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**

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.

. $H_2X + 2NaOH \rightarrow Na_2X + 2H_2O$.

(ii) Calculate *Mr* of **R**.

No. of moles OH- = 21.6 x 0.100 /1000 = 2.16 x 10^{-3} mol

No. of moles R = No. moles of H_2X = 2.16 x 10^{-3} /2 = 1.08 x 10^{-3} mol (in 25.0 cm^3)

No. of moles R in 250 cm3 =1.08 x 10^{-3} x 250/25 = 1.08 x 10^{-2} mol

1.08 x 10^{-2} mol of R = 1.25 g

1 mole of R = 1.25/1.08 x 10^{-2} = **116 g**

[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 ....S

[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**

----conc H_2SO_4 followed by H_2O ; or steam and H_3PO_4 catalyst

S into **U**

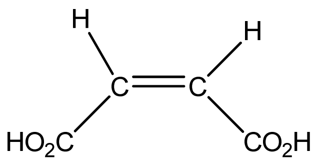
--- $KMnO_4$, cold dilute acidified or cold dilute alkaline

T into **S**

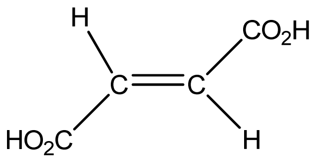
----Conc H_2SO_4 at 170 °C or heat with Al_2O_3

[3]

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



cis

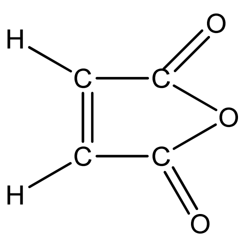


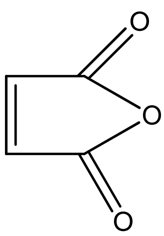
trans

[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]



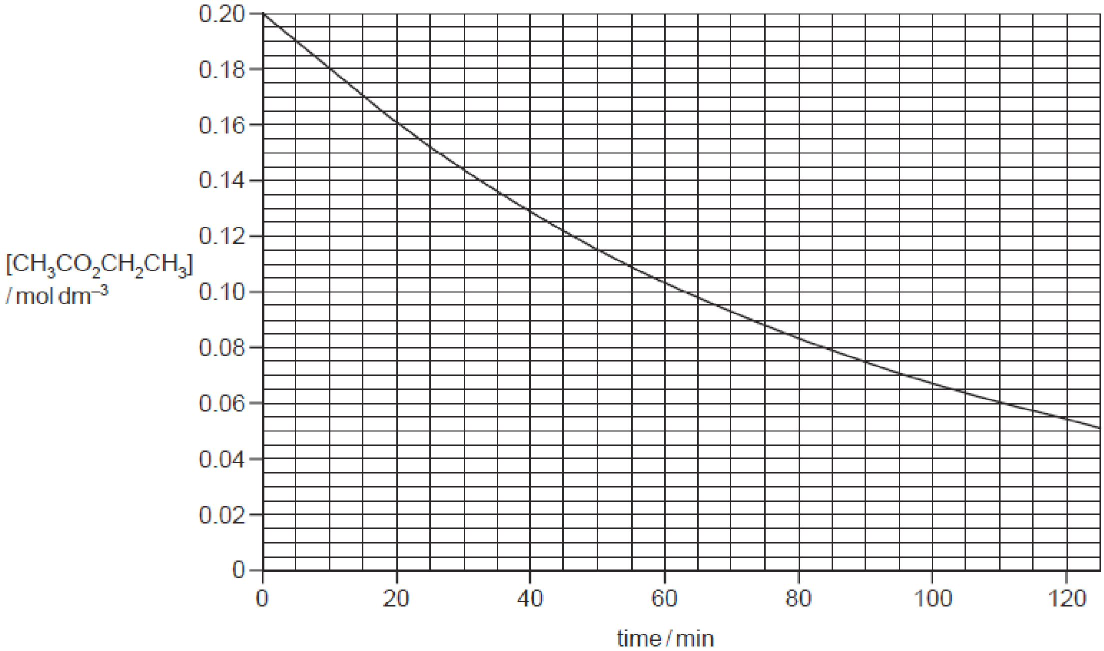


[Total: 10]

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}.



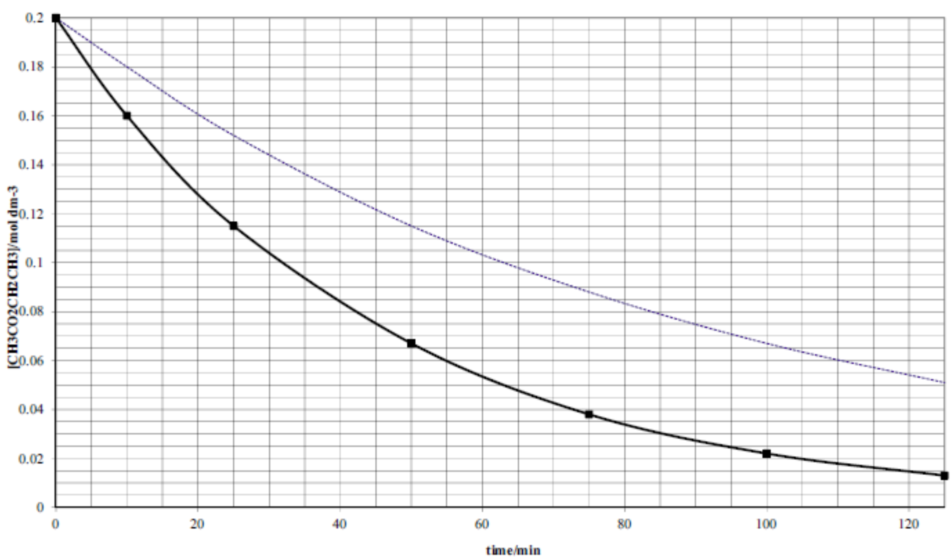
(a) When the second experiment was carried out using [HC*l*] = 0.2 mol dm^{-3}, the following results were obtained.

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.

Correct plotting of points and good best fit curve

(i)



plotting of points (–1 for any error – plotted to within ½ square) [1]
a good best fit curve [1]

(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.
Construct lines for two tangents and mention two values/ concentration doubled, rate doubled.
Or
Construction lines for two half lives. t ½ = 63 min (+/- 3 min) or 32 min +/- 3

Constant t ½

(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.

Initial rate (gradient) for expt 2 / Initial rate (gradient) for expt 1 = 2
Or ratio of $t_{½}$ = 2

Order wrt [HCl] = 1

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

rate = k $[CH_3CO_2CH_2CH_3]$ [HCl]

rate = 0.2/95 or 0.2/47

k = 2.1 x 10^{-3} / 0.2 x 0.1 = 0.11 (mol^{-1} dm^3 min^{-1})
k = 4.3 x 10^{-3} / 0.2 x 0.2 = 0.11 (mol^{-1} dm^3 min^{-1})

[7]

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

Water is solvent; its conc. do not change

....

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

.........HCl is a catalyst..

.... [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	46	0.789[a]	-1367.3	-277.1
liquid hydrogen	H_2	2	0.0711[b]		
octane	C_8H_{18}	114	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}.

2/24000 = 8.3 x 10^{-5} g cm^{-3}

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

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

....zero [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.

$C_8H_{18}(l) + 25/2\ O_2(g) \rightarrow 8CO_2(g)\ \ 9\ H_2O(l)$ [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 .

$\Delta H_c = 8\ \Delta H_f(CO_2) + 9\Delta H_f(H_2O) - \Delta H_f(\text{Octane})$

8(-393.5) + 9(-285.8) – (-250)

= -5470 kJ mol^{-1}

. [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

-726/32 = -22.69 kJ g-1

(ii) hydrogen gas

-285.8/2 = -142.9 kJ g-1

[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

-1367.3 x 0.789 / 46 = -23.5 kJ cm^{-3}

(ii) octane

-5470.2 x 0.703 / 114 = -33.7 kJ cm^{-3}

[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.

........At std conditions hydrogen should be gaseous not liquid

....[1]

[Total: 14]

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

(i) $Br_2(aq)$

Alkene;

(ii) Na(s)

Alcohol; carboxylic acids.

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

$CH_3CH(OH)$**-** ; CH_3CO-

(iv) 2,4-dinitrophenylhydrazine

RCHO or R_2CO.. ....

[4]

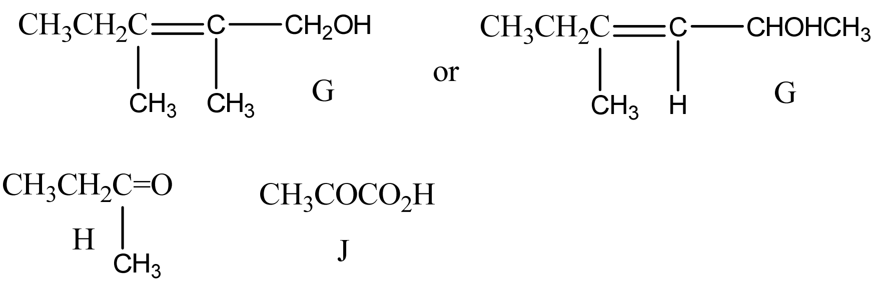
(b) Compound **G** has the molecular formula $C_7H_{14}O$. Treating **G** with hot, concentrated, acidified $KMnO_4(aq)$ produces two compounds, **H**, C_4H_8O, and **J**, $C_3H_4O_3$.
Four reagents in column 1 below were used to test these three compounds and the results are shown in the table below.

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]
5	**(a) ans**	P_4O_{10} reacts vigorously with water to give a solution of phosphorous acid, H_3PO_4. The pH of the resultant solution would be around 2. $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$ SiO_2 does not react with water and thus the pH remains at 7.

	(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 /°C	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]

	(b)ans	**W**: Giant ionic – conducts electricity in molten state due to presence of mobile ions; it is a basic oxide which hydrolyses a little to give an alkaline solution of pH =8 **X**: Giant covalent – does not conduct electricity in molten state as it has no ions; high melting point; does not react with water **Y**: Giant ionic – conducts electricity in molten state due to presence of mobile ions; is a basic oxide; reacts readily with water to give a very alkaline solution **Z**: Simple covalent – is an acidic oxide; low melting point indicates weak intermolecular forces; it reacts with water to give a very acidic solution.

(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]

(c)ans **(i)** $5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 2Mn^{2+} + 4H^+$

(ii) Solution turns from colourless to pink (due to one drop of excess $KMnO_4$)

(iii)

$$n_{MnO_4^-} = \frac{20.5}{1000} \times 0.02 = 4.100 \times 10^{-4} \text{ mol}$$

$$n_{SO_2} = 4.100 \times 10^{-4} \times \frac{5}{2} = 1.025 \times 10^{-3} \text{ mol}$$

$$[SO_2] = \frac{1.025 \times 10^{-3}}{25.0} \times 1000 = 0.0410 \text{ mol dm}^{-3}$$

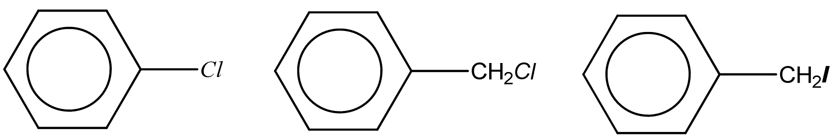
(d) A mixture of benzoic acid and sodium benzoate is sometimes used along with SO_2 as a preservative in foodstuffs.
Explain how the above mixture acts as a buffer solution.

[2]

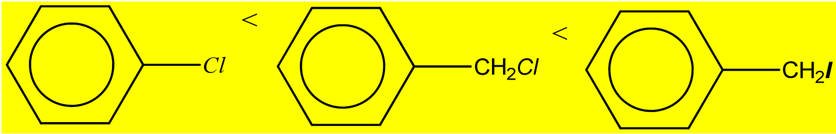
When acid H^+ is added to the buffer, it reacts with the large reservoir of benzoate ions to form benzoic acid, thus the pH decrease will be negligible.

When acid OH^- is added to the buffer, it reacts with the large reservoir of benzoic acid to form benzoate ions, thus the pH increase will be negligible.

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



[3]

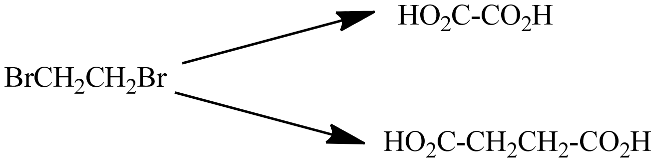


Ease of hydrolysis increases …
In chlorobenzene, the C-C*l* bond has partial double bond character due to delocalisation of the pi electrons in the benzene ring into the p orbitals of chlorine. Hence it is stronger and does not undergo hydrolysis.

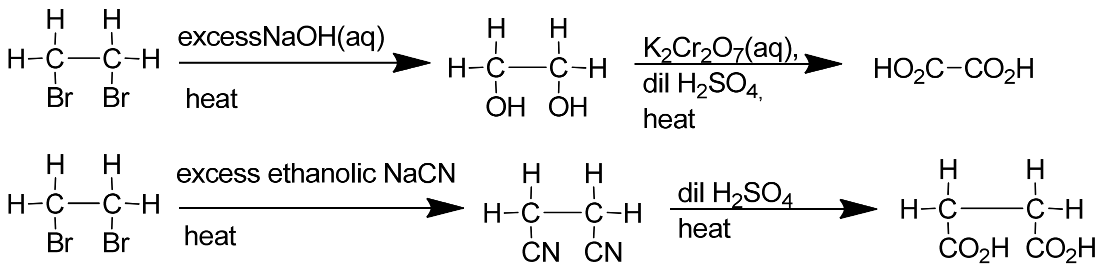
(Chloromethyl) benzene is hydrolysed by nucleophilic substitution of Cl, breaking C-Cl bond.

(Iodomethyl) benzene is hydrolysed more easily as C-I bond is weaker (with smaller bond energy than C-Cl) and thus beak more easily.

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



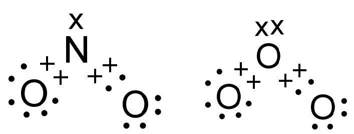
Total [20]



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

It is covalent bonding formed where one empty orbital overlap with another orbital with a pair of electrons.

(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]

Bond angle of O_3 is 115° since there are 2 bond pairs and 1 lone pair around the central O atom and bond pair – bond pair repulsion is weaker than lone pair – bond pair repulsion.

Bond angle of NO_2 is 118° since there are is 2 bond pairs and 1 lone electron around the central N atom. Since the repulsion between the bond pair and the lone electron is less than the repulsion between the bond pair and lone pair in O_3, bond angle is larger than in O_3.

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

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

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.

A low temperature will favour the forward reaction as the reaction is exothermic .

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

- If cooled, the rate of reaction will be too slow/ costly to cool gas
- activation energy of reaction is too high

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

[6]

CO	binds with oxygen carrying haemoglobin irreversibly thus toxic to body.
NO and NO_2	1. dissolves in water giving nitrous acid and nitric acid, as acid rain (pH < 5) it damage stone-works of buildings 2. help form **photochemical smog ;**respiratory problems in humans 3. NO_2 catalyzed the oxidation of atmospheric SO_2 ; the SO_3 dissolves in rain water forming sulfuric acid, acid rain (damage stone-works of buildings)

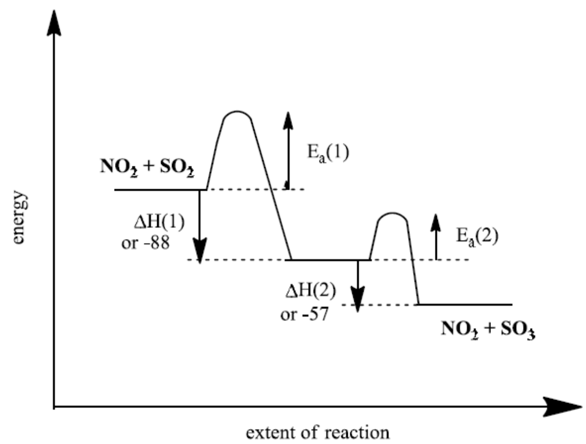
(c) NO_2 catayses the oxidation of SO_2 to SO_3.

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

$NO_2 + SO_2 \rightarrow NO + SO_3$ ΔH_1 = –88 kJ mol^{-1}
$NO + ½O_2 \rightarrow NO_2$ ΔH_2 = –57 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]



both E_a shown, with $E_a(1) > E_a(2)$ [1]
both ΔH shown, with ΔH(1) > ΔH(2) [1]

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

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

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.

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

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

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

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]

(f) **(i)** Amount of I_2 produced = $\frac{1}{2} \times \frac{15.0}{1000} \times 0.100 = 7.50 \times 10^{-4}$ mol

(f) **(ii)** Volume of O_3 present = $7.50 \times 10^{-4} \times 22.4 \times 10^3 = 16.8\ dm^3$

$\therefore$ Percentage of O_3 in the mixture = $\frac{16.8}{500} \times 100\ \% = 3.36\ \%$

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

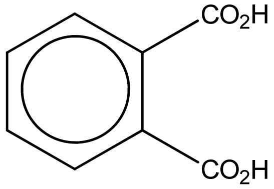
(i) Describe how you could ensure that only *either* the aldehyde or the carboxylic acid is produced during the oxidation process.

(i) The aldehyde can be obtained by reacting a primary alcohol with acidified $K_2Cr_2O_7$ under heating. The aldehyde is obtained by immediate distillation from the reaction mixture.

The carboxylic acid can be obtained by reacting the primary alcohol with acidified $K_2Cr_2O_7$ under reflux for several hours to ensure complete oxidation of the starting material.

(ii)

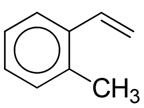
Compounds **L** and **M**, both C_9H_{10}, are oxidized by hot concentrated alkaline $KMnO_4$, followed by acidification, to give benzene-1,2-dicarboxylic acid, **P**.



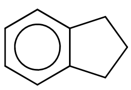
P

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

[4]



L



M

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]

$SiCl_4$: white solid or white/steamy fumes [1/2]
$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$ [1]
PCl_5: fizzes or white/steamy fumes [1/2]
$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$ [1]
$PCl_5 + H_2O$ (dropwise or moist air) $\rightarrow POCl_3 + 2HCl$

(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.

$$CH_3CHO + 2CH_3OH \overset{H^+}{\rightleftharpoons} CH_3CH(OCH_3)_2 + H_2O$$

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.(include units)

[5]

$K_c = [\text{acetal A}][H_2O] / [CH_3CHO][CH_3OH]^2$

$[H_2O] = 0.025$
$[H^+] = 0.05$
$[CH_3CHO] = 0.175$
$[CH_3OH] = 0.05$

$K_c = 1.4(3)$ mol^{-1} dm^3

(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]

(i) H_2O Ý $H^+ + OH^-$ / $2H_2O$ Ý$H_3O^+ + OH^-$

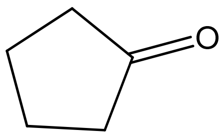
(ii) $Kc = [H^+][OH^-]/[H_2O]$
$[H_2O]$ is constant / in large excess
Negligible dissociation/ eqm far o left

(iii) $[H^+] = 7.16 \times 10^{-7}$ $mol\ dm^{-3}$
$pH = -log(7.16 \times 10^{-7}) = 6.15$

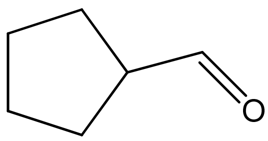
(iv) endothermic; $[H^+]$ higher at higher temp so eqm must have shifted right.

(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.

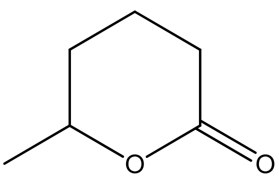
(i)

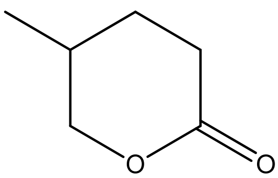


and



(ii)





[5]

Total [20]

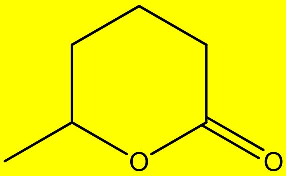
(i) Test: Mild oxidation of aldehydes using Tollens reagent or Fehlings reagent

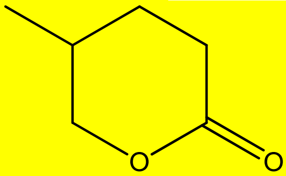
Observation: silver mirror observed with Tollens reagent on aldehydes; no silver mirror with ketones
Brick red ppt of Cu_2O with Fehlings reagent on aldehydes; no ppt with ketones.

Or oxidation with $K_2Cr_2O_7$ / $H_2SO_4(aq)$; orange solution turns green for aldehydes; ketones do not get oxidise and no color change occurs..

(ii)
Test:

1) dil H_2SO_4, heat or dil NaOH, heat (hydrolyse the ester group)
2) $I_2(aq)$, NaOH(aq), heat (test for presence of $CH_3CH(OH)$- group)

Yellow CHI_3 obtained for 

but no yellow crystals obtained for  .