



HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE
NAME

--

CT GROUP

15S

CENTRE
NUMBER

--	--	--	--

INDEX
NUMBER

--	--	--	--

CHEMISTRY

9647/03

Paper 3 Free Response

19 September 2016

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper

Data Booklet

INSTRUCTIONS TO CANDIDATES

Write your name and class on all the work you hand in.

Write in dark blue or black pen.

You may use a soft pencil for any diagrams, graphs or rough working.

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

Answer any **four** questions.

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

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.

<u>Write down the question numbers</u> for the questions attempted on the <u>cover page</u> provided.
--

Answer any **four** questions.

- 1 (a) Suggest and explain how the boiling points of 1-chlorobutane and 1-bromobutane differ from each other. [2]

- (b) (i) Define the term *standard enthalpy change of combustion*. [1]

- (ii) Use of the *Data Booklet* is relevant to this question.

In an experiment to determine the enthalpy change of combustion of bromobutane, a quantity of the fuel was burnt underneath a copper can containing 200 g of water. It was found that the temperature rose by 45.0 °C after 2.35 g of bromobutane had been burnt. The heat transfer was known to be only 80% efficient.

Calculate the enthalpy change of combustion of the bromobutane. Ignore the heat capacity of the copper can. [2]

- (c) An experiment was set up to study the reaction between 2-bromo-3-methylbutane and sodium hydroxide. The reagents used were **FA1**, containing 0.0100 mol dm⁻³ of 2-bromo-3-methylbutane and **FA2**, containing 0.0100 mol dm⁻³ NaOH. In each experiment, the reagents were dissolved in a suitable solvent to ensure good mixing. The results are recorded in the table below.

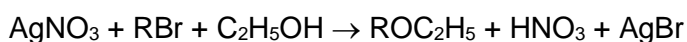
Expt	Volume of FA1 / cm ³	Volume of FA2 / cm ³	Volume of solvent / cm ³	Rate / mol dm ⁻³ s ⁻¹
1	10.0	30.0	60.0	7.40 × 10 ⁻⁷
2	5.0	20.0	25.0	9.86 × 10 ⁻⁷
3	10.0	5.0	35.0	4.93 × 10 ⁻⁷

- (i) Use the data in the table to deduce the order of reaction with respect to 2-bromo-3-methylbutane and sodium hydroxide. Hence, write a rate equation for this reaction. [3]
- (ii) With reference to your answer to (c)(i), describe the mechanism for the reaction between 2-bromo-3-methylbutane and sodium hydroxide. [3]
- (iii) Calculate the rate constant for the reaction, stating the units. [2]

- (d) In a separate experiment, a student performed the following qualitative analysis tests on three different bromoalkanes: 1-bromobutane, 2-bromobutane and 2-bromo-2-methylpropane. Different solvents were used for **Test 1** and **Test 2** and it was observed that the choice of solvents did have an effect on the type of reaction mechanisms undergone by the bromoalkanes.

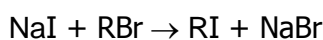
Test 1:

When silver nitrate was added to the bromoalkanes using ethanol as the solvent, silver bromide was precipitated for all three bromoalkanes at different rates.



Test 2:

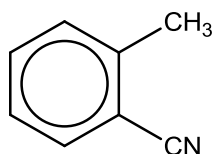
When sodium iodide in propanone solvent was added to the bromoalkanes, sodium bromide was precipitated for 1-bromobutane and 2-bromobutane at different rates, but not 2-bromo-2-methylpropane.



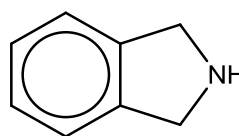
The observations for each test were recorded in the following table.

	Time taken for precipitate to appear	
	Test 1	Test 2
1-bromobutane	5 min	Almost immediately
2-bromobutane	3 min	5 min
2-bromo-2-methylpropane	Almost immediately	No precipitate

- (i) Different nucleophilic substitution mechanisms have been proposed for the reactions in the two tests.
- Considering the information provided, suggest the predominant mechanism undergone in each test. [1]
- (ii) Considering the structure of the bromoalkane, explain why the test results support your answer in (d)(i). [2]
- (iii) Considering the interactions involved with the solvent, explain why the suggested mechanism for **Test 1** occurs predominantly. [1]
- (e) 2-methylbenzonitrile can be used as a starting reagent to form compound **A**. Propose a synthesis route for the formation of compound **A** in no more than 3 steps, showing clearly the reagents, conditions and structures of the intermediates formed.



2-methylbenzonitrile



Compound **A**

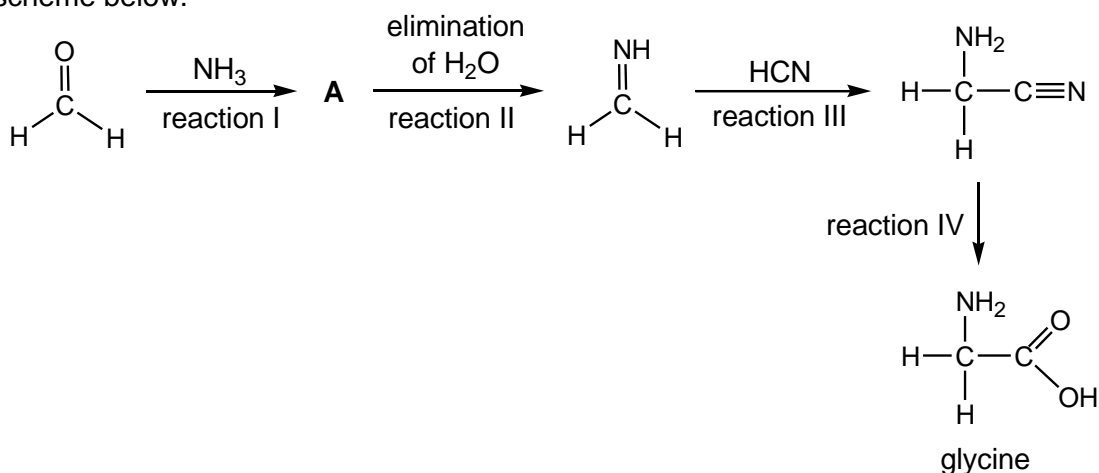
[3]

[Total: 20]

- 2 Ethanoic acid behaves as a weak acid in water, with $K_a = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$.
In contrast, ethanoate ion behaves as a weak base in water, with $K_b = 5.6 \times 10^{-10} \text{ mol dm}^{-3}$.

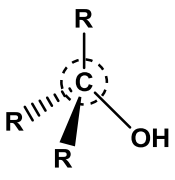
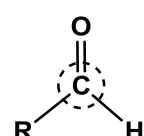
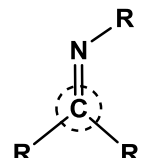
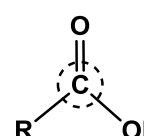
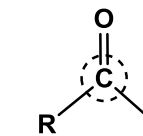
- (a) (i) Write the expressions for K_a and K_b of ethanoic acid and ethanoate ion respectively, and use these expressions to show that the product $K_a \times K_b$ has a constant value at a fixed temperature. [2]
- (ii) Compare the relative strength of ethanoate ion and water as bases, and explain with the aid of an equation, whether a solution of sodium ethanoate is acidic, alkaline, or neutral. [2]
- (iii) Calculate the pH of a solution which contains 0.50 mol dm^{-3} ethanoic acid and 0.50 mol dm^{-3} sodium ethanoate. [1]

- (b) The Strecker synthesis is a route to prepare amino acids. Glycine (2-aminoethanoic acid) can be prepared from methanal as shown in the reaction scheme below.



- (i) Suggest a structure for compound **A**. [1]
- (ii) The product of **reaction II** is an imine, which has a C=N bond. Methanal undergoes reaction with another compound **B** to form an orange solid **C** which also has a C=N bond. Name compound **B** and draw the structure of the orange solid **C**. [2]
- (iii) What *type of reaction* is occurring during **reaction III**? [1]
- (iv) State the reagents and conditions for **reaction IV**. [1]
- (v) Compound **D** is an isomer of glycine. Upon warming **D** with dilute sodium hydroxide, a gas which turns litmus blue is evolved. Draw the structure of **D**. [1]
- (vi) A carbonyl compound **E** can be used as the starting material to prepare another amino acid, alanine (2-aminopropanoic acid) using the Strecker synthesis. Draw the structure of **E**. [1]
- (vii) The synthesis of alanine in (b)(vi) produces a mixture of two optical isomers. State which one of the reactions, **I** to **IV**, gives rise to this mixture, and explain your choice briefly. [2]

- (c) In organic chemistry, the number of bonds that a given carbon atom has with electronegative atoms like O or N is called the functional group level of that carbon atom. Some examples are shown below, but there are many other possibilities.

Functional group level		
1	2	3
	 	 

(R = alkyl or aryl group or H atom)

- (i) State the functional group level of the carbon atom in methane and in carbon dioxide. [1]

Keeping track of the functional group level can be used to understand a large number of organic reactions.

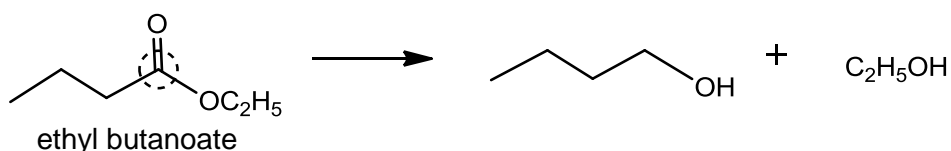
During **oxidation reactions**, the functional group level increases as C–H bonds are converted into new C–O bonds.

During **reduction reactions**, the functional group level decreases as C–O bonds are converted into new C–H bonds.

During **hydrolysis reactions**, the functional group level of every carbon remains the same.

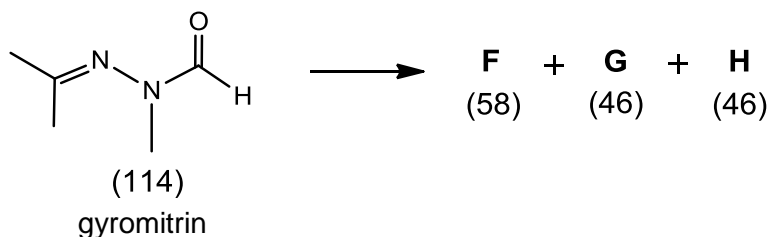
In each of the reactions in (c)(ii) and (c)(iii), no carbon-carbon bonds are broken or formed.

- (ii) Ethyl butanoate undergoes the following reaction to form two products. State the functional group level of the *circled* carbon atom at the start and end of the reaction, and hence deduce whether the reaction is an oxidation, a reduction, or a hydrolysis reaction.



[2]

- (iii) Gyromitrin, a toxin found in fungi, undergoes hydrolysis to give three different products, **F**, **G**, and **H**. Suggest structures for these products using their relative molecular masses (shown in brackets) and the functional group levels of the carbon atoms.



[3]

[Total: 20]

3 Use of the Data Booklet is relevant to this question.

In 2016, 4 new elements were added to the Periodic Table. Part of the Periodic Table showing information about the 4 new elements is shown below.

Key						
—		—		—	—	relative atomic mass
Nh		Mc		Ts	Og	atomic symbol
nihonium		moscovium		tennessine	oganesson	name
113		115		117	118	proton number

Mc, Ts, and Og were synthesised by accelerating calcium ions into atoms of heavier elements. Once in every few billion collisions, the nuclei of the 2 particles would fuse and give rise to the new element. For example, Ts was synthesised using berkelium (${}_{97}\text{Bk}$).

(a) (i) State the heavy element used in the synthesis of Mc. [1]

(ii) Based on the relative position of Ts in the Periodic Table, predict the physical state of Ts at room temperature. Give a brief explanation for your answer. [2]

(iii) Scientists have predicted the existence of superheavy elements above proton number 120 that are stable under standard conditions. One such element, if successfully synthesised in large quantities, would give rapid effervescence of a colourless gas in water, and its oxide would be basic in nature. The sulfate compound of the element would be insoluble in water.

State, with reasons, the group of the Periodic Table that this element is likely to belong. [2]

(b) Scientists are already working on the next element of proton number 119 using berkelium and titanium.

(i) Explain, using relevant electronic configurations, why titanium is considered a transition element but not zinc. [2]

(ii) Tetrahydrofuran (THF), $M_r = 72.1$, is a simple covalent molecule that behaves as a monodentate ligand. Titanium forms a complex with zero net charge with THF and chloride ligands. A 1.00 g sample of the complex was completely hydrolysed in water and filtered. The residue contained 2.99×10^{-3} mol of TiO_2 . The filtrate yields 1.72 g of silver chloride after treating with aqueous silver nitrate. Determine the coordination number of the central titanium of the complex. [3]

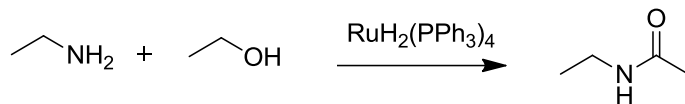
Calcium and titanium are both metals but differ in their chemical and physical properties.

- (c) (i) Compounds of calcium contain the Ca^{2+} ion. The corresponding ion of titanium is Ti^{3+} . Use relevant data from the *Data Booklet* to explain why Ca^{3+} compounds do not exist and Ti^{3+} compounds do. [3]
- (ii) Draw labelled diagrams to show the shapes of the orbitals in the **outermost** occupied quantum shell of a Ca^{2+} ion. [2]
- (iii) Explain why the melting point of titanium is higher than that of calcium. [2]
- (iv) Describe the observations when calcium is burned in air, and excess water is added to the resulting oxide. Write equations where appropriate and suggest the pH value of the aqueous solution formed. [3]

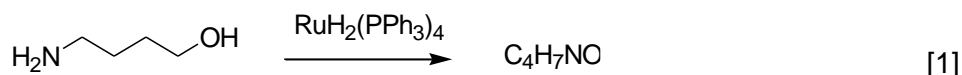
[Total: 20]

- 4 Transition metal catalysed reactions have emerged in recent years as powerful tools for preparing organic compounds from previously unavailable routes. Ruthenium-based catalysts have been at the heart of these advances.

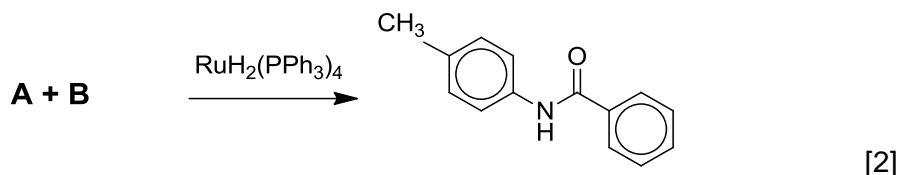
(a) The ruthenium(II) based catalyst $\text{RuH}_2(\text{PPh}_3)_4$, where $\text{PPh}_3 = \text{P}(\text{C}_6\text{H}_5)_3$, is able to catalyse the formation of an amide under suitable conditions, as shown in the scheme below.



(i) Draw the structure of the product for the reaction below.



(ii) $\text{RuH}_2(\text{PPh}_3)_4$ also catalyses the formation of the amide shown in the reaction scheme below. Draw the structures of compounds **A** and **B**.

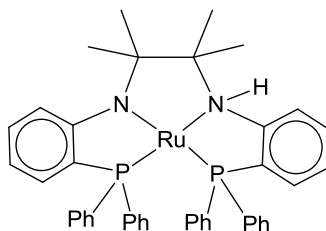


(iii) Propose a synthetic route for the formation of compounds **A** and **B**, using only methylbenzene as the starting compound in each case. [3]

(b) The catalyst $\text{RuH}_2(\text{PPh}_3)_4$ exhibits geometric isomerism. In the cis configuration, the H-Ru-H angle is 90° , while in the trans configuration, the H-Ru-H angle is 180° .

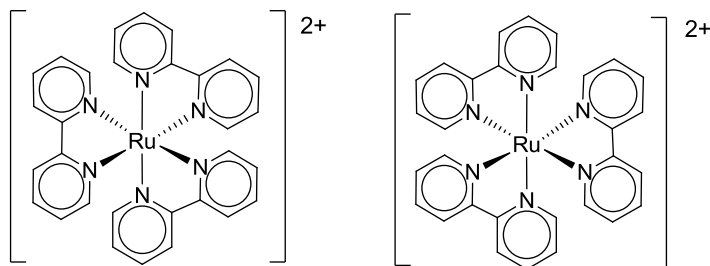
Draw labelled diagrams showing the structures of the two isomers. [2]

(c) In addition to $\text{RuH}_2(\text{PPh}_3)_4$, other ruthenium complexes like the one shown below, also proved to be effective in organic synthesis.

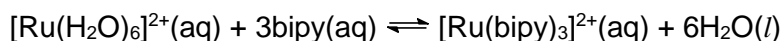


State the oxidation number of ruthenium in the complex above. [1]

- (d) The complex ion tris(bipyridine)ruthenium(II) is a catalyst which has received much attention because of its ability to exhibit optical isomerism. Two of its isomers are shown below.



- (i) Explain why the complex above exhibits optical isomerism. [1]
- (ii) Tris(bipyridine)ruthenium(II) cation contains three bipyridine rings, which can be represented by the symbol, bipy. The formation of tris(bipyridine)ruthenium(II) from aqueous ruthenium(II) ions is shown in the equation below. The enthalpy change for this reaction is approximately zero.



Deduce the sign of the entropy change, ΔS , and hence the sign of the free energy change, ΔG , in this reaction. [3]

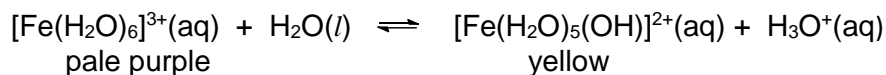
Iron is directly above ruthenium in the transition metal block of the Periodic Table.

- (e) Ligands are able to modify the difference in energy between the non-degenerate d-orbitals in an octahedral crystal field.

The following table lists the different colours of visible light and their corresponding wavelengths. The energy of light is inversely proportional to its wavelength.

Colour	violet	blue	green	yellow	red
Wavelength / nm	400	450	500	600	650

The equation below represents the hydrolysis of $\text{Fe}(\text{III})$ ions in water. The pale yellow colour of $\text{Fe}(\text{III})$ solutions observed commonly is actually due to the presence of the complex ion $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$, while unhydrolysed $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is pale purple in color.

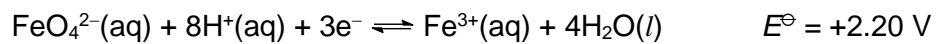


- (i) With reference to the colours of the two complexes above, explain which complex ion has a larger energy gap between their d-orbitals. [2]
- (ii) Electrons in both $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ exhibit a 'high spin' state, where electrons occupy the d-orbitals singly before starting to pair up in the lower energy d-orbitals.

Draw a suitable diagram to show the electron distribution in the 3d subshell of a Fe^{3+} ion in a 'high spin' **excited** state, where an electron from a lower energy d-orbital has been promoted to a higher energy d-orbital by absorbing light of a certain wavelength.

[1]

(f) K_2FeO_4 is a strong oxidising reagent which is dark red in colour.



Using relevant data from the *Data Booklet*, describe and explain the observations when the following solutions are mixed together in **I** and in **II** respectively. Calculate the E^\ominus_{cell} and write a balanced equation for any reaction occurred.

I K_2FeO_4 and H_2O_2

II KMnO_4 and $\text{Fe}(\text{NO}_3)_3$

[4]

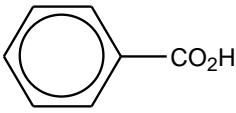
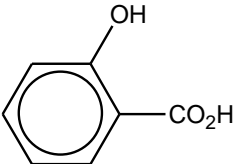
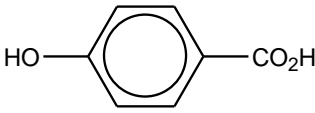
[Total: 20]

- 5 (a) Ag_2CO_3 is a sparingly soluble salt. A 100 cm^3 saturated solution of Ag_2CO_3 in water was found to contain $2.57 \times 10^{-4}\text{ mol dm}^{-3}$ of Ag^+ ions.

(i) Calculate the K_{sp} of Ag_2CO_3 and state its units. [2]

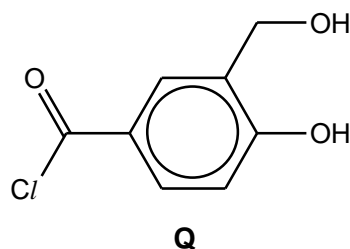
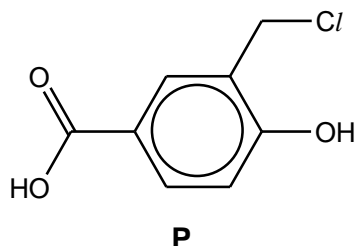
(ii) Hence, calculate the solubility of Ag_2CO_3 when 2.50 g of Na_2CO_3 solid was added to the solution above. [2]

- (b) The table below shows the $\text{p}K_{\text{a}}$ values of benzoic acid and its derivatives.

Acid	benzoic acid	2-hydroxybenzoic acid	4-hydroxybenzoic acid
Structure			
$\text{p}K_{\text{a}}$	4.20	2.98	4.58

Rank the three compounds in order of **increasing** acid strength and account for the trend. [3]

- (c) Compounds **P** and **Q** can be synthesised from 4-hydroxybenzoic acid.



Suggest the reagents and conditions for a reaction that could be used to distinguish between **P** and **Q**. You need to state how **each** of **P** and **Q** react. [2]

- (d) Heating compound **A**, $\text{C}_{13}\text{H}_{14}\text{O}_3$, under reflux with dilute H_2SO_4 produces compound **B**, $\text{C}_8\text{H}_8\text{O}$, and compound **C**, $\text{C}_5\text{H}_8\text{O}_3$.

B reacts with aqueous bromine to give compound **D**, $\text{C}_8\text{H}_7\text{O}_2\text{Br}_3$. On heating **B** with acidified KMnO_4 , 4-hydroxybenzoic acid and carbon dioxide gas are formed.

When **C** is heated with acidified KMnO_4 , compound **E** is the only organic product formed. Both **C** and **E** gave yellow precipitate when warmed with alkaline aqueous iodine. Treatment of **E** with aqueous Na_2CO_3 liberates carbon dioxide gas.

- (i) When vaporised in a suitable apparatus, 0.219 g of **E** occupied a volume of 70 cm^3 at $150\text{ }^\circ\text{C}$ and a pressure of 125 kPa .

Calculate the relative molecular mass of **E** and hence suggest a molecular formula for **E**, given that it contains 3 carbon atoms. [2]

- (ii) Suggest structures for **A** to **E**, explain your reasoning. [9]

[Total: 20]