CO}_3^{2-}$	$\text{CO}_2$ liberated by dilute acids
chloride, $\text{Cl}^-(\text{aq})$	gives white ppt. with $\text{Ag}^+(\text{aq})$ (soluble in $\text{NH}_3(\text{aq})$ );
bromide, $\text{Br}^-(\text{aq})$	gives pale cream ppt. with $\text{Ag}^+(\text{aq})$ (partially soluble in $\text{NH}_3(\text{aq})$ );
iodide, $\text{I}^-(\text{aq})$	gives yellow ppt. with $\text{Ag}^+(\text{aq})$ (insoluble in $\text{NH}_3(\text{aq})$ );
nitrate, $\text{NO}_3^-(\text{aq})$	$\text{NH}_3$ liberated on heating with $\text{OH}^-(\text{aq})$ and Al foil
nitrite, $\text{NO}_2^-(\text{aq})$	$\text{NH}_3$ liberated on heating with $\text{OH}^-(\text{aq})$ and Al foil; NO liberated by dilute acids (colourless NO $\rightarrow$ (pale) brown $\text{NO}_2$ in air)
sulfate, $\text{SO}_4^{2-}(\text{aq})$	gives white ppt. with $\text{Ba}^{2+}(\text{aq})$ (insoluble in excess dilute strong acids)
sulfite, $\text{SO}_3^{2-}(\text{aq})$	$\text{SO}_2$ liberated on warming with dilute acids; gives white ppt. with $\text{Ba}^{2+}(\text{aq})$ (soluble in excess dilute strong acids)

**(c) Tests for Gases**

<i>gas</i>	<i>Test and test results</i>
ammonia, $\text{NH}_3$	turns damp red litmus paper blue
carbon dioxide, $\text{CO}_2$	gives a white ppt. with limewater (ppt. dissolves with excess $\text{CO}_2$ )
chlorine, $\text{Cl}_2$	bleaches damp litmus paper
hydrogen, $\text{H}_2$	“pops” with a lighted splint
oxygen, $\text{O}_2$	relights a glowing splint
sulfur dioxide, $\text{SO}_2$	turns acidified aqueous potassium manganate(VII) from purple to colourless

**(d) Colour of halogens**

<i>halogen</i>	<i>colour of element</i>	<i>colour in aqueous solution</i>	<i>colour in hexane</i>
chlorine, $\text{Cl}_2$	greenish yellow gas	pale yellow	pale yellow
bromine, $\text{Br}_2$	reddish brown gas/liquid	orange	orange-red
iodine, $\text{I}_2$	black solid/purple gas	brown	purple