HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	**18S**
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9729/02

Paper 2 Structured Questions

18 September 2019

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** clearly in the spaces above.

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.

Answer all questions in the spaces provided in the Question Paper.

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

A Data Booklet is provided.

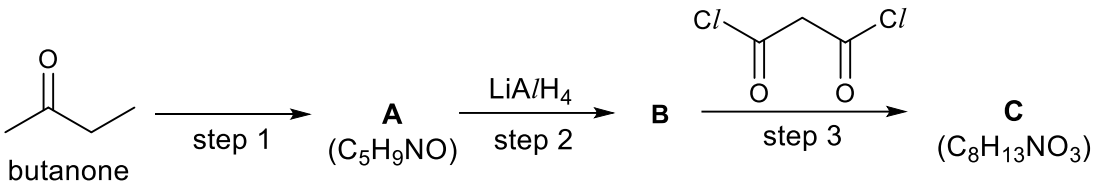
At the end of the examination, fasten all your work securely together.

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

For Examiner's Use	
1	/ 17
2	/ 13
3	/ 22
4	/ 23
s.f.	
units	
Total	/ 75

Calculator Model:

1 **(a)** Butanone can be converted to compound **C** via the following series of reactions.



(i) Suggest the reagents and conditions for step 1.

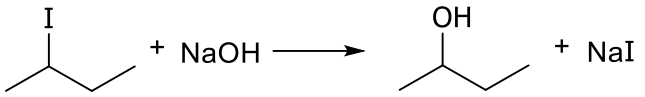
…… [1]

(ii) In the boxes below, draw the structures of compounds **A**, **B** and **C**.

A	**B**
C	

[3]

(b) 2-iodobutane is converted to its corresponding alcohol by heating with aqueous sodium hydroxide.



$\Delta H < 0$

The rate equation is:

rate = k[2-iodobutane][NaOH]

(i) Describe the mechanism of this reaction. In your answer you should show all charges and lone pairs and show the movement of electrons by curly arrows.

[3]

(ii) Draw a fully labelled reaction pathway diagram for the reaction between 2-iodobutane and sodium hydroxide.

[2]

(c) Describe and explain how the volatilities of the halogens vary from chlorine to iodine.

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..... [2]

(d) Some hydrogen halides are unstable to heat.

(i) Write an equation for the reaction undergone on heating a hydrogen halide.

…….. [1]

(ii) Describe and explain how the thermal stabilities of the hydrogen halides (HC*l*, HBr and HI) vary down the group.

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…… [2]

(e) When sodium thiosulfate, $Na_2S_2O_3$, is reacted with bromine, $NaHSO_4$ is formed. However, when $Na_2S_2O_3$ reacts with iodine, $Na_2S_4O_6$ is formed instead.

Use the following data, and data from the *Data Booklet*, to suggest an explanation for this difference.

$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$	$E^\ominus = +0.09$ V
$4SO_2 + 4H^+ + 6e^- \rightleftharpoons S_4O_6^{2-} + 2H_2O$	$E^\ominus = +0.51$ V
$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O$	$E^\ominus = +0.17$ V

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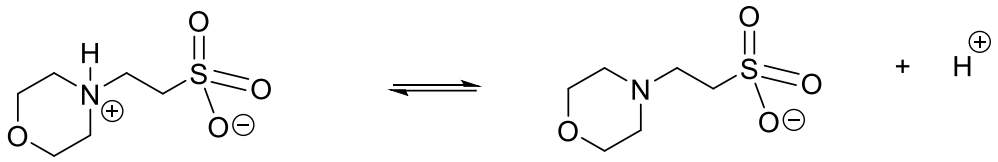
…… [3]

[Total: 17]

2 (a) 4-Morpholineethanesulfonic acid (MES) is commonly used to prepare buffer solutions. In aqueous solution, MES exists as a dipolar ion which dissociates to give H^+ ions:



4-Morpholineethanesulfonic acid
(MES)

FA 1 is a buffer solution prepared from MES with a pH of 5.5. The ratio of MES and its conjugate base is 4:1.

(i) Determine the pK_a of MES.

[1]

(ii) State the mole ratio of MES to its conjugate base if the pH = pK_a of MES.

[1]

A student titrated 10.0 cm^3 of **FA 1** with aqueous sodium hydroxide, and found that 20.0 cm^3 of aqueous NaOH was required for complete neutralisation.

(iii) What volume of aqueous NaOH should be added to 10.0 cm^3 of **FA 1** such that the pH of the resulting solution becomes equal to pK_a of MES?

[2]

(iv) Write an equation to show why the pH at equivalence point is more than 7.

[1]

(v) The pH of the solution at equivalence point is 9.4. Suggest a suitable indicator for the titration of **FA 1** with aqueous NaOH, giving a reason for your choice.

Indicators	Working range
Congo red	3.0 – 5.0
Cresolphthalein	8.2 – 9.8
Indigo carmine	11.4 – 13.0

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.....[2]

(b) Zymase, an enzyme that occurs naturally in yeasts, catalyses the fermentation of sugar into ethanol and carbon dioxide.

$$\text{sugar} \rightarrow \text{ethanol} + \text{carbon dioxide}$$

Fig. 2.1 shows the results of an investigation of the initial rate of fermentation of sugar by zymase. In the experiments, the initial concentration of sugar was varied but that of zymase was kept constant.

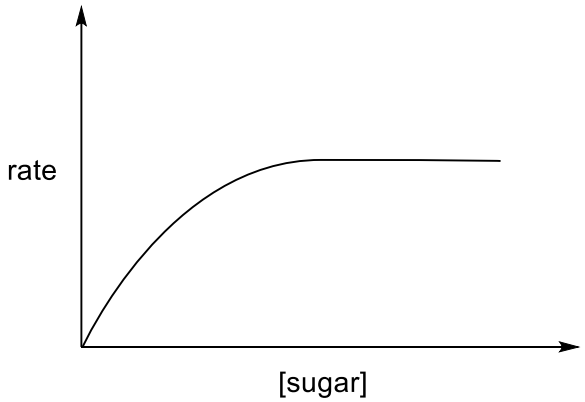

Fig. 2.1

(i) Explain fully the shape of the graph.

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.....[2]

(ii) Sketch on Fig. 2.1 the shape of the line you would expect when the amount of zymase added was increased. [1]

(iii) Three other experiments were carried out to measure the initial rates of fermentation at different concentrations of sugar and zymase. The results are shown in Table 2.2.

Table 2.2

Experiment	[sugar] /mol dm^{-3}	[zymase] /mol dm^{-3}	Relative initial rate
1	0.20	0.10	1
2	0.40	0.10	2
3	0.10	0.20	1

Deduce the orders of reaction with respect to sugar and zymase, showing how you arrive at your answers.

[3]

[Total:13]

3 This question is about alkynes, which are hydrocarbons that contain a carbon-carbon triple bond.

(a) In the past, ethyne gas, C_2H_2, was prepared from calcium carbide, CaC_2. Calcium carbide is a crystalline solid with a melting point of approximately 2160 °C.

(i) Draw the dot-and-cross diagram of CaC_2.

[1]

(ii) When excess water with a drop of universal indicator is added to some calcium carbide, ethyne is produced and the solution changes from green before the reaction, to blue after the reaction is complete.

Write an equation, with state symbols, for this reaction.

……[1]

(b) **(i)** Draw the structure of ethyne, showing correct geometry, and clearly indicate the bond angle in your drawing. State the type of hybridisation of the carbon atoms in ethyne.

Type of hybridisation of carbon: ……... [2]

(ii) Ethyne gas approaches ideal behavior at room temperature and pressure. Identify, and explain, **two** characteristics of ethyne that enable it to exhibit ideal gas behaviour.

……

……

……

……

……[2]

(c) When completely combusted, ethyne reacts with oxygen according to the following equation:

$$C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$$

A fixed-volume flask containing a mixture of ethyne and oxygen is connected to a manometer.

The manometer consists of a U-tube containing some liquid mercury, which is exposed to atmospheric pressure at one end. Initially, the mercury levels on both arms are at the same height, as shown in Fig. 3.1 below.

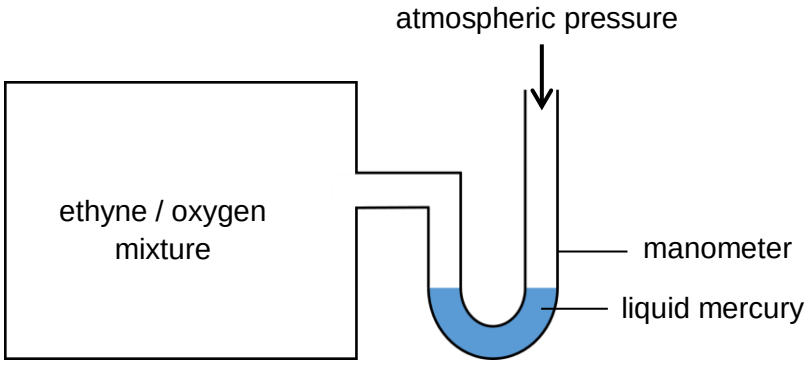


Fig 3.1

When the mixture in the flask was combusted, the final mercury levels in the manometer showed a difference in height of 65 mm. All measurements were made at room temperature and pressure. ["mm Hg" is a unit of pressure, where 760 mm Hg = 1 atm]

The initial partial pressures of ethyne and oxygen are *x* and *y* mm Hg respectively. After the combustion, the partial pressure of ethyne changed by *p* mm Hg.

(i) Express the total initial pressure in the flask in terms of *x* and *y* and state its value in mm Hg.

[1]

(ii) Express the total pressure after the combustion in terms of *x*, *y*, and *p*;

[1]

(iii) Hence, show that the difference in height of 65 mm in the mercury levels is due to a **decrease** in pressure inside the flask.

[1]

(iv) Determine the value of p to 1 decimal place.

[1]

(v) Hence, calculate

(I) the partial pressure, in mm Hg, of carbon dioxide formed after the combustion;

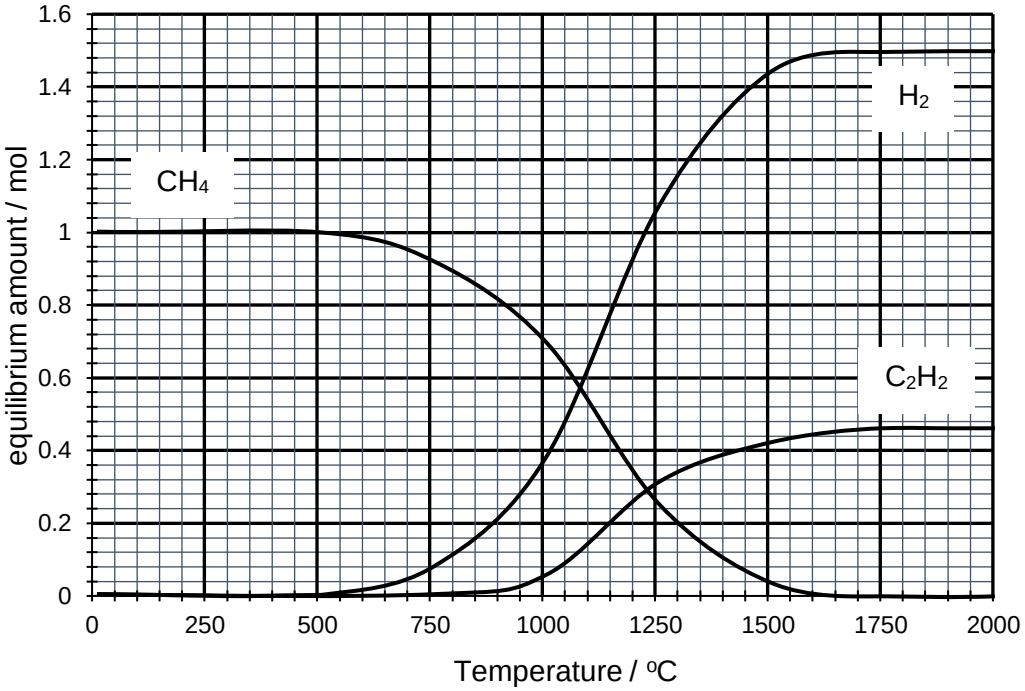
(II) the values of x and y, assuming all the oxygen was used up during the combustion, and only carbon dioxide and water were produced in the process.

[2]

(d) In more recent years, ethyne has been largely manufactured from methane. One such conversion only employs heat, and produces ethyne according to the following equilibrium:

$$2CH_4(g) \ll C_2H_2(g) + 3H_2(g) \text{ - - - - - - - - - - - - - - - (1)}$$

Equilibrium compositions during the conversion of methane to ethyne in a 0.100 m^3 vessel may be predicted using the simulated data below.



(i) Assuming the gases behave ideally in the range of temperatures shown in the graph, use the simulated data to calculate the pressure of hydrogen gas in the vessel at 1250 °C.

[2]

(ii) Show that, for equilibrium (1) at 1250 °C,

$$K_p = \frac{(n_{H_2})^3(n_{C_2H_2})}{(n_{CH_4})^2} \times \left(\frac{RT}{V}\right)^2$$

where
R is the molar gas constant
T is the temperature in the vessel
V is the volume of the vessel

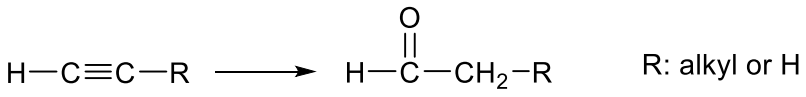
and hence, calculate K_p, showing its units.

[3]

(iii) State how the value of K_p for equilibrium (1) would change when the temperature is changed from 1250 °C to 1000 °C.

.....[1]

(e) Terminal alkynes can undergo hydroboration-oxidation reactions, as shown below.



(i) Draw and name the product formed when propyne, C_3H_4, undergoes hydroboration-oxidation.

name of product: .....[2]

(ii) Describe a simple chemical test to distinguish propyne from the product you have drawn in **(e)(i)**. You may assume that propyne reacts similarly to propene.

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.....[2]

[Total: 22]

4 Aromatic compounds like benzene tend to undergo electrophilic substitution reactions.

(a) Explain why aromatic compounds are reactive towards electrophiles but not nucleophiles.

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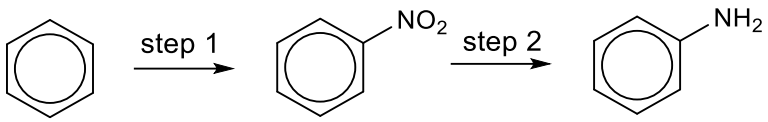
…… [1]

(b) Explain why aromatic compounds tend to undergo substitution reactions instead of addition reactions.

……

…… [1]

(c) Benzene is a starting material for the synthesis of phenylamine.



(i) State the reagents and conditions for steps 1 and 2.

step 1: ……

step 2: ……[2]

(ii) Phenylamine reacts readily with excess aqueous bromine to give a white solid **X**. Identify **X** and write a balanced equation for the reaction that occurs.

[2]

(iii) Suggest the order of reactivity of benzene, nitrobenzene and phenylamine with liquid bromine. Explain your answer.

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……

……

……[2]

(iv) Draw the structure of the monobrominated organic product formed when nitrobenzene reacts with liquid bromine.

[1]

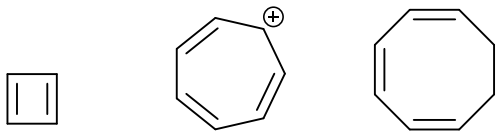
In 1931, the German chemist Erich Hückel formulated a theory to help determine if a species would be considered aromatic. This rule became known as Hückel's rule.

An aromatic species must satisfy all the following criteria:

1. It must be cyclic.
2. Every atom in the ring must have a p orbital.
3. Each p orbital must overlap the p orbitals from either side in a continuous fashion to form a closed loop, which means the structure has to be planar for effective overlap.
4. The cyclic system must contain (4n+2) delocalised π electrons, where n is 0 or a positive integer (1, 2, 3 etc.)

For example, benzene is aromatic because it satisfies all the four criteria, with 6 delocalised π electrons (n = 1).

(d) Consider the following species.



D **E** **F**

Which species are **not** aromatic? Explain your answer briefly.

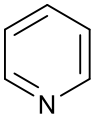
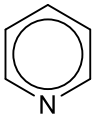
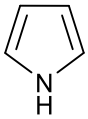
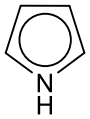
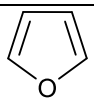
.....

.....

.....[2]

Table 4.1 shows information on three aromatic compounds which obey Hückel's rule.

Table 4.1

compound	hypothetical structure of compound	actual structure of compound	pK_b	resonance energy/ kJ mol^{-1}	boiling point/ ^{o}C
pyridine			8.6	134	115
pyrrole			13.6	100	129
furan				80	31

The hypothetical structures of the compounds in Table 4.1 assume that there is no delocalisation of π electrons in the rings. However, in reality, delocalisation of π electrons gives rise to the extra stability of the aromatic compounds. The resonance energy is defined as the energy difference between the actual structure and hypothetical structure of each compound.

(e) **(i)** All the carbon and nitrogen atoms in pyrrole are sp^2 hybridised.

Draw the arrangement of all the hybridised and unhybridised orbitals of the nitrogen atom in pyrrole. Label the orbitals clearly.

[2]

(ii) Pyrrole has six electrons in the delocalised π electron cloud.

How many electrons does the nitrogen atom in pyrrole contribute to the delocalised π electron cloud? You may find it useful to consider the hypothetical structure of pyrrole.

……[1]

(iii) The nitrogen atom in pyrrole has a lone pair of electrons. Suggest the orbital in which the lone pair resides.

……[1]

(iv) Hence, using your answers in **(e)(ii)** and **(e)(iii)**, suggest why the pK_b of pyrrole is so high.

……

……[1]

(f) **(i)** Furan can behave differently from benzene in its reactions. Under certain conditions, furan undergoes electrophilic addition instead of electrophilic substitution. Based on your answer in **(b)**, explain this phenomenon, using relevant data from Table 4.1.

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……[2]

(ii) Furan can form hydrogen bonds when added to ethanol. Draw a diagram to show how hydrogen bonding occurs between one molecule of furan and one molecule of ethanol and explain how this interaction arises.

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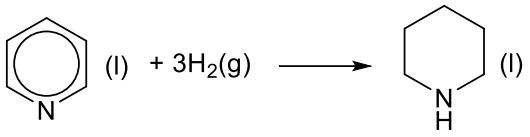
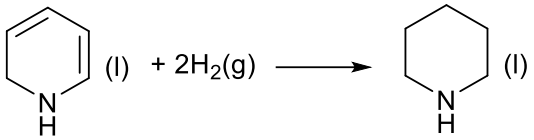
……[2]

(g) The enthalpy changes of hydrogenation of pyridine and compound **E** can be represented by the equations below:



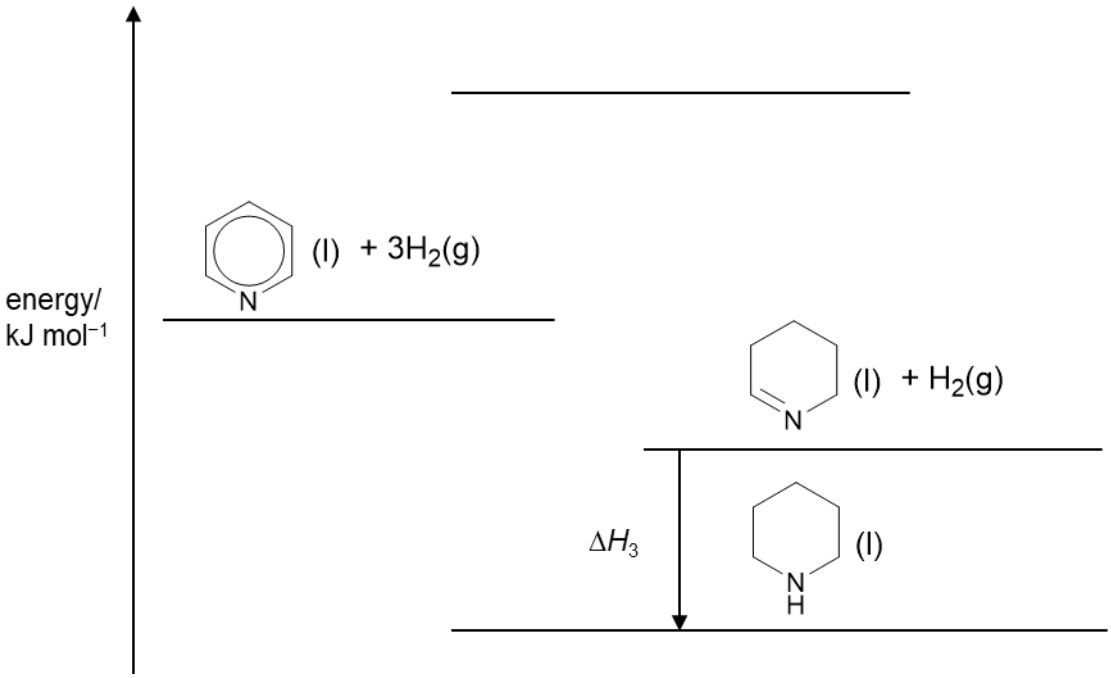
$\Delta H_1 = -194$ kJ mol^{-1}



$\Delta H_2 = -240$ kJ mol^{-1}

E

Using the information above and relevant data from Table 4.1, complete the energy diagram below and use it to calculate ΔH_3.



ΔH_3 = …….. kJ mol^{-1}

[3]

[Total: 23]

END OF PAPER