HWA CHONG INSTITUTION
C2 Preliminary Examination
Higher 2

CANDIDATE NAME		**CT GROUP**	2 3 S
CENTRE NUMBER	S	**INDEX NUMBER**	

CHEMISTRY **9729/03**

Paper 3 Free Response **11 September 2024**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your **name**, **CT group, centre number** and **index number** on all the work you hand in.

Write in dark blue or black pen.

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

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

DO **NOT** WRITE ON ANY BARCODES.

Answer all questions in the spaces provided in 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.

No. of sheets of writing paper submitted (write 0 if none)	
For Examiner's Use	
1	**/ 20**
2	**/ 19**
3	**/ 21**
Circle your option below	
4 / 5	**/ 20**
Deductions (s.f.)	
Deductions (units)	
Deductions (structures)	
Total	**/ 80**

Section A

Answer **all** questions in this section.

1 (a) Like Group 2 carbonates, Group 2 nitrates also undergo thermal decomposition according to the following equation:

$$M(NO_3)_2(s) \rightarrow MO(s) + 2NO_2(g) + \frac{1}{2} O_2(g) \qquad \Delta H > 0$$

(i) Draw a dot-and-cross diagram showing the bonding in $Mg(NO_3)_2$, clearly indicating any co-ordinate bonds it contains. [2]

(ii) Explain why the temperature for thermal decomposition of Group 2 nitrates increases down the group. [2]

(iii) Deduce, with reasoning, the sign of the entropy change of the reaction. Hence, suggest why high temperature is needed for thermal decomposition to take place. [2]

(iv) Using Table 1.1 and data from the *Data Booklet*, draw a Born-Haber cycle to calculate a value for the lattice energy of MgO. Show your working.

Table 1.1

	$\Delta H^\ominus$ / kJ mol^{-1}
1st electron affinity of oxygen	–142
2nd electron affinity of oxygen	+844
standard enthalpy change of atomisation of Mg(s)	+148
standard enthalpy change of formation of MgO(s)	–602

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(b) Describe the reactions, if any, of the oxides MgO, Al_2O_3 and P_4O_{10} with water. Write equations for any reaction and state the pH of the resultant mixtures. [3]

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(c) In the presence of $AlCl_3$, methylbenzene can undergo electrophilic substitution with halogens like chlorine.

(i) Explain why $AlCl_3$ can act as a Lewis acid. [1]

(ii) Draw the structures of the major organic products formed in the electrophilic substitution reaction between methylbenzene and chlorine. [1]

(iii) Write a balanced equation for the reaction between methylbenzene and hot acidified potassium manganate(VII). Use [O] to represent the oxidising agent. [1]

If the halogen is changed to iodine, electrophilic substitution of methylbenzene occurs much less readily. To increase its reactivity, reagents like iodine monochloride, ICl, in the presence of $AlCl_3$ are used instead.

(iv) Explain why ICl is more reactive in the electrophilic substitution of methylbenzene compared to I_2. [1]

(v) Draw the mechanism of the reaction between methylbenzene and ICl, showing the formation of the electrophile and any intermediates. Use curly arrows to indicate the movement of electron pairs, and show any relevant lone pairs. [3]

[Total: 20]

2 **(a)** Describe and explain the difference in reactivity of alkenes and carbonyl compounds towards nucleophilic reagents. [2]

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(b) In the pharmaceutical industry, understanding optical activity and addressing the effects of racemic mixtures is crucial in drug development.

(i) Explain why a racemic mixture is optically inactive. [2]

(ii) With reference to a reaction involving a suitable alkene **or** carbonyl compound of your choice, explain why a racemic mixture is obtained in the reaction.
Give the organic compound and reagents used, and draw structures to illustrate the type of stereoisomerism present in the product mixture. [3]

(iii) Stereoisomers of a drug such as ibuprofen often have different pharmacological activities. Suggest a reason for why this is so. [1]

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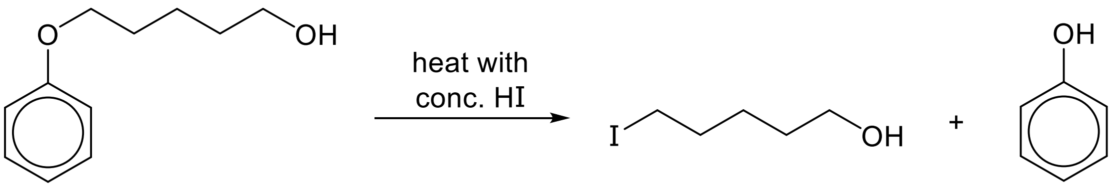
(c) Fig. 2.1 shows the reaction of compound **A** with hot concentrated hydroiodic acid.



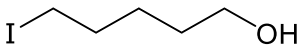
A **B**

Fig. 2.1

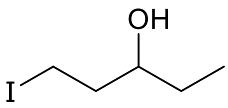
(i) Suggest the *type of reaction* that occurs during this reaction. [1]

(ii) Give the systematic name for **B**. [1]

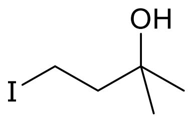
(iii) **C** and **D** are constitutional isomers of **B**. The three compounds may be distinguished via a two-step procedure.



B



C



D

I. In step 1, the three compounds are heated separately with acidified potassium dichromate(VI). State what would be observed for each compound.

II. The organic products formed from positive tests in step 1 are isolated for a further test in step 2. Suggest a reagent, other than 2,4-dinitrophenylhydrazine, that can be used to distinguish these products, and state the observations for each compound. [3]

(iv) Phenol can be converted to phenyl ethanoate via a two-step process. State the reactant required for each step of this process. [2]

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(d) Fig. 2.2 shows a synthetic scheme for the conversion of compound **E** to compounds **G** and **H**. In **E**, the R group could be at positions 2, 3 or 4 relative to the –OH group on the benzene ring.

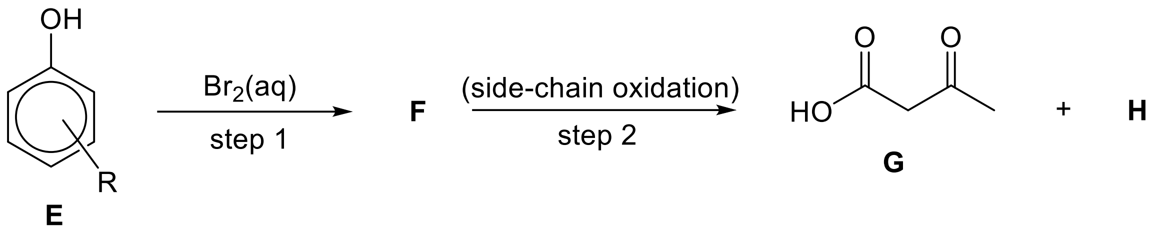

Fig. 2.2

(i) Draw the structure of the organic product formed when compound **G** is reacted with 2,4-dinitrophenylhydrazine. [1]

(ii) In step 1 of Fig. 2.2, the relative molecular mass of **E** changes from 178.0 to 335.8 in **F**, the major product of the reaction.
Deduce, with reasoning, the position of the R group relative to the –OH group in **E**. [1]

(iii) Based on your answer to **(d)(ii)** and the following information, suggest the structures of **F** and **H**, both of which contain brominated benzene rings.

- **G** and **H** are the only carbon-containing products formed when **F** undergoes side-chain oxidation in step 2
- one mole of **H** produces one mole of hydrogen gas on complete reaction with sodium metal
- **F** gives orange precipitate with 2,4-dinitrophenylhydrazine [2]

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[Total: 19]

3 **(a)** Explain why transition metal complexes are often coloured. [3]

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(b) **(i)** State the electronic configuration of chromium. [1]

(ii) Explain why chromium can exhibit a number of different oxidation states in its compounds. [1]

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(c) A black oxide CrO, dissolves readily in dilute acid to form a sky blue solution **A**. When left in the air, the solution changes to a green solution **B**. When a small amount of sodium hydroxide is added to **B**, a grey green precipitate **C** is formed. Upon the addition of excess sodium hydroxide, a complex $[Cr(OH)_6]^{3-}$ is formed which reacts with H_2O_2 to form a yellow solution, CrO_4^{2-}.

(i) Give the formula of the unknown chromium-containing species present in **A**, **B**, and **C**. [3]

(ii) What type of reaction occurs when CrO_4^{2-} is formed from $[Cr(OH)_6]^{3-}$? [1]

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(d) In an acidic medium, chromium(VI) exists as $Cr_2O_7^{2-}$.

(i) State one reason why aqueous Cr^{6+} ion does not exist. [1]

(ii) In aqueous solution, $Cr_2O_7^{2-}$ exists in equilibrium with CrO_4^{2-} as shown below.

$$Cr_2O_7^{2-}(aq) + H_2O(l) \rightleftharpoons 2CrO_4^{2-}(aq) + 2H^+(aq)$$

orange yellow

Describe the observation when an aqueous solution of $Cr_2O_7^{2-}$ is diluted with water. Explain your reasoning. [2]

(iii) With the aid of $E^\ominus$ values from the *Data Booklet*, explain why a reaction occurs when SO_2 is bubbled into acidified $K_2Cr_2O_7(aq)$. Write an equation for this reaction. [2]

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(e) A hydrated salt **E** (M_r = 399.7) contains 13.0 % of Cr, 27.0 % of H_2O and 60.0 % of Br by mass. An aqueous solution containing 0.400 g of **E** immediately gives 0.188 g of cream precipitate when treated with aqueous silver nitrate.

(i) Calculate the mole ratio of Cr: H_2O: Br in the hydrated salt **E**. [1]

(ii) Identify the cream precipitate and hence, determine the formula of the octahedral complex cation in the hydrated salt **E**. [3]

(iii) Given that the complex ion in **E** has a net dipole moment, draw the structure of this complex ion, showing clearly how the ligands are arranged around chromium. [1]

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(f) Fifty years ago, most sulfuric acid was manufactured by the "lead chamber process".

The chamber used in the process must not be made of steel as iron rapidly dissolves in concentrated sulfuric acid, whereas lead is only superficially attacked. With the aid of $E^{\ominus}$ values from the *Data Booklet*, explain why this is so. [2]

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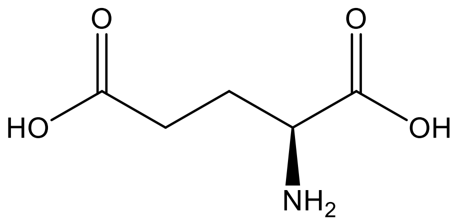
Section B

Answer **one** question from this section.

4 (a) The structure of glutamic acid is shown below.



glutamic acid

There are three pK_a values associated with glutamic acid: 2.19, 4.25 and 9.67.

A 10.0 cm^3 sample of the *fully protonated* form of glutamic acid is titrated against 0.100 mol dm^{-3} NaOH(aq). The titration curve is shown in Fig. 4.1.

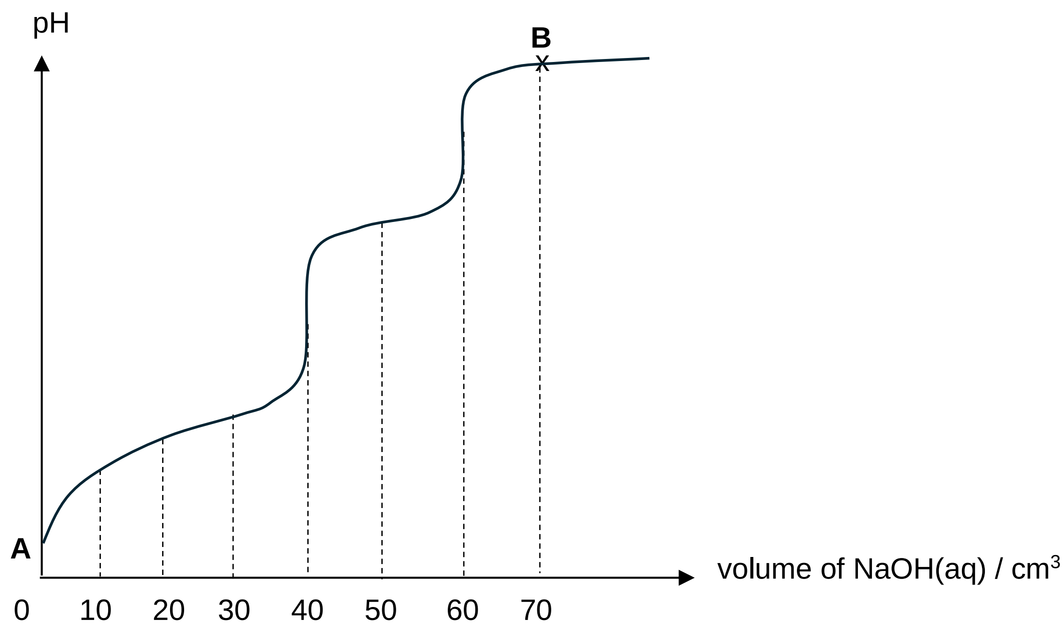


Fig. 4.1

(i) Define pK_a. [1]

(ii) When 60 cm^3 of NaOH is added, all three acidic groups are deprotonated. Calculate the concentration of glutamic acid in the given sample. [1]

(iii) Calculate the pH of glutamic acid at point **A**. [2]

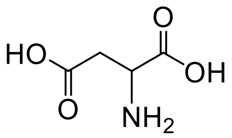
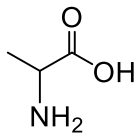
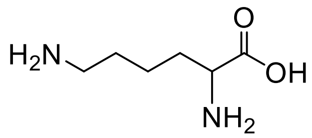
(iv) Draw the zwitterion of glutamic acid. [1]

(v) The isoelectric point (pI) is the pH where the amino acid exists primarily as the zwitterion. **On the titration curve in Fig. 4.1**, mark the point at which this occurs, with a cross. [1]

(vi) Calculate the pH at point **B**. [2]

(b) Table 4.1 gives the structures and pI values of three different amino acids.

Table 4.1

amino acid	 asp	 ala	 lys
pI	2.77	6.00	9.74

(i) Draw the structure of the tripeptide asp-ala-lys. The left-most end of the peptide should be a free $-NH_2$ group, while the right-most end is a free $-CO_2H$ group. [2]

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(ii) A mixture of the three amino acids in Table 4.1 can be separated via a process known as electrophoresis.

The amino acid mixture is placed in the centre of a strip of filter paper soaked in a buffer solution of pH 6.00 as shown in Fig. 4.2. Two electrodes are then placed in contact with the edges of the filter paper.

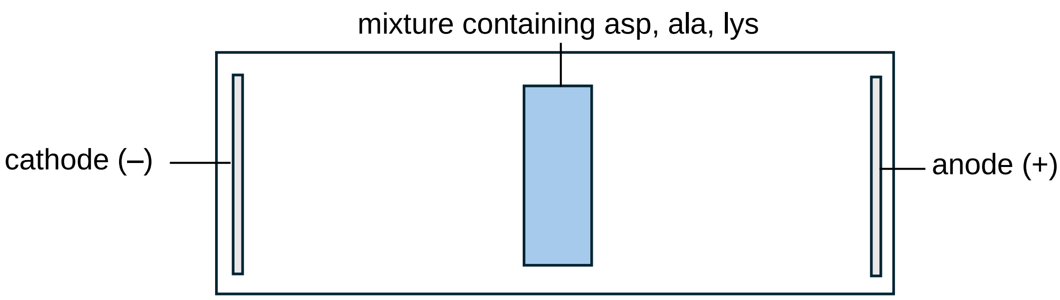

Fig. 4.2

By considering the net charge on the predominant form of each amino acid at pH 6.00, label the positions of the three amino acids at the end of the experiment **on Fig. 4.3**. [2]

Fig. 4.3

(c) Describe and explain the relative basicities of ethylamine, diethylamine and triethylamine in the gaseous state. [3]

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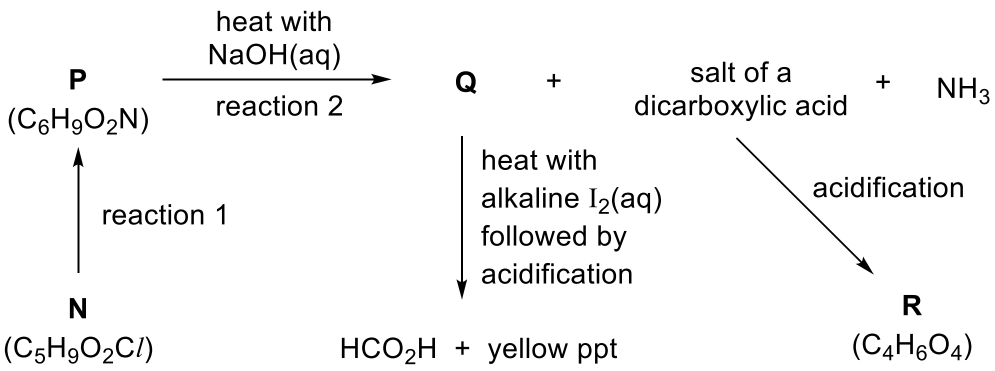
(d) Consider the reaction scheme below.



(i) By considering the change in molecular formulae of **N** to **P**, suggest the reagents and conditions for reaction 1. [1]

(ii) State the type of reaction for reaction 2. [1]

(iii) Suggest the structure of **Q**. [1]

(iv) Compound **P** does not rotate plane-polarised light and is insoluble in both dilute hydrochloric acid and aqueous sodium hydroxide at room temperature. Suggest the structures of **P** and **R**. [2]

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5 The Sabatier reaction is the catalytic reduction of carbon dioxide to produce methane.

$$CO_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2O(g)$$

(a) 1.00 mol of CO_2(g) was reacted with 4.00 mol of H_2(g) in a sealed vessel with a volume of 6.87 dm^3. The reaction mixture was allowed to reach *dynamic equilibrium* at a pressure of 30.0 bar and a temperature of 500 °C.

(i) Explain what is meant by the term *dynamic equilibrium*. [1]

(ii) Using the ideal gas equation, calculate the total number of moles of gas present at equilibrium. [2]

(iii) Hence, determine the partial pressures of each of the individual gases at equilibrium. [3]

(iv) Write an expression for the equilibrium constant K_p, for the Sabatier reaction, including units. [2]

(v) Calculate the value of K_p at 500 °C. [1]

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(b) In the Sabatier reaction, the proportion of products at equilibrium decreases as temperature increases.

(i) Deduce whether the Sabatier reaction is endothermic or exothermic. Explain your reasoning. [1]

(ii) Sketch the graph of the K_p value against temperature. [1]

(iii) How would the K_p value change if the total pressure decreases? Explain your answer. [1]

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(c) State an advantage of using the hydrogen-oxygen fuel cell to generate electricity as compared to coal-fired power plants. [1]

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(d) In recent years, there has been breakthroughs in producing methane-oxygen fuel cells that require lower operating temperatures, by changing the catalyst used at the anode. An example of a methane-oxygen fuel cell is shown in Fig. 5.1 below.

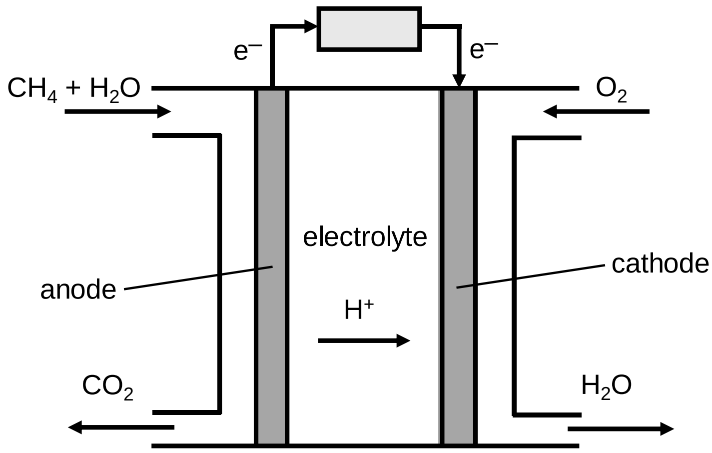

Fig. 5.1

The half-equations for the reactions at the anode and cathode are given by equations 1 and 2 respectively:

equation 1 $CH_4(g) + 2H_2O(l) \rightarrow CO_2(g) + 8H^+(aq) + 8e^-$ $\Delta G^\ominus_1 = +131.2\ kJ\ mol^{-1}$

equation 2 $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

The overall equation of the reaction in the fuel cell is given by equation 3:

equation 3 $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

(i) Use relevant data from the *Data Booklet* to calculate the standard Gibbs free energy change, $\Delta G^\ominus_2$, for the reaction in equation 2. [2]

(ii) Hence, determine the standard Gibbs free energy change, $\Delta G^\ominus_3$, for the reaction in equation 3, and $E^\ominus_{cell}$ for the methane-oxygen fuel cell. $\Delta G^\ominus$ can be used in the same manner as $\Delta H^\ominus$ in a Hess' law cycle but $E^\ominus$ cannot. [2]

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(e) The Sabatier reaction and the methane-oxygen fuel cell both require the use of transition metals as heterogeneous catalysts.

Transition metal compounds can also act as homogeneous catalysts. For instance, the catalytic role of Fe^{2+} in the reaction between I^- and $S_2O_8^{2-}$ is well-known.

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

Using relevant data from the *Data Booklet*, suggest a transition metal cation, other than Fe^{2+} or Fe^{3+}, that can catalyse this reaction. Include relevant chemical equations and calculations to support your answer. [3]

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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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