Name:		Class:	

ST ANDREW'S JUNIOR COLLEGE

Preliminary Examinations

Chemistry **8872/2**

Higher 1 **11 Sep 2017**

Paper 2 **1300 − 1500**

Candidates answer on separate paper.

Additional Materials: Writing paper, graph paper, Data Booklet

READ THESE INSTRUCTIONS FIRST
Write your name and civics group 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.

Section A:
Answer **all** the questions in this section in the spaces provided.

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

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.

For Examiners use only:

Section A		Section B	
Question	**Marks**	**Question**	**Marks**
1	/9	1	/20
2	/14	2	/20
3	/7	3	/20
4	/10		
Total	/40	Total	/40
TOTAL (Section A + Section B)			/80

This document consists of **17** pages including a blank page.

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Section A

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

1. Apricot kernels containing glycoside amygdalin turns into deadly hydrogen cyanide acid, HCN, when the kernel is crushed. High doses of hydrogen cyanide can cause coma with seizures and cardiac arrest, leading to death in a matter of minutes. A fatal dose for a human can be as low as 1.50 mg kg^{-1} of body weight.

(1 mg = 1.00 x 10^{-3} g)

The forensics department of the local law enforcement agency was trying to determine the cause of death of a 90 kg deceased man who was found at home on the couch with a few empty packets of apricot kernels lying on the ground.

A typical human has 70 cm^3 of blood per kg of body mass. A 10 cm^3 sample of blood was obtained from the body and dissolved to form 25 cm^3 of solution. The amount of HCN can be determined through the amount of Fe^{2+} present in the blood. The Fe^{2+} required 1.70 cm^3 of 0.00100 mol dm^{-3} acidified $Na_2Cr_2O_7$ solution for complete reaction.

(a) Write a balanced redox equation between Fe^{2+} and $Cr_2O_7^{2-}$. **[1]**

……

(b) Show by oxidation number that the reaction in **(a)** is a redox reaction. **[2]**

……

……

(c) Calculate the number of moles of hydrogen cyanide, HCN, in the 25 cm^3 of solution. **[2]**

1 **(d)** Calculate the number of moles of hydrogen cyanide, HCN, in the body of the deceased man. **[1]**

(e) Calculate the concentration of HCN in mg kg^{-1} and hence determine if the cause of death was due to hydrogen cyanide poisoning. **[3]**

[Total: 9]

2. This question is about nitrogen and its compounds.

(a) NO_2 is highly reactive and usually exists in the more stable form of N_2O_4.

(i) Draw a diagram to illustrate the shape of the molecule, N_2O_4, and state the bond angle about the N atom. **[2]**

Bond angle: ……....

(ii) Draw the dot-and-cross diagram of NO_2 and hence suggest a reason why NO_2 is expected to be highly reactive. **[2]**

……..

……..

(iii) Explain why the bond angle for NO_2 is greater than 120°. **[2]**

……..

……..

……..

2 (b) At room temperature and pressure, NO_2 dimerises to form dinitrogen tetraoxide, N_2O_4, as shown below:

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H < 0$$

(i) Write the expression for the equilibrium constant, K_c, for the above equilibrium, stating its units. **[2]**

Units: ……

(ii) At 298 K and 101 kPa, 1.00 g of NO_2 was placed in the reaction chamber initially. When equilibrium was established, the gaseous mixture was found to occupy a volume of 0.317 dm^3 and showed an average M_r of 77.3. The average M_r of the mixture can be calculated using the following expression, **[2]**

$$\text{Ave } M_r = \frac{[n_{eqm}\,(NO_2) \times M_r(NO_2)] + [\,n_{eqm}\,(N_2O_4) \times M_r(N_2O_4)]}{\text{Total number of moles at equilibrium}}$$

where n_{eqm} = number of moles at equilibrium

Fill in the table below and use the expression given above to solve for the value of *y*.

	NO_2	N_2O_4
Initial/ mol		
Change/ mol	$-2y$	$+y$
Equilibrium/ mol		y

2 (b) (iii) Hence, calculate the value of K_c. **[2]**

(iv) Describe how the average M_r will be affected when pressure decreases. **[2]**

……..

……..

……..

[Total: 14]

3. Many biological processes only occur within a narrow range of pH values. The pH of different fluids found in the body is given below:

Body Fluid	pH
Saliva	6.8
Blood	7.4
Stomach juices	1.0 - 3.0
Intestinal juices	8.5

(a) Calculate the hydroxide ion concentration in intestinal juices. **[2]**

(b) The low pH in the human stomach is due to the existence of hydrochloric acid, which is known to be a *strong Brønsted-Lowry acid*. Explain the terms in italics. **[2]**

……

……

……

(c) The body maintains the pH of blood within a narrow range of values. Death could result if the blood pH decreases below 6.8 or increases above 7.8. The need to maintain the pH within a narrow range of values requires the use of a buffer. In blood, the main buffering system is the H_2CO_3 / HCO_3^- buffer.

(i) What do you understand by the term *buffer* solution? **[1]**

……..

……..

3 **(c)** **(ii)** Write equations to show how the H_2CO_3/HCO_3^- buffer system regulates the acidity on the addition of a small amount of H^+ and OH^-. **[2]**

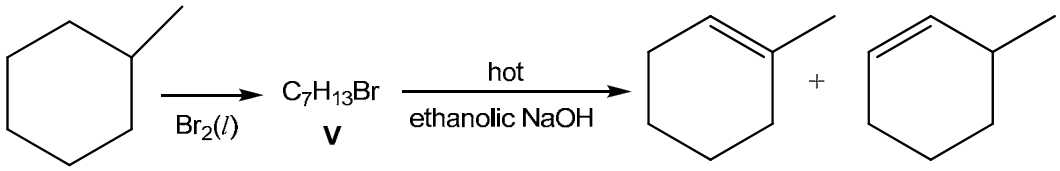
……..

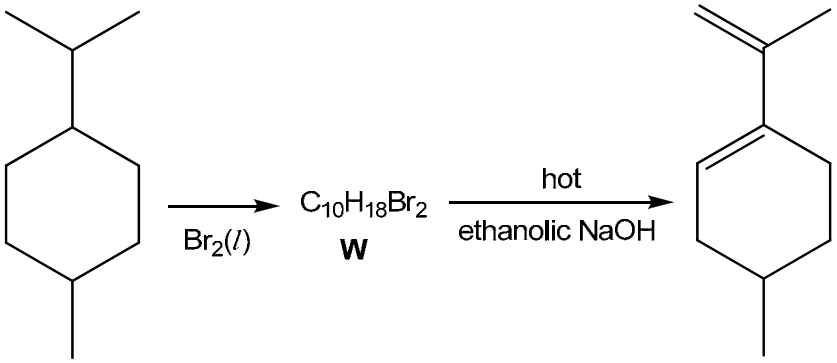
……..

……..

[Total: 7]

4. Alkenes are very useful compounds and can be used as fuels and in the manufacture of a wide variety of polymers. The following reactions involve the formation of some alkenes.





only 1 product formed

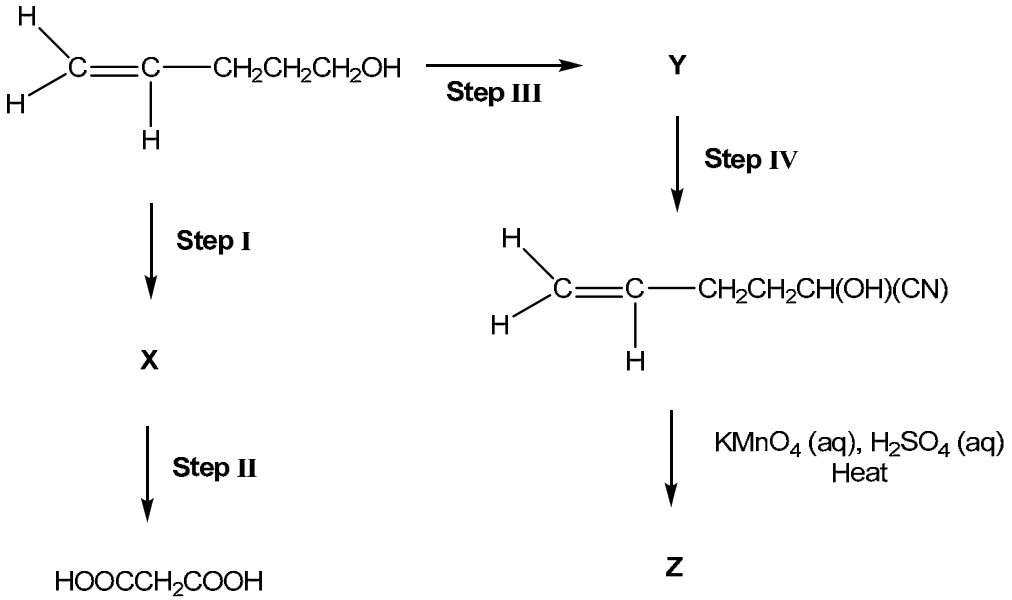
(a) What is the type of reaction for the reaction of the hydrocarbons with $Br_2(l)$ to form **V** and **W?** **[1]**

……

4 **(b)** Suggest the skeletal structure of **V** and **W.** **[2]**

Structure **V**	Structure **W**

(c) The flow chart below involves the reaction of pent-4-en-1-ol.



4 (c) (i) Draw the structural formulae of **X**, **Y** and **Z**. **[3]**

Structure **X**	Structure **Y**
Structure **Z**	

(ii) State the reagents and conditions for steps **I – IV** in the spaces provided. **[4]**

	Reagents and Conditions
Step I	
Step II	
Step III	
Step IV	

[Total: 10]

--- END OF SECTION A ---

Section B

Answer 2 out of 3 questions.

1. The Andrussow oxidation is invented by Leonid Andrussow in which methane and ammonia react in the presence of oxygen, over platinum catalyst, to produce hydrogen cyanide.

$$2CH_4(g) + 2NH_3(g) + 3O_2(g) \rightarrow 2HCN(l) + 6H_2O(l)$$

(a) Draw the dot-and-cross diagram for HCN. State the shape and bond angle. **[3]**

(b) **(i)** Calculate the standard enthalpy change of the above reaction using the data below. **[2]**

	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
CH_4	–74.9
NH_3	–45.9
HCN	+130.5
H_2O	–285.8

(ii) Using data from the *Data Booklet*, calculate another value for the standard enthalpy change of the above reaction. **[3]**

(iii) Explain why the two values differ in **(b)(i)** and **(b)(ii)**. **[1]**

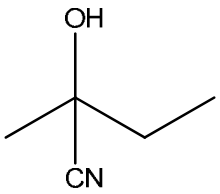
(c) The data below shows the boiling points of HCN and NaCN, and their solubility in water.

	Boiling Point / °C	Solubility in water
HCN	25.6	Miscible
NaCN	1496	Miscible

(i) Explain, in terms of structure and bonding, the difference between the boiling points of HCN and NaCN. **[3]**

(ii) Explain with the aid of a diagram the solubility of NaCN in water. **[3]**

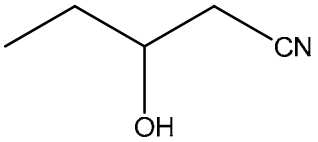
1 (d) Hydrogen cyanide is used as a reagent in the formation of cyanohydrin. The structure below shows an example of a cyanohydrin.



(i) Draw the structure of the organic compound that forms the cyanohydrin above. **[1]**

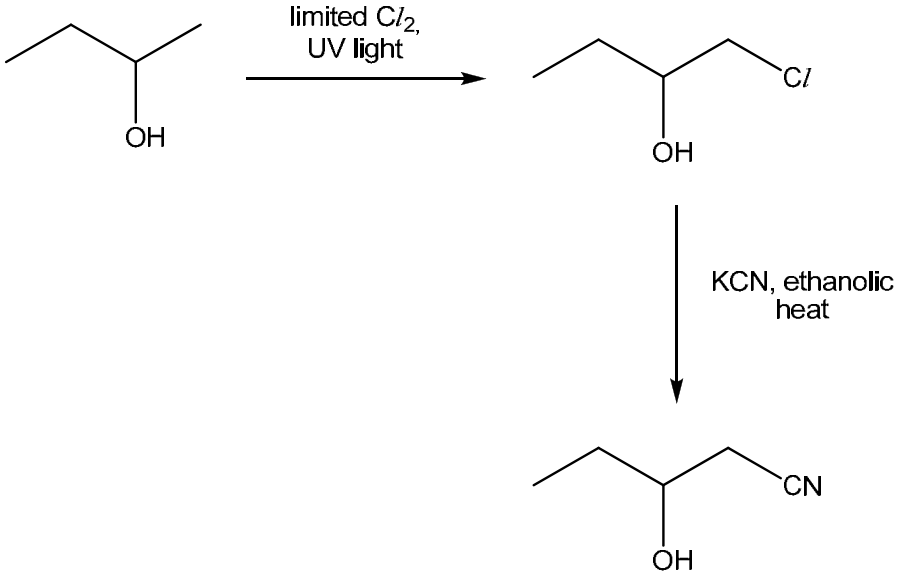
(ii) Suggest why the reaction needs to be performed at a low temperature. **[1]**

(iii) The structure below is an isomer of the cyanohydrin above. **[2]**



Outline a simple chemical test to distinguish between the two compounds.

(iv) A student suggested that the isomer can be synthesised in the following reaction scheme. Suggest why this synthesis is not the best method. **[1]**



[Total: 20]

2. Rocket propellant is a high oxygen containing fuel, whose combustion takes place, in a definite and controlled manner with the evolution of a huge volume of gas. There are four main types of chemical rocket propellants: solid, storable liquid, cryogenic liquid and liquid monopropellant. Solid propellant rocket has a higher propellant density than liquid propellant rocket.

(a) Suggest an advantage of using a solid propellant rocket rather than a liquid propellant rocket. **[1]**

During the 1950s, researchers in the United States developed ammonium perchlorate composite propellant, a type of solid propellant. This mixture is made up of finely ground ammonium perchlorate, fine aluminium powder and polybutadiene acrylonitrile.

(b) Ammonium perchlorate undergoes mild heating according to the equation below.

$$4NH_4ClO_4(s) \rightarrow 4HCl(g) + 2N_2(g) + 5O_2(g) + 6H_2O(l)$$

(i) Calculate the volume of gases formed when 25 g of ammonium perchlorate is heated. (All volumes are measured at room temperature and pressure.) **[2]**

(ii) Suggest why strong heating may lead to an explosion. **[1]**

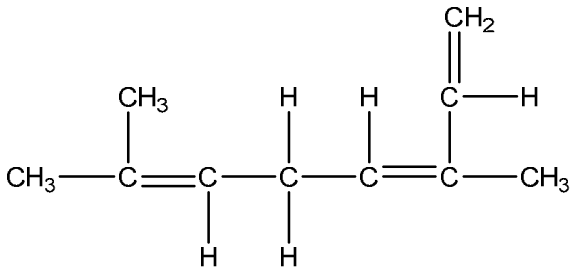
(c) **(i)** Explain why the first ionisation energy of magnesium is higher than that of aluminium. **[2]**

(ii) Explain the difference in electrical conductivity of magnesium, aluminium and silicon. **[2]**

The Soviet utilised syntin, a liquid propellant, for Soyuz U2, is a type of carrier rocket, until 1995. Syntin comprises of synthetic cyclopropane, $C_{10}H_{16}$.

(d) When 0.75 g of cyclopropane undergoes complete combustion, the increase in temperature of 250 cm^3 of water is 18°C and has an efficiency is 85%. Calculate the standard enthalpy change of combustion of cyclopropane. **[3]**

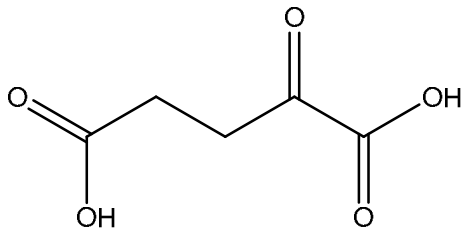
(e) Ocimene is an isomer of syntin with the following structure.



(i) Draw the cis and trans isomers of Ocimene. **[2]**

(ii) Explain why ocimene is able to exhibit cis-trans isomerism. **[2]**

2 **(f)** **W** is another isomer of syntin, with a molecular formula of $C_{10}H_{16}$. When **W** reacts with hot acidified potassium manganate(VII), it forms 2 moles of gas **X**, **Y**, and the product shown below **[5]**



X forms a white precipitate when it reacts with aqueous calcium hydroxide.

Y, C_3H_6O, forms a yellow precipitate when it reacts with aqueous alkaline iodine. **Y** also forms an orange precipitate when it reacts with 2,4–dinitrophenylhydrazine. However, **Y** does not form a sliver mirror when it is warmed with Tollens' Reagent.

Deduce the structures of **W**, **X** and **Y**.

[Total: 20]

3 **(a)** A solution of hydrogen peroxide in aqueous HC*l* slowly oxidises bromide ions according to the equation below.

$$H_2O_2 + 2Br^- + 2H^+ \rightarrow Br_2 + 2H_2O$$

The rate of reaction was followed by measuring the concentration of the remaining hydrogen peroxide after fixed time intervals. Two experiments were carried out, starting with different concentrations of bromide ions. The following results were obtained.

Time / min	Experiment 1 $[Br^-] = 1.00$ mol dm^{-3}	Experiment 2 $[Br^-] = 1.50$ mol dm^{-3}
	$[H_2O_2]$/ mol dm^{-3}	$[H_2O_2]$/ mol dm^{-3}
0	0.0100	0.0100
40	0.0078	0.0069
80	0.0061	0.0048
120	0.0048	0.0033
160	0.0037	0.0023
200	0.0028	0.0016

(i) Using the same axes, plot graphs of $[H_2O_2]$ against time for the two experiments. **[2]**

(ii) Use your graphs to determine the order of reaction with respect to $[H_2O_2]$ and to $[Br^-]$, showing your workings clearly. **[4]**

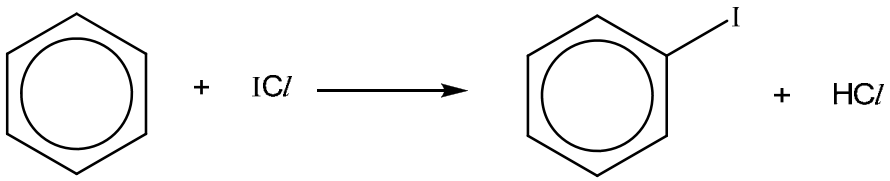
(iii) In another separate experiment, it was found that the order of reaction with respect to [HC*l*] is zero, write the rate equation for the reaction. **[1]**

(iv) Sketch a graph of rate against concentration of H_2O_2. **[1]**

(v) Explain, with an appropriate sketch of the Boltzmann distribution, how an increase in temperature affects the rate of reaction. **[3]**

(b) Explain the difference in ionic radius between Br^- and I^-. **[2]**

3 **(c)** Aromatic halogenation with iodine monochloride, IC*l*, produces aryl iodide.



This reaction is typically catalysed by aluminium chloride when it reacts with iodine monochloride to produce the electrophile I^+.

$$IC\mathit{l} + A\mathit{l}C\mathit{l}_3 \longrightarrow [A\mathit{l}C\mathit{l}_4]^- + I^+$$

(i) Draw the structure of $[A\mathit{l}C\mathit{l}_4]^-$ and suggest in terms of bonding how $[A\mathit{l}C\mathit{l}_4]^-$ is formed from $A\mathit{l}C\mathit{l}_3$. **[2]**

(ii) When sodium carbonate is added to a solution of $A\mathit{l}C\mathit{l}_3$, effervescence was seen. Explain the observation with the aid of relevant equations. **[3]**

(iii) Ethanolic silver nitrate is added to iodobenzene and iodopropane in two separate test tubes. Yellow precipitate is seen immediately in one of the test tubes, whereas no precipitate is seen in the other test tube. Explain the observations. **[2]**

[Total: 20]

--- THE END ---