HWA CHONG INSTITUTION
C1 Promotional Examination
Higher 2

NAME		**CT GROUP**	**18S**

CHEMISTRY

9729/02

Paper 2 Structured questions

2 October 2018

1 hour 5 minutes

Candidates answer on the Question Paper.

Additional Materials: Data Booklet.

READ THESE INSTRUCTIONS FIRST

Write your name and CT group 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, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided on 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 EXAMINERS' USE ONLY

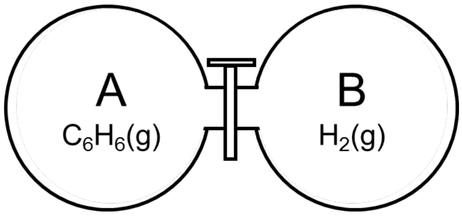
Paper 1	Paper 2		Paper 3	
Multiple Choice	**Structured**		**Free Response**	
	Q1	/ 10	Q1	/ 20
	Q2	/ 14	Q2 / 3	/ 20
	Q3	/ 16		
	Deductions		Deductions	
/ 20	**Subtotal:**	**/ 40**	**Subtotal:**	**/ 40**

This document consists of **12** printed pages.

Answer **all** the questions.

1 Cyclohexane can be produced by reacting benzene with hydrogen under certain conditions.

$$C_6H_6(g) + 3H_2(g) \rightleftharpoons C_6H_{12}(g)$$



Vessel A contains benzene gas at a pressure of x atm and vessel B contains hydrogen gas at a pressure of 5.67 atm. The flasks were kept at a temperature of 600 K.

When the two flasks are connected and the gases mixed in the presence of a suitable catalyst with the temperature maintained at 600 K, they react to give gaseous cyclohexane. It was found that at equilibrium, the partial pressures of cyclohexane and benzene were 0.61 atm and 2.70 atm respectively.

(a) **(i)** Write an expression for K_p for this equilibrium.

[1]

(ii) Find the partial pressure of hydrogen at equilibrium, given that K_p = 0.0305 atm^{-3}.

[1]

(iii) The two vessels have a combined volume of 6.0 dm^3.

Show that the volume of vessel B is 4.0 dm^3 and hence determine x.

[3]

(b) Using relevant bond energy data from the *Data Booklet*, calculate the enthalpy change for the reaction of benzene gas and hydrogen gas to give cyclohexane gas.

[2]

(c) Deduce how the K_p will change if:

I the catalyst was removed:

....

....

....

II the temperature was increased:

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[3]

[Total: 10]

2 Methylbenzene reacts with liquid bromine under different reaction conditions to produce different brominated products.

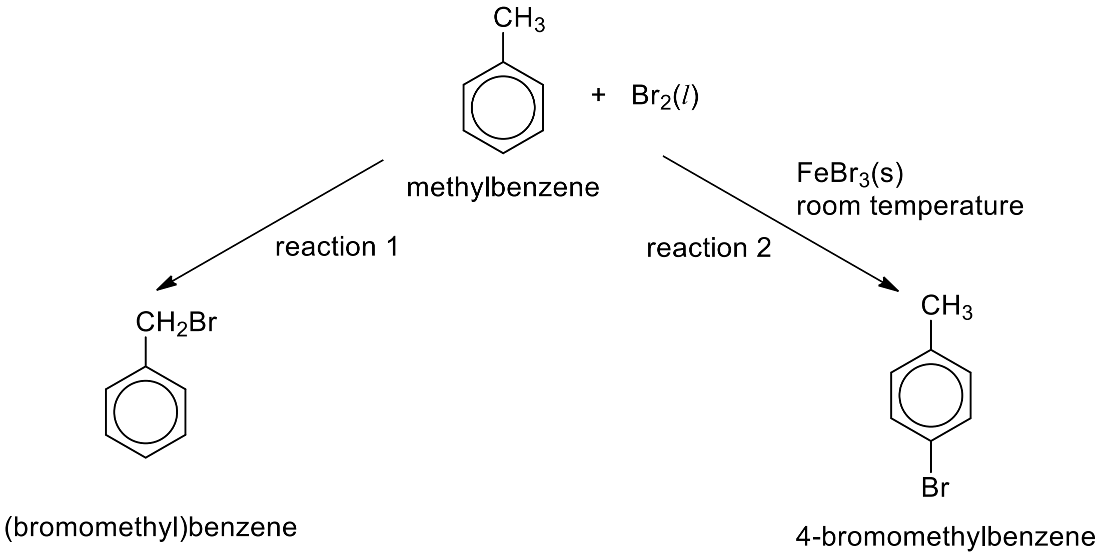

Fig. 2.1

(a) State the conditions required in reaction 1.

....[1]

(b) Explain why the liquid bromine used in reaction 1 should be limited in quantity.

....

....[1]

(c) **(i)** Describe the mechanism for reaction 2 between methylbenzene and liquid bromine to form 4-bromomethylbenzene, showing clearly any intermediates that may be formed and use curly arrows to indicate the movement of electron pairs.

[3]

(ii) With reference to your answer in **c(i)**, explain why the slow step has fairly high activation energy.

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…………………………………………………………………………………………………[1]

(d) 4-bromomethylbenzene is one of the two major products formed in reaction 2. Draw the structure of the other major product.

[1]

(e) Explain the relative ease of methylbenzene undergoing reaction 2 compared to benzene.

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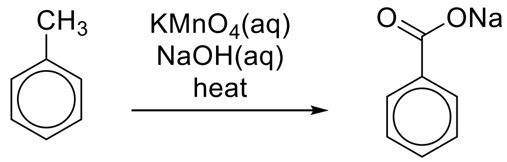
…………………………………………………………………………………………………[2]

(f) When methylbenzene is heated with aqueous potassium manganate(VII) and aqueous sodium hydroxide, sodium benzoate is produced via a side-chain oxidation reaction.



methylbenzene sodium benzoate

The reaction does not go to completion, and the desired sodium benzoate can be separated from unreacted methylbenzene via the following steps.

1. The reaction mixture is filtered to remove the brown solid MnO_2.
2. Hexane is added to the filtrate, and the mixture is shaken.
3. When left to stand, the mixture forms two immiscible layers, the hexane layer and the aqueous layer. The two layers are then separated using a separatory funnel.

(i) Explain why sodium benzoate is soluble in the aqueous layer in step 3.

....

....[1]

Benzoic acid can be obtained from sodium benzoate found in the aqueous layer by adding a reagent.

(ii) Suggest the reagent to be added to sodium benzoate to give benzoic acid.

....[1]

(iii) Briefly describe how the benzoic acid formed can be separated from the reagent in **f(ii)**.

You may find the following information useful.

Benzoic acid is not soluble in hexane but is soluble in the solvent diethyl ether. Diethyl ether is immiscible with water.

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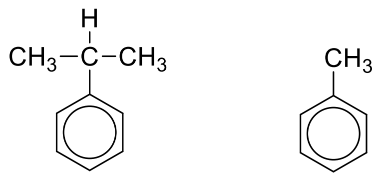
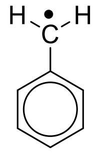
....[1]

(iv) A study found that **X** undergoes side-chain oxidation more readily than methylbenzene.



X methylbenzene

The mechanism for the side-chain oxidation of methylbenzene may involve the following radical intermediate.



Explain fully why the presence of a radical intermediate in the mechanism is consistent with the results of the above study.

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....

....

....[2]

[Total: 14]

3 Hydrogen is a clean and environmentally friendly fuel. The sunlight-driven water splitting reaction that separates water into its constituent elements is therefore of interest to scientists.

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g) \qquad (1)$$

(a) Calculate $\Delta G^\ominus$ for reaction (1) at 298 K and hence explain why this reaction needs to be driven by sunlight.

Standard enthalpy change of formation of $H_2O(l)$ = -286 kJ mol^{-1}
Standard entropy change of formation of $H_2O(l)$ = -163 J K^{-1} mol^{-1}

....

....[2]

The oxygen evolution reaction as depicted by half-equation (2) below is one of the processes involved in the water splitting reaction.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (2)$$

This process has a high kinetic barrier and a catalyst is needed to produce oxygen at fast rates.

In order to investigate the efficiency of the catalyst, an experiment was performed where water was oxidized using a powerful chemical oxidant such as cerium ammonium nitrate (CAN), $(NH_4)_2Ce(NO_3)_6$.

Fig. 3.1 shows the experimental setup.

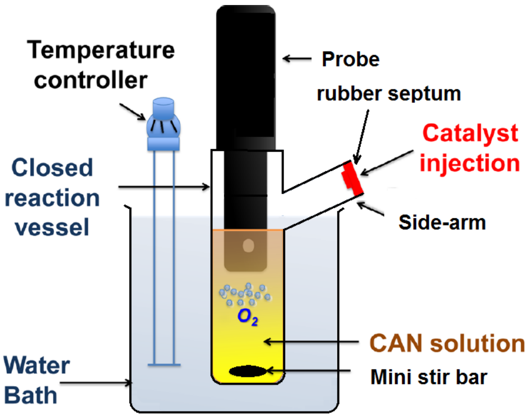

Fig. 3.1

25.0 cm^3 of 0.0220 mol dm^{-3} acidified CAN solution was placed in a constant temperature water bath. Excess nitrogen gas was bubbled into the CAN solution through the side-arm inlet. This was followed by injection of 1.00 cm^3 of an oxygen-free aqueous solution of the catalyst. A timer was started immediately and the concentration of dissolved oxygen produced was monitored using the probe at regular time intervals.

(b) **(i)** Suggest why it was necessary to bubble nitrogen gas into the CAN solution before the start of the experiment.

…………………………………………………………………………………………

……………………………………………………………………………………[1]

(ii) A student tried to add the catalyst by removing the rubber septum and pouring the solution down the side-arm. He was advised by his mentor to inject the catalyst through the rubber septum instead.

Explain why it was necessary to add the catalyst into the reaction vessel via injection.

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……………………………………………………………………………………[1]

(iii) At the end of the reaction, the concentration of dissolved oxygen was found to be 0.169 g dm^{-3}.

If cerium is the only element in CAN that has undergone reduction during the reaction, calculate the final oxidation state of cerium in the cerium-containing product.

[3]

(c) The rate equation for this reaction is shown below.

$$\text{rate} = k[\text{CAN}]^m[\text{catalyst}]^n$$

As CAN is present in large excess, this rate equation can be simplified as

$$\text{rate} = k'[\text{catalyst}]^n$$

$$\text{where } k' = k[\text{CAN}]^m$$

The rate equation may also be expressed in logarithmic form:

$$\lg(\text{rate}) = \lg k' + n \lg[\text{catalyst}]$$

To determine the efficiency of the catalyst, a series of experiments was carried out using the same method as described above but with varying concentrations of the catalyst.

Fig. 3.2 shows the plot of lg (rate) against lg [catalyst] for the series of experiments performed.

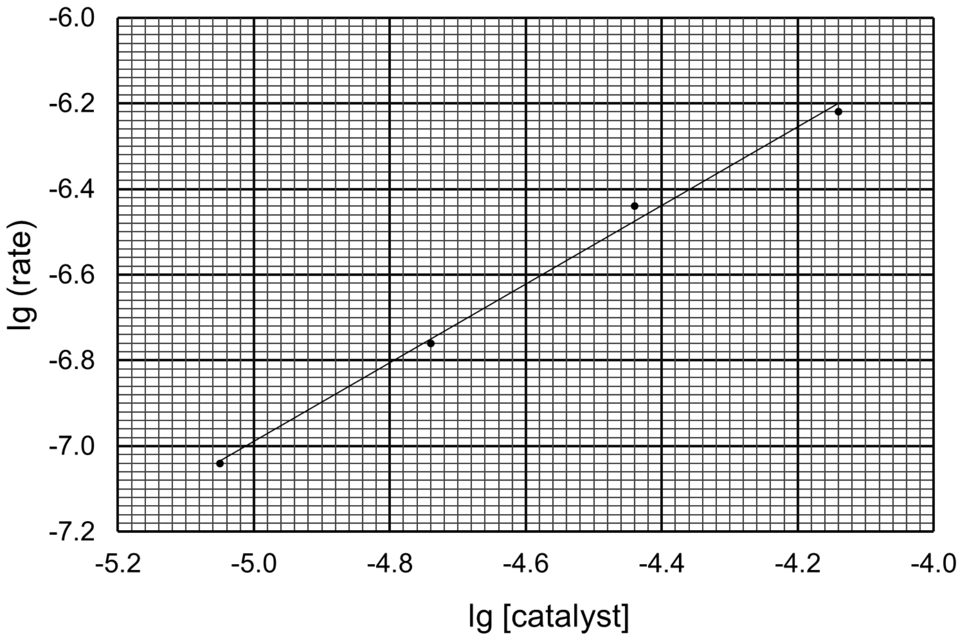

Fig. 3.2

(i) By using the graph given, determine the order of reaction with respect to the catalyst. Show your working clearly.

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……………………………………………………………………………………………[1]

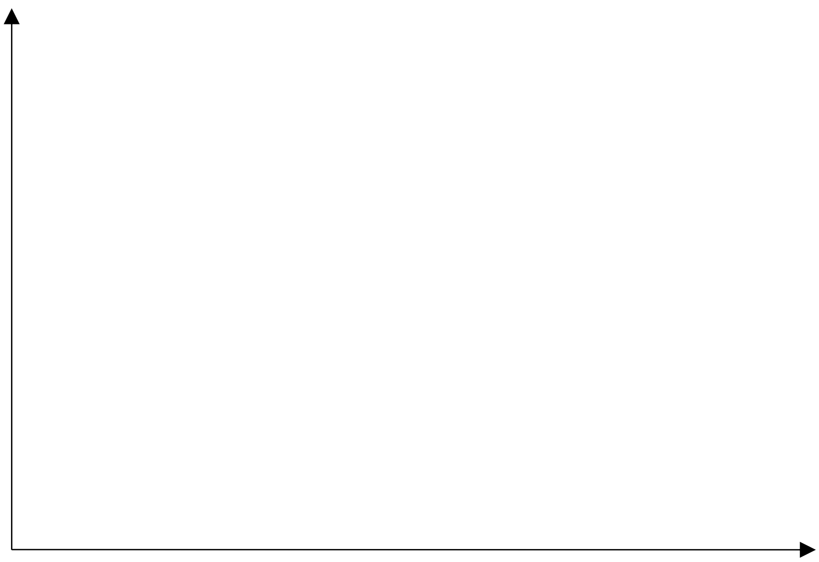
(ii) The efficiency of the catalyst is given by its turnover frequency (TOF).

$$\text{TOF} = \frac{\text{rate of change of } [O_2]}{[\text{catalyst}]}$$

By using the graph given, calculate TOF, in s^{-1}, for the catalyst used.

TOF = ………………………. s^{-1}
[1]

(d) With the aid of a sketch of the Boltzmann distribution, explain how an increase in temperature increases the rate of a chemical reaction.



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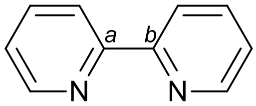
…………………………………………………………………………………………..[3]

(e) 2,2'-bipyridine was one of the reactants used to synthesise the catalyst in this experiment. It can exist in both the *cis* and *trans* configuration. The structure below shows the *cis* configuration.



2,2'-bipyridine

(i) Draw a labelled diagram to show the orbitals involved in bonding around the carbon atom labelled *a*, and state the type of hybridisation involved.

[2]

(ii) Using your answer in **(e)(i)**, explain why there is restricted rotation about the bond between the carbon atoms labelled *a* and *b*.

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……………………………………………………………………………..………[1]

(iii) Draw the *trans* configuration of 2,2'-bipyridine.

[1]

[Total: 16]

~END OF PAPER~