TEMASEK JUNIOR COLLEGE
2022 JC2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME	

CENTRE NUMBER	S					INDEX NUMBER					

Chemistry **9729/02**

Paper 2 Structured Questions **25 August 2022**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number and name in the spaces at the top of this page.
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** the questions in the spaces provided on the Question Paper.
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.

For Examiner's Use		
Paper 1		**/30**
Paper 2	**Q1**	**/9**
	Q2	**/14**
	Q3	**/10**
	Q4	**/8**
	Q5	**/20**
	Q6	**/14**
	Total	**/75**
Paper 3		**/80**
TOTAL (%)		**/100**

This document consists of **23** printed pages and **1** blank page.

Answer **all** the questions in the space provided.

1 **(a)** Element **W** is from Period 5 of the Periodic Table. The first eight ionisation energies of element **W**, in kJ mol^{-1}, are

869 1800 2690 3610 5720 6670 12000 13800

(i) Identify element **W** and explain your answer.

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.... [2]

(ii) Explain the difference between the first ionisation energy of element **W** compared to the element to its left on the Periodic Table.

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(b) The chlorides of elements in Period 3 of the Periodic Table show different behaviours on addition to water.

(i) Describe and explain the reactions of aluminium chloride, $AlCl_3$, and phosphorus pentachloride, PCl_5, with excess water.

Write equations for any reactions that occur.

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.... [3]

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(ii) The reaction of PCl_5 with limited amount of water involves step-wise substitution of –C*l* with –OH.

Write the overall balanced equation for the reaction of PCl_5 with limited amount of water. Hence, suggest a three-step reaction sequence for this reaction.

Overall equation: ....

Step 1: ....

Step 2: ....

Step 3: ....

[2]

[Total: 9]

2 Boron trifluoride, BF_3, and aluminium fluoride, AlF_3, differ markedly in their physical properties.

compound	melting point / °C
BF_3	–127
AlF_3	1291

(a) **(i)** State the type of bonding present in each of these compounds and draw 'dot-and-cross' diagrams in the boxes below to illustrate this bonding.

Type of bonding: …………………………..	Type of bonding: …………………………..
BF_3	AlF_3

[2]

(ii) Outline the principles of the Valence Shell Electron Pair Repulsion theory.

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.... [2]

(iii) Boron trifluoride forms a compound with ammonia.

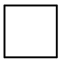
Use the Valence Shell Electron Pair Repulsion theory to predict and draw the likely shape of the product formed from this reaction.

Shape of product: ………………………………………………………………

[2]

Cyclobutane is an example of a cyclic alkane. While itself has no commercial or biological significance, more complex derivatives of cyclobutane are important in biology and biotechnology.

Cyclobutane decomposes to ethene as shown by the following equation.



$$\text{(g)} \rightarrow 2CH_2{=}CH_2\text{(g)} \qquad \Delta H^{\ominus}_{\text{decomp}}$$

A student planned to determine $\Delta H^{\ominus}_{\text{decomp}}$ by using the standard enthalpy changes of combustion of cyclobutane and ethene, represented by $\Delta H^{\ominus}_{c}$(cyclobutane) and $\Delta H^{\ominus}_{c}$(ethene) respectively. Both substances are gases at 298 K.

$\Delta H^{\ominus}_{c}$(ethene) was previously determined to be –1411 kJ mol^{-1} in a flame calorimetric experiment.

To determine $\Delta H^{\ominus}_{c}$(cyclobutane), the student decided to conduct another flame calorimetric experiment under the same conditions.

There are two stages to this experiment.

Stage I : Calibration of calorimeter (i.e. copper can, water and other components in the calorimeter)

In the experiment, the calorimeter must first be calibrated by determining its heat capacity, ***C***, which is the amount of heat required to raise the temperature of the calorimeter by 1 K.

Stage II : Determination of $\Delta H^{\ominus}_{c}$(cyclobutane) using the calibrated calorimeter.

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The student carried out the flame calorimetric experiment using the calorimeter. Part of his results is shown below.

Stage I, using ethene as the fuel,

- change in temperature of water = 33.8 °C
- mass of gaseous ethene burnt = 1.00 g

Stage II, using cyclobutane as the fuel,

- change in temperature of water = 32.9 °C
- mass of gaseous cyclobutane burnt = 1.00 g

(b) **(i)** Use the above information and experimental results to calculate the heat capacity, ***C***, of the calorimeter.

[2]

(ii) Use your answer to **(b)(i)** to determine $\Delta H_c^{\ominus}$(cyclobutane).

[2]

(iii) Hence, calculate the standard enthalpy change of decomposition of cyclobutane to ethene, $\Delta H^{\ominus}_{decomp}$.

[1]

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(c) **(i)** Use data from the *Data Booklet* and the $\Delta H^{\ominus}_{decomp}$ obtained in **(b)(iii)** to calculate the actual C–C bond energy in cyclobutane.

[You may assume that the difference between the C–H bond energy in cyclobutane and in ethene, and the difference between the C=C bond energy from the *Data Booklet* and in ethene are insignificant.]

[2]

[Turn over

(ii) Suggest an explanation for the difference between the average C–C bond energy from the *Data Booklet* and the actual value calculated in **(c)(i)**.

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.... [1]

[Total: 14]

3 **(a)** SO_2 gas is found in air near volcanoes. 213 cm^3 of SO_2 collected at r.t.p. near a volcano required 25.0 cm^3 of 0.120 mol dm^{-3} acidified potassium dichromate(VI) solution for complete reaction.

Calculate the final oxidation state of sulfur in the product mixture.

[2]

(b) The Contact process is an important industrial method of manufacturing sulfuric acid.

The key stage of the Contact process is the reaction between sulfur dioxide and oxygen:

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g) \qquad \text{--------} \quad \text{Equation 1}$$

Table 3.1 shows how the percentage of sulfur trioxide in the equilibrium mixtures varies with temperature as well as the volume of the reaction vessels.

Table 3.1

Temperature /°C	Percentage of sulfur trioxide in the equilibrium mixture for vessel		
	A	**B**	**C**
800	1.68	0.009	0.88
700	2.98	0.016	1.54
600	5.70	0.032	3.02
500	11.9	0.077	6.71

Using the data in Table 3.1,

(i) explain whether the forward reaction is exothermic or endothermic.

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....[2]

(ii) explain and rank the three vessels in order of decreasing volume.

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A mixture containing 2 moles of SO_2 and 1 mole of O_2 was heated in a closed 3.60 dm^3 flask at 500 °C and allowed to reach equilibrium. The flask was then rapidly cooled to liquefy SO_3.

After removing gaseous SO_2 and O_2, excess water was carefully added to the liquid SO_3, causing the following reaction to occur:

$$SO_3(l) + H_2O(l) \rightarrow H_2SO_4(aq) \qquad \text{--------} \quad \text{Equation 2}$$

The resulting solution was made up to 250 cm^3 in a standard volumetric flask. 25.0 cm^3 of this solution was titrated with 5.00 mol dm^{-3} NaOH and required 38.50 cm^3 for complete neutralisation.

(iii) Calculate the equilibrium amount of SO_3 at 500 °C.

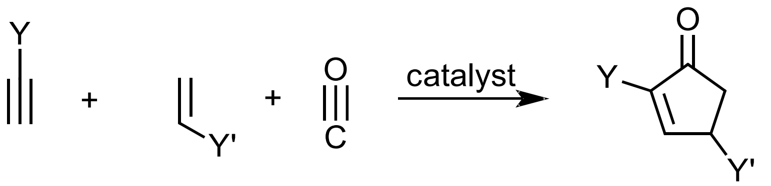
[2]

(iv) Hence, calculate a value for the equilibrium constant, K_c, of equation 1.

[2]

[Total: 10]

4 **(a)** The Pauson-Khand reaction is a gas phase reaction between an alkyne, an alkene and carbon monoxide to form a cyclic carbonyl compound, as shown in Fig. 4.1.



where Y and Y' can be C*l* or H.

Fig. 4.1

An organic compound **A** was produced from the Pauson-Khand reaction. The compound has the following composition by mass; 51.5 % C, 13.7% O, 30.5% C*l* and 4.3% H. The relative molecular mass of **A** is 116.5.
Upon heating with ethanolic $AgNO_3$, **A** gave a white precipitate.

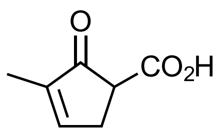
(i) Determine the molecular formula of **A** and draw its structural formula.

[2]

(ii) Draw a diagram to show the orbitals of the carbonyl carbon in compound **A**. State the type of hybridisation involved.

Type of hybridisation: .... [1]

(b) Another possible product of the Pauson-Khand reaction is shown below:



B

Draw the organic product formed when **B** reacts with each of the following.

(i) cold $KMnO_4$(aq) in KOH(aq)

(ii) $LiAlH_4$

[2]

(c) A flask with a volume of 100 cm^3 was first weighed with air filling the flask, and then with another gas **Z**, filling the flask. The results, measured at 26 °C and 1.00×10^5 Pa are shown.

Mass of flask containing air	= 47.930 g
Mass of flask containing **Z**	= 47.989 g
Density of air	= 0.00118 g cm^{-3}

Calculate the relative molecular mass of **Z**.

[3]

[Total:8]

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5 **(a)** The 'bromine clock' involves a reaction between bromide ions and bromate(V) ions in acid solution:

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

The reaction can be monitored by adding phenol and a constant volume of methyl red to all the experiments.

Phenol reacts immediately with the bromine as it is produced. Once all the phenol added has reacted, the bromine that is subsequently produced will oxidise the methyl red causing the disappearance of the red colour in the reaction mixture.

A series of experiments were carried out to investigate the order of reaction with respect to $[BrO_3^-]$ and the results obtained are shown in Table 5.1.

Table 5.1

Expt	Volume of BrO_3^- / cm^3	Volume of Br^- / cm^3	Volume of H^+ / cm^3	Volume of phenol / cm^3	Volume of deionised water / cm^3	Time taken for the colour of methyl red to disappear /s
1	5.0	5.0	10.0	1.0	11.0	82
2	10.0	5.0	10.0	1.0	6.0	42
3	10.0	5.0	10.0	2.0	5.0	x

(i) Write an equation for the reaction between phenol and bromine water.

[1]

(ii) Deduce the order of reaction with respect to $[BrO_3^-]$. Explain your reasoning.

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....[1]

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(iii) Using your answer in **(a)(ii)**, calculate the value of x.

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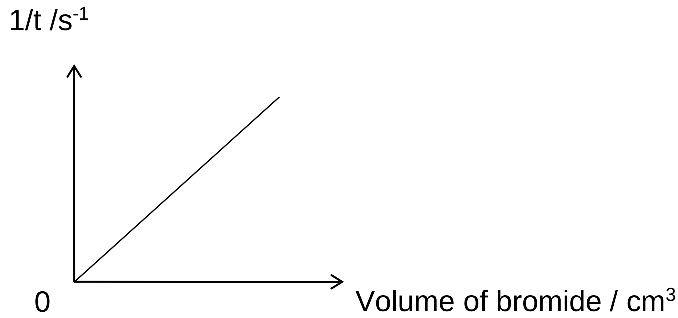
(iv) Another series of experiments were conducted with varying volumes of bromide ions and large excess of BrO_3^- and H^+. The total volume of the mixture was kept constant. The results obtained were used to plot a graph of 1/t against the volume of bromide.



Deduce the order with respect to [Br^-], explain your reasoning.

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....[1]

(v) Given that the unit of the rate constant is $mol^{-3}\ dm^{9}\ s^{-1}$, deduce the order with respect to [H^+].

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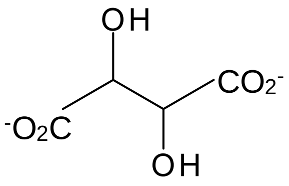
....[1]

(b) The reaction between $S_2O_8^{2-}$ and tartrate ions is catalysed by iron(III) ions and the overall equation is as shown.



$+ 3S_2O_8^{2-} + 2H_2O \rightarrow 2CO_2 + 2HCO_2^{-} + 6H^{+} + 6SO_4^{2-}$

Tartrate ions

Write equations to illustrate how iron(III) ions catalyses the reaction.

[2]

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(c) Methyl red is a pH indicator. It is red when the pH is less than 4.4 and yellow when the pH is above 6.2.

In microbiology, methyl red is used to identify bacteria that produces acids from the metabolism of glucose. The type of acid produced depends on the specific enzymatic pathways present in the bacteria.

All the bacteria initially metabolise glucose to pyruvic acid, CH_3COCO_2H. After which, some bacteria use the mixed acid pathway to metabolise pyruvic acid while other bacteria use the butanediol fermentation pathway. The products formed and the colour of methyl red are shown in Table 5.2.

Table 5.2

Metabolism pathway	Products formed per mole of glucose	Colour of methyl red
Mixed acid pathway	4 mol of acids (mainly lactic acid, $CH_3CH(OH)CO_2H$, and ethanoic acid), 1 mol of ethanol, 1 mol of CO_2 1 mol of H_2	Red
Butanediol fermentation pathway	1 mol of acid	Yellow

(i) Explain the colours of methyl red shown in Table 5.2.

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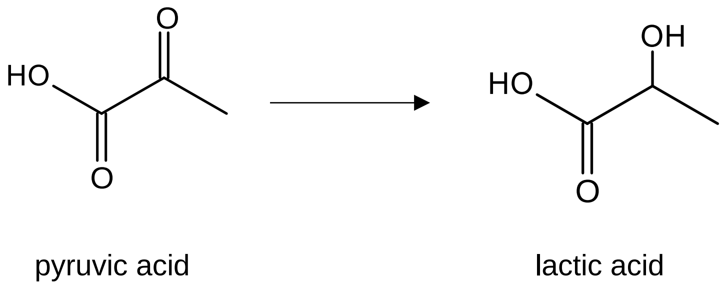
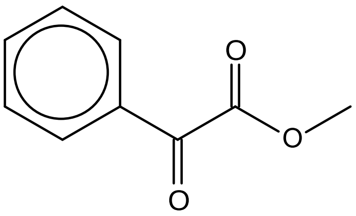
....[1]

(ii) State the reagent and condition to obtain lactic acid from pyruvic acid.



Reagent and condition: ....[1]

(iii) Suggest the reagents and conditions, including the structures of the intermediates, for the synthesis of compound **Y** from pyruvic acid.



compound **Y**

[3]

(d) Table 5.3 shows the pK_a values of some compounds, including phenol.

Table 5.3

Compound	pK_a
Phenol	10.0
Phenylmethanol, $C_6H_5CH_2OH$	15.4
Phenylmethanethiol, $C_6H_5CH_2SH$	9.93

(i) Suggest how the acidities of phenol and phenylmethanol compare with each other.

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(ii) Suggest a reason why the pK_a for $C_6H_5CH_2SH$ is much lower than that for $C_6H_5CH_2OH$.

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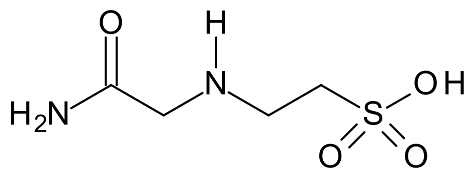
(e) ACES, $C_4H_{10}N_2O_4S$, is another compound containing sulfur.



ACES

ACES has a pK_a value of 6.88.

(i) Draw the structure of the product formed when dilute hydrochloric acid is added to ACES at room temperature.

[1]

(ii) Draw the structure of the conjugate base of ACES.

[1]

(iii) The pH of a solution of ACES is 2.2.

Calculate the ratio of [conjugate base of ACES] to [ACES].

[1]

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(iv) 0.0200 mol of the conjugate base of ACES is dissolved in 100 cm^3 of deionised water. 50 cm^3 of 0.300 mol dm^{-3} of hydrochloric acid was added to the solution.

Given that the conjugate base reacts with hydrochloric acid in a 1:1 stoichiometry, calculate the pH of the solution.

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[2]

[Total: 20]

6 The Gabriel synthesis is a 3-step approach to synthesis amines. Phthalimide is used as the main reactant, which has a nitrogen atom flanked by two carbonyl groups.

Propylamine is obtained from the Gabriel synthesis method as shown in Fig. 6.1.

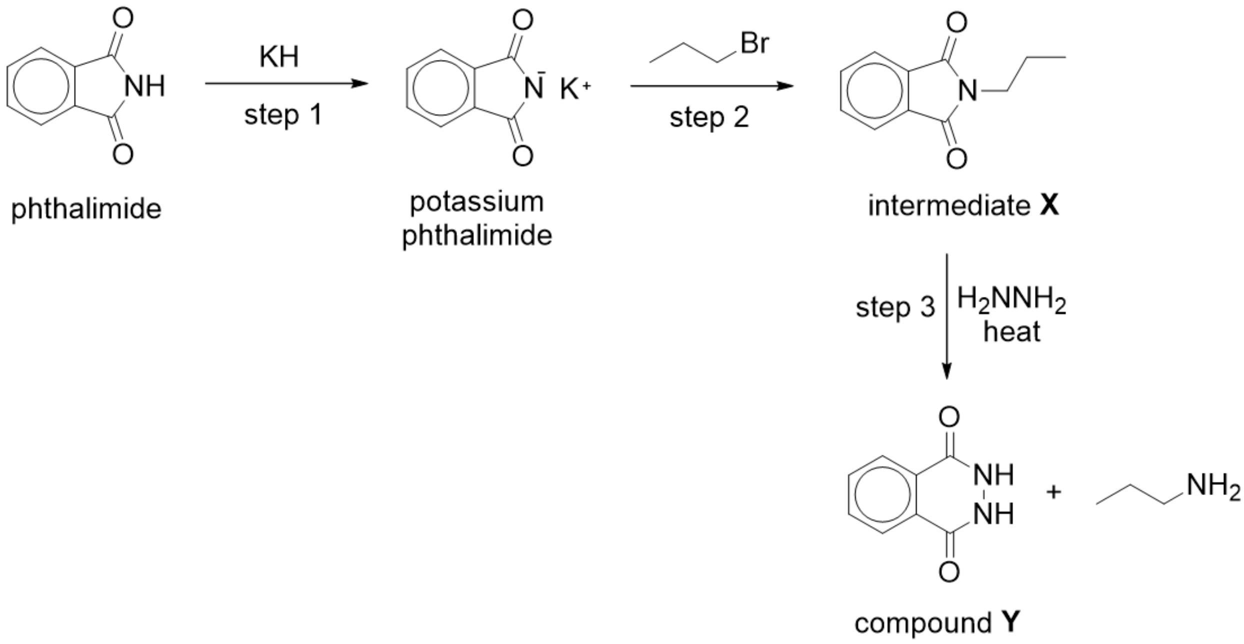

Fig. 6.1

(a) **(i)** State the role of phthalimide in the above reaction in step 1.

....[1]

(ii) With reference to the product formed in step 1, explain why phthalimide is able to function as the role identified in **(a)(i)**.

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....[1]

(b) Step 2 of Gabriel synthesis is a nucleophilic substitution reaction.

With reference to the structures of relevant reactants, explain why potassium phthalimide does not react with 2-bromo-2-methylpropane at all.

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....[2]

(c) Suggest another reagent and condition used to liberate the free amine from intermediate **X** in the last step.

Construct a balanced equation for this reaction, showing the structures of all reactants and products.

[2]

(d) A sample contains both propylamine and compound **Y** after the Gabriel synthesis shown in Fig. 6.1. A student decides to purify propylamine from the impure sample and starts by adding an equal volume of dilute hydrochloric acid, with stirring, to the sample.

Some physical data for various compounds are given in Table 6.1.

Table 6.1

	propylamine	water	compound **Y**
Density / g cm^{-3}	0.719	1.0	1.3
Boiling point / ^oC	47.8	100.0	523.5

(i) With reference to structure and bonding, explain the purpose of the addition of dilute hydrochloric acid in the purification process.

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(ii) Starting with the mixture from **(d)(i)**, plan an experiment to purify propylamine from the impure mixture.

Your plan should include details of:

- how propylamine is obtained in its anhydrous liquid form; and
- suitable apparatus used.

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(e) A student made the following statement in his journal

"Using a 2:1 mole ratio of bromomethane and potassium phthalimide in the Gabriel synthesis method will produce a dimethylamine."

Comment on the validity of the student's statement.

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....[2]

[Total: 14]

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