VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATIONS
Higher 1

CANDIDATE NAME ……

CT GROUP ……

CHEMISTRY 8872/02

Paper 2 **16 September 2014**

Candidates answer Section A on the Question Paper. **2 hours**

Additional Materials: Answer Paper
Graph Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
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.

Section B
Answer **two** questions on separate answer paper.

The number of marks is given in brackets [ ] at the end of each question or part question.

FOR EXAMINER'S USE			
Section A		**Section B**	
A1		**B4**	
A2		**B5**	
A3		**B6**	
		Total	**/ 80**

This document consists of **13** printed pages and **1** blank page.

Section A

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

1 **(a)** Describe the bonding in ethyne, CH≡CH, in terms of orbital overlap. You may draw a diagram to illustrate your answer.

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[3]

(b) Bond energies for some multiple bonds are listed below.

Bond	Bond energy / kJ mol^{-1}
C=C	610
C≡C	840
N≡N	994

Explain why C≡C is a stronger bond than C=C but a weaker bond than N≡N.

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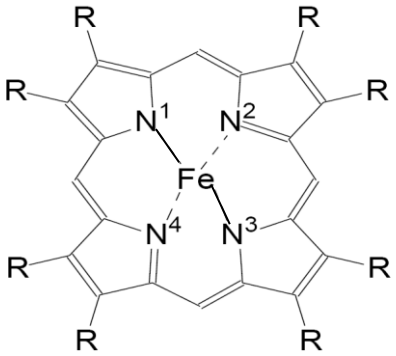
[2]

(c) Haemoglobin is an important protein present in the red blood cell, which is responsible for transport of oxygen in the body. It contains a haem group and a metal centre as shown below. The four N atoms and the Fe atom are planar.



(i) State the nature of the bonding around the iron atom.

Type of bond between Fe atom and N^1: ……..……...

Type of bond between Fe atom and N^2: ……..……

(ii) One molecule of haemoglobin (Hb) binds up to four oxygen molecules to form oxyhaemoglobin ($Hb(O_2)_4$), as shown in the following equation.

$$Hb(aq) + 4O_2(g) \rightleftharpoons Hb(O_2)_4(aq) \qquad \text{------ (1)}$$

By applying *Le Chatelier's Principle*, explain how oxygen molecules are transported from the lungs to the body tissues.

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(iii) The percentage saturation of haemoglobin is defined as the percentage of haemoglobin present in the blood that has been converted to oxyhaemoglobin.

With reference to equilibrium (1), state and explain how the percentage saturation of haemoglobin changes when temperature increases.

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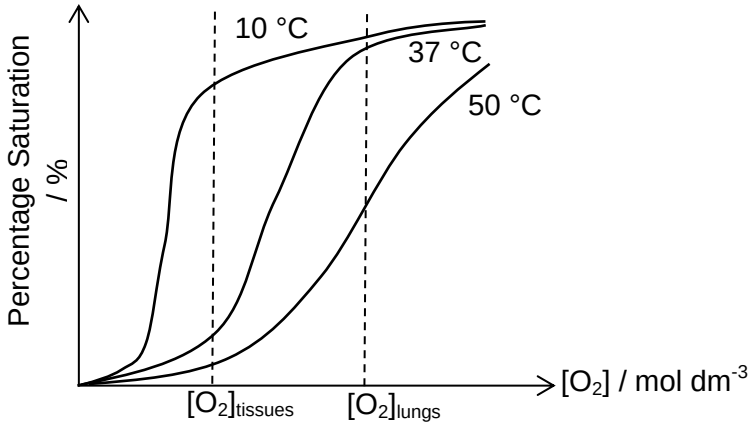
(iv) The relationship between the percentage saturation of haemoglobin and concentration of oxygen in blood at different temperatures is shown below.



Suggest the optimum temperature at which haemoglobin operates. Explain your answer.

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[8]

[Total: 13]

2 **(a)** Sodium azide, NaN_3, is the gas–forming component in many car airbag systems. On heating, it decomposes to give nitrogen gas which expands the air bag.

The concentration of sodium azide may be determined by titration against iodine under suitable conditions as shown by the following equation.

$$2N_3^-(aq) + I_2(aq) \rightarrow 3N_2(g) + 2I^-(aq)$$

A 0.800 g sample of sodium azide was dissolved in water and made up to 100 cm^3. To a 25.0 cm^3 portion of this solution, 25.0 cm^3 of acidified 0.100 mol dm^{-3} $I_2(aq)$ was added. The excess of iodine reacted completely with 22.00 cm^3 of 0.100 mol dm^{-3} sodium thiosulfate. The equation for the reaction of iodine with thiosulfate ions is as follows.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

(i) Calculate the amount of iodine that reacted with 25.0 cm^3 of sodium azide solution.

(ii) Calculate the percentage purity by mass of the sodium azide.

[4]

(b) **(i)** A hydride of nitrogen, **Q**, contains 12.5% of hydrogen by mass. Find its empirical formula.

(ii) When **Q** is heated very strongly, it decomposes into its elements. 10 cm^3 of **Q** produces 30 cm^3 of products (all volumes are measured under the same conditions).

What is the molecular formula of **Q** and the oxidation state of nitrogen in **Q.**

(iii) **Q** is an unstable compound which will disproportionate to give two nitrogen–containing products when heated gently. The oxidation numbers of nitrogen in the two products are 0 and –3 respectively. Write a balanced equation for the reaction and use oxidation numbers to explain what is meant by *disproportionation* in this reaction.

[5]

(c) On Planet Uranus, it is postulated that the number of subshells associated with each principal quantum number and the respective energy levels of the subshells are similar to that on Earth. Each orbital contains a maximum of two electrons. However, the number of orbitals that make up a subshell may or may not be identical to that on Earth.

Figure 1 represents the sketch of the successive ionisation energies of **all** the electrons of an element **T** on Planet Uranus.

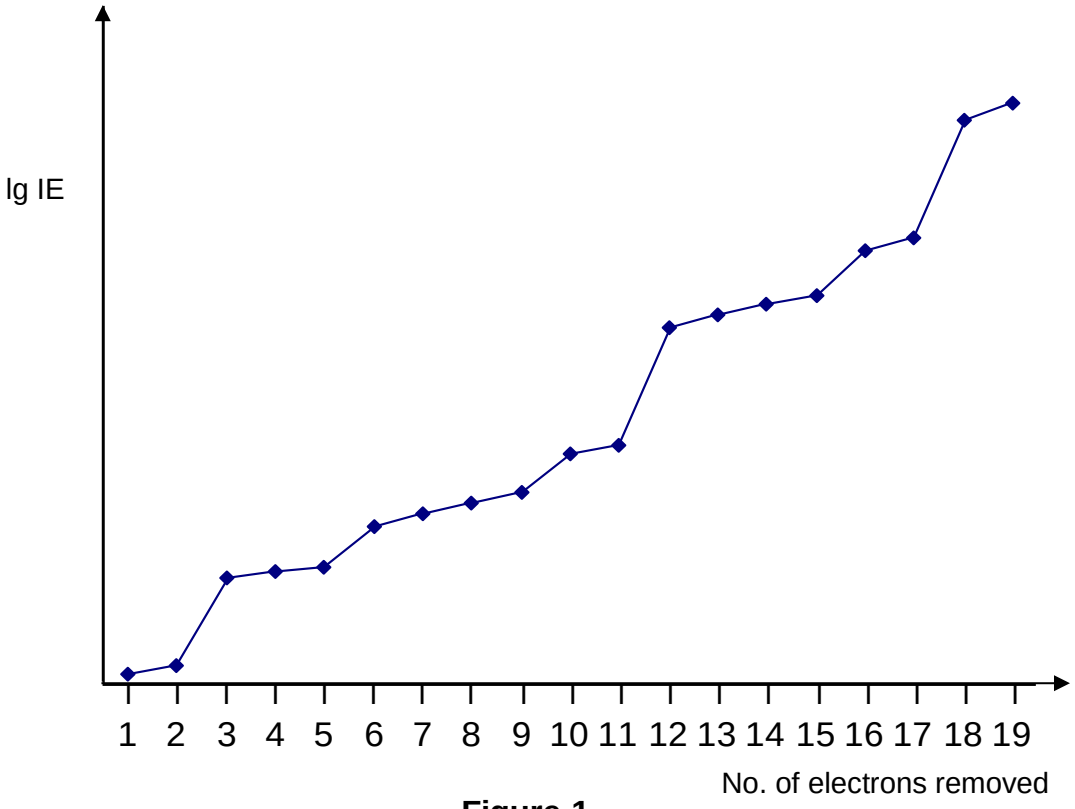

Figure 1

(i) With the aid of a relevant equation, explain what is meant by the *third ionisation energy* of element **T**.

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(ii) By interpreting Figure 1, suggest with reasoning, which period of the Periodic Table element **T** belongs to.

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(iii) Using Figure 1, deduce the number of 2p orbitals present in element **T**.

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(iv) State the full electronic configuration of element T.

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[5]

[Total: 14]

3 This question is on the reactions of the hydrocarbons and their halogen derivatives.

(a) What do you understand by the term *bond energy*?

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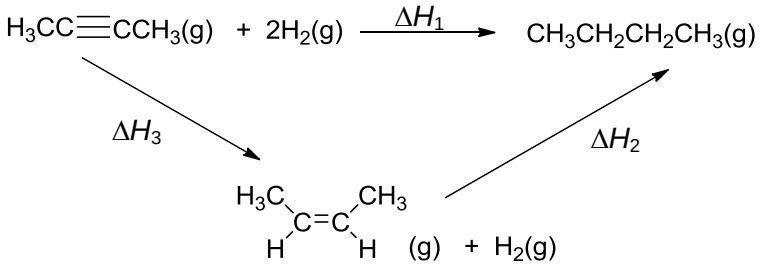
[1]

(b) The hydrogenation of the hydrocarbons, butyne and *cis*–but–2–ene, are shown in the energy cycle below.



(i) Use the bond energy values from the *Data Booklet* to calculate ΔH_1.

(ii) Calculate ΔH_2, given that the enthalpy change of formation of gaseous *cis*–but–2–ene and gaseous butane are –8 kJ mol^{-1} and –127 kJ mol^{-1} respectively.

(iii) By using your answers to **(b)(i)** and **(b)(ii),** calculate ΔH_3.

[4]

(c) Gas used in camping stoves is available in canisters, which contain mainly butane.

(i) When 3.40 g of butane was used to heat 500 g of water, it was found that the temperature of water increased by 44 °C. Assuming that the specific heat capacity of water is 4.2 J K^{-1} cm^{-3}, calculate the enthalpy change of combustion of butane.

(ii) The standard enthalpy change of combustion of butane is –2877 kJ mol^{-1}. Suggest a reason for the difference between this value and that obtained in **(c)(i)**.

The standard enthalpy changes of combustion, $\Delta H_c^{\ominus}$, for some common fuels are given below.

fuel	formula	M_r	$\Delta H_c^{\ominus}$ / kJ mol^{-1}	$\frac{\Delta H_c^{\ominus}}{M_r}$ / kJ g^{-1}
methane	CH_4	16	–890	–55.6
ethanol	CH_3CH_2OH	46	–1367	–29.7
butane	C_4H_{10}	58	–2877	–49.6
octane	C_8H_{18}	114	–5470	–48.0

(iii) Explain why $\Delta H_c^{\ominus}$ values become more exothermic with M_r.

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(iv) Explain why ethanol has a much less exothermic $\frac{\Delta H_c^{\ominus}}{M_r}$ compared to alkanes.

……

……

[5]

(d) Upon irradiation of ultra–violet light, 2,4–dimethylpentane undergoes monochloro–substitution.

(i) Draw the structural formula of all the possible monochlorinated products.

(ii) Predict the mole ratio of the monochlorinated products in **(d)(i)**.

……

(iii) With reference to structures drawn in **(d)(i)**, indicate those that form only one organic product when reacted with hot ethanolic KOH.

[3]
[Total: 13]

Section B

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

4 **(a)** 3–fluoroprop–2–enoic acid, $CHF=CHCO_2H$, is used as building blocks of polymers, which shows exceptional mechanical and optical properties. This compound can exhibit *geometric isomerism*.

(i) What do you understand by the term *geometric isomerism*?

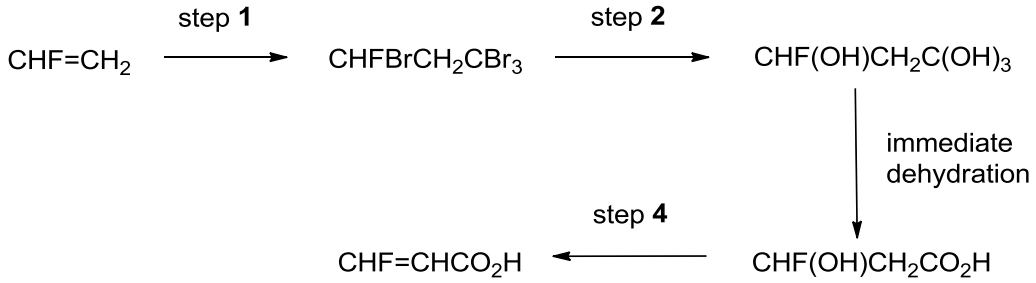
(ii) Draw the possible geometric isomers of the above compound.

(iii) The geometric isomers differ in some physical properties, including boiling point. By considering the bonding and structure of the above isomers, suggest and explain which isomer will have a higher boiling point.

(iv) Suggest how the acidity of 3–fluoroprop–2–enoic acid might compare to that of $CHF=CHCH_2OH$?

[5]

(b) 3–fluoroprop–2–enoic acid can be obtained from fluoroethene as shown below:



(i) Suggest the reagents required for steps **1**, **2** and **4**.

(ii) Explain why the $CHF=CHCO_2H$ dissolves better in aqueous NaOH than water.

(iii) 0.422 g of an organic compound, $C_3H_xI_y$ (M_r = 422) is subject to alkaline hydrolysis. After cooling the products, excess dilute HNO_3(aq) is added and then $AgNO_3$(aq) is added. The mass of the precipitate, AgI formed is 0.705 g. Determine the values of x and y.

[6]

(c) The acid–base properties of the oxides of Period 3 elements show a distinctive trend across the period.

Illustrate the above statement with reference to the oxides, Na_2O, Al_2O_3 and P_4O_{10}. Write relevant equations for the reactions involved and discuss how the bonding in Al_2O_3 accounts for its acidic or basic character.

[5]

(d) Alloys of aluminium and magnesium are often used in the aircraft manufacture because of their high strength and low density.

A 1.50 g sample of one such alloy was reacted with an excess of aqueous sodium hydroxide and the volume of hydrogen given off was measured. 1.50 dm^3 of gas was produced at room temperature and pressure.

(i) The aluminium containing product of this reaction is the same as that from the reaction between aluminium oxide and sodium hydroxide. Based on this information, construct relevant half equations and hence write the equation for the reaction between aluminium and sodium hydroxide.

(ii) Calculate the percentage by mass of aluminium in the sample of alloy.

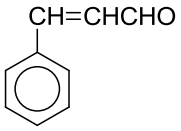
[4]
[Total: 20]

5 **(a)** When hydrocarbon **P,** $C_{10}H_{12}O$ is heated with acidified potassium manganate (VII), compound **Q**, C_8H_8O is obtained as the **only** organic product. **P** gives effervescence when sodium metal is added. When **P** is treated with gaseous HBr, compound **R**, $C_{10}H_{12}Br_2$ is formed. When **Q** is added to 2,4–dinitrophenylhydrazine, an orange precipitate is obtained.

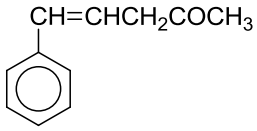
Deduce the structures for each lettered compound, **P**, **Q** and **R** and give an account of the chemistry involved.

[6]

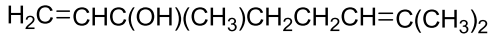
(b) Recent research has suggested that cinnamon could be an effective pesticide against the larvae of mosquitoes, thus helping in the fight against malaria. Each of the following three compounds, which are present in cinnamon, appears to be effective as a pesticide.



A



B



C

For each of the compounds **A** to **C**, state the reagents and conditions which would distinguish it from the other two and describe the observations that would be seen.

[4]

(c) The acid–catalysed hydrolysis of methyl methanoate may be represented by the equation:

$$HCO_2CH_3 + H_2O \overset{H^+}{\rightleftharpoons} HCO_2H + CH_3OH$$

When the hydrolysis was carried out in the presence of excess aqueous hydrochloric acid in a constant–temperature bath, the following results were obtained.

Time / min	Fraction of methyl methanoate remaining
0	1.00
10	0.62
20	0.38
30	0.24
40	0.14
50	0.08
60	0.05
70	0.03
80	0.02

(i) Explain what is meant by the term '*order of reaction*'.

(ii) Plot an appropriate graph to show that the reaction is first–order with respect to ester and hence determine the rate constant for the reaction.

(iii) Sketch a labelled reaction pathway diagram for the uncatalysed hydrolysis reaction given that the activation energy of the forward reaction is +152 kJ mol^{-1} and that for the reverse reaction is +184 kJ mol^{-1}.

Determine the enthalpy change of the reaction.

(iv) On your sketch in **(c)(iii)**, draw the reaction pathway of the acid catalysed reaction. Label this clearly.

(v) With the help of a Maxwell Boltzmann distribution, explain how the use of a catalyst may help to speed up the rate of this reaction.

[10]
[Total: 20]

6 (a) Vitamin C, $C_6H_8O_6$, also known as ascorbic acid, is a monobasic acid. When 500 mg tablet of vitamin C is swallowed, it dissolves in the stomach before being absorbed into the bloodstream. The stomach may be assumed to contain 1.00 dm^3 of 0.100 mol dm^{-3} hydrochloric acid. 0.0794% of the vitamin C tablet is ionised in the stomach.

(i) Determine the acid dissociation constant K_a of vitamin C.

(ii) Blood has a pH of 7.35 and is saturated with carbon dioxide. Concentration of H_2CO_3 in blood is 3.20×10^{-3} mol dm^{-3}. The equilibrium reaction acts as a buffer.

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- ; \quad K_a = 4.5 \times 10^{-7} \text{ mol dm}^{-3}$$

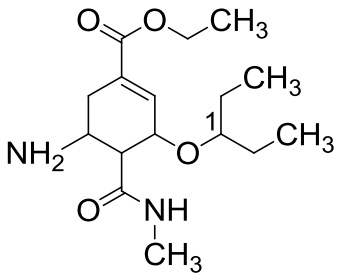
With the aid of balanced equations, explain clearly how this buffering action minimizes the change in pH on the addition of either acid or alkali.

(iii) Calculate the concentration of HCO_3^- in the blood.

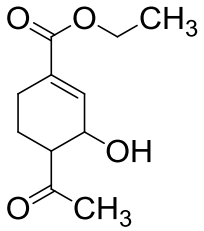
(iv) Explain qualitatively how the extent of ionisation of vitamin C changes as it moves from the stomach to the bloodstream.

[9]

(a) Oseltmivir (Tamiflu) is an antiviral drug that slows the spread of non-resistant strains of the influenza virus between cells in the body. It blocks the action of a viral enzyme called neuraminidase and has since been indicated for the treatment of H5N1 and H1N1 infection. The standard adult dosage is 75 mg twice daily. Compound **C** is a derivative of Oseltamivir that may be investigated for antiviral activities.



Oseltamivir
M_r= 312.4

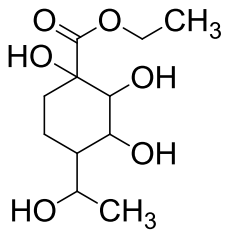


Compound C

(i) A male adult patient has been put on a 1 week oseltamivir treatment. Calculate the total number of moles of oseltamaivir taken by this patient over the period of treatment.

(ii) State the shape and bond angle about the carbon atom labelled '1'.

(iii) Compound **D** can be synthesised from **C** in two steps. Give the reagents, conditions and intermediates for this two–step synthesis. Name the types of reactions involved.



Compound D

(iv) Draw the organic products formed when compound **C** is reacted with
(I) hot aqueous alkaline iodine

(II) hot aqueous acidic $KMnO_4$

(v) Write the balanced equation for the reaction of compound **C** with 2,4–dinitrophenylhydrazine.

[11]
[Total: 20]