HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	**20S**
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9729/03

Paper 3 Free Response

16 September 2021

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, name and CT group 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** 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.

No. of sheets of writing paper submitted (write 0 if none)	

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	
1	**/ 21**
2	**/ 18**
3	**/ 21**
Circle your option below	
4 / 5	**/ 20**
Deductions	
Total	**/ 80**

Section A

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

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1 (a) With the aid of the Boltzmann distribution, explain how an increase in temperature will affect the rate constant of a reaction. [3]

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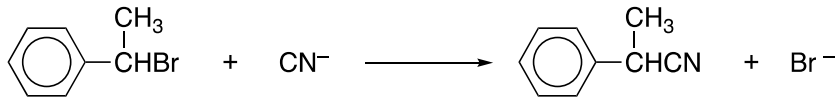
(b) Bromoalkanes can react with sodium cyanide to form nitriles. Depending on the structure of the bromoalkane, the reaction can proceed via the S_N1 or S_N2 mechanism.

Reaction 1 follows the S_N1 mechanism under certain conditions.

reaction 1



(i) Describe the mechanism for *reaction 1*. In your answer, show all relevant charges, lone pairs, dipoles and show the movement of electron pairs by using curly arrows. [2]

(ii) Hence, write the rate equation for *reaction 1*. [1]

(iii) What is meant by the term *order of reaction*? [1]

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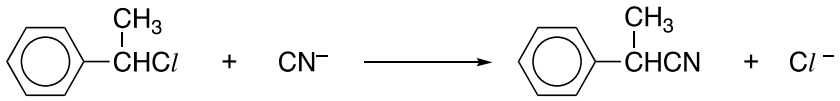
(iv) An experiment is carried out to study the kinetics of *reaction 1*. The concentration of the bromoalkane is monitored at timed intervals, with sodium cyanide present in large excess.

Sketch a suitable graph and show clearly on the graph how the results of the experiment can be used to confirm the reaction is first order with respect to the concentration of the bromoalkane. [2]

(v) The reaction below follows the same mechanism as *reaction 1*.

reaction 2 

Predict the relative rates of *reaction 1* and *reaction 2* under identical conditions, giving your reasoning. [1]

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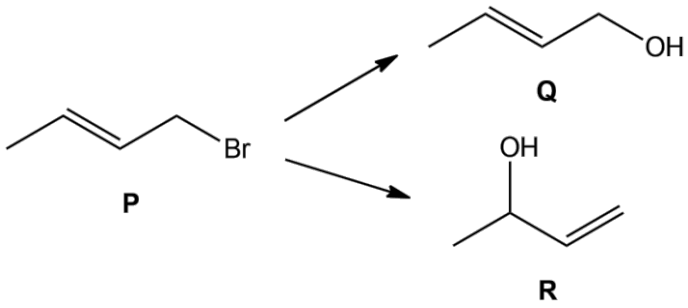
(c) When another bromoalkane, **P**, reacts with aqueous sodium hydroxide, the reaction could occur via both S_N1 and S_N2 mechanisms. Two products, **Q** and **R**, are obtained.



(i) Name compound **P**. [1]

(ii) Explain why compound **P** can react via the S_N1 mechanism, even though it is a primary bromoalkane. Hence suggest how product **R** may be formed in the reaction. Use the concept of delocalisation in your answer. [2]

(iii) State the type of stereoisomerism shown by product **R** and draw its stereoisomers. [2]

(iv) Compound **P** can react with ethylamine to form compound **S**, $C_6H_{13}N$. Draw the displayed formula of compound **S**. [1]

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(d) Although they have similar formulae, the following two compounds have differently shaped molecules.

PBr_3 ClF_3

Use the Valence Shell Electron Pair Repulsion (VSEPR) theory to predict the shape of each molecule. Draw appropriate diagrams to illustrate the shapes and label the bond angles in your diagrams. [5]

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[Total: 21]

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2 (a) (i) State the relative charges and relative masses of protons, neutrons and electrons. [2]

(ii) Describe the distribution of mass and charges within an atom. [1]

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(b) (i) Explain the general trend in ionic radii down Group 2. [2]

(ii) Describe and explain the trend in the thermal stabilities of the Group 2 carbonates. [3]

(iii) Write an equation, with state symbols, for the thermal decomposition of calcium carbonate. [1]

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For Examiner's use

(c) Define the term *mole*. [1]

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(d) 0.15 g of a solid mixture containing only $MgCO_3$ and $BaCO_3$ was shaken with excess aqueous hydrochloric acid. 35.00 cm^3 of carbon dioxide was collected at 30.0°C and 1 bar.

(i) Calculate the amount of carbon dioxide, in moles, that was collected. [2]

(ii) Hence, determine the mole fraction of $MgCO_3$ in the mixture. [3]

(iii) The mole fraction of $MgCO_3$ in the solid mixture can also be determined by indirect (back) titration.

Outline how you would determine the mole fraction of $MgCO_3$ using the indirect titration method.

No details regarding quantities, use of specific glassware, or calculations are required. [3]

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3 (a) Describe and explain the acid-base behaviour of aluminium oxide, Al_2O_3.

Write equations for all the reactions you choose to illustrate your answer. [4]

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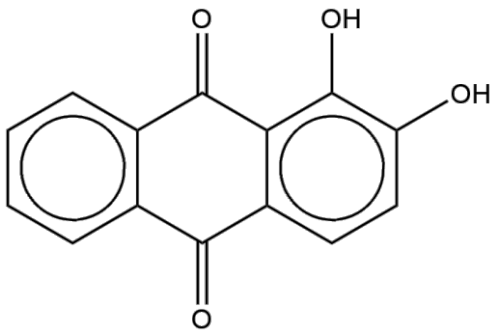
(b) Alizarin is a red dye with the structure shown below.



alizarin

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Alizarin is used to dye cotton red in the presence of aluminium ions. Fig. 3.1 shows how Al^{3+} is bonded to alizarin and the hydroxyl groups of cotton.

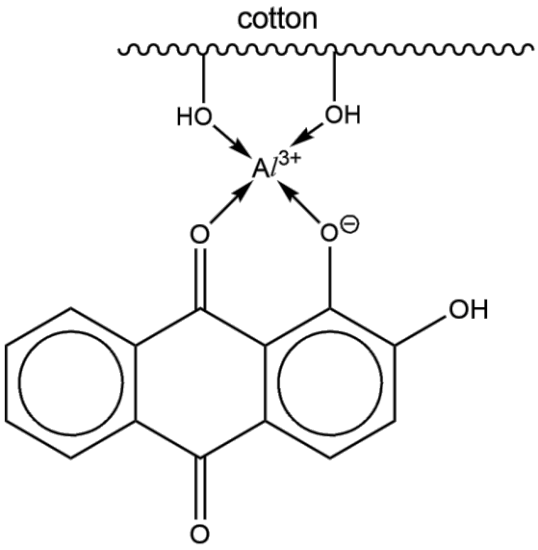

Fig. 3.1

(i) Explain how Al^{3+} behaves as an acid when forming the structure in Fig 3.1. [1]

(ii) Explain why alkaline conditions are needed for alizarin molecules to bond with Al^{3+} ions. [2]

(iii) A piece of cloth dyed red with alizarin was placed in a basin containing boiling water. It was observed that very little red dye enters the water.

Suggest a substance that could be added such that more dye enters the water. [1]

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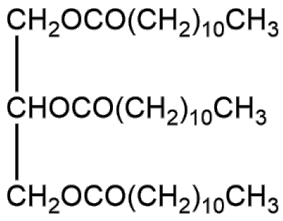
(c) Coconut oil contains a large amount of compound **G**.



G

G can be converted into soap by heating it with aqueous sodium hydroxide, NaOH, to form a sodium salt, **H**, which remains dissolved in the solution. **H** is precipitated out as a solid by adding sodium chloride, NaC*l*.

(i) Give the structural formula of **H**. [1]

You may represent **H** as Na^+A^- for the rest of this question.

(ii) The solubility of **H** in water is 0.108 mol dm^{-3} at 24 °C.

Calculate a value for the solubility product, K_{sp}, of **H** at 24 °C. [1]

(iii) Explain why adding NaC*l* to a solution of **H** causes solid **H** to precipitate out. [1]

(iv) Use your answer in **(c)(ii)** to determine the minimum mass of solid NaC*l* that is needed to precipitate solid **H** when added to 500 cm^3 of a 1.00×10^{-2} mol dm^{-3} solution of **H** at 24 °C. [2]

(v) Explain why the solubility of **H** in water is lower than the solubility of NaC*l* in water. [1]

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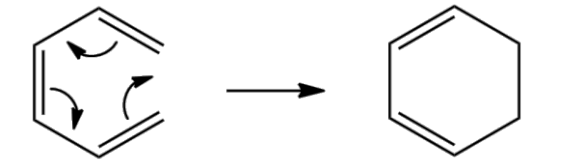
(d) Double bonds that alternate with single bonds are said to be conjugated. For example, 1,3-butadiene is a conjugated diene, whereas 1,4-pentadiene is a non-conjugated diene.

1,3-butadiene 1,4-pentadiene

An electrocyclic reaction involves the cyclisation of a conjugated alkene. Fig. 3.2 shows the movement of electron pairs, represented by curly arrows, when 1,3,5-hexatriene undergoes this reaction. During this reaction, a new σ bond is formed, the number of π bonds decreases by one, and the remaining π bonds change position.



1,3,5-hexatriene 1,3-cyclohexadiene

Fig. 3.2

(i) 2-methyl-1,3-butadiene is a conjugated alkene and undergoes the electrocyclic reaction to form compound **J**.

2-methyl-1,3-butadiene

Suggest the structure of compound **J**. [1]

(ii) Compound **K**, C_8H_{12}, is a conjugated alkene and undergoes the electrocyclic reaction to form compound **L** which contains a 6-membered ring.

One mole of **K** reacts with 3 moles of liquid bromine in the dark. On treatment with hot concentrated potassium manganate(VII), $KMnO_4$, **K** forms CO_2 and compound **M**, $C_2H_4O_2$.

$$\underset{\mathbf{K}}{C_8H_{12}} \xrightarrow{KMnO_4} \underset{\mathbf{M}}{2C_2H_4O_2} + 4CO_2$$

When **L** was treated with hot concentrated $KMnO_4$, it forms CO_2 and compound **N**, $C_6H_{10}O_4$. **N** does not give an orange precipitate with 2,4-dinitrophenylhydrazine.

$$\underset{\mathbf{L}}{C_8H_{12}} \xrightarrow{KMnO_4} \underset{\mathbf{N}}{C_6H_{10}O_4} + 2CO_2$$

K, **L** and **N** are symmetrical molecules.

Use the information above to suggest structures for compounds **K**, **L**, **M** and **N**, explaining the reactions described. [6]

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[Total: 21]

Section B

Answer **one** question from this section.

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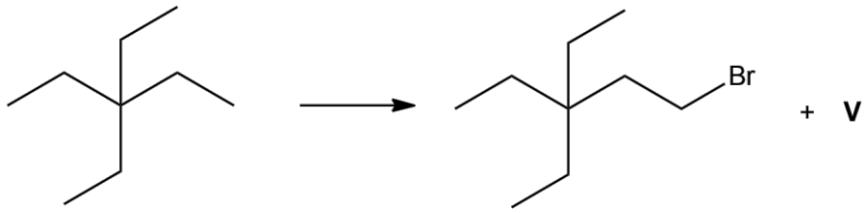
4 (a) Bromine reacts with alkanes in the presence of light.

(i) Outline the mechanism of the reaction between propane and bromine to form 2-bromopropane. [4]

3,3-diethylpentane reacts with bromine to give two monobromoalkanes, **U** and **V**.



3,3-diethylpentane **U**

(ii) Draw the structure of **V** and state its isomeric relationship to **U**. [2]

(iii) Predict the relative proportions of **U** and **V** formed in the above reaction. Explain your answer. [2]

(iv) When the bromination is carried out and the products are analysed, it is found that the mole ratio of **U** : **V** is about 1:1.

Suggest an explanation for the difference between this ratio and the one you gave in **(a)(iii)**. [1]

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(b) An equimolar mixture of bromine and hydrogen was heated at 700 K until equilibrium was established. The equilibrium mixture was found to contain 77.65 % by mass of HBr.

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g) \quad \Delta H < 0$$

(i) Write an expression for the equilibrium constant, K_c, for this reaction and calculate its value. [5]

(ii) State and explain how the composition of the equilibrium mixture would change if there were an increase in

I the pressure at constant temperature

II the temperature [2]

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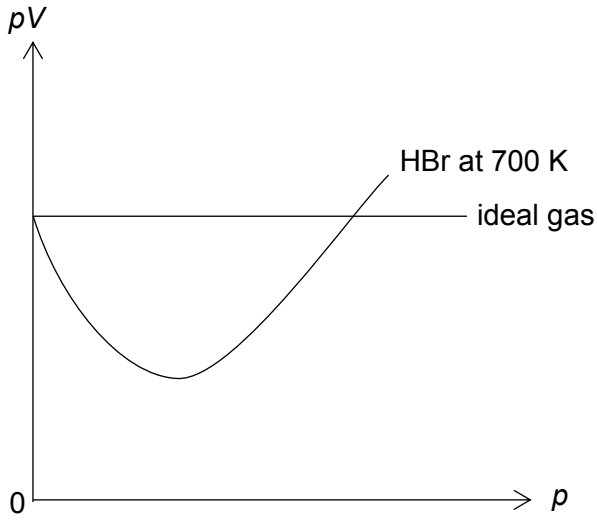
(c) **(i)** Explain, in terms of intermolecular forces and molecular size, the conditions necessary for a gas to approach ideal behavior. [2]

(ii) The value of pV is plotted against p for HBr gas at 700 K, where p is the pressure and V is volume of the gas.



Copy the diagram and sketch the corresponding graphs for the ideal gas and HBr gas when the temperature is raised to 800 K. [2]

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5 (a) Describe the mode of action of iron as a heterogeneous catalyst in the Haber Process. [3]

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(b) State **two** d-block elements whose isolated gaseous **atoms** in the ground state have the same number of electrons in the 3d subshell as an isolated gaseous Fe^{3+} ion. [1]

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(c) When solid hydrated iron(III) salts containing $[Fe(H_2O)_6]^{3+}$ ions are dissolved in water, an acidic solution is obtained due to the following equilibrium.

$$[Fe(H_2O)_6]^{3+} + H_2O \ll [Fe(H_2O)_5(OH)]^{2+} + H_3O^+$$

(i) State the relationship between $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_5(OH)]^{2+}$ ions. [1]

(ii) A 0.15 mol dm^{-3} solution of aqueous iron(III) chloride has a pH of 1.78. Calculate the acid dissociation constant, K_a, of $[Fe(H_2O)_6]^{3+}$. [2]

(iii) When 0.10 g of solid sodium hydroxide is added to 50 cm^3 of the solution in **(c)(ii)**, a buffer solution of pH 2 to 3 is obtained and no precipitation occurs.

Use your answer in **(c)(ii)** to calculate the pH of this buffer solution. [3]

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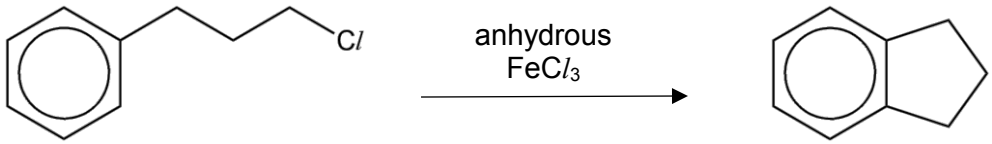
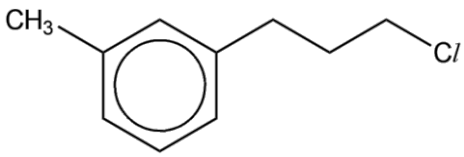
(d) **(i)** When anhydrous iron(III) chloride is added to compound **A**, an intramolecular electrophilic substitution occurs to form **B**.



A **B**

Describe the mechanism for the formation of **B** from **A**. In your answer, you should show all charges and lone pairs and show the movement of electrons by curly arrows. [3]

(ii) Compound **C** also undergoes the above reaction in the presence of anhydrous iron(III) chloride.



C

Predict the reactivity of **C** in this reaction compared to that of **A**, giving your reason. [1]

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(e) Compound **D**, $C_9H_{11}Cl$, is an isomer of **A**. Warming **D** with NaOH(aq) produces alcohol **E**, which does not react with excess acidified $Na_2Cr_2O_7$.

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Compound **F** can be formed from **D** or from **E** in one step. The M_r of **D** is 30.9% larger than the M_r of **F**.

(i) Draw the structures of **E** and **F**, giving your reasoning. [4]

(ii) State the reagents and conditions required to convert **D** to **F**, and **E** to **F**. [2]

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Additional answer space

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

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