HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	**16S**
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9729/03

Paper 3 Free Response

18 September 2017

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
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.

Section A

Answer **all** questions.

Section B

Answer **one** question.

Begin each question on a **new sheet of writing paper**.

A Data Booklet is provided.

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

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.

Circle the question numbers for the questions that you have attempted on the cover page provided.

Section A

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

1 (a) *Azurite* is a deep blue copper-containing mineral. For many centuries, finely ground rock containing azurite has been used as a pigment in blue paints. Azurite is a mixture of copper(II) carbonate and copper(II) hydroxide. The formula of pure azurite is $Cu_3(CO_3)_2(OH)_2$, which has a relative formula mass of 344.5.

The percentage by mass of pure azurite in a sample of finely ground rock can be determined by back titration. 3.70 g of the sample is added to 100 cm^3 of 0.425 mol dm^{-3} sulfuric acid. The resulting solution was made up to 250 cm^3 with distilled water. 25.0 cm^3 of the diluted solution required 26.50 cm^3 of 0.100 mol dm^{-3} sodium hydroxide for neutralization.

Dilute sulfuric acid reacts with pure azurite as shown in the following equation.

$$Cu_3(CO_3)_2(OH)_2(s) + 3H_2SO_4(aq) \rightarrow 3CuSO_4(aq) + 4H_2O(l) + 2CO_2(g)$$

Calculate the percentage by mass of pure azurite in the sample. You may assume that azurite is the only substance in the rock that reacts with sulfuric acid. [3]

(b) The brick-red precipitate, Cu_2O, dissolves in concentrated ammonia solution to form a colourless complex ion **P**, $[Cu(NH_3)_x]^{n+}$, which has a linear geometry about the central metal ion. When left exposed to air, the colourless complex ion **P** turns into a deep blue solution, containing the complex ion $[Cu(NH_3)_4]^{2+}$.

(i) State the value of x and write the formula of complex ion **P**. [2]

(ii) With the help of the *Data Booklet*, write the two half equations, and hence the overall equation for the reaction of the colourless complex ion **P** to form $[Cu(NH_3)_4]^{2+}$. [2]

(c) Iodine and chlorine react together to give iodine trichloride.

$$I_2(s) + 3Cl_2(g) \rightarrow 2ICl_3(s)$$

(i) Construct a fully labelled energy cycle relating the reactants and products of this reaction to their gas phase atoms. Use your cycle to calculate the average bond energy of the I–Cl bond in ICl_3.

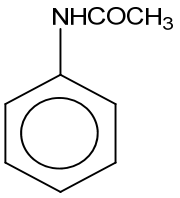
Your cycle should include relevant data from the *Data Booklet* together with the following data.

standard enthalpy change of formation ($\Delta H_f^{\ominus}$) of $ICl_3(s)$	= –81 kJmol^{-1}
enthalpy change of sublimation of $I_2(s) \rightarrow I_2(g)$	= +38 kJmol^{-1}
enthalpy change of sublimation of $ICl_3(s) \rightarrow ICl_3(g)$	= +60 kJmol^{-1}

[4]

(ii) The standard Gibbs free energy of formation, $\Delta G_f^{\ominus}$, of $ICl_3(s)$ is –40.4 kJmol^{-1}. Calculate $\Delta S_f^{\ominus}$ and comment on its sign with respect to the reaction. [2]

(d) The antipyretic (fever-reducing) drug *antifebrin* can be made via a 3-step synthetic route, starting from benzene.



antifebrin

(i) State the 3 types of reactions involved (in sequence) in the formation of antifebrin from benzene. [3]

(ii) Draw the structures of the products formed when antifebrin was subjected to prolonged heating with dilute sulfuric acid. [1]

[Total: 17]

2 Thiols are a group of organic compounds which may be represented as $C_nH_{2n+1}SH$ or RSH, where R is an alkyl group.

(a) In an experiment a sample of thiol was completely burnt in a stoichiometric amount of oxygen. The product mixture was collected in a 1.65 dm^3 flask at 110 °C and 1 atm total pressure. The partial pressure of sulfur dioxide was found to be 16.9 kPa.

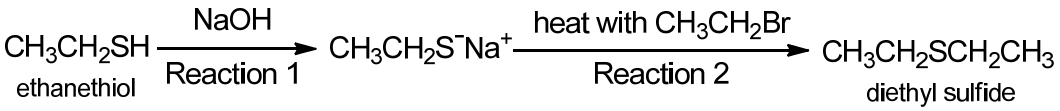
(i) Write a balanced equation for the complete combustion of one mole of a thiol with *n* carbon atoms. [1]

(ii) Show that when a thiol with *n* carbon atoms is completely burnt in a stoichiometric amount of oxygen, the mole fraction of sulfur dioxide in the product mixture is $1/(2n+2)$. Assume that all products are gaseous. [1]

(iii) Use the above data, together with the information in **(ii)** to deduce the value of *n* for the thiol burnt in the experiment. [1]

(iv) Hence find the mass of thiol burnt. [2]

(b) Thiols are suitable starting materials for the synthesis of organic sulfides. An example is given below.



(i) How would the acid strength of ethanethiol compare to that of ethanol, given that Reaction 1 is effectively complete? [1]

(ii) State the type of reaction occurring in Reaction 2. [1]

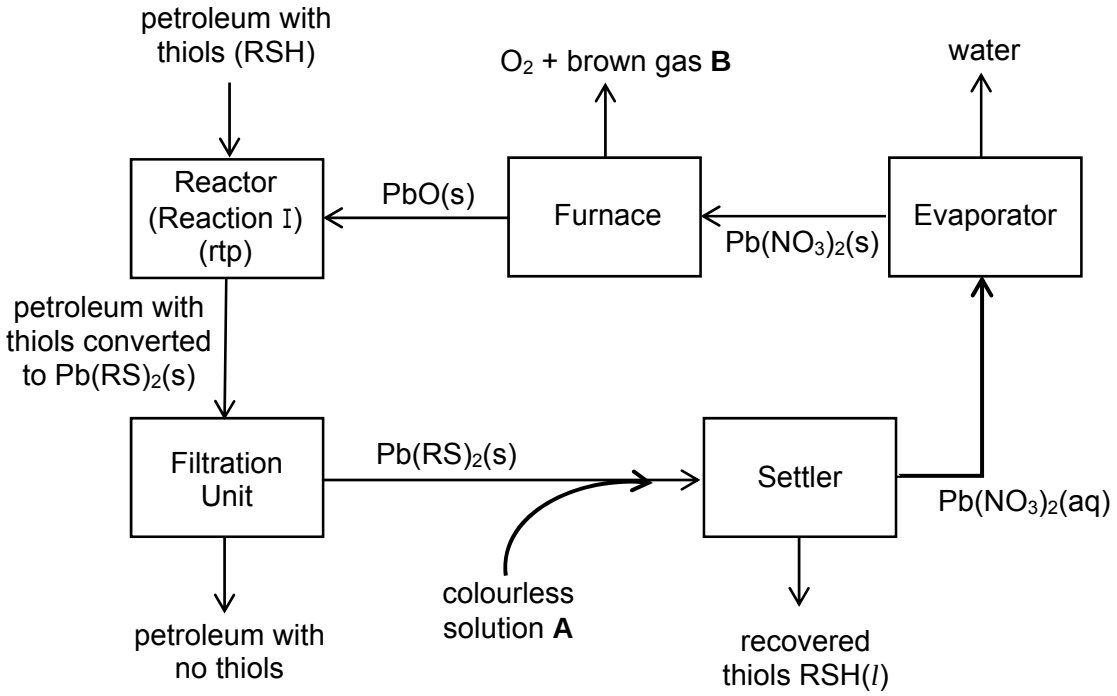
(iii) Suggest why Reaction 1 was carried out in the above synthesis. [1]

(iv) Give **two** reasons to explain why ethylphenyl sulfide, $C_6H_5SCH_2CH_3$, cannot be obtained by changing bromoethane in Reaction 2 to bromobenzene. [2]

(c) The following diagram shows a process which may be used for the removal and recovery of thiols from petroleum. The process utilizes the reaction between thiols and lead(II) oxide, as given in the equation below.

$$2RSH(l) + PbO(s) \rightleftharpoons Pb(RS)_2(s) + H_2O(l) \qquad \text{Reaction I}$$

As the equilibrium position for Reaction I lies very much towards the products, the overall recovery of thiols in the process is high.



(i) State the role of lead(II) oxide in Reaction I. [1]

(ii) Comment on the sign and magnitude of $\Delta G^{\ominus}$ for Reaction I. [2]

(iii) Suggest the identity of colourless solution **A** and brown gas **B**. [2]

(iv) Suggest the temperature in the furnace, explaining your reasoning with the use of relevant data from the *Data Booklet*. For reference, copper(II) nitrate and barium nitrate decompose at 170 °C and 630 °C respectively. [4]

(d) Thermal cracking, which is a process where large alkane molecules are broken down into smaller alkanes and alkenes, proceeds via a free radical mechanism.

The following are reactions which are thought to occur, using propane as the starting alkane.

$CH_3CH_2CH_3 \rightarrow \bullet CH_3 + \bullet CH_2CH_3$ -- (A)

$CH_3CH_2CH_3 \rightarrow \bullet H + \bullet CH_2CH_2CH_3$ -- (B)

$\bullet CH_3 + CH_3CH_2CH_3 \rightarrow CH_4 + \bullet CH_2CH_2CH_3$ -- (C)

$\bullet CH_2CH_3 \rightarrow \bullet H + CH_2{=}CH_2$ -- (D)

$\bullet CH_3 + CH_2{=}CH_2 \rightarrow \bullet CH_2CH_2CH_3$ -- (E)

$\bullet CH_3 + \bullet CH_3 \rightarrow CH_3CH_3$ -- (F)

$2 \bullet CH_2CH_3 \rightarrow CH_3CH_3 + CH_2{=}CH_2$ -- (G)

(i) Reactions (A) and (B) are termed initiation steps. With the use of the *Data Booklet*, deduce which one is more likely to occur. [1]

(ii) Of reactions (C) to (G), identify those which may be termed propagation steps in the mechanism. [1]

(iii) Which gas, if detected in the product mixture, would offer support for the occurrence of both Reactions (B) and (D)? [1]

(iv) Explain why Reaction (G) may be termed a disproportionation. [1]

[Total: 23]

3 Phosphorus forms a wide range of compounds that are essential for life and have many applications in the industry and in the laboratory.

(a) Many detergents contain sodium dodecylbenzenesulfonate, $C_{18}H_{29}SO_3Na$ (M_r = 348), that can react with calcium ions in 'hard' water to give a precipitate, making the detergent ineffective.

The solubility product, K_{sp}, for $(C_{18}H_{29}SO_3)_2Ca(s)$ is given by

$$[Ca^{2+}][C_{18}H_{29}SO_3^-]^2 = 1.20 \times 10^{-17} \text{ mol}^3 \text{ dm}^{-9}$$

A particular brand of detergent contains 17.4% by mass of sodium dodecylbenzenesulfonate. The manufacturer states that in 'hard' water, 1.00 g of the detergent should be used with 1.00 dm^3 of water. A typical sample of 'hard' water contains 2.50×10^{-4} mol dm^{-3} of Ca^{2+}.

You may assume that the volume of 1.00 g of detergent is negligible compared to 1.00 dm^3 of 'hard' water.

(i) Explain why it is not necessary to include the concentration of $(C_{18}H_{29}SO_3)_2Ca(s)$ in the K_{sp} expression. [1]

(ii) Explain whether a precipitate will form when 1.00 g of the detergent is added to 1.00 dm^3 of 'hard' water. [3]

(iii) Calculate the maximum concentration of Ca^{2+} in 'hard' water for the detergent to be effective when it is used as recommended by the manufacturer. [1]

In order for detergents to be used in 'hard' water, sodium tripolyphosphate, $Na_5P_3O_{10}$, is added as a water softening agent. It 'softens' water by complexing with the calcium ions which can help to prevent the formation of precipitate.

$$Ca^{2+}(aq) + P_3O_{10}^{5-}(aq) \rightleftharpoons CaP_3O_{10}^{3-}(aq) \qquad K_c = 7.70 \times 10^8 \text{ mol}^{-1} \text{ dm}^3$$

(iv) Write an expression for the equilibrium constant of the above reaction. [1]

(v) Some solid sodium tripolyphosphate was added to 'hard' water containing the detergent. After forming the complex, the concentration of $P_3O_{10}^{5-}$ decreased to **one-tenth** of its original value at equilibrium.

Using the K_c value, calculate the concentration of Ca^{2+} in the equilibrium mixture. [1]

(vi) Hence, with reference to your answers in **(a)(iii)** and **(a)(v)**, comment on whether the amount of solid sodium tripolyphosphate added was sufficient to make the detergent effective. [1]

(b) Phosphorus also forms a class of compounds with nitrogen known as phosphazenes.

A commercially available phosphazene is $(Cl_2PN)_3$ which is the starting material for many biomedical polymers. It can be synthesized by reacting PCl_5 with NH_4Cl. HCl is formed as a byproduct.

(i) Write an equation for the synthesis of $(Cl_2PN)_3$. [1]

(ii) $(Cl_2PN)_3$ has a cyclic backbone consisting of alternating phosphorus and nitrogen atoms. Each chlorine atom forms a single bond with a phosphorus atom.

Draw the structure of $(Cl_2PN)_3$. [1]

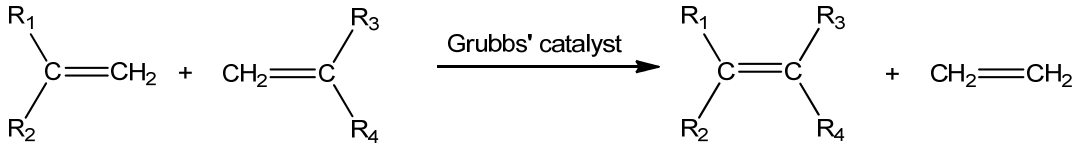
(iii) Like PCl_5, $(Cl_2PN)_3$ undergoes a similar reaction with water, forming $(PN(OH)_2)_3$.

Suggest the type of reaction undergone by $(Cl_2PN)_3$ and predict what would be observed when a few drops of water was added to $(Cl_2PN)_3$. [2]

(iv) The atomic radii of P, N and Cl are listed in the *Data Booklet*.

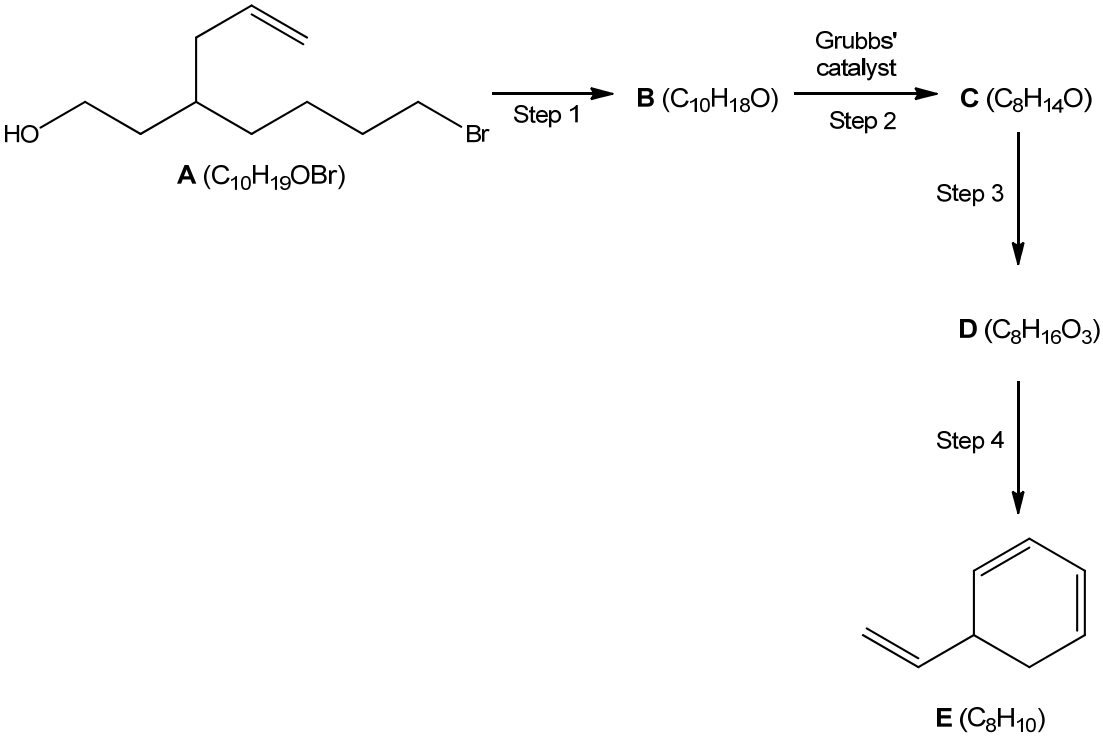
State and explain the differences between the atomic radii of these three atoms. [2]

(c) Many transition metal complexes contain phosphorus-containing ligands. An example is the Grubbs' catalyst that is used in alkene metathesis, a reaction that involves the redistribution of carbon-carbon double bonds.



(R_1, R_2, R_3 and R_4 are alkyl groups)

The reaction scheme below shows the synthesis of compound **E** via alkene metathesis. Compound **A** is the only starting organic compound.



Compound **C** is a cyclic compound that reacts with one mole of PCl_5. Compound **D** reacts with three moles of PCl_5.

(i) Draw the structures of compounds **B**, **C** and **D**. [3]

(ii) State the reagents and conditions for Steps 1, 3 and 4. [3]

[Total: 20]

Section B

Answer **one** question from this section.

4 (a) Organic compounds like ethanol can be used as fuels in fuel cells.

In an ethanol fuel cell, an aqueous solution of ethanol undergoes oxidation at the anode, which is layered with a metal catalyst, to produce carbon dioxide gas and hydrogen ions, while oxygen undergoes reduction at the cathode.

(i) Write a half equation for the reaction that occurs at the anode in the ethanol fuel cell. [1]

(ii) Describe the mode of action of the metal catalyst that helps to increase the rate of reaction at the anode in the fuel cell. [4]

(iii) Draw a fully labelled diagram of a separate electrochemical cell you would set up in order to measure the standard reduction potential, $E^{\ominus}_{CO_2/ethanol}$. [3]

(iv) Deduce how $E^{\ominus}_{CO_2/ethanol}$ will change when the pH in the CO_2/ethanol half-cell increases. [2]

(b) **A,** $C_6H_8O_3$, is a fungal metabolite that is known to inhibit the formation of biofilms. To determine its identity, **A** was boiled in dilute HC*l* to give **B**, $C_6H_{10}O_4$.

(i) The degree of unsaturation uses the molecular formula of an organic compound to find the number of double/ triple bonds or rings present in the compound. A double bond or a ring accounts for one degree of unsaturation, while a triple bond accounts for two degrees of unsaturation.

The degree of unsaturation for a compound $C_xH_yO_z$ is found using this expression: ½ (2 + 2x – y).

Calculate the degree of unsaturation of **A** and of **B.** [2]

(ii) Deduce the **functional groups** present in **B**. Provide supporting evidence from the information below.

- **B** reacts with Na_2CO_3 to give effervescence.
- When **B** was warmed with alkaline I_2(aq), a yellow precipitate was observed.
- No orange precipitate was formed upon reaction of **B** with 2,4–dinitrophenylhydrazine.
- When **B** was heated with acidified $K_2Cr_2O_7$, it formed **C**, $C_6H_6O_4$. However, when acidified $KMnO_4$ was used instead, **D**, $C_5H_4O_5$ was produced.
- Both **C** and **D** formed an orange precipitate when reacted with 2,4–dinitrophenylhydrazine. [3]

(iii) By considering the reaction of **A** to give **B** and your answer in **b(ii)**, deduce the identity of the functional group present in **A** that is **not** present in **B**. [1]

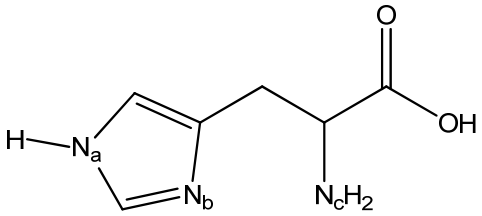
(iv) **A** was subjected to a series of tests. The observations are recorded in the table below.

Test	Observation
Br_2 (aq)	Yellow solution decolourised
$SOCl_2$	White fumes of HCl observed
I_2, NaOH(aq), heat	No yellow ppt
2,4–dinitrophenylhydrazine	No orange ppt observed
Na_2CO_3(aq)	No effervescence observed

Using all the information in **(b)**, suggest the structures of **A**, **B**, **C** and **D**. [4]

[Total: 20]

5 Histidine is one of the essential amino acids that is present in many proteins and enzymes. It exists as a crystalline solid with a melting point of 282 °C. There are three pK_a values associated with histidine: 1.82, 6.00 and 9.17.



histidine

(a) Account for the crystalline state and high melting point of histidine in terms of its structure and bonding. [3]

(b) State the hybridisation of the nitrogen atom N_b and sketch a diagram showing all the hybrid orbitals around it. [2]

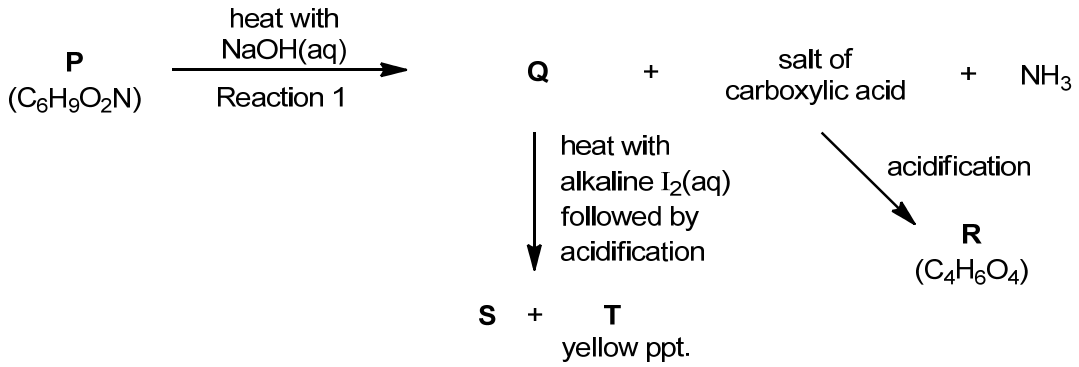
(c) **(i)** In the fully protonated form of histidine, nitrogen atoms N_b and N_c are protonated. N_a is not considered basic.

Sketch the titration curve obtained when 20 cm^3 of the fully-protonated form of histidine is titrated with 60 cm^3 of NaOH(aq) of the same concentration. Your sketch should show clearly where the three pK_a values occur and mark the isoelectric point of histidine on your sketch with an "**X**". [3]

(ii) Calculate the final pH, to 2 decimal places, of the resultant solution obtained when 10 cm^3 of 0.010 mol dm^{-3} NaOH was added to 100 cm^3 of a solution of 0.10 mol dm^{-3} histidine at pH 6.

You may represent the acid as HA and the conjugate base as A^- in your working. [3]

(d) Compound **P** does not rotate plane-polarised light and is insoluble in both dilute hydrochloric acid and aqueous sodium hydroxide at room temperature. The following scheme shows reactions of compound **P** and its products.



(i) State the type of reaction that occurs in Reaction 1 and identify **two** possible functional groups in **P** which can produce ammonia in this reaction. [2]

(ii) Draw the structures of compounds **P** to **T.** [5]

(iii) On treatment of **P** with hydrogen and a platinum catalyst, compound **U**, $C_6H_{13}NO_2$, is produced. However, reaction of **P** with lithium aluminium hydride forms **Q** and compound **V**, $C_4H_{11}NO$. Both **Q** and **V** contain a common functional group. Suggest the structures of **U** and **V**. [2]

[Total: 20]