Catholic Junior College
JC2 Preliminary Examination
Higher 2

CANDIDATE NAME	
CLASS	2T

CHEMISTRY 9729/02

Paper 2 Structured Questions

August 2021

2 hours

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.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

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

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use		
Paper 1		30
Paper 2	Q1	/14
	Q2	/8
	Q3	/12
	Q4	/9
	Q5	/15
	Q6	/17
		75
Paper 3		80
Paper 4		55
OVERALL (100%)		
Grade		

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

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.

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

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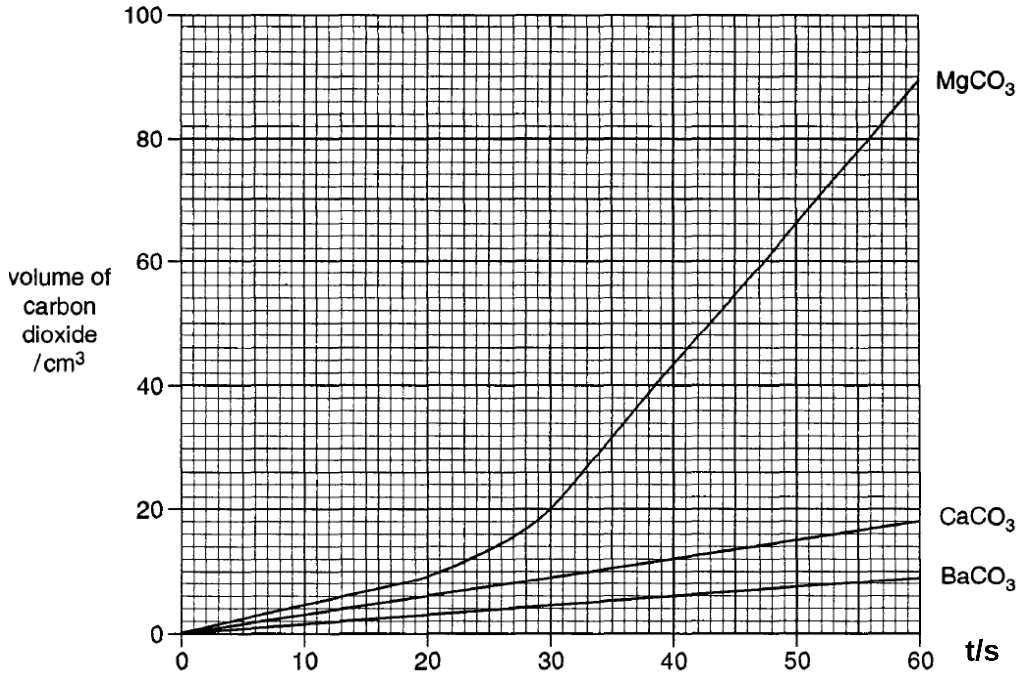
(c) A student investigates the thermal decomposition of the carbonates of Group 2 elements. He separately heats the carbonates of magnesium, calcium and barium and records the total volume of carbon dioxide collected every 10 seconds. In each experiment, he uses the same amount, in moles, of each carbonate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

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

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(d) The student wanted to perform the same investigation on the carbonates of the elements in Group 13 but found that $Al_2(CO_3)_3$ does not exist at room temperature. Suggest a reason for this.

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

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……………………………………………………………………………………………[2]

(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.

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(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.

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[Total: 14]

2 **(a)** **(i)** Calculate the average oxidation number of sulfur in sodium thiosulfate, $Na_2S_2O_3$.

[1]

(ii) Draw the structure of a thiosulfate anion, $S_2O_3^{2-}$, with a single central S atom, and clearly label the actual oxidation number of each S atom.

[2]

(b) Thiosulfate anions undergo disproportionation as shown.

$$S_2O_3^{2-} + H_2O \rightarrow SO_4^{2-} + HS^- + H^+$$

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

[2]

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

$S_4O_6^{2-}$ / $S_2O_3^{2-}$ $E^{\ominus} = +0.09$ V

MnO_4^{-} / Mn^{2+} $E^{\ominus} = +1.52$ V

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

Strongest oxidising agent: ……………………………………………………………..[1]

Strongest reducing agent: ……………………………………………………………..[1]

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

……………………………………………………………………………………[1]

[Total: 8]

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

The reaction between peroxodisulfate(VII) ions, $S_2O_8^{2-}$, and iodide ions, I^-, is represented by the following equation:

$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

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.

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....[1]

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

....

....

....[1]

(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.

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....[3]

(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.

Reaction 1: $2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$

Reaction 2: $I_2 + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

During an experiment to determine the rate equation, different concentrations of KI, and $Na_2S_2O_8$ 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.

....

....[1]

(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: ....

against: .... [1]

(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.

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

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

[1]

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

[2]

[Total: 12]

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:

$$\text{ROH} \xrightarrow[\text{step } \mathbf{1}]{\text{NaH}} \text{RO}^-\text{Na}^+ \xrightarrow[\text{step } \mathbf{2}]{\text{R'X (alkyl halide)}} \text{ROR'}$$

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

.... [1]

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

.... [1]

(iii) Using 1-chloropropane as the alkyl halide and $CH_3CH_2O^-$ 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.

[3]

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

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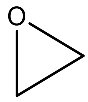
.... [1]

(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 Willamson ether synthesis with a low yield because it is unstable. Suggest why epoxyethane is unstable.

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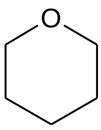
…………………………………………………………………………………… [1]

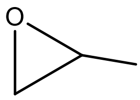
(ii) In the boxes below, suggest the structure of the organic reagent used to synthesise each of the following ethers via intramolecular Williamson ether synthesis.

I



Organic reagent:

II



Organic reagent:

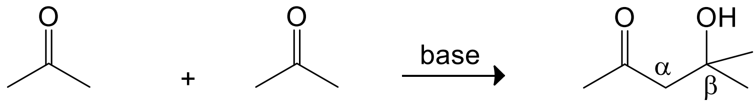
[2]

[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.

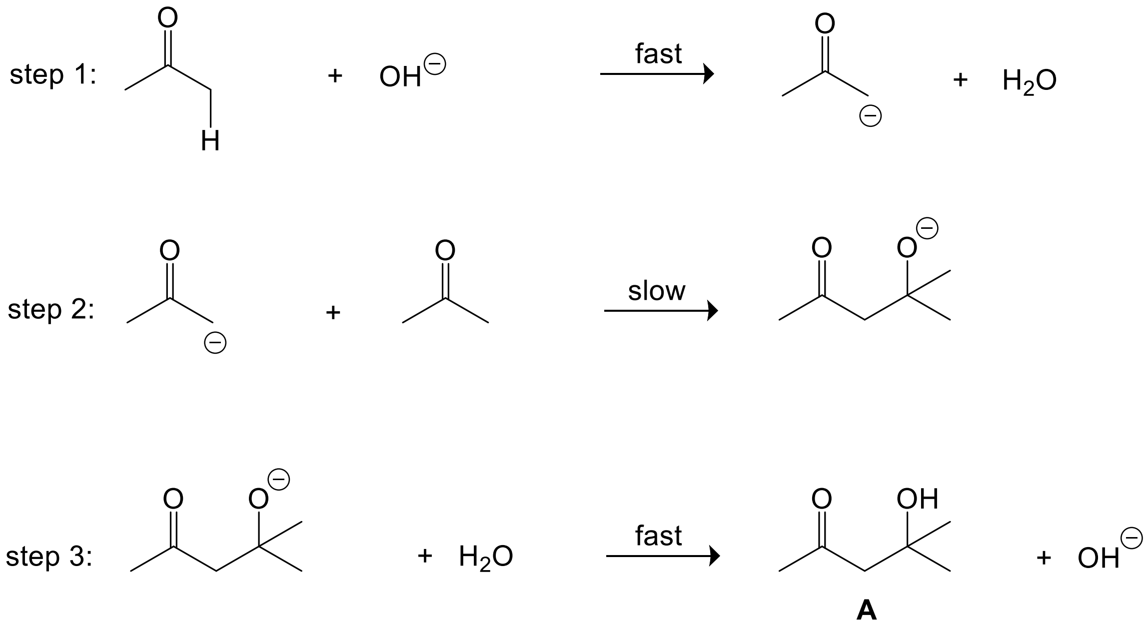
The reaction combines two carbonyl compounds to form a new β–hydroxy carbonyl compound, also known as *aldols*, which are commonly found in many important molecules, whether naturally occurring or synthetic.

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



Aldol **A**

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



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

.... [1]

(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]

(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 value 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)	**D** (M_r = 102)

(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.

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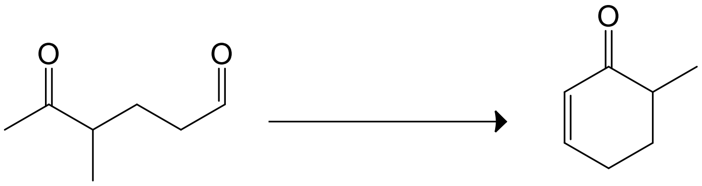
(b) At a higher temperature, the carbonyl compounds can undergo Aldol Condensation reaction, which involves the loss of a water molecule from the aldol product obtained earlier and results in the formation of an alkene functional group between the α and β carbons.

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

(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.



Q

(i) State the hybridisation of the carbon atom in C=C and draw the hybrid orbitals of this carbon atom.

[2]

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

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……………………………………………………………………………………………[2]

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

[2]

[Total: 15]

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 dm^3 of PBS with some missing quantities.

Step 1: Add 8.00 g of Na*Cl*, 0.200 g of K*Cl*, certain amount of KH_2PO_4 and Na_2HPO_4. The initial pH will be at 7.94

Step 2: Add a certain amount of H*Cl* 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 $H_2PO_4^-$ and HPO_4^{2-} are related by the following equilibrium.

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \qquad pK_a = 7.20$$

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.

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....[3]

(ii) Calculate the ratio of $[HPO_4^{2-}]/[H_2PO_4^-]$ at the initial pH.

[2]

(iii) Calculate, to **four** significant figures, the amount of Na*Cl* and K*Cl* (in moles) separately present in 1 dm^3 of PBS.

[2]

(iv) Hence, using your answers in **(a)(iii)** and taking into account the total amount of Na^+ ions, calculate the initial amount of Na_2HPO_4 and subsequently the initial amount of KH_2PO_4 that should be added at step 1.

[2]

(v) Using your answers in **(a)(iii)** and taking into account the total amount of Cl^- ions, calculate the amount of H*Cl* added.

[1]

(vi) Hence, show with calculation, that the final ratio of $[HPO_4^{2-}]/[H_2PO_4^-]$ is 1.56 after H*Cl* is added in step 2.

[1]

(vii) Maximum buffer capacity of a phosphate buffer is when $[HPO_4^{2-}] = [H_2PO_4^-]$. Compare and comment on the buffer capacity of the phosphate solution at the end of step 1 and at the end of step 2.

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.... [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 mol dm^{-3} $AgNO_3$ as titrant and 1.50 mol dm^{-3} K_2CrO_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_2CrO_4	1.12×10^{-12}

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

[1]

(ii) If 1.00 cm^3 of K_2CrO_4 was added at the start of titration, calculate the concentration of CrO_4^{2-}(aq) ions at the end-point and determine if Ag_2CrO_4 precipitate will form at the end-point.

[3]

(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.

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....[1]

[Total: 17]

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