	TEMASEK JUNIOR COLLEGE		
	2024 JC2 PRELIMINARY EXAMIN	ATION	
	Higher 2		TEMASEK JUNIOR COLLEGE
CANDIDATE NAME		CLASS	

CENTRE	
NUMBER	

INDEX NUMBER

Chemistry

Paper 3 Free Response Questions

9729/03 11 September 2024

2 hours

Candidates answer on the Question Paper.

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Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, 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. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A

Answer **all** questions.

Section B

Answer **one** question.

A Data Booklet is provided.

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

At the end of the examination, fasten all your work securely together.

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

For Examiner's Use		
Paper 3	Q1	/19
	Q2	/19
	Q3	/22
	Q4	/20
	Q5	/20
	Total	/80

This document consists of 28 printed pages.

Section A

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

1

In Group 14 of the Periodic Table, the elements at the top of the group, carbon to (a) germanium, have very different properties from those at the bottom, tin and lead. For instance, carbon to germanium tend to adopt oxidation states of +4, whereas the heavier elements, such as tin and lead, exhibit the +2 oxidation states.

(i) Table 1.1 shows the melting points of the elements of Group 14.

element	С	Si	Ge	Sn	Pb
melting point / °C	>3550	1410	937	232	327

Carbon, silicon and germanium each forms a solid with the same type of structure. Using structure and bonding and the information from the Data Booklet, suggest why the melting points of these elements decrease from carbon to germanium. [2]

Table 1.1

Carbon forms many allotropes such as graphite and diamond. Recent scientific research has found that replacing the graphite electrodes with graphene in lithium-ion batteries can DO NOT WRITE IN THIS MARGIN extend battery life. Graphene is a single, one atom thick layer of graphite.

- Explain why graphene can conduct electricity along the plane. (ii)
- (iii) State and explain how you would expect the bond strength of carbon-carbon bonds in graphene to differ when compared with that in diamond. [2]

[1]

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(b)	Carb Calci	on forms carbide anion, C_2^{2-} in calcium carbide while silicon mostly forms Si ⁴⁺ ions. ium carbide is a crystalline solid with a melting point of approximately 2160 °C.	
	(i)	Draw the dot-and-cross diagram of C_2^{2-} . [1]	
	(ii)	When some calcium carbide is added to excess water with a drop of Universal Indicator, ethyne gas, C_2H_2 , is produced. The solution changes from green to blue after the reaction is complete.	DO N
		Write an equation, with state symbols, for this reaction. [2]	OT WRI
	(iii)	In a particular experimental set-up, a beam of ${}^{12}C_2{}^{2-}$ ions was deflected by an angle of -2.45°. Assuming an identical set of conditions, calculate the angle of deflection for ${}^{28}Si^{4+}$ ions. [2]	TE IN THIS MARGIN
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(C) Using the data from Data Booklet, describe and explain the reducing strength of Group 2 elements from magnesium to strontium. [3]

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- (d) Aluminium chloride is used as a catalyst for the reaction between methylbenzene and 2-chloropropane to form two constitutional isomers L and M with the formula $C_{10}H_{14}$.
 - Suggest the mechanism for this reaction to form the major product, L. Show all charges (i) and relevant lone pairs and show the movement of electron pairs using curly arrows. [3]

L and M are formed in a 60:40 ratio. Suggest why L is the major product. (ii)

noropropane to form two constitutional isomers \mathbf{L} and \mathbf{W} with the formula $C_{10} \square_{14}$.	DO
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(e)	(i)	Write an equation for the reaction of with acidified KMnO ₄ .	
()	(ii)	Name the oxidised product formed in (a)(i)	
	()		['] <i>2</i>
			[Total: 19]

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2 Many chemical processes release waste products into the atmosphere. Scientists are developing new catalysts to convert these emissions into useful products, such as methanol which can be used as a fuel.

An equation for the synthesis of methanol is given below.

 $CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g)$ $\Delta H = -49 \text{ kJ mol}^{-1}$

- (a) (i) State and explain the effect on the position of equilibrium when the temperature is increased. [2]
 - (ii) State and explain the effect on the position of equilibrium when the pressure is increased. [1]

[1]

[2]

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(iii) Write an expression for K_p of the reaction.

1.0 mol of carbon dioxide and 3.0 mol of hydrogen were sealed in a container. After the mixture had reached equilibrium, at a pressure of 500 kPa, the amount of methanol produced was 0.86 mol.

- (iv) Determine the mole fraction of methanol when the system reached equilibrium. [2]
- (v) Hence, calculate the K_p value, stating its units.
- (vi) Suggest one possible environmental advantage of this reaction. Explain your answer. [1]

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(b) The standard enthalpy change of formation of some species are given in Table 2.1.

Table 2.1

compound	$\Delta H_{f^{\theta}}/ kJ mol^{-1}$
CO ₂ (g)	-394
H ₂ O(g)	-242

- (i) Define standard enthalpy change of formation.
- (ii) Write an equation to represent the standard enthalpy change of formation of CH₃OH(g). [1]
- (iii) Use the enthalpy change of reaction for the synthesis of methanol and the data provided in Table 2.1 to calculate the standard enthalpy change of formation of CH₃OH(g).

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[1]

- (c) (i) State two assumptions of ideal gas behaviour.
 - (ii) Fig. 2.1 shows the graphical plot of pV = nRT for $CO_2(g)$ at 500K as a function of pressure. On the same axes provided in Fig 2.1, sketch the graph for $H_2O(g)$ at 500K.

[1]

[1]





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- (d) Carbon dioxide can be formed by thermal decomposition of carbonates and hydrogen carbonates. The thermal decomposition of potassium hydrocarbonate, KHCO₃, proceeds according to reaction 1.

Reaction 1: $2KHCO_3(s) \rightarrow K_2CO_3(s) + CO_2(g) + H_2O(I)$ ΔH_1

The enthalpy change of this reaction cannot be measured directly. It is calculated from the enthalpy changes of other reactions, as shown in reactions 2 and 3.

Reaction 2: $K_2CO_3(s) + 2HCl(aq) \rightarrow 2KCl(aq) + CO_2(g) + H_2O(l)$	$\Delta H_2 = -34.0 \text{ kJ mol}^{-1}$
Reaction 3: KHCO ₃ (s) + HC $l(aq) \rightarrow KCl(aq) + CO_2(g) + H_2O(I)$	$\Delta H_3 = +32.8 \text{ kJ mol}^{-1}$

- (i) Suggest why it is not possible to measure ΔH_1 for the decomposition reaction directly. [1]
- (ii) Construct a suitable energy cycle to determine the enthalpy change of reaction 1. [2]
- (iii) State and explain the sign of entropy change of reaction 2. [1]
- (iv) Hence, state and explain whether reaction 2 is spontaneous at all temperatures. [1]

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[Total: 19]

3 (a) Singapore is one of 197 countries that signed the Montreal Protocol, a treaty to reduce the production and consumption of chlorofluorocarbons (CFCs).

Outline the environmental consequence of releasing chlorofluorocarbons into the atmosphere. [1]

(b) Pentane has many applications, including acting as a replacement for CFCs.
 When pentane is reacted with chlorine in the presence of *uv* light, three mono-chlorinated compounds, W, X and Y are formed.



Compounds W is not chiral while compound Y is produced as a racemic mixture.

- (i) Compound W only forms pent-1-ene in an elimination reaction.
 Deduce the structure of W and state the reagent and condition for the elimination reaction.
 [2]
- (ii) Draw three-dimensional structures for the enantiomers of compound Y and suggest why a racemic mixture is formed. [2]
- (iii) Suggest how the pair of enantiomers differ in their physical properties.

[1]

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(c) Pent-1-ene also reacts with chlorine in the presence of *uv* light. Two of the products are 3-chloropent-1-ene and 4-chloropent-1-ene.







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4-chloropent-1-ene

- (i) Draw the structures of the organic radical intermediates leading to the formation of 3-chloropent-1-ene and 4-chloropent-1-ene. [1]
- (ii) Hence, suggest why 3-chloropent-1-ene is formed in larger quantity. [1]
- (iii) 1-chloropent-1-ene is an isomer of 3-chloropent-1-ene.

Suggest an identification test to distinguish 1-chloropent-1-ene from 3-chloropent-1-ene. State the positive observation for this test. [2]

(d) In biological systems, oxygen accepts an electron to form superoxide. An enzyme regulates the level of superoxide by catalysing its decomposition to hydrogen peroxide and oxygen.

Explain how the rate of this enzyme-catalysed reaction varies with [superoxide]. [2]

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(e) Benzenediazonium chloride, $C_6H_5N_2Cl$, decomposes in water as shown in the following equation.

$$C_6H_5N_2Cl$$
 (aq) + $H_2O(I) \rightarrow C_6H_5OH(aq) + N_2(g) + HCl(aq)$

A solution of 0.0750 mol dm⁻³ of $C_6H_5N_2Cl(aq)$ decomposes at a constant temperature of 50 °C.

The volume of nitrogen gas, $N_2(g)$, collected is recorded every 5 minutes for 45 minutes as shown in the graph in Fig. 3.1.





- (ii) Hence, calculate the concentration of $C_6H_5N_2Cl$ (aq) at 32 min. [1]
- (iii) Calculate the rate constant for the reaction and include its units. [1]
- (iv) On Fig. 3.1, draw the graph produced if the same volume of half the concentration of $C_6H_5N_2Cl(aq)$ decomposes at a constant temperature of 50 °C. All other conditions remained unchanged. [1]
- (v) The reaction was repeated at 20 °C.

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Sketch the Boltzmann distribution and explain how a decrease in temperature affects the rate. [3]

(vi) The effect of temperature on the rate of the reaction is given by the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}}$$

where k = rate constant, $E_a = activation$ energy, R = molar gas constant,

T = temperature in Kelvin and A = Arrhenius constant

The value of the rate constant at 20 °C is 2.58×10^{-3} . Using your answer to (iii), calculate the activation energy of this reaction.

If you were unable to obtain an answer in **(e)(iii)**, use the value of 0.06.

[2]

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Section B

Answer **one** question from this section.

4 (a) Barium meals are given to patients prior to receiving an X-ray imaging. The main component in barium meals is barium sulfate.

At 30°C, 0.285 mg of barium sulfate is found to dissolve in 100 cm³ water to form a saturated solution.

(i) Calculate the solubility product, K_{sp} , of barium sulfate at 30°C. [2]

[1]

(ii) A small amount of sodium sulfate is added to the saturated solution in (a).Explain how the solubility of barium sulfate would change.

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(b) Imines are a group of organic molecules which are common intermediates in many biological reactions, where they are often referred to as Schiff bases.

Imines can be synthesised from the reaction between carbonyl compounds and primary amines, in the presence of acid catalyst.



where R_1 , R_2 and R_3 are H, alkyl or aryl groups

The mechanism for the formation of imines follows a 3-step reaction.

- Step 1 Nucleophilic addition between the carbonyl compound and primary amine occurs, producing a dipolar intermediate.
- Step 2 The dipolar intermediate undergoes proton transfer, forming a neutral molecule, followed by protonation of an oxygen atom
- Step 3 Expulsion of water (a good leaving group) and forming of C=N bond, followed by regeneration of the acid catalyst to form the imine.

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(i) Using appropriate curly arrows, illustrate the 3-step mechanism for the formation of the imine when butanone reacts with ethylamine.

Show clearly the charges and lone pair of electrons as well as structure of intermediate formed. [3]

(ii) The mechanism above is highly sensitive to pH of the reaction medium. Figure 4.1 below shows the rate of formation of imine at various pH.



Fig 4.1	0
With reference to the mechanism and information above, suggest explanatio the rate of reaction is very slow at very low pH and at very high pH.	ns why [2]

(c) Under certain conditions, an imine undergoes tautomerisation to form an enamine.



imine



Ζ

Imine and enamine are known as tautomers of each other.

In the presence of an acid catalyst, dicarbonyl compound **X** reacts with hydrazine, N_2H_4 , in a similar reaction as **(b)** to form intermediate **Y**, which tautomerises to form **Z**.

Y and Z are tautomers of each other.



(i) Draw the structure of intermediate **Y**.

(ii) Hence, deduce the structure of dicarbonyl compound **X**.

(iii) Compounds P and Q are isomers of X.



Suggest a simple chemical test which could be used to give a positive observation for **P**. [1]

[1]

[1]

The 5-membered ring structure of Z behaves like a benzene ring.

Draw the structure of product V.

- (iv) With reference to the structure of Z, suggest why Z is more likely to exist than its tautomer. [1]
- (v) Z reacts with hot alkaline potassium manganate(VII) to form a single ionic product V, $C_5H_2N_2O_4Na_2$.

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[1]

(d) A, C_5H_8O , and B, $C_5H_6O_4$, are cyclic compounds. Both give C, $C_5H_6O_5$, upon heating with acidified potassium manganate(VII).

A and **B** each exists as a pair of enantiomers but not **C**. 1 mole of **A** and **B** each produces 0.5 mole of H_2 gas while 1 mole of **C** produces 1 mole of H_2 gas when excess sodium metal is added.

A decolourises aqueous bromine in the dark. **B** reacts with sodium carbonate to form $C_5H_5O_4Na$ and reacts with hot aqueous NaOH to form $C_5H_6O_5Na_2$. Only **C** gives orange solid with Brady's reagent.

[7]

Deduce the structures of **A**, **B** and **C** and explain your reasoning.

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5 (a) The use of *Data Booklet* is relevant to this question.

When iron is heated with chlorine, $FeCl_3$ is produced. However, when heated with iodine, FeI_2 is produced instead.

- (i) Explain why when iron is heated with iodine, FeI_2 is produced but not FeI_3 . [2]
- (ii) Draw a fully labelled diagram to show how the standard electrode potential of the Fe³⁺(aq)/Fe²⁺(aq) system could be measured. Show the direction of electron flow in the circuit.
 [3]
- (iii) A few drops of acidified potassium manganate(VII) is added to the Fe³⁺(aq)/Fe²⁺(aq) half-cell. Predict and explain how the cell potential would change. [2]
- (iv) FeC l_3 is a dark brown solid which dissolves in water to give an acidic solution. This solution is often used, in the electronics industry, to dissolve the copper used in printed circuit boards.

Explain, with the aid of a chemical equation, why aqueous $FeCl_3$ is acidic. [2]

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(b) Chloroethane can be made by reacting PCl_3 with ethanol, via nucleophilic substitution mechanism.

 $PCl_3 + CH_3CH_2OH \rightarrow CH_3CH_2Cl + HOPCl_2$

- (i) The mechanism is thought to involve these steps:
 - The first step involves a nucleophilic attack on P by the oxygen atom of ethanol with simultaneous P-C*l* bond cleavage to form a positively charged intermediate.
 - The second step involves a nucleophilic attack on a carbon atom by the C*l*⁻ ion with simultaneous C-O bond cleavage to form the products.

Use the information given above to suggest a mechanism to show how chloroethane is formed. Show relevant lone pairs and dipoles and use curly arrows to indicate the movement of electron pairs. [3]

[1]

(ii) Explain why chlorobenzene cannot be made in the same way using phenol and PCl_3 .

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- (c) Compound X, C₉H₁₁NO₂, rotates plane polarised light and reacts with the following reagents:
 - aqueous bromine to give compound Y, C₉H₉NO₂Br₂
 - sodium carbonate to give a salt
 - PCl₅ to give a 5-membered cyclic compound Z

Compound **X** does not react with neutral $FeCl_3$.

Deduce the structural formulae of compounds **X**, **Y** and **Z**. [7]

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