HWA CHONG INSTITUTION
Preliminary Examination
Higher 1

CANDIDATE NAME		**CT GROUP**	**13S**

CHEMISTRY

8872/02

Paper 2

15 September 2014

2 hours

Candidates answer **Section A** on the Question Paper.

Additional Materials: Data Booklet
Writing paper

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 a pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue, correction fluid or tapes.

Section A

Answer **all** questions.

Section B

Answer **two** questions on separate answer paper.
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**				**TOTAL**
Multiple Choice	**Section A (Structured)**		**Section B (Free Response)**		
	Q1	/10	Q5	/ 20	
	Q2	/9	Q6	/ 20	
	Q3	/14	Q7	/ 20	
	Q4	/7			
/ 30	**Subtotal**	**/ 40**	**Subtotal**	**/ 40**	**110**

This question booklet consists of **13** printed pages.

Section A

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

1 Compound **R** is a weak diprotic (dibasic) acid which is very soluble in water.

(a) A solution of **R** was prepared which contained 1.25 g of **R** in 250 cm^3 of solution. When 25.0 cm^3 of this solution was titrated with 0.100 mol dm^{-3} NaOH, 21.60 cm^3 of the alkali were needed for complete reaction.

(i) Using the formula H_2X to represent **R**, construct a balanced equation for the reaction between H_2X and NaOH.

.....

(ii) Calculate *M*r of **R**.

[3]

(b) Three possible structures for **R** are shown below.

S	**T**	**U**
$HO_2CCH{=}CHCO_2H$	$HO_2CCH(OH)CH_2CO_2H$	$HO_2CCH(OH)CH(OH)CO_2H$

Deduce from your answer in a(ii) which of the structures, **S**, **T** or **U**, correctly represents the structure of the acid, **R**.

R is represented by .....

[1]

(c) It is possible to convert **S**, **T**, or **U** into one another.

State the reagent(s) and essential conditions that would be used for the following conversions

S into **T**

S into **U**

T into **S**

---

[3]

(d) The acid **S** shows stereoisomerism. Draw structures to show this isomerism. Label each isomer.

[2]

(e) When one of the isomers of **S** is heated at 110 °C in the absence of air, a cyclic compound **V**, with molecular formula $C_4H_2O_3$, is formed.
The other isomer of **S** does not react at this temperature.
Suggest the displayed formula of **V**.

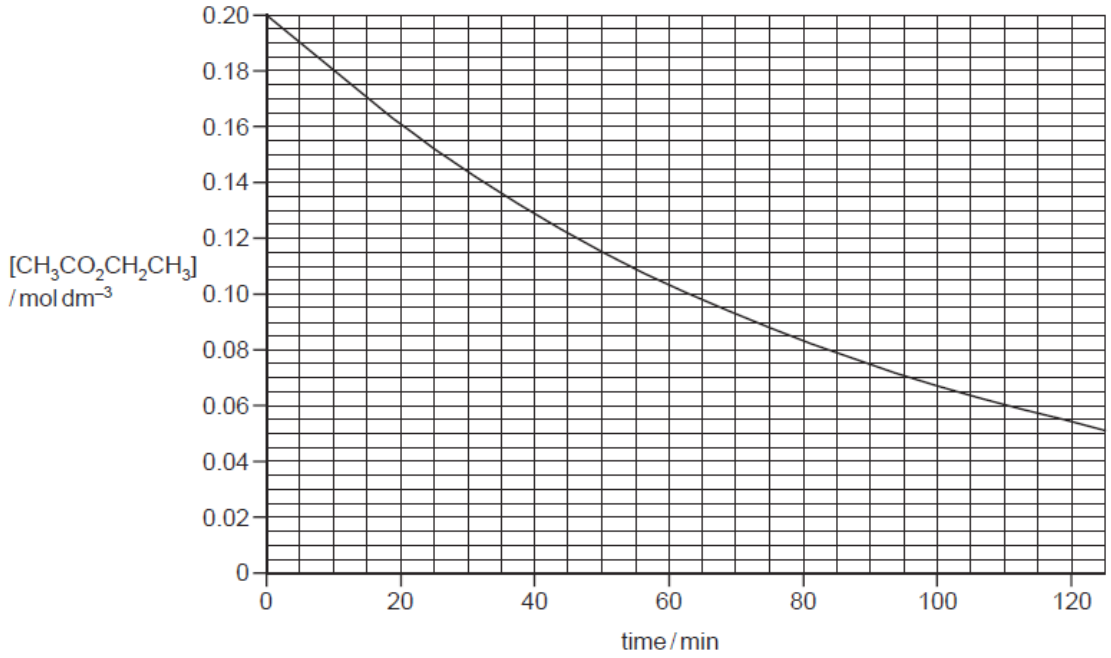
[1]

[Total: 10]

2 Ethyl ethanoate is hydrolysed slowly by water in the following acid-catalysed reaction.

$$CH_3CO_2CH_2CH_3 + H_2O \xrightarrow{H^+} CH_3CO_2H + CH_3CH_2OH$$

The concentration of ethyl ethanoate was determined at regular time intervals as the reaction progressed.
Two separate experiments were carried out, with different HC*l* concentrations.
The following graph shows the results of an experiment using [HC*l*] = 0.1 mol dm^{-3}.



(a) When the second experiment was carried out using [HC*l*] = 0.2 mol dm^{-3}, the following results were obtained.

Time/min	$[CH_3CO_2CH_2CH_3]$ / mol dm^{-3}
0	0.200
10	0.160
25	0.115
50	0.067
75	0.038
100	0.022
125	0.013

(i) Plot these data on the axes above, and draw a line of best fit.

(ii) Use one of the graphs to show that the reaction is first order with respect to $CH_3CO_2CH_2CH_3$.
Show all your working, and show clearly any construction lines you draw on the graphs.

(iii) Use the graphs to calculate the order of reaction with respect to HC*l*.
Show all your working, and show clearly any construction lines you draw on the graphs.

(iv) Write the rate equation for this reaction, and calculate the value of the rate constant.

rate =

[7]

(b) (i) Why is it **not** possible to determine the order of reaction with respect to water in this experiment?

.....

.....

(ii) Although $[CH_3CO_2CH_2CH_3]$ decreases during each experiment, [HC*l*] remains the same as its initial value.
Why is this?

.....

..... [2]
[Total: 9]

3 Table 1.1 gives some data on four fuel sources: methanol, ethanol, hydrogen and octane. Octane can serve as a rough approximation of petrol.

Table 1.1

name	**formula**	**molar mass / g mol^{-1}**	**density / g cm^{-3}**	**ΔH□ /kJ mol^{-1}**	**ΔH□ / kJ mol^{-1}**
methanol	CH_3OH	32	0.793[a]	-726.0	-239.1
ethanol	C_2H_5OH		0.789[a]	-1367.3	-277.1
liquid hydrogen	H_2	2	0.0711[b]		
octane	C_8H_{18}		0.703[a]		-250.0

[a] At 298 K and 1 bar pressure
[b] At 20 K and 1 bar pressure

(a) Insert the missing molar mass values in the table 1.1.

[1]

(b) Calculate the density of **gaseous** hydrogen at 298 K and 1 bar pressure.
Assume 1 mole of any gas occupies 24 dm^3 at 298 K and 1 bar pressure.
Give your answer in g cm^{-3}.

.....g cm^{-3} [1]

(c) What is the value of the standard enthalpy of formation of hydrogen **gas**, H_2?

.....
[1]

(d) Use the information in Table 1.2 to give the value of the standard enthalpy of combustion of hydrogen.

Table 1.2

name	**ΔH□ /kJ mol^{-1}**
water	-285.8
carbon dioxide	-393.5

(e) Write down the chemical equation that represents the *standard enthalpy of combustion* of octane. Include state symbols.

..... [2]

(f) Use the enthalpy of formation data in Table 1.1 and Table 1.2 and the equation in (e) to calculate the standard enthalpy of combustion of octane, ΔH□ .

. [3]

(g) An important property of a fuel, especially when the fuel has to be lifted (such as in aviation), is the energy released on combustion *per gram* of fuel.
Calculate the enthalpy change of combustion per gram of fuel at 1 bar pressure and 298 K for methanol and hydrogen gas.

(i) methanol

(ii) hydrogen gas

[2]

(h) Another important characteristic of a fuel, especially when there is a fuel tank of limited size, is the energy released on combustion *per cm*^{3} of fuel.
Calculate the enthalpy change of combustion per cm^3 of fuel for ethanol and octane.

(i) ethanol

(ii) octane

[2]

(i) Explain why, given the data in the question, it is not strictly possible to make a fair comparison of the energy released per cm^3 of liquid hydrogen with the other fuels.

.....

.....[1]

[Total: 14]

4 **(a)** State the functional groups positively identified by the following.

(i) $Br_2(aq)$

.....

(ii) Na(s)

.....

(iii) $I_2(aq) + OH^-(aq)$

.....

(iv) 2,4-dinitrophenylhydrazine

..... [4]

(b) Compound **G** has the molecular formula $C_7H_{14}O$. Treating **G** with hot, concentrated, acidified $KMnO_4(aq)$ produces two compounds, **H**, C_4H_8O, and **J**, $C_3H_4O_3$.
Four reagents in column 1 below were used to test these three compounds and the results are shown in the table below.

test reagent	result of test with		
	compound **G**	compound **H**	compound **J**
$Br_2(aq)$	decolourises	no reaction	no reaction
Na(s)	fizzes	no reaction	fizzes
$I_2(aq) + OH^-(aq)$	no reaction	yellow precipitate	yellow precipitate
2,4-dinitrophenylhydrazine	no reaction	orange precipitate	orange precipitate

(c) Based on the results of the tests in the table, suggest **structures** for compounds **G**, **H** and **J**.

G $C_7H_{14}O$
H, C_4H_8O
J, $C_3H_4O_3$

[3]
Total [7]

Section B

Answer **two** questions from this section on separate answer paper.

5 **(a)** Describe the reactions, if any, of the oxides P_4O_{10} and SiO_2 with water. Include the approximate pH value of any resulting solutions, and write equations for any reactions that occur.

[3]

(b) The structures of oxides can be simple or giant, and their bonding can be covalent or ionic. Use these terms to describe the structure and bonding in each of the oxides **W, X, Y and Z**. Explain your reasoning in each case.

Oxide	Melting point /^oC	Electrical conductivity when molten	Reaction with water	Resulting pH
W	2850	Good	Very little	8
X	1720	Poor	None	7
Y	1280	Good	Exothermic	14
Z	580	Poor	Exothermic	1

[4]

(c) 25.0 cm^3 of a solution formed by dissolving SO_2 in water was titrated with 0.0200 mol dm^{-3} $KMnO_4$. 20.5 cm^3 of this $KMnO_4$ solution were required for the end point.

(i) Use the Data Booklet to write an equation for the reaction between SO_2 and MnO_4^- ions in this titration.

(ii) Describe how you would recognise the end-point during this titration.

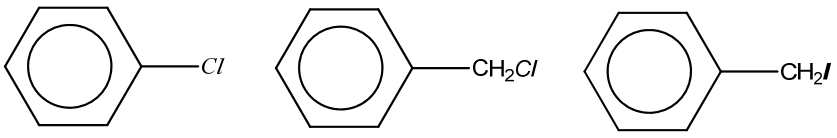
(iii) Use your equation from **(c)(i)** and the data above to calculate the concentration of SO_2 in mol dm^{-3} in the solution.

[4]

(d) A mixture of benzoic acid and sodium benzoate is sometimes used along with SO_2 as a preservative in foodstuffs.
Explain how the above mixture acts as a buffer solution.

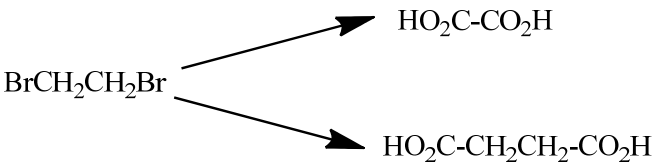
[2]

(e) Describe and explain the relative ease of hydrolysis of the following three halogen compounds.



[3]

(f) Suggest synthetic routes to the following dicarboxylic acids starting from 1, 2–dibromoethane. [4]



Total [20]

6 (a) (i) Explain what is meant by the term dative bonding, in terms of orbital overlap?

(ii) Both NO_2 and O_3 molecules contains a dative covalent bonding. Draw dot and cross diagrams to show their bonding. Include all lone pairs in your diagrams.

(iii) Suggest a value for the bond angle in each of the above two molecules, giving reasons for your choice

[5]

(b) In the catalytic converter of a car engine's exhaust system, the following reaction occurs.

$$2NO(g) + 2CO(g) \text{ Ý } N_2(g) + 2CO_2(g) \quad \Delta H = -745 \text{ kJ mol}^{-1}$$

The temperature in a catalytic converter is high.

(i) State the effect, if any, on the position of equilibrium if the temperature is lowered. Give a reason for your answer.

(ii) The gases from the engine are **not** cooled before entering the converter. Explain why this is so.

(iii) State two environmental impacts the gas emissions will cause if no catalytic converter was installed in the car?

[6]

(c) NO_2 catayses the oxidation of SO_2 to SO_3.

The reaction between SO_2, NO_2 and O_2 occurs in two steps.

$NO_2 + SO_2 \rightarrow NO + SO_3 \quad \Delta H_1 = -88 \text{ kJ mol}^{-1}$
$NO + ½O_2 \rightarrow NO_2 \quad \Delta H_2 = -57 \text{ kJ mol}^{-1}$

The activation energy of the first reaction, E_{a1}, is higher than that of the second reaction, E_{a2}.
Construct a fully-labeled reaction pathway diagram for this reaction, labeling E_{a1}, E_{a2}, ΔH_1 and ΔH_2.

[2]

(d) Ozone is usually made by passing oxygen gas through a tube between two highly charged electrical plates.

$$3O_2(g) \downarrow 2O_3(g)$$

The reaction does not go to completion, so a mixture of the two gases results.
The concentration of O_3 in the mixture can be determined by its reaction with aqueous KI.

$$O_3 + 2KI + H_2O \downarrow I_2 + O_2 + 2KOH$$

The iodine formed can be estimated by its reaction with sodium thiosulfate.

$$2Na_2S_2O_3 + I_2 \downarrow Na_2S_4O_6 + 2NaI$$

When 500 cm^3 of an oxygen/ozone gaseous mixture at s.t.p. was passed into an excess of aqueous KI, and the iodine titrated, 15.0 cm^3 of 0.100 mol dm^{-3} $Na_2S_2O_3$ was required to discharge the iodine colour.

(i) Calculate the amount in moles of iodine produced.

(ii) Hence calculate the percentage of O_3 in the gaseous mixture.

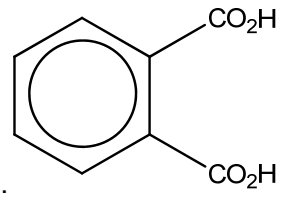
[3]

(e) Oxidation is an important reaction in organic chemistry. Both aldehydes and carboxylic acid can be prepared by the oxidation of alcohols with acidified $K_2Cr_2O_7$.

(i) Describe how you could ensure that only *either* the aldehyde or the carboxylic acid is produced during the oxidation process.

(ii)

Compounds **L** and **M**, both C_9H_{10}, are oxidized by hot concentrated alkaline $KMnO_4$, followed by acidification, to give benzene-1,2-dicarboxylic acid, **P**.



P

Compound **L** reacts with $H_2(g)$, but compound **M** does not.
Suggest structures for compounds **L** and **M**

[4]

Total [20]

7 (a) Describe the reactions, if any, of silicon(IV) chloride and phosphorus(V) chloride with water.
Write equations for any reactions that occur.

[3]

(b) Acetals are compounds formed when aldehydes are reacted with an alcohol in the presence of an acid catalyst. The reaction between ethanal and methanol was studied in the inert solvent dioxan.

$$CH_3CHO + 2CH_3OH \xrightarrow{H^+} CH_3CH(OCH_3)_2 + H_2O$$
ethanal methanol acetal **A**

In an experiment, the concentrations of the reactants and products were measured. The results are shown in the table below.

	$[CH_3CHO]$ / mol dm^{-3}	$[CH_3OH]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	[acetal **A**] / mol dm^{-3}	$[H_2O]$ / mol dm^{-3}
at start	0.20	0.10	0.05	0.00	0.00
at equilibrium	(0.20-**x**)			**x**	
at equilibrium				0.025	

(i) Write an expression for the equilibrium constant, Kc, for the reaction.

(ii) Using the [acetal **A**] as given, 0.025 mol dm^{-3}, calculate the equilibrium concentrations of **all** the other reactants and products.

Hence, calculate a value for K_c.

[5]

(c) Pure water conducts electricity slightly, so it must be ionised to a small extent.

(i) Write an equation for the dissociation of water.

(ii) Use the equation in **(c)(i)** to write an expression for the equilibrium constant, K_c , for this reaction.
Use this expression to show that $K_w = [H^+][OH^-]$. Justify and explain your reasoning.

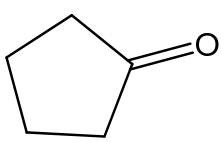
(iii) At 373 K the ionic product of water, K_w, has a value of 51.3×10^{-14} mol^2 dm^{-6}.
Use this information to calculate the pH of water at 373 K.
Give your answer to 3 significant figures.

(iv) At 298 K the pH of water is 7.00 . Use this information to state whether the dissociation of water is endothermic or exothermic and explain your answer.

[7]

(d) Suggest methods by which the following compounds could be distinguished from each other by chemical tests. The distinguishing of the pairs may rely on a preliminary breaking-up of the compounds, and subsequent testing of the reaction products.

(i)



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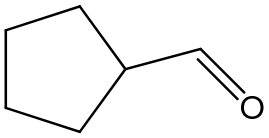
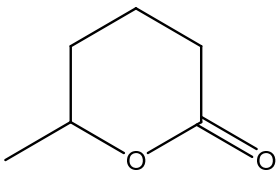
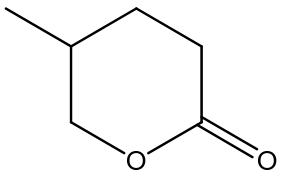


(ii)





[5]

Total [20]