CATHOLIC JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATIONS
Higher 2

CANDIDATE NAME

CLASS 2T

CHEMISTRY 9647/02

Paper 2 Structured Questions **Tuesday 21 August 2012**
2 hours

Candidates answer on the Question Paper.
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class in the boxes provided above.
Write in dark blue or black pen on both sides of the paper. **[PILOT FRIXION ERASABLE PENS ARE NOT ALLOWED]**
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. Write your answers in the space provided.
A Data Booklet is provided.
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 of the question.

For Examiner's Use			
Paper 1			**/ 40**
Paper 2	**Q 1**	**/ 12**	
	Q 2	**/13**	
	Q 3	**/21**	
	Q 4	**/12**	
	Q 5	**/14**	**/ 72**
Paper 3	**Q 1**	**/20**	
	Q 2	**/20**	
	Q 3	**/20**	
	Q 4	**/20**	
	Q 5	**/20**	**/ 80**
Total			**/ 192**

This document consists of **17** printed pages and **0** blank page.

[Turn over

Eggshells are rich in calcium carbonate and make good plant fertilisers to replenish calcium, an essential nutrient in plant growth. The eggshells are normally crushed and sprinkled around the plants. The shells will slowly decompose and enrich the soil. The decomposition of $CaCO_3$(s) may be represented as:

$CaCO_3$(s) ® CaO(s) + CO_2(g)

In the laboratory, all Group II carbonates, ***M***CO_3, can be decomposed by heating to give the corresponding oxide, ***M***O, and carbon dioxide, CO_2.

You are to design an experiment to investigate how the rate of decomposition of Group II carbonates varies down the group.
In addition to the standard apparatus available in a school laboratory for gas collection, you are provided with the following materials,

- samples of carbonates of magnesium, calcium, strontium and barium,
- a stopwatch

(a) Briefly describe how you would measure the rate of decomposition of the different carbonates in order to enable comparison.

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(b) Draw a diagram of the apparatus and experimental set up that you would use to carry out the experiment. Show clearly the following:

- the apparatus used to heat the carbonate, and
- how the carbon dioxide will be collected.

Label each piece of apparatus used, indicating its size or capacity.

[2]

(c) The temperature of the Bunsen flame varies depending on the ratio of the fuel to oxygen burnt. Besides keeping to the same fuel to oxygen ratio, suggest how you would control another factor in the heating to ensure a fair comparison of the rate of decomposition of different carbonates.

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(d) Other than the use of safety goggles, state one hazard that must be considered when planning the experiment and suggest how you would keep this risk to a minimum.

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(e) With reference to the apparatus in **(b)**, show how you would calculate the mass of each carbonate used in the experiment.
[M_r: $MgCO_3$ = 84.3; $CaCO_3$ = 100.1; $SrCO_3$ = 147.6; $BaCO_3$ = 197.0]

[2]

[Turn over

(f) Draw a table with appropriate headings (and units) to show the data you would record and the values you would calculate in order to plot a suitable graph to show the variation in the rates of decomposition of the carbonates.

Sketch, and explain, the shape of the graph you would expect from your results. Label clearly the axes.

Explanation:

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[Total: 12]

2 **(a)** Carbon dioxide is used in beverage carbonation. Cylinders of pressurised carbon dioxide are used to produce carbonated drinks. One such cylinder has an internal volume of 3.0 dm^3 and contains 4.6 kg of carbon dioxide.

(i) Calculate the pressure (in Pascals) the carbon dioxide gas would exert inside the cylinder at 28 °C.

(ii) To find the pressure of a fixed amount of carbon dioxide gas under certain conditions, the van der Waals' equation given below should be used.

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

Without further calculation, explain how the pressure obtained using the van der Waals' equation would differ from that in **(a)(i)**.

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[3]

(b) Real gases like carbon dioxide can be liquefied at low temperatures just by applying pressure. Gases can be liquefied by pressure alone if the temperature is below their critical temperature, T_c. At temperatures above T_c, the gas cannot be liquefied, regardless of the pressure applied. The critical temperature of carbon dioxide is 31.1 °C.

(i) Explain why real gases like carbon dioxide can be liquefied just by applying pressure.

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(ii) By considering structure and bonding, suggest a value for the critical temperature of methane and give a reason for your choice.

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(c) Beyond the critical temperature and pressure, carbon dioxide exists as a supercritical fluid, a state that resembles a gas but has density closer to that in the liquid phase. Carbon dioxide is now well established as a solvent for use in extraction.

(i) Suggest a reason why supercritical carbon dioxide is preferred as a solvent to extract caffeine from solid coffee over organic solvents like benzene.

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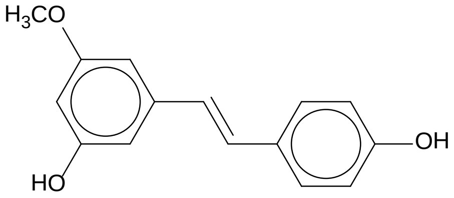
(ii) Suggest why small amounts of ethanol need to be added to supercritical carbon dioxide to increase the solubility of polyphenols for extraction. An example of a polyphenol is shown below.



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[2]

(d) Ethanedioate ions, $C_2O_4^{2-}$, can be oxidised by hot acidified aqueous potassium manganate(VII) to form carbon dioxide.

(i) Draw the structure of ethanedioate ions, $C_2O_4^{2-}$, and give the bond angle around the central carbon atom.

(ii) Construct a balanced equation for the reaction between ethanedioate ions and hot acidified potassium manganate(VII).

(iii) 1.63 g of a salt, $KHC_2O_4 \cdot H_2C_2O_4$, was dissolved in distilled water and made up to 250 cm^3 solution. Calculate the volume of 0.020 mol dm^{-3} $KMnO_4$ required to react with 20.0 cm^3 of the $KHC_2O_4 \cdot H_2C_2O_4$ solution.
[M_r of $KHC_2O_4 \cdot H_2C_2O_4 = 218.1$]

[4]

(e) **(i)** The reaction between acidified potassium manganate(VII) and ethanedioate ions is usually carried out at a higher temperature of 60 °C. Suggest why the rate of this reaction is slow at room temperature.

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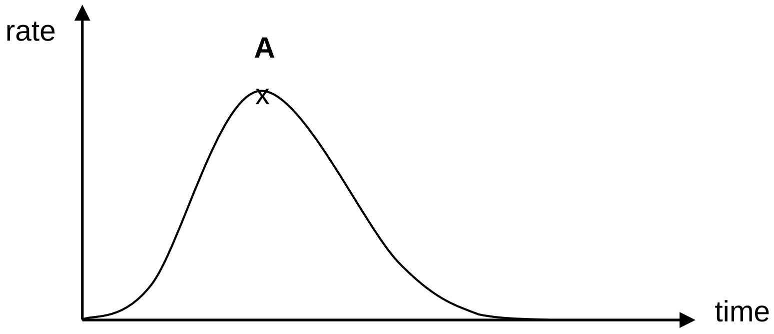
The graph of rate against time for the reaction between acidified potassium manganate(VII) and ethanedioate ions is shown below.



(ii) Suggest the species responsible for the increase in rate of reaction before point **A**, and identify the property which enables it to act as a catalyst in this reaction.

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[2]

[Total: 13]

3 Iron is the fourth most common element in the Earth's crust, and has many applications throughout the history of mankind. In nature, iron exists in many different mineral ores, consisting of iron in either +2 or +3 oxidation state. In prehistoric era, iron compounds were more commonly used as pigment without further purification. Limonite, which has the general formula of $FeO(OH){\cdot}nH_2O$, was used as a yellow pigment as early as 10 000 B.C.

(a) **(i)** Complete the electronic configuration of Fe^{3+}.

$1s^2$ ……………………..…………………

(ii) Briefly explain why iron in mineral ores is found in variable oxidation states, but for s-block elements, for example calcium, there is usually only one oxidation state.

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(b) A mineralogist dissolved 100 g of a certain pure limonite in concentrated HC*l* to form a yellow solution. It was found that 3.2 mol of HC*l* had reacted based on the equation,

$$FeO(OH).nH_2O + 4HCl \text{ ® } FeCl_4^- + (n+2)H_2O + H^+$$

(i) State the formula of this limonite (with n as an integer): ……………………….

(ii) Suggest the shape of $FeCl_4^-$: ………………….……………..

(iii) Explain, with reference to $FeCl_4^-$, why transition element complexes are coloured.

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[5]

(c) In recent times, with much better understanding of chemistry, iron and its compounds are widely used as catalysts and reagents in synthesis of chemicals. In particular, the ferrate(VI) ion, FeO_4^{2-}, is a strong oxidising agent that is used in green chemistry and water purification due to its non-toxic by-products.

Ferrate(VI) ions are not stable in acidic conditions and easily oxidise water to give oxygen. Hence, they are often produced in an alkaline medium.

Some $E^\ominus$ data of chlorate(I) and ferrate(VI) ions are given below.

$FeO_4^{2-} + 8H^+ + 3e^- \rightleftharpoons Fe^{3+} + 4H_2O$	$E^\ominus = +2.20$ V
$FeO_4^{2-} + 4H_2O + 3e^- \rightleftharpoons Fe(OH)_3 + 5OH^-$	$E^\ominus = +0.80$ V
$2ClO^- + 4H^+ + 2e^- \rightleftharpoons Cl_2 + 2H_2O$	$E^\ominus = +1.63$ V
$ClO^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$	$E^\ominus = +0.89$ V

(i) By selecting relevant $E^\ominus$ data from the *Data Booklet* and using the information above, explain with suitable calculation,

I why ferrate(VI) ions are not stable in acidic conditions,

II why it is feasible to form potassium ferrate(VI), K_2FeO_4, by reacting KC*l*O with $Fe(OH)_3$ in the presence of KOH.

(ii) Hence write a balanced overall equation for the formation of K_2FeO_4**.**

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(iii) Would you expect an acidified solution of K_2FeO_4 to be a stronger or weaker oxidising agent compared to an acidified solution of $KMnO_4$? Support your answer with relevant $E^\ominus$ values from the *Data Booklet*.

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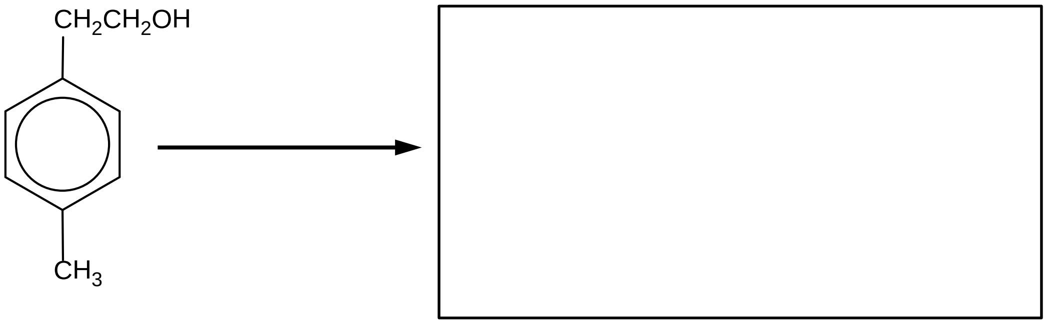
(iv) Hence draw the structure of the possible organic product formed when hot acidified purple K_2FeO_4 reacts with the following compound and suggest the expected observations.



Observations: ……………………………………………………………………………………

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[8]

(d) White light contains all the colours in the visible spectrum. Each of these colours is associated with a certain wavelength, l . The formula relating energy and wavelength is,

$$E = \frac{hc}{\lambda}$$

where $h = 6.626 \times 10^{-34}$ J s,

$c = 3.00 \times 10^{8}$ m s^{-1}

l has the unit of m.

Wavelength, l (10^{-9} m)	**Colour of light**
400	Violet
450	Blue
500	Green
550	Yellow
600	Orange
650	Red

(i) By considering the appearance of green iron(II) compounds and yellow iron(III) compounds, state the colour of light absorbed for these compounds.

Iron(II) ……………………………… Iron(III) ………………………………

(ii) Hence, calculate the energy associated with the respective colours absorbed.

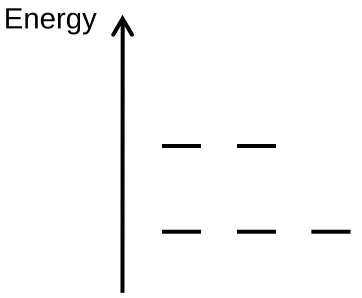
Energy of colour absorbed by

Iron(II) compounds: ……………………….

Iron(III) compounds: ……………………….

(iii) Using your answer in **(d)(ii),** complete the diagram below to show the relative energies of the d-orbitals, and the electronic distribution of the metal ion in each compound. In each case, label clearly the energy required for the promotion of an electron from the lower energy d-orbitals to the higher energy d-orbitals.

Assume that all electrons occupy the lower energy orbitals before the higher energy orbitals.

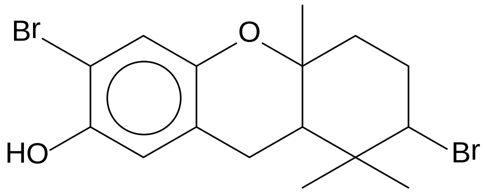


Iron(II) compound

Iron(III) compound

[5]
[Total: 21]

4 Cymobarbatol is an antimutagenic agent isolated from the marine algae *Cymopolia barbata*. The structure of cymobarbatol is shown below.



Cymobarbatol

(a) Name **two** functional groups, other than phenyl and ether, which are present in the cymobarbatol molecule.

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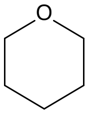
(b) Identify the chiral carbons in cymobarbatol molecule by placing an asterix (*) against each chiral carbon on the structure above. [1]

(c) Draw the structural formula of each organic product formed when cymobarbatol is treated with the following reagents.

In each reaction, assume that the  ring remains unaltered.

(i) ethanolic NaOH, heated under reflux

(ii) concentrated ethanolic NH_3, heated in a sealed tube

[2]

[Turn over

(d) Cymobarbatol will also react with aqueous NaOH under reflux condition.

(i) Given that one mole of cymobarbatol reacts with two moles of aqueous NaOH, write a balanced equation for this reaction.

(ii) When the bromine atoms in cymobarbatol are replaced by iodine atoms, how would you expect the rate of its hydrolysis reaction to compare to that of cymobarbatol? Explain your answer.

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(iii) Describe the expected observations when aqueous $AgNO_3$, followed by concentrated aqueous ammonia, is subsequently added to the resultant mixture in **(d)(i)**. Explain your answer with relevant equations.

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[7]

[Total: 12]

5 There are a number of structural isomers of molecular formula $C_nH_nO_2$. In particular, one of the isomers, **B**, is used as a tincture in perfumes and as a food additive.

(a) To find the value of *n*, a 1.00 g sample of **B** was burned in an excess of oxygen, and the gases produced were first passed through a U-tube containing P_4O_{10} (to absorb the water vapour) and then bubbled through concentrated NaOH(aq). The P_4O_{10} in the U-tube **increased** in mass by 0.529 g.

(i) Write an equation for the reaction of P_4O_{10} with water vapour and state the pH of the resultant solution.

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(ii) Suggest why anhydrous $CaCl_2$ **cannot** be used in place of P_4O_{10} in the U-tube.

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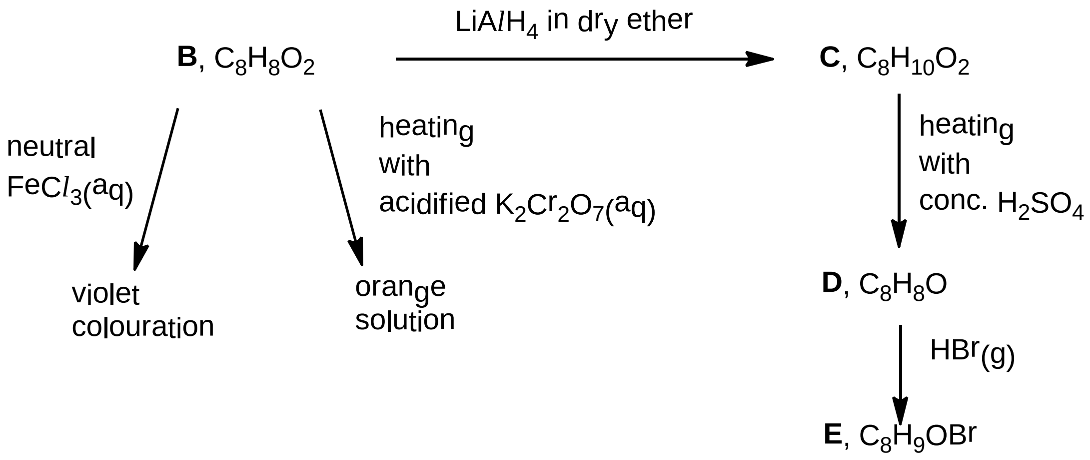
(iii) Calculate the number of moles of water produced.

(iv) Use the above data to show that the value of *n* = 8.

[5]

(b) A reaction scheme involving compound **B** is shown below.



(i) Based on the above information, draw three possible structural isomers of **B**, which are labelled as **B1**, **B2** and **B3** in the boxes below.

B1	**B2**	**B3**

(ii) Based on the structural isomer **B1**, draw the structural formulae of **C**, **D** and **E**.

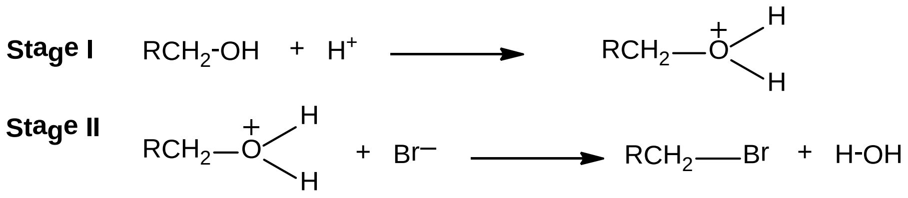
C	**D**	**E**

[6]

(c) A structural isomer of **D**, C_8H_8O, which is labelled as **F**, contains a C-O-C bond. **F** does **not** react with HBr(g).

(i) Suggest a structural formula of **F**.

(ii) Although **F** does not react with HBr(g), it can react with concentrated HBr(aq). The reaction of **F** with concentrated HBr(aq) is similar to the reaction of primary alcohols with concentrated HBr(aq). The process involves the following two stages:



Suggest a mechanism for the **Stage II** process in the reaction of **F** with concentrated HBr(aq), including curly arrows to denote movement of electrons, and all charges. You do **not** need to draw the 3-dimensional representation of the molecules involved.

[3]

[Total: 14]