

Catholic Junior College
JC2 Preliminary Examination
Higher 2

CANDIDATE
NAME

CLASS

CHEMISTRY

9729/02

Paper 2 Structured Questions

August 2021

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

MARK SCHEME AND WORKED SOLUTIONS

This document consists of **16** printed pages.

- 1 (a) Calcium is a Group 2 element. Table below shows the radius of the calcium atom and the radius of the calcium ion.

Element	Radius / pm
Ca	197
Ca ²⁺	100

Explain the difference in size between calcium atom and calcium ion.

Ca²⁺ has one quantum shell less than that of Ca atom. Hence the outer electrons are more strongly attracted by its nucleus. [1]

Most students only explain that Ca is bigger than Ca²⁺ due to higher number of quantum shells. They need to be made aware that the attractive force of nucleus on the valence electrons plays a part in affecting the size of atom.

A number of students mistaken Principal Quantum Shell as Subshell.

- (b) Describe and explain the trend in ionic radii down Group 2.

Ionic radii increase down group 2 due to increasing number of electron shells

and hence also increasing shielding effect. [1] These increases outweigh the

increase in nuclear charge. Hence, weaker electrostatic attraction of the

valence electrons by the nucleus. [1] [2]

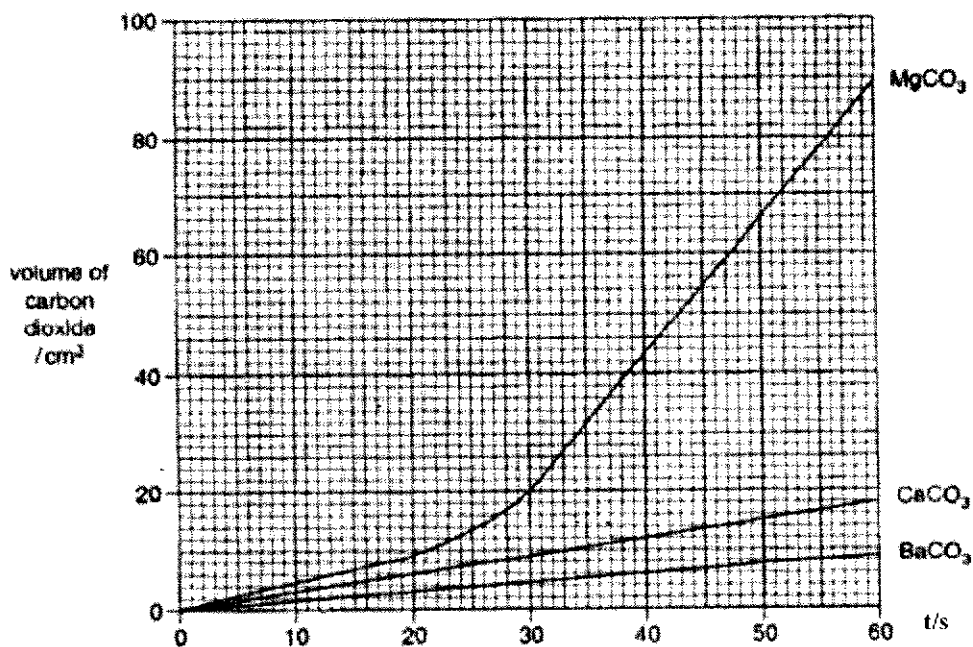
Most students failed to compare the effect of Increasing Nuclear Charge and that of Increasing Shielding Effect down the group. They need to be made aware that the Increase in Shielding Effect Outweighs Increase in Nuclear Charge.

A number of students mistaken Nuclear Charge as the Net Positive Charge of Cation.

Most students failed to describe the effect of Increase in Shielding Effect on the Electrostatic Forces of Attraction between Nucleus and Electrons.

- (c) A student investigates the thermal decomposition of the carbonates of Group 2 elements. He separately heats the carbonates of magnesium, calcium and barium and records the total volume of carbon dioxide collected every 10 seconds. In each experiment, he uses the same amount, in moles, of each carbonate and uses the hottest flame of a Bunsen burner.

The graph of his experimental results is given below.



- (i) Write an equation to represent the thermal decomposition of barium carbonate, indicating clearly the state symbols.

$$\text{BaCO}_3 (\text{s}) \rightarrow \text{BaO} (\text{s}) + \text{CO}_2 (\text{g})$$
 [1]

Almost all students are able to provide correct answer.

- (ii) Identify the least thermally stable carbonate and explain how the graph supports your answer.

MgCO₃ is the least thermally stable. [1]

The gradient of the graph for MgCO₃ is steepest. [1]

Or

Given the same amount of carbonates, MgCO₃ produce the most CO₂ upon thermal decomposition. [1]

[2]

Almost all students are able to provide correct answer.

Very few students misinterpret "Least Thermally Stable" compound as one that gives off least amount of gaseous products.

- (d) The student wanted to perform the same investigation on the carbonates of the elements in Group 13 but found that $\text{Al}_2(\text{CO}_3)_3$ does not exist at room temperature. Suggest a reason for this.

With its small size and high charge, Al^{3+} cation has a very high charge density [1].

Thus, Al^{3+} is able to polarise the electron cloud of the large carbonate anion (or CO_3^{2-}) and hence the C-O bond is weakened to such a large extent [1] such that $\text{Al}_2(\text{CO}_3)_3$ decomposes readily to give Al_2O_3 and CO_2 even at room temperature.

[2]

A number of students are able to relate the non-existence of $Al_2(CO_3)_3$ to the fact that it is very Thermally Unstable at room temperature, hence it is due to Large Extent of Polarisation of Anion Electron Cloud by Al^{3+} with Very High Charge Density.

A number of students have the misconception that non-existence of $Al_2(CO_3)_3$ is due to very low lattice energy of the ionic compound. They failed to understand that low lattice energy only results in the compound having low melting point. However the compound still exists but in molten state.

- (e) Compare and explain the difference between the lattice energy of barium carbonate and magnesium carbonate.

$$L.E \propto \frac{q_+ q_-}{r_+ + r_-}$$

Both the cations and anions are doubly charged/ have the same charge.

Ionic radius: $Ba^{2+} > Mg^{2+}$ [1]

Thus, the lattice energy of $BaCO_3$ is less exothermic/ smaller in magnitude [1] than that of $MgCO_3$.

[2]

Most students are able to relate Lattice Energy of the compounds to the expression: $L.E \propto \frac{q_+ q_-}{r_+ + r_-}$

Most students are able to compare the ionic size of Ba^{2+} and Mg^{2+} .

Most students failed to use the terms "More Exothermic" or "More Endothermic" to compare lattice energies of compounds.

- (f) The first ionisation energies of Group 2 elements are given below:

Group 2 Elements	1 st I.E/ kJ mol^{-1}
Be	900
Mg	736
Ca	590
Sr	548

Explain why the first ionisation energies decrease in magnitude down Group 2.

Down Group 2,

- Nuclear charge increases
- The atomic radius increases as outermost electron is in a higher principal quantum shell. Thus, the outermost electron is further from the nucleus.
- The number of inner shells of electrons increases, thus the outermost electron is better shielded by the inner shells of electrons
- Distance from nucleus and better shielding outweighs greater nuclear charge.
- Therefore, the outermost electron becomes less strongly attracted by the positive nucleus and so, less energy is required to remove the electron. $\therefore 1^{\text{st}} I.E$

[1]

[1]

[2]

Most students failed to compare the effect of Increasing Nuclear Charge and that of Increasing Shielding Effect down the group. They need to be made aware that the Increase in Shielding Effect Outweighs Increase in Nuclear Charge.

A number of students mistaken Nuclear Charge as the Net Positive Charge of Group 2 ions.

A few students mistaken that the Nuclear Charge of atoms remains constant down the group.

Most students failed to describe the effect of Increase in Shielding Effect on the Electrostatic Forces of Attraction between Nucleus and Valence Electrons.

- (g) Lithium nitrate is the only Group 1 nitrate that decomposes on heating, in the same way as Group 2 nitrates. Suggest a reason for why its behaviour is similar to Group 2 nitrates, and give an equation for its decomposition.



Reason for the behaviour:

Li⁺ and Mg²⁺ have similar charge densities (Li⁺ has very small ionic radius, smaller charge but also smaller ionic radius than Mg²⁺, so high charge density similar to Mg²⁺ but unlike other Group 1 metals). Hence, Li⁺ shares a diagonal relationship with Mg²⁺ (from Group 2) and show similar chemical reactions. [1]

[2]

Most students failed to provide correct equation for the Thermal Decomposition of Nitrates.

A number of students are able to explain that the thermal decomposition of Group 1 nitrate is related to polarisation of nitrate anion by Li⁺ cation. However, most of them failed to compare it with that of Group 1 cations.

Most students failed to provide the explanation that it due to Similar Charge Densities of Li⁺ and Mg²⁺.

[Total: 14]

- 2 (a) (i) Calculate the average oxidation number of sulfur in sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$.

Let average oxidation number of sulfur be x .

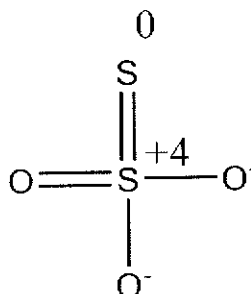
$$2(+1) + 2x + 3(-2) = 0$$

$$x = +2 \quad [1]$$

This was generally well done, except for a minority of students who reversed the sign, or did not show working.

[1]

- (ii) Draw the structure of a thiosulfate anion, $\text{S}_2\text{O}_3^{2-}$, with a single central S atom, and clearly label the actual oxidation number of each S atom.



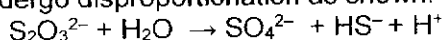
[1 correct structure, 1 correct oxidation numbers]

A very small minority of students drew the correct structure - with one single central S atom surrounded by the 4 other atoms, where the 2 extra negative charges are on O atoms (more electronegative), and all atoms apart from the central S achieved octet while the central S can expand the octet. Some gave a dot and cross diagram which doesn't show structure.

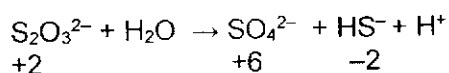
A number of students did not label the oxidation numbers of the S atoms, or gave numbers that did not average out to +2.

[2]

- (b) Thiosulfate anions undergo disproportionation as shown.



By considering the change in oxidation states in all the sulfur-containing species, deduce the number of moles of electrons involved in this reaction.



4 moles of electrons are transferred.

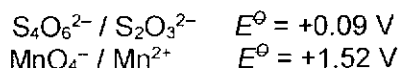
Many students got at least 1 mark here for working out the oxidation states of the 2 products and/or the change in oxidation states. Some students thought that 8 moles of electrons were transferred, although it would be easier to understand the reaction as having the same 4 moles of electrons being lost by 1 S to the other.

Some students considered the change in each S atom from +4 to +6 and 0 to -2, but then in that case the change in oxidation state is due to the surrounding atoms O and H, and the electrons should be counted separately, hence $2+2 = 4$ moles of electrons involved.

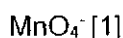
Common mistakes which were either due to carelessness or weak mental sums: finding oxidation no. of S in HS^- to be 0 or -1, or S in SO_4^{2-} to be +3.

[2]

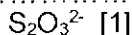
- (c) The values of standard reduction potentials are given for the following redox systems.



- (i) Among the species above, identify the strongest oxidising agent and the strongest reducing agent.



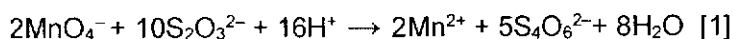
Strongest oxidising agent: [1]



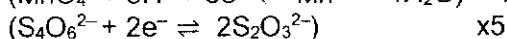
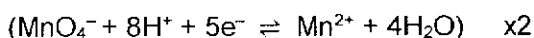
Strongest reducing agent: [1]

A majority of students got 1-2 marks here, although some students gave 2 species for each answer eg. $\text{MnO}_4^- / \text{Mn}^{2+}$

- (ii) With reference to the *Data Booklet*, write a balanced ionic equation for the most spontaneous reaction involving the 4 species above.



..... [1]



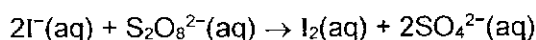
Some students obtained the correct equation even if c)(i) was wrong. Most common mistakes were forgetting to multiply one of the coefficients, or reversing $\text{S}_2\text{O}_3^{2-}$ and $\text{S}_4\text{O}_6^{2-}$. A small minority of students reversed the equation completely, or a very small number gave a half equation or another equation that didn't involve the 4 species above.

Quite a number of students included state symbols, showing awareness that species in an ionic equation have to be aqueous for any spectator ions to cancelled off, but there was no penalty if state symbols were not shown.

[Total: 8]

- 3 (a) Use of the *Data Booklet* is relevant to this question.

The reaction between peroxodisulfate(VII) ions, $\text{S}_2\text{O}_8^{2-}$, and iodide ions, I^- , is represented by the following equation:



This reaction is catalysed by adding a suitable transition metal species which acts as a homogeneous catalyst for the reaction.

- (i) Suggest why the above reaction requires the addition of a catalyst.

The reaction has **high activation energy** due to electrostatic repulsion

between the two negatively charged ions, $\text{S}_2\text{O}_8^{2-}$ and I^- . [1] *owtte*

..... [1]

Only a small number of students managed to score this mark.

Common errors include

- explain why catalyst is added rather than why reaction requires a catalyst.
- calculate E^\ominus_{cell} and state that reaction is not feasible even when $E^\ominus_{\text{cell}} > 0$
- breaking of bonds or endothermic reaction

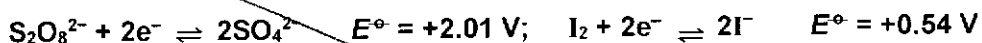
(ii) Explain why the transition metal can be used as a homogeneous catalyst?

The transition metal ion is able to exist in various oxidation states thus facilitating the formation of intermediates via alternative pathways of lower activation energy [1] owtte

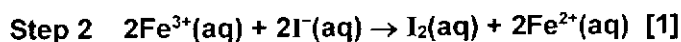
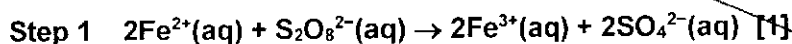
[1]

CLT – question removed.

(iii) By considering suitable E^\ominus values from the *Data Booklet*, suggest a catalyst for the reaction between $S_2O_8^{2-}$ and I^- ions, and write equations to show how the homogeneous catalysis occurs.



A possible catalyst is $FeSO_4(aq)$ [1] not chlorides, which can be oxidised by peroxodisulfate; BOD if give $Fe^{2+}(aq)$ or $Fe^{3+}(aq)$

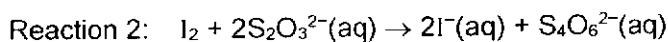
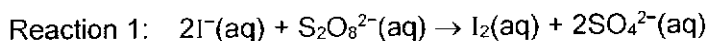


[3]

CLT – question removed.

(b) The rate of reaction between $S_2O_8^{2-}$ and I^- ions may be studied using the iodine clock reaction, which make use of the property that iodine forms an intense blue complex with starch.

In the iodine clock reaction, the following set of reactions take place and a colour change involving the starch-iodine complex happens after a fixed amount of iodine is produced, allowing the kinetics of the reaction to be determined.



During an experiment to determine the rate equation, different concentrations of KI, and $Na_2S_2O_3$ are mixed according to the following table. The rates for the colour change in each solution are shown below.

flask	$[I^-]$ / mol dm ⁻³	$[S_2O_8^{2-}]$ / mol dm ⁻³	rate / s ⁻¹
1	0.10	0.10	0.0222
2	0.10	0.20	0.0434
3	0.10	0.30	0.0665
4	0.15	0.05	0.0167
5	0.20	0.15	0.0675

(i) Suggest what was done in the experiment to ensure a fixed amount of iodine is produced.

By adding the same volume / fixed volume of $Na_2S_2O_3$ in each reaction flask. [1] owtte

[1]

Only a small handful managed to score the mark for this part of the question.

Common errors include

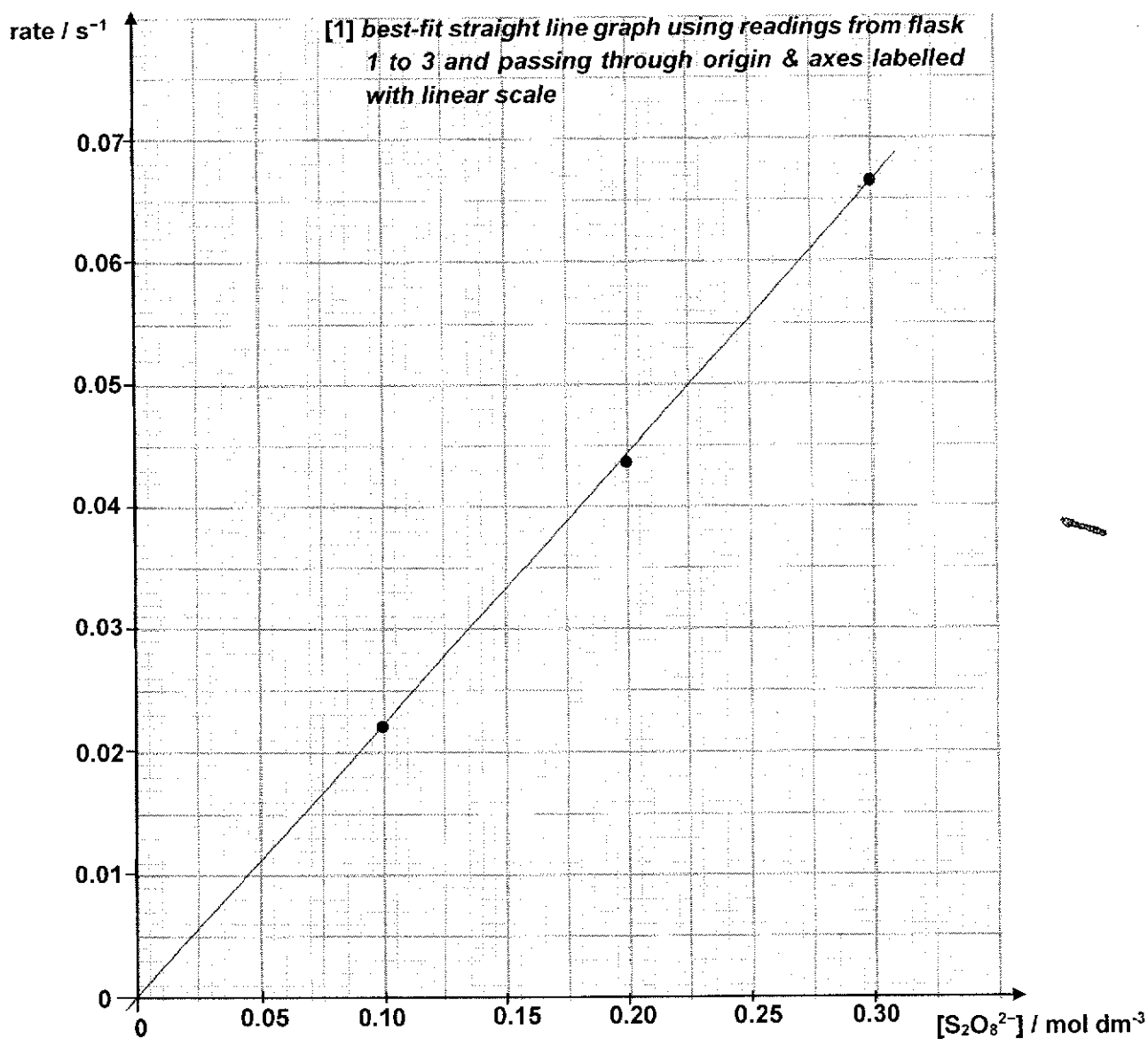
- Adding water to keep total volume of reaction mixture constant
- Adding excess KI
- Peroxodisulfate as limiting reagent

(ii) Deduce two sets of variables from the table whose values can be plotted to obtain the order of reaction with respect to $S_2O_8^{2-}$.

plot: rate / s^{-1}
 against: $[S_2O_8^{2-}] / \text{mol dm}^{-3}$ [1]

Majority were able to score the mark for this part of the question.

(iii) On the grid provided, plot a graph using the variables in (b)(ii) to determine the order of reaction with respect to $S_2O_8^{2-}$. Label the axes clearly.



1 [1]

Order of reaction with respect to $S_2O_8^{2-}$: [2]

Most were able to score the mark for this part of the question.

Common errors include

- Plotting for all 5 flasks rather than for flask 1 to 3 only
- Line not passing through origin
- Zig-zag line joining all 5 points

(iv) By using a non-graphical method, deduce the order of reaction with respect to I^- .

Let the rate equation be $\text{rate} = k [S_2O_8^{2-}] [I^-]^x$

Using data from flask 3 and 5,

$$\frac{\text{rate 5}}{\text{rate 3}} = \frac{k (0.15)(0.20)^x}{k (0.30)(0.10)^x} = \frac{0.0685}{0.0665}$$

$$2^x = \frac{0.0685}{0.0665} \times \frac{0.30}{0.15} = 2.06$$

$$\therefore x = 1$$

Order of reaction with respect to $I^- = 1$ [1] *with appropriate working*

Common errors include

- Simply quoting values from the table, but without any explanation how the values are used to arrive at the conclusion that reaction is 1st order
- Work out order w.r.t. peroxydisulfate instead of iodide
- Inability to manipulation mathematical calculation involving indices.

[1]

(v) Hence or otherwise, write the rate equation and calculate a value for the rate constant, k , stating clearly the units.

Rate equation is $\text{rate} = k [S_2O_8^{2-}] [I^-]$ [1]

$$k = \frac{\text{rate}}{[I^-][S_2O_8^{2-}]} = \frac{0.0222}{(0.10)(0.10)} = 2.22 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1} \text{ [1] value with units}$$

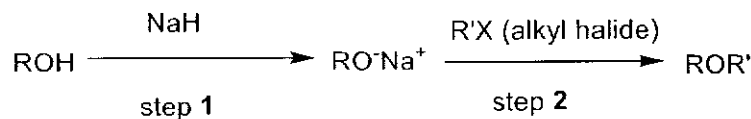
Most were able to score the marks for this part of the question.

[2]

[Total: 42 8]

- 4 Ethers have the general formula, R-O-R' (where R and R' are alkyl or aryl groups). The most useful method of preparing ethers is by the Williamson ether synthesis, in which an alkoxide ion (RO⁻) reacts with a primary alkyl halide (R'X) in an S_N2 mechanism.

(a) A reaction scheme is shown below:



- (i) State the type of reaction for step 1.

acid-base reaction/neutralisation/redox

[1]

The part was well done. Most were able to see that ROH donated a proton and is hence a Bronsted acid.

- (ii) Suggest why step 1 is necessary in the Williamson ether synthesis.

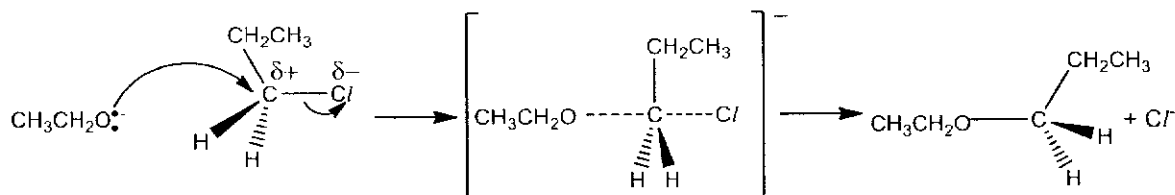
To generate the alkoxide ion, which is a **stronger nucleophile**

[1]

The part was well done.

- (iii) Using 1-chloropropane as the alkyl halide and CH₃CH₂O⁻ as the alkoxide ion, describe the mechanism for step 2 of the Williamson ether synthesis.

Show all charges and relevant lone pairs of electrons and show the movement of electron pairs by using curly arrows.



[1] Lone pair, partial charges, arrows

[1] Transition state correctly drawn

[1] inversion in configuration, show nucleophile attacking from the rear

[3]

There were only a small handful of candidates who managed to give all the required details. Most common mistakes included omitting partial charges, precision of arrows drawn and omitting sign of transition state. The drawing of the inversion of configuration was also a challenge for many candidates. Students are reminded that the geometry needs to be shown for S_N2 mechanism.

- (iv) The same reaction in (a)(iii) was repeated using iodopropane instead of chloropropane. State and explain the effect on the rate of reaction.

The rate of reaction using iodopropane will be faster.

The C-I bond is weaker, thus less energy is needed to break the bond. [1] [1]

This was a typical explanation type question but there were many candidates who failed to address the key concept. Explicit link to the strength of C-X bond must be made.

- (b) Epoxides are cyclic ethers commonly used in organic reactions. Epoxyethane is the simplest epoxide and has the structure as shown:



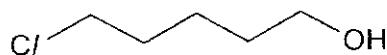
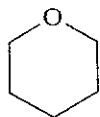
- (i) Epoxyethane can be synthesised via an intramolecular Williamson ether synthesis with a low yield because it is unstable. Suggest why epoxyethane is unstable.

Epoxyethane has a highly strained three-membered ring which makes it reactive/unstable. [1]

Most candidates were able to identify that there was a ring or angle strain due to the 3-membered ring. However, there were some scripts which revolved around lone-pair lone-pair repulsion instead. A number of scripts had incomplete reasoning.

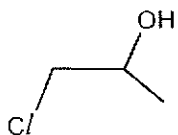
- (ii) Suggest the organic reagent to synthesise each of the following ethers via intramolecular Williamson ether synthesis.

I



II





Students had difficulties spotting the pattern and working backwards to identify the reactant. Students are expected to recognise the C-O bond was formed and hence break the C-O bond and add back a H to the O and add the halogen to get the organic molecule. Note that since this is an intramolecular reaction, both alcohol and halogenoalkane functional group are present on the same molecule. Only a small handful managed to get II correct. Since the product is asymmetrical, it matters which C-O bond was broken. Students needed to draw the one that contains a primary halogenoalkane, which was a clue given in the question stem.

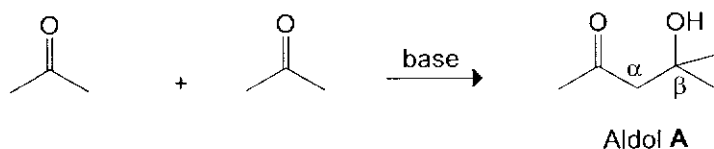
[2]

[Total: 9]

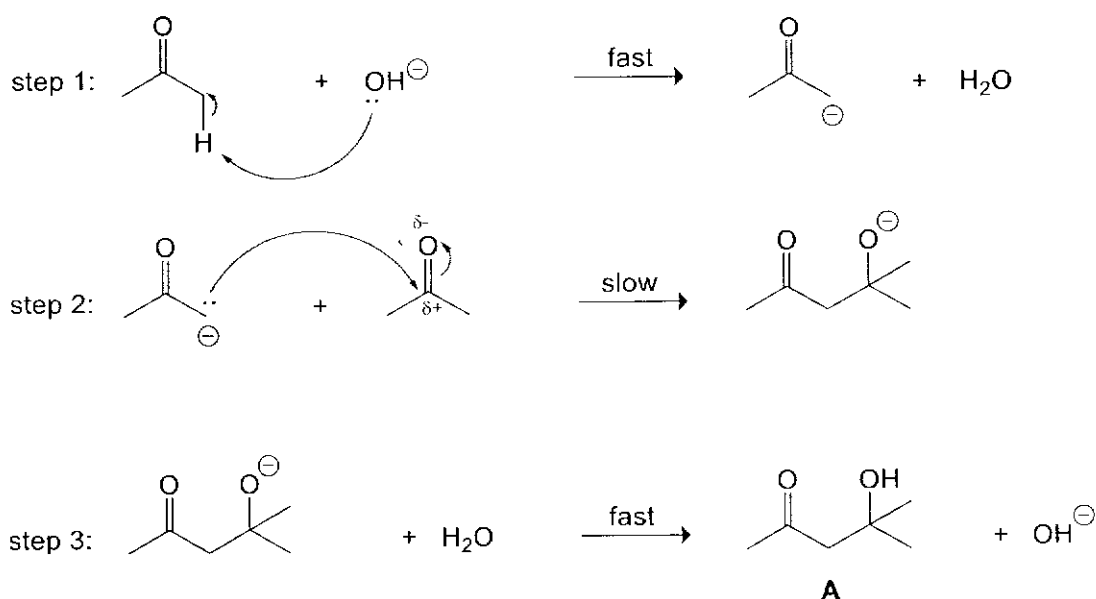
- 5 (a) The Aldol Addition reaction is important in organic synthesis as it provides a method for linking two smaller molecules by introducing a carbon-carbon bond between them.

The reaction combines two carbonyl compounds to form a new β -hydroxy carbonyl compound, also known as *aldols*, which are commonly found in many important molecules, whether naturally occurring or synthetic.

One example of Aldol Addition reaction between two propanone molecules to form an aldol **A** is shown in the equation below.



The following shows the mechanism for the Aldol Addition reaction involving two propanone molecules.



Very few answers received full credit for this question. There were many random arrows drawn. Students can consider the actual bonds broken and bonds formed to determine where the curly arrows should be drawn.

Common mistakes include

- Forgetting to draw lone pair on both or one of the O atoms
- Forgetting to label partial charges on C=O bond
- Using half-arrows even though no radicals are involved
- Labelling partial charges on charged ions

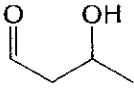
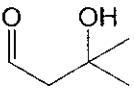
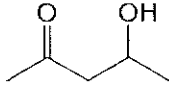
- (i) State the type of reaction that has occurred in step 2 of the mechanism.

nucleophilic addition [1]

[1]

Surprisingly a variety of answers were seen here. For a new reaction given, students are reminded to first try to relate to functional groups and reactions learnt in the syllabus and determine if it is a similar reaction.

- (ii) Complete the mechanism for steps 1 and 2 by showing the movement of electron pairs using curly arrows on the diagram shown above. Indicate all partial charges and relevant lone pairs. [2]
[1] each step
- (iii) When this reaction is carried out using a mixture of propanone and ethanal, three other compounds are formed in addition to compound **A**. Compound **B** has M_r of 88, while compounds **C** and **D** have M_r value of 102. Draw the structures of these three products labelled as **B**, **C** and **D**. [3]

		
B ($M_r = 88.0$)	C ($M_r = 102.0$)	D ($M_r = 102.0$)

Very few correct answers with many students leaving this part blank. Students need to refer to the reaction scheme given earlier and consider the changes when ethanal was added to the mixture. Many unrelated structures were given with totally different functional groups. The structures should not be drawn using the given M_r values as the only information.

- (iv) Suggest two chemical tests that could be used to distinguish the three products from each other. You should state clearly the observations for each test.

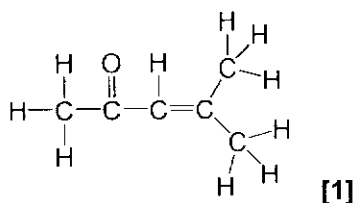
Add $I_2(aq)$, $NaOH(aq)$ to all three compounds separately and warm. Compound **B** and **D** will produce yellow ppt. but not compound **C**. [1]

Add Tollens' solution and warm. Compound **B** and **C** will produce silver mirror but not compound **D**. [1]

Many students left this part blank along with the previous part. No credit given if all three structures were not given as compounds **C** and **D** are not fixed. Suggested tests also need to be able to differentiate between all three compounds. Common mistakes include not stating the observations for all compounds or writing 'no visible observations'. It is also surprising to see a number of students writing 'reflux' or 'distillation' in their answers. Students are reminded that the tests conducted should be simple test tube tests. [2]

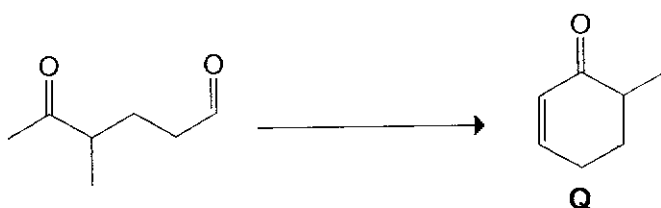
- (b) At a higher temperature, the carbonyl compounds can undergo Aldol Condensation reaction, which involves the loss of a water molecule from the aldol product obtained earlier and results in the formation of an alkene functional group between the α and β carbons.

Draw the displayed formula of the product formed from the Aldol Condensation involving two propanone molecules. [1]



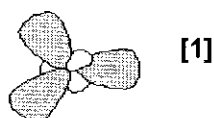
Many wrong structures were given, probably due to no reference made to Aldol A given earlier in the question. Common mistakes include answering with skeletal formula or not showing the bonds in the $-\text{CH}_3$ groups.

- (c) Intramolecular Aldol Condensation reaction can also occur to give a cyclic unsaturated carbonyl compound when a dicarbonyl compound with a sufficiently long carbon chain is used. An example of such a reaction is given below.



- (i) State the hybridisation of the carbon atom in $\text{C}=\text{C}$ and draw the hybrid orbitals of this carbon atom.

sp^2 [1]



[2]

Type of hybridisation was well answered but many never seen before diagrams were drawn for the hybrid orbitals. Some students also misread the question and tried to draw the overlapping of orbitals to form the $\text{C}=\text{C}$, which was not asked here.

- (ii) What type(s) of stereoisomerism can compound Q exhibit, and how many stereoisomers of each type(s) are there?

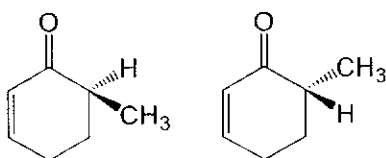
Enantiomerism [1]

2 enantiomers [1]

[2]

Poor understanding of stereoisomerism was seen here. There were many answers linking to constitutional isomerism with a large number of isomers drawn in the later part. Cis-trans isomerism is not exhibited when the $\text{C}=\text{C}$ is in a cyclic ring (of >8 carbon atoms).

(iii) Draw the structures of the stereoisomers of compound Q.



[1] each

[2]

[Total: 15]

The most common mistake was not drawing the bonds around the chiral carbon using wedge and dashed lines. Students are also reminded to be more careful when copying the structure. 5 and 7 member rings were seen, along with a different C=C position.

6 Among the typical ingredients in vaccine are four ionic salts, which makes up the phosphate-buffered saline (PBS).

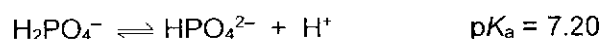
A student found incomplete instructions for preparing 1 dm³ of PBS with some missing quantities.

Step 1: Add 8.00 g of NaCl, 0.200 g of KCl, certain amount of KH₂PO₄ and Na₂HPO₄. The initial pH will be at 7.94

Step 2: Add a certain amount of HCl to the solution to reach the pH that is similar to the pH of blood in human body.

The resultant buffer solution also has ion concentrations similar to that in human body, with 0.157 mol dm⁻³ of Na⁺ and 0.1423 mol dm⁻³ of Cl⁻.

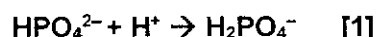
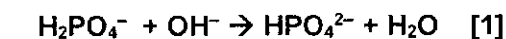
The ions H₂PO₄⁻ and HPO₄²⁻ are related by the following equilibrium.



With the above information and further calculations from (a)(ii) to (v), the student managed to prepare the desired PBS solution.

(a) (i) Explain what the term buffer means, and write two equations to describe how the PBS can act as a buffer.

A buffer is a solution in which then pH remains almost constant on dilution and when a small amount of acid or base is added. [1]



This was generally well answered. Usual common errors of missing out
 1) pH remains "almost" constant
 2) the key word of "small amount" of acid or base added. [3]

For the equations, the specific conjugate acid (H₂PO₄⁻) and conjugate base (HPO₄²⁻) are to be used to remove OH⁻ and H⁺ respectively. Furthermore, candidates should take note of balancing the equations and the correct ionic charge of the species.

- (ii) Calculate the ratio of $[\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-]$ at the initial pH.

$$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \quad [1]$$

$$7.94 = 7.20 + \log_{10} \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

$$0.74 = \log_{10} \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

$$\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 10^{0.74} = 5.50 \quad [1]$$

[2]

Most candidates were not able to process this calculation, and missed the fact that it is a buffer solution. Incorrect attempts tend to include $K_a = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$ and solved by using $[\text{H}^+] = [\text{HPO}_4^{2-}]$ which is incorrect in a buffer solution.

For those who used the Henderson-Hasselbalch equation (which is expected to be well known) may have forgotten how to convert $y = \log_{10} x$ into $10^y = x$

- (iii) Calculate, to four significant figures, the amount of NaCl and KCl (in moles) separately present in 1 dm³ of PBS.

$$M_r \text{ of NaCl} = 23.0 + 35.5 = 58.5$$

$$\text{Amount of NaCl} = \frac{8.0}{58.5} = 0.1368 \text{ mol [1]}$$

$$M_r \text{ of KCl} = 39.1 + 35.5 = 74.6$$

$$\text{Amount of KCl} = \frac{0.200}{74.6} = 2.681 \times 10^{-3} \text{ mol [1, 4 s.f. for both] [2]}$$

Part (iii) and (i) were the best performing parts of the question. Careless mistake of not giving 4s.f. and using incorrect A_r were the occasional errors here.

- (iv) Hence, using your answers in (a)(iii) and taking into account the total amount of Na⁺ ions, calculate the initial amount of Na₂HPO₄ and subsequently the initial amount of KH₂PO₄ that should be added at step 1.

$$\text{Total amount of Na}^+ \text{ in buffer solution} = 0.157 \text{ mol}$$

$$\text{Amount of Na}^+ \text{ due to Na}_2\text{HPO}_4 = 0.157 - 0.1368 = 0.0202 \text{ mol}$$

$$\text{Amount of Na}_2\text{HPO}_4 = \frac{0.0202}{2} = 0.0101 \text{ mol [1, e.c.f. 3 s.f.]}$$

(accept 0.0100 mol if 0.137 mol was used in calculations)

$$\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 5.50, \text{ let amount of KH}_2\text{PO}_4 \text{ be } x$$

$$\frac{\left(\frac{0.0101}{1}\right)}{\left(\frac{x}{1}\right)} = 5.50$$

$$x = \frac{0.0101}{5.50}$$

$$= 1.84 \times 10^{-3} \text{ mol [1] ecf amount of Na}_2\text{HPO}_4 \text{ and ratio from (ii)}$$

Candidates found this challenging, especially in finding amount of KH₂PO₄, as many did not use the ratio found in (ii).

While common error of not dividing by 2 was seen in finding amount of Na₂HPO₄, a surprisingly significant minority thought NaCl had formed Na₂HPO₄ instead of using the total amount of Na⁺ as guided and also understanding that these salts were added separately.

- (v) Use your answers in (a)(iii) and taking into account the total amount of Cl⁻ ions, calculate the amount of HCl added.

$$\text{Total amount of Cl}^- \text{ in buffer solution} = 0.1423 \text{ mol}$$

$$\text{Amount of HCl added} = \text{amount of Cl}^- \text{ due to HCl}$$

$$= 0.1423 - 0.1368 - 2.681 \times 10^{-3}$$

$$= 2.82 \times 10^{-3} \text{ mol [1, e.c.f., 3 or 4 s.f.]}$$

[1]

Despite error in (iv), candidates who attempted and were clear on the sources of Cl⁻ ions. i.e. NaCl, KCl and HCl, had managed to solve this easily.

- (vi) Hence, show with calculation, that the final ratio of $[\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-]$ is 1.56 after HCl is added in step 2.

$$\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = \frac{\left(\frac{0.0101 - 2.82 \times 10^{-3}}{1}\right)}{\left(\frac{1.84 \times 10^{-3} + 2.82 \times 10^{-3}}{1}\right)} = \frac{7.28 \times 10^{-3}}{4.66 \times 10^{-3}} = 1.56 \text{ [1] e.c.f (v) and (vi)}$$

Only the most able candidates managed to arrive at the correct answer here, understanding the full picture of how the final ratio can be derived.

It has to be noted that

- 1) Some HPO_4^{2-} (the conjugate base) had reacted away with H^+ added and
- 2) Some H_2PO_4^- had formed due to the reaction.

[1]

- (vii) Maximum buffer capacity of a phosphate buffer is when $[\text{HPO}_4^{2-}] = [\text{H}_2\text{PO}_4^-]$. Compare and comment on the buffer capacity of the phosphate solution at the end of step 1 and at the end of step 2.

The phosphate solution has a **higher buffer capacity at the end of step 2** compared to at the end of step 1, as the ratio of $[\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-]$ is closer to 1, which is when $[\text{HPO}_4^{2-}] = [\text{H}_2\text{PO}_4^-]$. [1, owtte]

.. [1]

At the end of step 2, the PBS can remove OH^- better than at end of step 1.

Most answers were incorrect or incomplete (lacking explanation or understanding about how the ratio of $[\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-]$ related to buffer capacity).

However, regardless of the ability shown in the earlier parts, it was clear to some candidates that the ratio of 1.56 given at end of step 2 (as in part (vi)) indicated a higher capacity of the buffer as compared to the end of step 1.

- (b) Mohr's method is a type of titration to determine the concentration of Cl^- in a sample. The same student carried out this titration with $0.100 \text{ mol dm}^{-3} \text{ AgNO}_3$ as titrant and $1.50 \text{ mol dm}^{-3} \text{ K}_2\text{CrO}_4$ as indicator.

He conducted the titration by pipetting 10.0 cm^3 of the phosphate-buffered saline (PBS) into a conical flask and added K_2CrO_4 indicator. Upon adding AgNO_3 , white precipitate is immediately formed and the end-point is indicated by the first appearance of a red precipitate of Ag_2CrO_4 . At the end-point, a saturated solution of AgCl is present. Based on his calculation, it will take 14.25 cm^3 of AgNO_3 to reach the end-point.

This titration works on the nature of sparingly soluble silver salt, and the relevant K_{sp} values are below:

compound	K_{sp}
AgCl	1.77×10^{-10}
Ag ₂ CrO ₄	1.12×10^{-12}

- (i) Calculate the concentration of Cr⁻(aq) ions that remains in the solution at the end-point of the titration, assuming that $[Ag^+(aq)] = [Cr^-(aq)]$.

$$K_{sp} \text{ of AgCl} = [Ag^+(aq)][Cr^-(aq)]$$

$$[Cr^-(aq)] = \sqrt[2]{1.77 \times 10^{-10}} = 1.33 \times 10^{-5} \text{ mol dm}^{-3} \text{ [1]}$$

[1]

Many incorrect calculations were based on amount of Ag⁺ added instead, showing a lack of understanding that most of the Ag⁺ added had already formed AgCl ppt as stated in the question stem.

Candidates should consider that if ppt is formed from the solution, the solution is now saturated, hence the concentration of ions remaining in the solution can be derived from K_{sp} .

- (ii) If 1.00 cm³ of K₂CrO₄ was added at the start of titration, calculate the concentration of CrO₄²⁻(aq) ions at the end-point and determine if Ag₂CrO₄ precipitate will form at the end-point.

$$[CrO_4^{2-}] = \frac{1.50 \times \frac{1}{1000}}{\frac{10 + 14.25 + 1.00}{1000}} = 0.0594 \text{ mol dm}^{-3}$$

[1, no marks for 0.0619 (missed 1 cm³ for total vol)]



$$\text{Ionic product} = [Ag^+]^2[CrO_4^{2-}]$$

$$= (1.33 \times 10^{-5})^2 (0.0594) = 1.05 \times 10^{-11} > 1.12 \times 10^{-12} \text{ [1, ecf } [CrO_4^{2-}]]$$

As ionic product of Ag₂CrO₄ > K_{sp} of Ag₂CrO₄ precipitation will occur [1, e.c.f]

[3]

This part was poorly attempted, perhaps due to a lack of time.

Incorrect answers for $[CrO_4^{2-}]$ ranged from totally ignoring the change in volume, to missing out the 10 cm³ sample, and some instances of 14.5 cm³ used as titre value.

Evidence of rushed work continue to surface in ionic product calculation with incorrect $[Ag^+]$ used, either as two times of answer in (i) or using 0.100 mol dm⁻³ instead.

Finally in justification of precipitation, mistakes include not using ionic product at all, or thinking that when $IP < K_{sp}$, precipitate will form, or not able to compare the values in standard form.

- (iii) The sample's pH range must be between 6.5 and 9 for Mohr's method titration to be conducted. Suggest a reason why it should not be conducted at a higher pH.

At a higher pH, $[OH^-]$ will be higher, and the Ag⁺ ions added may form an insoluble brown precipitate (Ag₂O), thus resulting in an inaccurate titre value obtained. [1]

ver

..... [1]

Only a handful of candidates appreciated that OH^- may form ppt with metal ions and hence affect the reaction. Majority of the incorrect attempts positioned this as pH range of indicator, as if it was an acid-base titration.

[Total: 17]