HWA CHONG INSTITUTION
C1 Promotional Examination
Higher 2

NAME		CT GROUP	17S

CHEMISTRY

9729/03

Paper 3 Free Response

27 September 2017

1 hour 15 minutes

Candidates answer on separate paper.

Additional Materials: Answer Paper, Graph Paper, Cover Page and Data Booklet.

READ THESE INSTRUCTIONS FIRST

Write your 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, graphs or rough working.

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

Section A

Answer **all** questions.

Section B

Answer **one** question.

Begin each question on a **new piece** of paper.

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

A Data Booklet is provided.

You are reminded of the need for good English and clear presentation in your answers.

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

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

Section A

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

1 Dienes are hydrocarbons which contain two C=C double bonds. Table 1.1 shows some data for hexa-1,3-diene, hexa-1,5-diene and hexane.

Table 1.1

	$CH_2{=}CHCH{=}CHCH_2CH_3$ hexa-1,3-diene	$CH_2{=}CHCH_2CH_2CH{=}CH_2$ hexa-1,5-diene	$CH_3(CH_2)_4CH_3$ hexane
Boiling point / C	73	60	68
$\Delta H_{vaporisation}$ / kJ mol^{-1}	+29.5	+28.3	+28.9
Bond energy of each C=C / kJ mol^{-1}	531	608	N.A.

(a) **(i)** State the type of stereoisomerism exhibited by hexa-1,3-diene. Draw the structures of the stereoisomers. [2]

(ii) By considering the arrangement of orbitals in hexa-1,3-diene, suggest why the bond energy of the C=C double bond is smaller for hexa-1,3-diene than hexa-1,5-diene. [1]

(b) Platinum is often used when hydrogenation of alkenes is carried out at room temperature.

(i) State the role of platinum in this reaction. [1]

(ii) With the aid of a sketch of the Boltzmann distribution, explain how the presence of platinum affects the rate constant of the reaction. [3]

(c) **(i)** Using suitable values from Table 1.1, calculate the entropy change of vaporisation, $\Delta S_{vaporisation}$, at the boiling point of hexa-1,5-diene. [2]

(ii) Write a balanced chemical equation with state symbols to represent the standard enthalpy change of hydrogenation, $\Delta H^{o}_{hydrogenation}$, for hexa-1,5-diene to be converted to hexane.

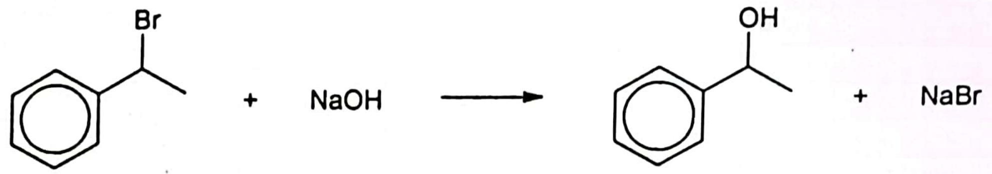
Hence, by using suitable values from Table 1.1 and the *Data Booklet*, calculate $\Delta H^{o}_{hydrogenation}$. [3]

(d) Draw the displayed formula of the organic products formed when hexa-1,3-diene and hexa-1,5-diene are heated separately with acidified $KMnO_4(aq)$. Label your answers clearly.

Give the balanced equation of this reaction for hexa-1,5-diene. [3]

[Total: 15]

2 Compound **A** reacts with sodium hydroxide to form 1-phenylethanol as shown below.



A

1-phenylethanol

(a) The rate of reaction can be followed by doing a series of titration. The *order of reaction* with respect to **A** and NaOH can then be determined.

Table 2.1 lists the concentrations of the different reactants in the reaction mixture for two experiments.

Table 2.1

Experiment	initial [A] / mol dm^{-3}	initial [NaOH] / mol dm^{-3}
1	0.10	0.010
2	0.20	0.010

At fixed intervals of time, 10.0 cm^3 of the reaction mixture was pipetted out into a conical flask containing 7.50 cm^3 of 0.020 mol dm^{-3} HC*l*. The resulting mixture was then titrated with a solution of 0.010 mol dm^{-3} aqueous NH_3, which reacts with the excess unreacted HC*l*.

The results are tabulated as shown in Table 2.2.

Table 2.2

time / min	V_t, volume of NH_3(aq) used in titration / cm^3		$(V_n - V_t)$ / cm^3	
	Experiment 1	Experiment 2	Experiment 1	Experiment 2
15	5.90	6.80		
30	6.80	8.60		
45	7.70	10.40		
60	8.60	12.20		
∞	V_n	V_n	▨	▨

(i) Explain the meaning of the term *order of reaction*. **[1]**

(ii) Show that V_n, the volume of NH_3(aq) used for titration when the reaction between **A** and NaOH is complete, is 15.00 cm^3. **[1]**

(iii) What is the simple relationship between $(V_n - V_t)$ and the remaining [NaOH]? **[1]**

(iv) Copy and complete the fourth and fifth columns of Table 2.2 on your answer paper.

On the graph paper provided, plot on the same axes the graphs of $(V_n - V_t)$ against time for Experiments 1 and 2. Use 2 cm to represent 10 min and 1.00 cm^3 on the x-axis and y-axis respectively.

Draw a line of best fit for each experiment and label your graphs clearly. **[2]**

(v) Using your graph, deduce the order of reaction with respect to

I: NaOH
II: **A**

Show all your working clearly. [3]

(vi) Hence, write the rate equation for the reaction, and state the units of the rate constant. [2]

(vii) A student suggested modifying the experiment as an alternative to the one described above. He claimed that his method was less tedious and less time-consuming.

"At fixed intervals of time, 10.0 cm^3 of the reaction mixture was pipetted out into a conical flask. The mixture was then titrated with a solution of 0.010 mol dm^{-3} HC*l* to determine [NaOH] at each time interval. A graph of [NaOH] against time can then be plotted"

Suggest why his method would not work. [1]

(b) Aromatic compounds **B**, **C** and **D** are constitutional isomers of **A**, with molecular formula C_8H_9Br.

B, **C** and **D** react with hot alkaline $KMnO_4$, followed by acidification to give **E**, **F** and **G** respectively, which all have the same molecular formula of $C_8H_6O_4$. **E** has a much lower melting point than **F** and **G**.

(i) Using the information given above, draw the three possible structures with the molecular formula $C_8H_6O_4$. [1]

(ii) Based on the structures you have drawn, suggest which one is **E**, explaining your answer. [2]

(iii) Hence, draw the structure of **B**. [1]

[Total: 15]

Section B

Answer **one** question from this section.

3 (a) (i) State and explain the trend of first ionisation energy down Group 13. [2]

(ii) Draw labeled diagrams to illustrate the shapes and orientation of all the orbitals occupied by the electrons in the outermost quantum shell of Al^{3+}. [2]

(b) (i) $AlCl_3$ is a solid which sublimes at 180 °C. AlF_3, on the other hand, is a solid which melts at 1291 °C.

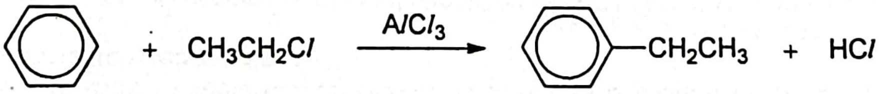
Account for these observations in terms of structure and bonding. [3]

(ii) Using the following data, draw an energy cycle to calculate the lattice energy of AlF_3(s).

Enthalpy change of formation of AlF_3(s)	–1510 kJ mol^{-1}
Enthalpy change of formation of Al^{3+}(aq)	–538 kJ mol^{-1}
Enthalpy change of formation of F^-(aq)	–335 kJ mol^{-1}
Enthalpy change of hydration of Al^{3+}(g)	–4690 kJ mol^{-1}
Enthalpy change of hydration of F^-(g)	–506 kJ mol^{-1}

[4]

(c) Aluminium chloride is used as a catalyst in the preparation of ethylbenzene by the reaction of benzene with chloroethane via Friedel-Crafts alkylation.

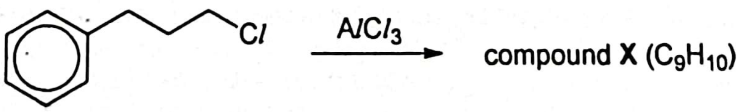


ethylbenzene

The first step is the reaction between CH_3CH_2Cl and $AlCl_3$ as shown below:

$$CH_3CH_2Cl + AlCl_3 \rightarrow CH_3CH_2^+ + AlCl_4^-$$

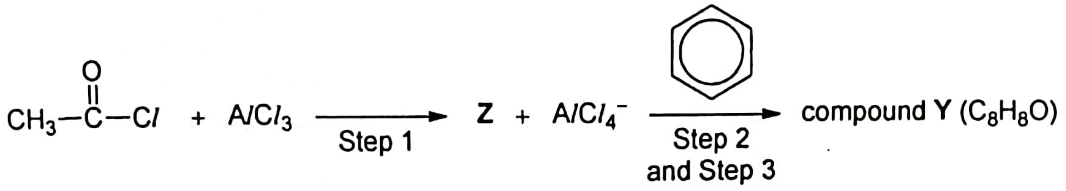
(i) Suggest the structure of compound **X** for the following reaction.



[1]

$AlCl_3$ reacts in a similar way with ethanoyl chloride, CH_3COCl, producing an intermediate **Z** that can then attack a benzene ring. This reaction produces compound **Y** with the formula C_8H_8O.

The outline of the mechanism is given below.



(ii) Suggest the structures of the intermediate **Z** and compound **Y**. [2]

(iii) Describe the mechanism of Step 2 and Step 3. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows. [2]

(iv) Given that the overall reaction is exothermic, draw the energy profile diagram for Step 2 and Step 3.

On the diagram, label the reactants, intermediates and products, and the activation energy, E_a, for each step. [2]

(d) Describe a simple chemical test to distinguish between cyclohexene and benzene. You should state the reagents and conditions for the test, and describe the expected observations for each compound. [2]

[Total: 20]

4 The water-gas shift reaction describes the process of reacting carbon monoxide and water vapour to form carbon dioxide and hydrogen.

$$CO(g) + H_2O(g) \;=\; CO_2(g) + H_2(g)$$

(a) In an experiment, an equimolar mixture of carbon monoxide and water vapour was placed in a vessel.

(i) Assuming that 70% of carbon monoxide has reacted at equilibrium, calculate the mole fraction of each of the gases at equilibrium, and hence show that the average relative molecular mass of the resulting gas mixture is 23.0. [2]

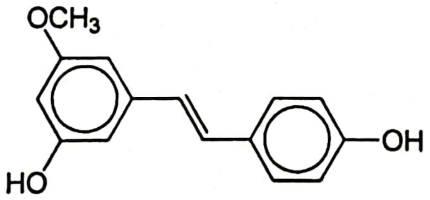
(ii) Given that the reaction was performed in a 30.0 dm^3 vessel and the equilibrium pressure and temperature were found to be 6.50 atm and 50.0 °C respectively, calculate the density of the gas mixture at equilibrium by using the ideal gas equation. [2]

(b) **(i)** A real gas such as carbon dioxide can be liquefied at room temperature just by applying pressure.

Explain why the application of pressure causes the gas to liquefy. [2]

(ii) One of the uses of liquid carbon dioxide is to act as a solvent in the extraction of polyphenols from tea leaves.

Suggest why small amounts of ethanol should be added to liquid carbon dioxide in the extraction of polyphenols such as the molecule below.



[1]

(c) Ethanol can be synthesised in the laboratory through the hydration of ethene using concentrated sulfuric acid catalyst, according to the equation below.

$$CH_2{=}CH_2(g) + H_2O(l) \rightarrow C_2H_5OH(l) \qquad \Delta H^\circ_r$$

(i) Draw the structure of sulfuric acid, H_2SO_4, showing its shape. State the shape about each central atom. [2]

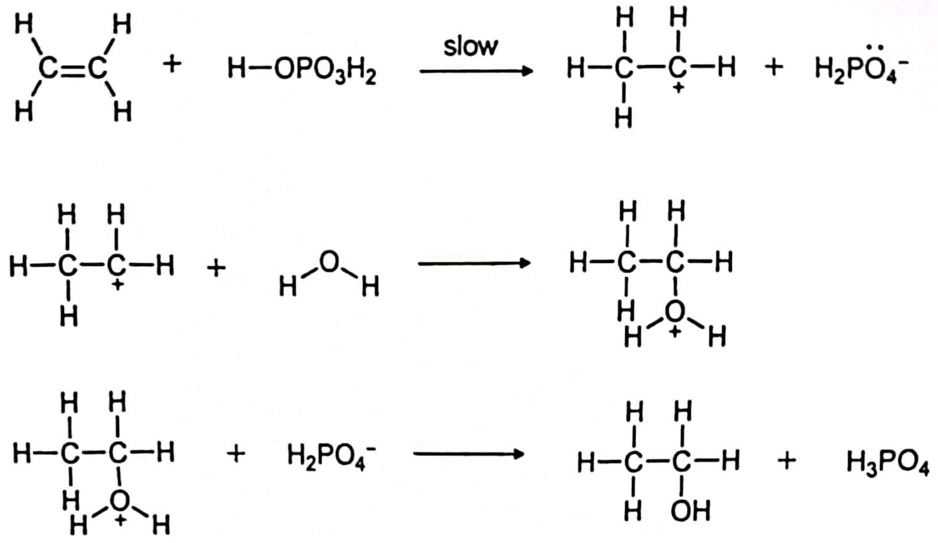
(ii) When burned in a limited supply of air, ethanol forms carbon monoxide and water.

$$C_2H_5OH(l) + 2O_2(g) \rightarrow 2CO(g) + 3H_2O(l) \qquad \Delta H^\circ_1 = -834 \text{ kJ mol}^{-1}$$

Using enthalpy change data ΔH°_1 as well as those given below, draw an energy cycle to calculate the standard enthalpy change of hydration of ethene, ΔH°_r.

Standard enthalpy change of combustion of $CH_2{=}CH_2(g)$ = –1411 kJ mol^{-1}
Standard enthalpy change of combustion of $CO(g)$ = –283 kJ mol^{-1} [3]

(d) Another method of hydrating ethene to produce ethanol involves using concentrated phosphoric acid catalyst. The mechanism for this process is similar to the one in the reaction of alkenes with hydrogen halides, with elementary steps as shown below.



(i) State the type of reaction undergone in the hydration of ethene. [1]

(ii) Copy the equations above onto your answer paper and complete the mechanism of this reaction by showing curly arrows, dipoles and any relevant lone pairs. [3]

(iii) With reference to the mechanism above, draw the structure of the two possible carbocation intermediates if the reactant used was propene instead of ethene, and explain which would be the intermediate leading to the major product. [2]

(iv) Describe a simple chemical test to distinguish between propene and propane. You should state the reagents and conditions for the test, and describe the expected observations for each compound. [2]

[Total: 20]

END OF PAPER