



VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE
NAME

CT GROUP

CHEMISTRY

9729/03

Paper 3 Free Response

21 September 2020

Candidates answer on the Question Paper.
Additional Materials: Data Booklet

2 hours

READ THESE INSTRUCTIONS FIRST

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

Write in dark blue or black pen.

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

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

Section A

Answer **all** the questions.

Section B

Answer **one** question.

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.

For Examiner's Use		
Section A	1	/ 20
	2	/ 21
	3	/ 19
Section B	4 OR 5	/ 20
Total		/ 80

This document consists of **25** printed pages and 1 blank page.

Section A

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

1 Chlorine is in Group 17 and undergoes many reactions.

(a) Sketch and label, separately, the $3p_z$ and $3d_{x^2-y^2}$ orbitals present in chlorine. [2]

(b) An element **A** reacts with chlorine to form ACl_2 . The electronic configuration of A^{2+} is $[\text{Kr}]4d^{10}$. Identify the element **A**. [1]

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(c) The following reaction occurs when chlorine dissolves in water.



When solutions of chlorine are used for water purification, the pH of these solutions are kept near to pH 7 by the addition of a base.

Chlorine is dissolved in water to produce 1000 cm^3 of a solution containing 0.170 mol of HClO and 0.170 mol of HCl .

A buffer solution is then prepared by adding 0.200 mol of $\text{NaOH}(\text{s})$ to this solution. The NaOH reacts initially with the HCl . The remaining NaOH then reacts with HClO .

(i) Write two equations to explain how this buffer is able to maintain a relatively constant pH when a few drops of $\text{H}^+(\text{aq})$ or $\text{OH}^-(\text{aq})$ are added to it. [1]

(ii) Calculate the pH of the buffer solution. [K_a of HClO is $2.9 \times 10^{-8} \text{ mol dm}^{-3}$.] [1]

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- (d) A sample of an alkane, RH, and limited amount of chlorine are mixed together and irradiated with ultraviolet light. The mechanism involved two propagation steps.



Some data for the enthalpy change of reaction and the activation energy of the two propagation steps of an alkane, RH, are given below.

Step	$\Delta H / \text{kJ mol}^{-1}$	$E_a / \text{kJ mol}^{-1}$
Propagation step 1	+4	17
Propagation step 2	-109	4

Use the data provided to sketch the energy profile diagram of the two propagation steps of the chlorination of RH. Indicate all the given energy changes, reactants, intermediates and products on the diagram. [3]

- (e) In the laboratory, there are three bottles labelled **B**, **C** and **D**. Each bottle contains one of the following chemicals, $\text{Cl}_2(\text{aq})$, $\text{NaI}(\text{aq})$ and $\text{KBr}(\text{aq})$.

Three tests were carried out using the chemicals in the bottles. The results are summarised in the table below.

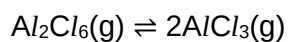
test	procedure	observation
1	mix chemical in bottle B with chemical in bottle C	colourless solution obtained
2	mix chemical in bottle B with chemical in bottle D	yellow solution obtained
3	mix chemical in bottle C with chemical in bottle D	yellow solution obtained

- (i) Deduce which bottle contains $\text{Cl}_2(\text{aq})$. Write equations to support your reasoning. [2]

- (ii) Suggest a reagent that could be added separately after performing test 2 and test 3 to confirm the identities of the chemicals in the bottles. State the observations clearly. [2]

This image shows a full page of a handwriting practice worksheet. It consists of multiple sets of three horizontal dashed lines, providing a guide for letter height and placement. The lines are evenly spaced across the entire page, which is otherwise blank.

- (f) Solid aluminium chloride sublimes at 180 °C. In the vapour phase, an equilibrium is established between aluminium chloride and its dimer.



At 400 °C and 1 atm, 0.84 g of the equilibrium gaseous mixture occupies 268 cm³.

- (i) Calculate the average relative molecular mass of the gaseous mixture. [2]
- (ii) Use your answer in (f)(i) to determine the degree of dissociation, α , of Al_2Cl_6 . [1]
- (iii) Write an expression for the equilibrium constant, K_p , for the dissociation of Al_2Cl_6 . [1]
- (iv) Hence, calculate the equilibrium constant, K_p , for the dissociation of Al_2Cl_6 at 400 °C, including its units.

If you were unable to calculate the degree of dissociation of Al_2Cl_6 in **(f)(ii)**, assume $\alpha = 0.456$. This is not the correct value of α . [2]

- (v) State and explain the effect of increasing the temperature on the average M_r of the equilibrium mixture. [2]

This image shows a full page of white paper with horizontal dashed lines, typical of primary-ruled notebook paper. The lines are evenly spaced and run across the width of the page. There are no margins, text, or other markings on the paper.

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- 2 (a) By means of a fully labelled diagram, show how the standard electrode potential of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ system can be measured by using a standard hydrogen electrode. [3]

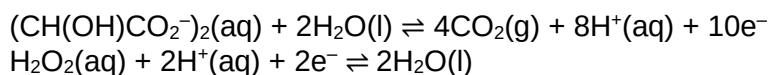
- (b) (i) When solid Fe and H_2O_2 are mixed together, the following reaction may occur.



Using data from the *Data Booklet*, write the equation for another possible reaction that might occur between solid Fe and H_2O_2 . Calculate the $\Delta G^\ominus$ per mole of Fe for this reaction. Hence, deduce which oxidation state of Fe is more likely to be formed with H_2O_2 . [4]

- (ii) Tartrate ions, $(\text{CH}(\text{OH})\text{CO}_2^-)_2$ can be oxidised by hydrogen peroxide to carbon dioxide and water using pink $\text{Co}^{2+}(\text{aq})$ ions as catalyst. During the reaction, the solution turns green due to formation of $\text{Co}^{3+}(\text{aq})$ before changing back to pink at the end of the reaction.

The two half-equations for the redox reaction between tartrate ions and hydrogen peroxide are shown below.



State the type of catalysis that has taken place and suggest a two-step mechanism to show the role of $\text{Co}^{2+}(\text{aq})$ ions in this reaction. [2]

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- [illegible]

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- (d) In an experiment, water is added to a test tube containing the solid remaining after magnesium carbonate has been heated. Dilute sulfuric acid is then added to the test tube.

The above procedure is repeated to the solid remaining after barium carbonate has been heated.

Describe all the observations made in both the experiments and give the formulae of all the species formed. [3]

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- (e) Compound **E**, $\text{C}_4\text{H}_5\text{NO}$ is non-chiral and insoluble in either acid or base. When reacted with lithium aluminium hydride, **E** forms compound **F**, $\text{C}_4\text{H}_{11}\text{NO}$. **F** reacts with ethanoyl chloride to form compound **G**, $\text{C}_8\text{H}_{15}\text{NO}_3$. When **G** is heated with acidified potassium dichromate, it forms compound **H**, which is soluble in both dilute hydrochloric acid and aqueous sodium hydroxide.

Deduce the structures of compounds **E**, **F**, **G** and **H**, explaining the reactions described. [6]

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[Total: 21]

3 This question is about silicon and its compounds.

- (a) Elemental silicon adopts a structure analogous to diamond. Describe this structure, including the type of bonding and shape around each Si atom. [2]

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- (b) Explain why the first ionisation energy of silicon is smaller than that of phosphorus but the first electron affinity of silicon is numerically greater than that of phosphorus. [2]

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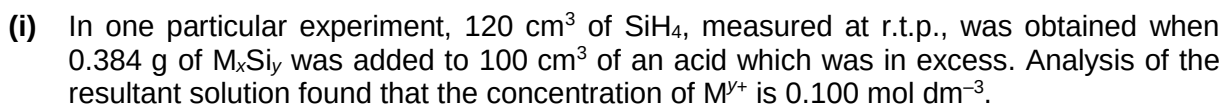
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(ii) The structure of silicide ion is thought to be a tetrahedron with four silicon atoms. Each Si atom forms single covalent bonds with the other three Si atoms. All the Si atoms achieve octet configuration. Draw the structural formula of this silicide ion, indicating clearly the bond between the atoms and its overall charge. [1]

[illegible]

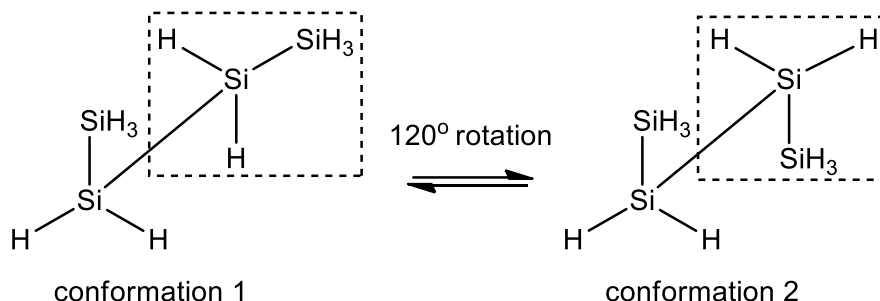
- (d) By controlling the reaction conditions, the reaction of metal silicides described in (c) can also produce longer-chain silanes. The physical data of some silanes are given in **Table 3.1** below.

Table 3.1

silane	formula	M_r	boiling point / °C	melting point / °C	density at 25 °C / g cm ⁻³
monosilane	SiH ₄	32.1	-112	-185	gas
disilane	Si ₂ H ₆	62.2	-14	-132	gas
trisilane	Si ₃ H ₈	92.3	53	-117	0.743
tetrasilane	Si ₄ H ₁₀	122.4	108	-90	0.793
n-pentasilane	Si ₅ H ₁₂	152.5	153	-72.8	0.827
cyclopentasilane	Si ₅ H ₁₀	150.5	194	-10.5	0.963

- (i) Unlike alkanes, the formation of silanes larger than heptasilane has proven difficult due to their instability. With reference to the *Data Booklet*, suggest why silanes (Si_nH_{2n+2}) are less stable than alkanes (C_nH_{2n+2}). [1]
- (ii) The Si–Si single bond in silanes can be rotated through different angles, resulting in the formation of different conformational isomers.

Two of the conformational isomers of disilane are shown below.



Straight-chain silanes have more conformational isomers compared to cyclic silanes with the same number of Si atoms.

Use the given information on conformational isomers to explain why cyclopentasilane has an unexpectedly higher boiling point than n-pentasilane. Support your answer with an additional data from **Table 3.1**. [2]

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- (e) The element, silicon, is used extensively as a semiconductor in the computer and microelectronics industries. One of the methods to make silicon involves thermal decomposition of monosilane, SiH_4 , at high temperatures of at least 500°C to deposit silicon on the computer chips.



- (i) Using the following data and data from the *Data Booklet*, construct an energy level diagram to determine the average bond energy of Si–H in monosilane.

	$\Delta H / \text{kJ mol}^{-1}$
enthalpy change of atomisation of Si	+456
standard enthalpy change of formation of $\text{SiH}_4(\text{g})$	+34.3

[3]

- (ii) Suggest and explain the sign of the standard entropy change of decomposition of monosilane, ΔS° .

[1]

- (iii) Calculate the standard Gibbs free energy change, ΔG° , for the decomposition of monosilane. Hence, suggest why high temperatures are needed for this decomposition. The numerical value of ΔS° for this decomposition of monosilane is $75.5 \text{ J K}^{-1} \text{ mol}^{-1}$

[2]

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(f) Silicon tetrafluoride, SiF_4 , a *Lewis acid*, reacts readily with fluoride ion to form species such as SiF_5^- and SiF_6^{2-} .

(i) What is meant by the term *Lewis acid*? [1]

(ii) Suggest why $\text{Si}(\text{CH}_3)_4$ does not react similarly with fluoride. [1]

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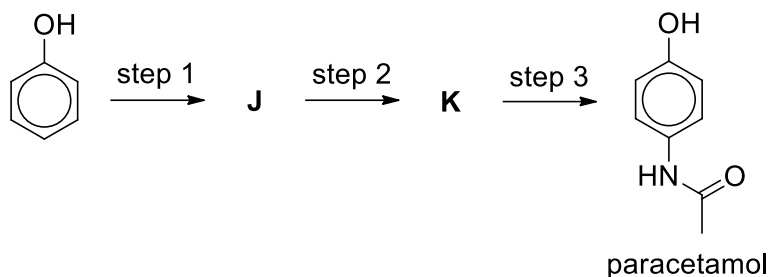
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[Total: 19]

Section B

Answer **one** question from this section.

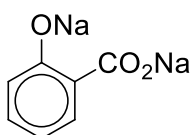
- 4 (a)** Phenol is a valuable industrial commodity for the synthesis of various useful materials and compounds. For example, paracetamol, a medication used to treat pain and fever, can be prepared from phenol via a three-step synthesis as shown below.



- (i) Suggest the structures of compounds **J** and **K**, and the reagents and conditions for steps 1, 2 and 3. [4]
- (ii) Identify one possible organic side product with the molecular formula, $\text{C}_6\text{H}_4\text{N}_2\text{O}_5$, formed in step 1. Suggest one way to minimise its formation. [2]

[illegible]

- (b)** Phenol is also used to make aspirin with compound **L** as an intermediate in the synthesis. Compound **L** is formed by heating phenol with CO_2 and NaOH strongly under pressure.



L

This reaction occurs in the following three steps.

Step 1: Phenol undergoes acid-base reaction with hydroxide ion.

Step 2: CO_2 functions as an electrophile.

Step 3: The anion of **L** is formed.

- (i) Suggest the mechanism for this reaction, showing all charges and using curly arrows to show the movement of electron pairs in each step. [3]

- (ii) Explain why hydroxide ion is needed in this reaction so that the second step can occur more readily. [1]

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- $$\text{C}_6\text{H}_5\text{OH}(\text{l}) + 3\text{H}_2(\text{g}) \longrightarrow \text{C}_6\text{H}_{11}\text{OH}(\text{l})$$
- cyclohexanol

Given that the above enthalpy change of reaction is -210 kJ mol^{-1} and the enthalpy change of combustion of cyclohexanol is $-2215 \text{ kJ mol}^{-1}$, calculate the enthalpy change of combustion of hydrogen. [1]

[illegible]

(d) The pH values of 0.10 mol dm⁻³ of the following salt solutions are shown in the table below.

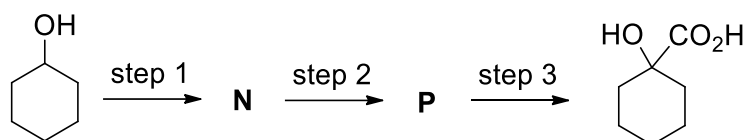
salt	pH
$\text{CH}_3\text{CH}_2\text{NH}_3\text{Cl}$	5.82
NH_4Cl	5.13
$\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$	2.81

- (i) Suggest an explanation for the different pH values of the three solutions. [3]
- (ii) Use the data provided in the table to calculate the pK_a of $C_6H_5NH_3^+$. [2]

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[Total: 20]

5 (a) A 3-step synthesis is shown below.

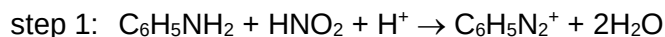


Suggest the structures of compounds **N** and **P**, and the reagents and conditions for the three steps. [4]

[illegible]

- [illegible]

- (c) Phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, is an important substance used in many industrial processes. It can react with dilute nitrous acid, HNO_2 , at room temperature to give a diazonium salt, $\text{C}_6\text{H}_5\text{N}_2^+$, as shown in step 1.



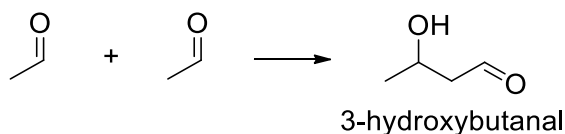
The diazonium salt formed is not stable and it can decompose on heating as shown in step 2.



- (i) Write a balanced equation for the overall reaction when phenylamine is heated with aqueous HNO_2 . [1]
- (ii) Outline briefly how the initial rate of the reaction in **(c)(i)** could be measured. [2]
- (iii) A student conducted an experiment and determined that the rate equation for the reaction in **(c)(i)** is $\text{rate} = k[\text{C}_6\text{H}_5\text{NH}_2][\text{HNO}_2][\text{H}^+]$. Assuming that both steps are elementary steps, deduce if the rate equation can be used to determine which step is the slow step. [2]

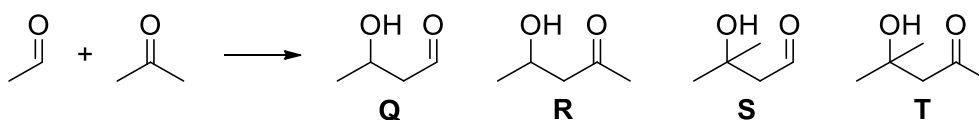
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- (d) Aldol reaction is commonly used to lengthen a carbon chain. It is based on the property that the C–H group next to a C=O group is often acidic and can be cleaved heterolytically in the presence of a base, such as sodium hydroxide. For example, ethanal can react with itself to give 3-hydroxybutanal as shown below.

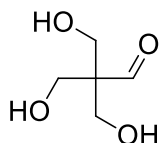


- (i) Draw the skeletal formula of the product formed when propanal undergoes aldol reaction in the presence of a base. [1]

An aldol reaction that starts with two different carbonyl compounds are of little synthetic importance because this reaction gives a mixture of products. For example, when ethanal and propanone undergo aldol reaction in the presence of sodium hydroxide, a mixture of four different products is formed as shown below.



- (ii) The product mixture obtained in the above reaction was separated. Suggest how you could distinguish these products using not more than three simple chemical tests. You are allowed to use negative results to identify the products. [3]
- (iii) Suggest how many different organic products are formed when propanone and butanone undergo aldol reaction in the presence of sodium hydroxide. [1]
- (iv) Suggest the two carbonyl compounds with no more than 2 carbon atoms in each of them that can be used to prepare the following compound using the aldol reaction.



[1]

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Additional answer space

If you use the following page to complete the answer to any question, the question number must be clearly shown.

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