HWA CHONG INSTITUTION
C1 Promotional Examination
Higher 2

NAME		**CT GROUP**	**16S**

CHEMISTRY

9729/03

Paper 3 Free Response

30 September 2016

1 hour 20 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.

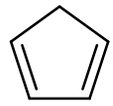
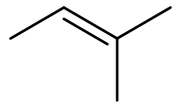
1 **(a)** When 2-methylbutane is reacted with chlorine gas in the presence of sunlight, several mono-chlorinated products are formed.

(i) Draw the structures of all possible mono-chlorinated products. [2]

(ii) Explain which of the products you have drawn in **(i)** was formed via the most stable radical. [1]

(iii) Hence, describe the mechanism for the formation of the product you identified in **(ii)**. [3]

(b) A student has forgotten to properly label bottles known to contain the following two organic compounds:

	Compound
A	Cyclopenta-1,3-diene 
B	2-methylbut-2-ene 

Describe a simple chemical test that would allow the student to distinguish between **A** and **B**. [2]

(c) A 2.00 g impure sample of yttrium(III) oxide, Y_2O_3 (M_r = 225.8), was known to be contaminated with a little hydrated yttrium(III) carbonate, $Y_2(CO_3)_3 \cdot 3H_2O$ and other inert material. After the sample was left exposed to moist air for several days, it was reweighed and found to have increased in mass. The change in mass was due to the conversion of some of the oxide to form compound **Q**.

The resulting sample was completely dissolved in 35.00 cm^3 of 2.00 mol dm^{-3} hydrochloric acid, releasing 16.40 cm^3 of gas (measured at standard temperature and pressure) in the process. After all the gas was released, the resulting solution required 19.65 cm^3 of 1.00 mol dm^{-3} sodium hydroxide solution for complete neutralisation.

The following information may be relevant:

- Balanced equation for reaction of yttrium(III) oxide with hydrochloric acid:

$$Y_2O_3 + 6HCl \rightarrow 2YCl_3 + 3H_2O$$

- **Q** is made up of yttrium, oxygen and hydrogen only.
- When separately reacted with a mineral acid, **Q** and yttrium(III) oxide form the same products.
- The conversion of the oxide to form **Q** does not result in any change of oxidation state.

(i) Calculate the amount of acid that reacted with the sample. [1]

(ii) Calculate the amount of acid that reacted with the yttrium(III) carbonate. [1]

(iii) **Q** consists of 63.5% yttrium and 2.14% hydrogen by mass. Identify **Q** and write an equation for its formation from the oxide. [2]

(iv) Hence, or otherwise, determine the percentage purity of the original sample of yttrium(III) oxide. [3]

[Total: 15]

2 **(a)** Potassium manganate(VII) and hydrogen peroxide react to give oxygen gas as follows:

$$2MnO_4^-(aq) + 5H_2O_2(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5O_2(g) + 8H_2O(l)$$

A thermometric titration between potassium manganate(VII) and hydrogen peroxide was carried out. The temperature of the reaction mixture was followed as acidified potassium manganate(VII) was added in 4.00 cm^3 aliquots to 25.0 cm^3 of 1.00 mol dm^{-3} hydrogen peroxide. The results of the titration are shown in Table 2.1.

Table 2.1

Volume of $KMnO_4$ added / cm^3	Highest Temperature obtained / °C
0.00	31.0
4.00	37.0
8.00	44.0
12.00	50.0
16.00	54.0
20.00	49.0
24.00	44.0
28.00	38.0
32.00	33.0

(i) Use the data given in Table 2.1 to plot a graph of temperature / °C against volume of $KMnO_4$ / cm^3. [2]

(ii) From the graph, determine the maximum temperature obtained and the volume of $KMnO_4$ at which the maximum temperature obtained occurs. Show your working on your graph. [2]

(iii) Using your answer to **(ii)**, determine the enthalpy change of reaction per mole of hydrogen peroxide. Give your answer to the nearest whole number in kJ mol^{-1}. [3]

(b) Describe and explain the trend of the first ionisation energies of the elements in Period 3 as fully as you can. [4]

(c) Describe the bonding and structure in the substances given below and their effects on the melting points, making use of the data given in Table 2.2.

Table 2.2

Substance	**Formula**	**Melting point / °C**
Argon	Ar	−189
Hydrogen peroxide	H_2O_2	−0.43
Diamond	C	3350

[4]

[Total: 15]

Section B

Answer **one** question from this section.

3 Phosgene, $COCl_2$, carbon monoxide and chlorine are all toxic gases. Despite their toxicities, these compounds are important starting materials in the synthesis of pharmaceutical and other organic compounds.

(a) (i) Draw a 'dot-and-cross' diagram to show the bonding in phosgene. [1]

(ii) Sketch a diagram showing all the hybrid orbitals around the carbon atom in phosgene. [1]

(b) Phosgene can dissociate to form carbon monoxide and chlorine.

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$$

0.200 mol of phosgene was placed into a rigid reaction vessel of volume 12.5 dm^3 and allowed to dissociate at a temperature of 770 K. The total amount of gas at equilibrium was found to be 0.319 mol.

(i) Calculate the equilibrium concentrations of $COCl_2$, CO and Cl_2, and the percentage of $COCl_2$ dissociated at 770 K. [4]

(ii) Write the expression for the equilibrium constant, K_c, for the above reaction and calculate its value at 770 K, showing its units clearly. [3]

(iii) The standard Gibbs free energy change of reaction, $\Delta G_r^{\ominus}$, for the above dissociation is $+67.7 \times 10^3$ J mol^{-1}. The relationship between the equilibrium constant and the standard Gibbs free energy change of this reaction can be expressed as:

$$\Delta G_r^{\ominus} = -RT \ln K$$

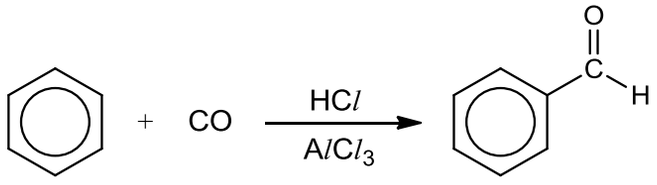
where K in the above expression is the numerical value of K_c.

Calculate the value of K for the dissociation of $COCl_2$ at 298 K. [1]

(iv) Using your answers to **(ii)** and **(iii)**, deduce whether the forward or backward reaction will be favoured when the temperature of the equilibrium mixture is decreased from 770 K to 298 K.

Hence, deduce the sign of the enthalpy change of reaction, ΔH, for the dissociation of phosgene. [2]

(c) Benzaldehyde, C_6H_5CHO, is an aromatic compound with a characteristic almond-like odour, and hence has found use as a flavouring agent. Benzaldehyde may be synthesised by the Gatterman–Koch reaction, a Friedel–Crafts acylation involving the reaction between carbon monoxide and benzene in the presence of hydrogen chloride and aluminium chloride as catalysts.

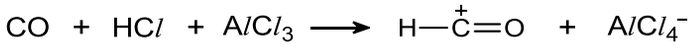


benzaldehyde

The mechanism for the reaction may be described as follows:

- Generation of the electrophile, HCO^+.
- Reaction between the electrophile and benzene to form a carbocation intermediate in the rate-determining step.
- Loss of a proton from the carbocation intermediate to regenerate HCl and $AlCl_3$.

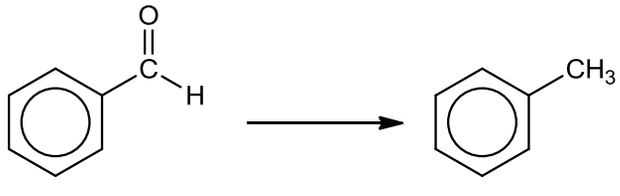
(i) The electrophile, HCO^+, is generated from the reaction between carbon monoxide, hydrogen chloride and aluminium chloride:



Using the theories of acids and bases, state the roles of CO and $AlCl_3$ in the above reaction. [2]

(ii) Describe the mechanism of the reaction between the electrophile in **(i)** and benzene to form benzaldehyde, showing clearly the movement of electrons, the structure of the intermediate formed, as well as the regeneration of the catalysts. [3]

(iii) Benzaldehyde may undergo further reaction to form methylbenzene, as shown below.



methylbenzene

State the type of reaction that benzaldehyde undergoes and justify your answer. [2]

(iv) Another method of producing methylbenzene from benzene involves the direct Friedel–Crafts alkylation of benzene. By considering the reactivities of methylbenzene and benzene, suggest why it is difficult to obtain a high yield of methylbenzene using this method. [1]

[Total: 20]

4 The stratosphere is a region of upper atmosphere that extends from 16 to 50 km above sea level, with a temperature of about 270 K at higher altitude. In this region, oxygen molecules absorb high-energy ultraviolet radiation and break up to form oxygen atoms. Some of these oxygen atoms react with oxygen molecules to produce ozone (O_3) in Reaction 1 shown below.

Reaction 1: $O + O_2 \rightarrow O_3$ $\quad \Delta H_1' = -160$ kJ mol^{-1}

(a) Draw the 'dot-and-cross' diagram of ozone, stating its shape and bond angle. [2]

(b) Within the stratosphere, ozone can be broken down to regenerate molecular oxygen as shown in Reaction 2.

Reaction 2: $O + O_3 \rightarrow 2O_2$ $\quad \Delta H_2'$

Using $\Delta H_1'$ and relevant data from the *Data Booklet*, construct an energy cycle to calculate the standard enthalpy change for this reaction, $\Delta H_2'$. [2]

(c) High-flying supersonic aircraft release NO into the stratosphere. The mechanism below shows how Reaction 2 occurs in the presence of NO.

Step I: $NO + O_3 \rightarrow NO_2 + O_2$
Step II: $NO_2 + O \rightarrow NO + O_2$

(i) State the role of NO in this mechanism. [1]

(ii) This reaction is found to be overall second order. Identify the rate-determining step in the given mechanism and give a reason to justify the overall order. [1]

(iii) The rate of Reaction 2 is found to be slower when taking place in the stratosphere as compared to in a laboratory for the same concentrations of NO and O_3.

With the help of a Maxwell–Boltzmann diagram, suggest a reason for this observation. [4]

(d) The following question describes reactions of a volatile hydrocarbon **P**.

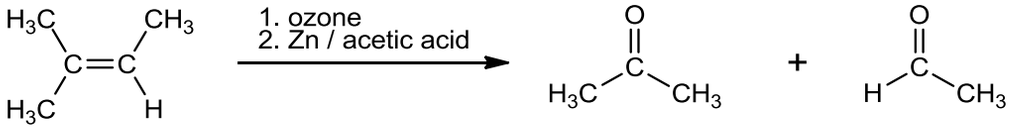
(i) 10 cm^3 of **P** was exploded in excess oxygen. A contraction of 30 cm^3 occurred after the combustion. On passing the gaseous products through aqueous sodium hydroxide, a further contraction of 60 cm^3 occurred. (All volumes of gases were measured at room temperature and pressure).

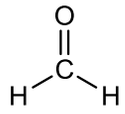
Show that the molecular formula of **P** is C_6H_8. [2]

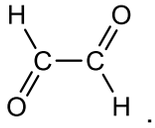
(ii) When 0.25 g of **P** is reacted with 225 cm^3 of hydrogen gas over a platinum catalyst at room temperature and pressure, **Q** is formed.

When **P** is added to aqueous bromine, the solution is decolourised and **R** is formed.

Ozonolysis is an organic reaction where the unsaturated bonds of alkenes are cleaved with ozone. The example below shows the products formed after an alkene is reacted with ozone followed by zinc in acetic acid.



When **P** undergoes ozonolysis, the only organic products formed are 

and 

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Deduce the identities of **P**, **Q** and **R** and explain the chemistry involved. [8]

[Total: 20]

END OF PAPER