VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATIONS
Higher 2

CANDIDATE NAME .....

CT GROUP .....

CHEMISTRY **9647/02**

Paper 2 Structured **13 September 2016**

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

Additional Materials: 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.

Answer **all** questions.
A Data Booklet is provided.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	
2	
3	
4	
5	
6	
Total	

This document consists of **16** printed pages and **0** blank page.

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

1 Planning (P)

When potassium manganate(VII) reacts with sodium ethanedioate, a redox reaction occurs as shown below:

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O \quad \text{—— reaction 1}$$

A product that is generated during the course of the reaction and helps to speed up the reaction rate is known as an autocatalyst. The autocatalyst for the above reaction is Mn^{2+}.

The kinetics of this reaction can be investigated by determining the concentration of MnO_4^- over the course of the reaction. Fixed aliquots (portions) of the reaction mixture are withdrawn at regular time intervals and added to an excess of potassium iodide.

The MnO_4^- in the aliquots reacts with excess iodide as shown below.

$$2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O \quad \text{—— reaction 2}$$

The amount of iodine formed can then be determined by titration with the sodium thiosulfate solution as shown below.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} \quad \text{—— reaction 3}$$

The volume of sodium thiosulfate used is proportional to the concentration of MnO_4^-.

(a) In this experiment, both sodium ethanedioate and sulfuric acid are used in large excess. Explain the purpose of using a large excess of sodium ethanedioate and sulfuric acid.

……

……

[1]

(b) Using the information given above, you are required to write a plan for the determination of the concentration of MnO_4^- at regular timing intervals.

You may assume that you are provided with the following:

- 0.0500 mol dm^{-3} potassium manganate(VII), $KMnO_4$
- 0.500 mol dm^{-3} sodium ethanedioate, $Na_2C_2O_4$
- 1.00 mol dm^{-3} sulfuric acid, H_2SO_4
- 0.200 mol dm^{-3} potassium iodide, KI
- solid $Na_2S_2O_3$
- starch indicator
- stopwatch
- apparatus and chemicals normally found in a school or college laboratory.

Your plan should include:

- justification for
  - the volume of each reactants to be used in **reaction 1** so as to allow a minimum of **6 aliquots** of the reaction mixture to be withdrawn and the concentration of MnO_4^- in each aliquot to be determined;
  - the intended concentration of the sodium thiosulfate, $Na_2S_2O_3$, to be used;
- brief, but specific, details of the apparatus you would use, bearing in mind the levels of precision they offer;
- an outline of how the results would be obtained;
- a sketch of the graph you would expect to obtain.

[10]

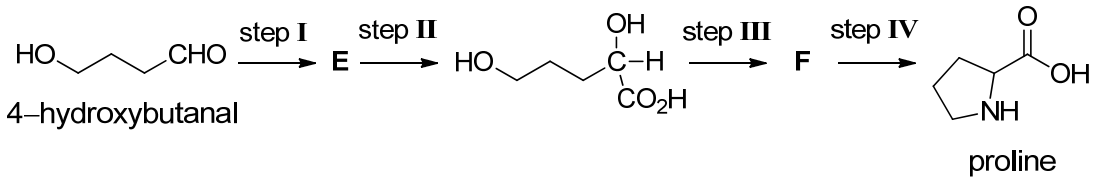
(c) The order of reaction with respect to MnO_4^- can be determined by initial rate method. Use your graph in **(b)**, suggest how the initial rate can be determined.

……

……...[1]

[Total: 12]

2 **(a)** Proline (pro) is one of the naturally occurring amino acids. It can be synthesised from 4–hydroxybutanal in 4 steps.



4–hydroxybutanal

proline

(i) Suggest the structures of **E** and **F.**

E

F

[2]

(ii) Suggest the reagents and conditions required for the following steps.

step **I**: ……

step **III**: ……..

step **IV**: ……...[3]

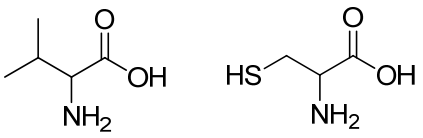
(b) The two pK_a values associated with proline are 2.0 and 10.5.

Make use of these pK_a values to suggest the major species present in the solution of proline with the following pH values.

pH 1	pH 7	pH 12

[3]

(c) The structures of amino acids, valine (val) and cys are shown below.



(i) Draw the structure of val–pro–cys peptide.

[2]

(ii) State the possible R group interactions that val–pro–cys may have with another val–pro–cys peptide.

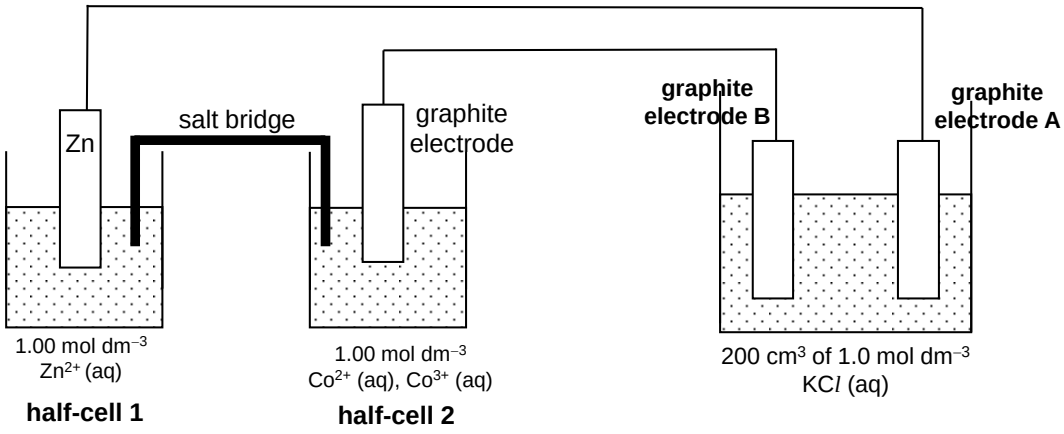
……

……

……[2]

[Total: 12]

3 **(a)** A student used the following setup in an attempt to produce chlorine gas using potassium chloride solution.



(i) Using relevant data from the *Data Booklet*, predict the type of redox reaction that occurs at each half–cell. State the polarity at the graphite electrodes **A** and **B**.

Half–cell **1**: …….

Half–cell **2**: …….

Graphite electrode **A**: …….

Graphite electrode **B**: ……. [2]

(ii) 20 cm^3 of hydrogen gas was collected on one of the electrodes after 10 minutes at room temperature and pressure. Assuming 20% of the hydrogen gas was lost during collection, calculate the current produced by the battery setup.

[2]

(iii) With reference to relevant data from the *Data Booklet*, explain the absence of chlorine being discharged on the other electrode.

……

……

…….. [1]

(b) 20 cm^3 of a gas mixture containing gaseous ethanol, carbon monoxide and excess oxygen was burned completely. There was a contraction of 1 cm^3. When the product mixture was passed through sodium hydroxide, there was a further contraction of 6 cm^3. All gas volumes are measured at 400 K and 1 atm.

Determine the molar composition of the ethanol and carbon monoxide in this gas mixture.

[3]

[Total: 8]

4 Magnesium and beryllium are Group II elements but beryllium behaves differently from that of magnesium. There is said to be a 'diagonal relationship' between beryllium and aluminium as they show similar chemical behaviour due to their similarities in electronegativity and charge density.

(a) **(i)** When a few drops of water are added to solid beryllium chloride, steamy white fumes are evolved and a white solid remains, which is insoluble in water.

Write a balanced equation for this reaction.

…….. [1]

(ii) When a large amount of water is added to solid beryllium chloride, a clear, weakly acidic solution is obtained. Explain.

……

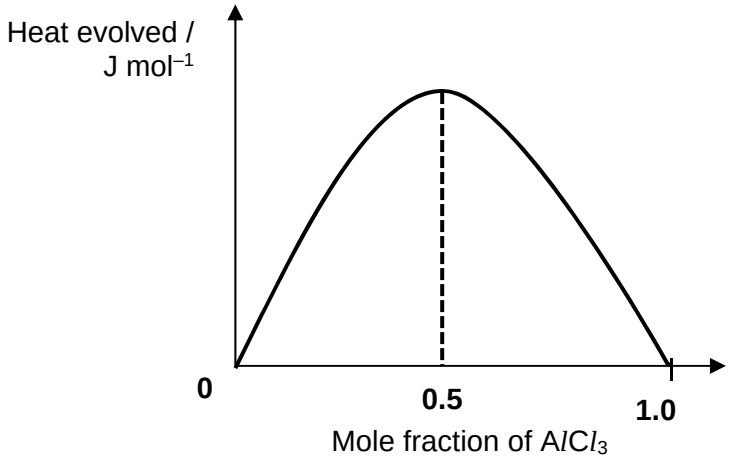
…….. [1]

(iii) At 750 °C, the relative molecular mass of gaseous beryllium chloride corresponds to the formula $BeCl_2$. At 550 °C, gaseous beryllium chloride exists as a mixture of $BeCl_2$ and **Y** (relative molecular mass of **Y** is 160).

Determine the molar composition of gaseous beryllium chloride at 550 °C which has a relative molecular mass of 100. Draw a diagram to illustrate the nature of the bonding in **Y** and indicate the value of the bond angle about Be.

[2]

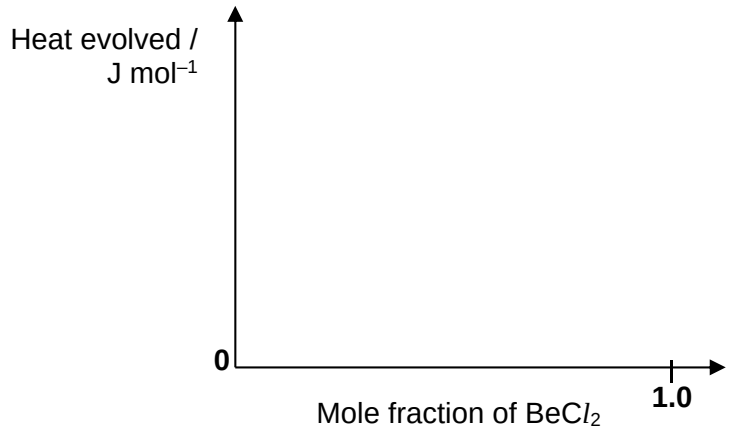
(iv) When aluminium chloride, $AlCl_3$, is mixed with ammonia, compound **Z** is formed and the reaction is exothermic. The diagram below shows the relationship between the heat evolved per mole of the mixture and the mole fraction of $AlCl_3$.



Draw a diagram to show the bonding in a molecule of compound **Z**.

[1]

(v) Sketch a labelled diagram similar to **(a)(iv)** that you would expect to obtain when A*l*C*l*$_3$ is replaced by BeC*l*$_2$.

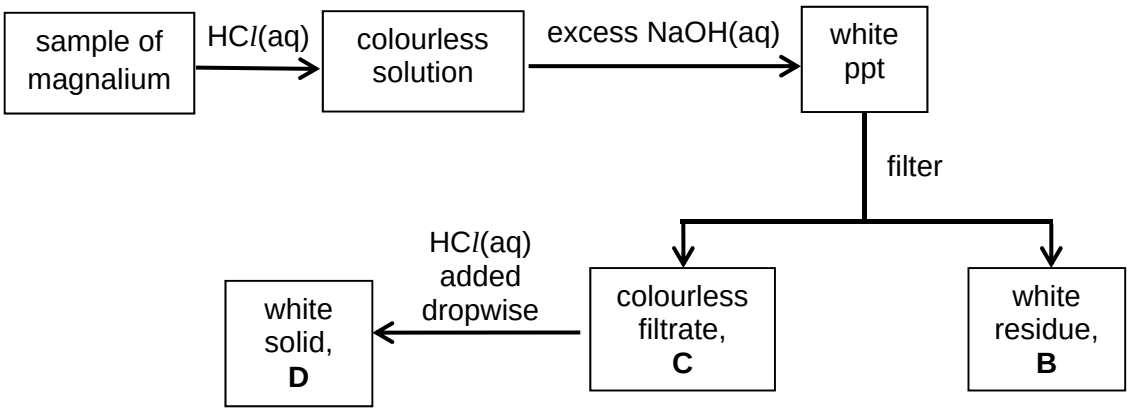


[1]

(vi) Write a balanced equation of a chlorination reaction in Organic Chemistry that uses anhydrous BeC*l*$_2$ as a catalyst.

[1]

(b) Magnalium is an alloy of aluminium and magnesium which is used in boat-building. The diagram below shows some reactions of magnalium.



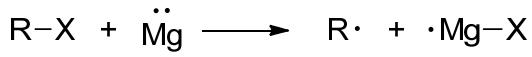
Identify **B**, **C** and **D.**

B: …….. **C**: …….. **D**: …….. [3]

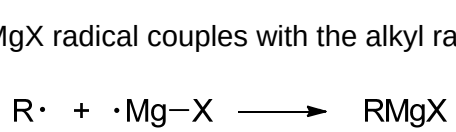
(c) Grignard reagents, RMgX, can be prepared by the reaction of magnesium with halogenoalkane, RX, using dry ether as the solvent.

The mechanism of the reaction involves two steps.

Step **1**: It involves the transfer of one electron from Mg to the halogen X followed by the homolytic fission of the carbon–halogen bond. This forms MgX, which is a radical.



Step **2**: MgX radical couples with the alkyl radical formed in step **1**.



(i) Draw curve arrows to show the movement of electrons in step **1** of the mechanism given above.

[1]

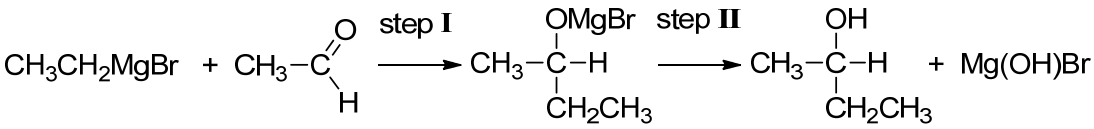
(ii) Suggest which step in the mechanism is the rate–determining step. Explain your answer.

……

……

…… [1]

Grignard reagents can be used to prepare alcohols from carbonyl compounds as shown by the reaction of CH_3CH_2MgBr with ethanal below:



(iii) What type of reaction takes place in steps **I** and **II**?

step **I**: ……

step **II**: ……[2]

(iv) The variation of the rate constant *k* with temperature for the reaction of CH_3CH_2MgBr with ethanal is given below:

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where E_a denotes the activation energy in J mol^{-1}, R is the gas constant, and T is the temperature in Kelvin.

Given that at 25 ^oC, the rate constant and activation energy of the reaction is 9.16 x 10^{-3} mol^{-1} dm^3 s^{-1} and 102 kJ mol^{-1} respectively.

Explain, with calculations, the effect of temperature change on the rate of the reaction when the temperature is raised by 5 ^oC.

……

……

…… [2]

(v) Draw the structural formula of the Grignard reagent that will react with butan–2–one to form 3–methylpentan–3–ol in a similar two–step reaction.

[1]

(vi) Suggest why $CH_3CO(CH_2)_3CH_2Br$ and magnesium cannot be used to prepare the Grignard reagent $CH_3CO(CH_2)_3CH_2MgBr$.

……

……..[1]

(vii) Ethanal is oxidised to ethanoic acid by acidified potassium dichromate. Using data from the Data Booklet and the data below, calculate $E^{\ominus}_{cell}$ of the reaction.

$$E^{\ominus}(CH_3CO_2H|CH_3CHO) = +0.92 \text{ V}$$

Hence, explain why the reaction takes place only in the presence of heat.

……

……

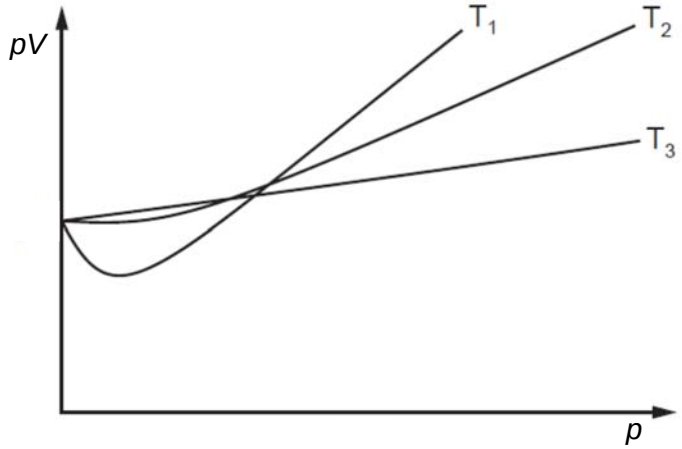
……

…… [2]

[Total: 20]

5 **(a)** The relationship $pV = nRT$ can be derived from the laws of mechanics by assuming ideal behaviour for gases.

The graph represents the relationship between pV and p for a real gas at three different temperatures, T_1, T_2 and T_3.



(i) Draw **one** line on the graph to show what the relationship should be for the same amount of an ideal gas and state which of T_1, T_2 or T_3 is the lowest temperature.

Lowest Temperature: …….. [1]

(ii) State and explain the effect of pressure on the extent to which a gas deviates from ideal behaviour.

……

…….. [1]

(b) A flask with a volume of 100 cm^3 was first weighed with air filling the flask. The same flask was then weighed with only gas, **Y**, filling the flask. The results, measured at 26 ^oC and 1.00×10^5 Pa, are shown.

Mass of flask containing air = 47.930 g
Mass of flask containing **Y** = 47.989 g
Density of air = 0.00118 g cm^{-3}

Calculate the relative molecular mass, M_r, of **Y**.

[2]

(c) In recent years there has been worldwide interest in the possible extraction of 'shale gas' (a form of natural gas) as an important energy source.

One of the problems associated with using shale gas is its variable composition. **Table 1** shows the percentage composition of shale gas from four different sources **J**, **K**, **L** and **M**.

Table 1

source	CH_4	C_2H_x	C_3H_y	CO_2	N_2
J	80.3	8.1	2.3	1.4	7.9
K	82.1	14.0	3.5	0.1	0.3
L	88.0	0.8	0.7	10.4	0.1
M	77.5	4.0	0.9	3.3	14.3

In the formula above, ***x*** and ***y*** are variables.

(i) Draw the structures of **three** possible compounds with the formula C_3H_y.

[1]

(ii) Which source of shale gas, **J**, **K**, **L** or **M**, will provide the most energy when burned? Explain your answer.

……

…… [1]

(iii) Suggest one method by which carbon dioxide can be removed from shale gas.

……

…… [1]

Table 2 shows a comparison of the relative amounts of pollutants produced when shale gas, fuel oil and coal are burned to produce **the same energy**.

Table 2

air pollutant	shale gas	fuel oil	coal
CO_2	117	164	208
CO	0.040	0.033	0.208
NO_2	0.092	0.548	0.457
SO_2	0.001	1.12	2.59
particulates	0.007	0.84	2.74

(iv) Suggest why shale gas produces the smallest amount of CO_2.

……

…… [1]

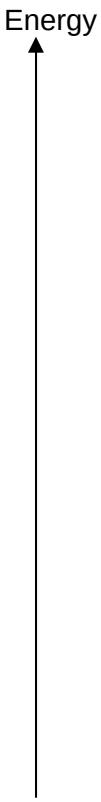
(v) Explain which of the three fuels, shale gas, fuel oil or coal, is the largest contributor to 'acid rain'.

……

…… [1]

(d) Use the following data and data from the *Data Booklet* to construct a labelled energy level diagram to determine the lattice energy of Fe_2O_3.

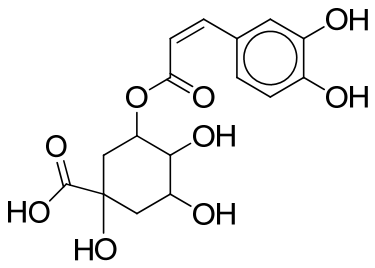
enthalpy change of $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$	–1644 kJ mol^{-1}
enthalpy change of atomisation of Fe(s)	+414 kJ mol^{-1}
electron affinity of the oxygen atom	–141 kJ mol^{-1}
electron affinity of the O^- ion	+844 kJ mol^{-1}



[4]

[Total: 13]

6 **(a)** Coffee beans contain chlorogenic acid.

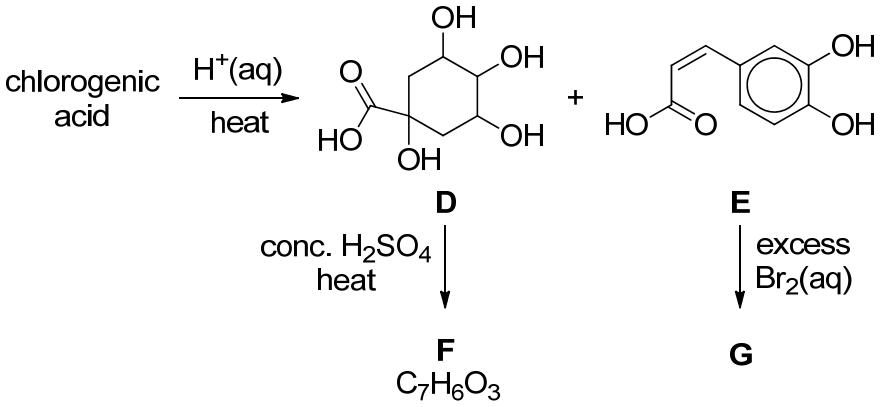


chlorogenic acid

(i) How many moles of $H_2(g)$ will be evolved when 1 mol of chlorogenic acid reacts with an excess of sodium metal?

…… [1]

On heating with dilute aqueous acid, chlorogenic acid produces two compounds **D** and **E**.



When compound **D** is heated with concentrated H_2SO_4, compound **F**, $C_7H_6O_3$, is formed.

Compound **F** does not decolourise cold dilute acidified $KMnO_4$ but reacts with $Br_2(aq)$.

When compound **E** is treated with an excess of $Br_2(aq)$, compound **G** is produced.

(ii) If the test with cold dilute acidified $KMnO_4$ had been positive, which functional group would this have shown to be present in **F**?

…… [1]

(iii) Suggest the structures for compounds **F** and **G**, and draw them in the relevant boxes below.

$C_7H_6O_3$ **F**	**G**

[2]

(b) Allyl alcohol, $CH_2=CHCH_2OH$, is a colourless liquid which is soluble in water.

Crotyl alcohol, $CH_3CH=CHCH_2OH$, is a colourless liquid.

(i) Describe how you would distinguish between allyl alcohol and crotyl alcohol. The compounds may be distinguished by a preliminary chemical reaction followed by a subsequent testing of the reaction products. Include clearly the reagents, conditions and observations for each compound.

……

……

……

…… [2]

(ii) Allyl alcohol may be converted into propanal by using a ruthenium(IV) catalyst in water.

$$CH_2=CHCH_2OH \xrightarrow{\text{ruthenium(IV)}} CH_3CH_2CHO$$

State the type of reaction and explain your answer.

……[1]

[Total: 7]