



CATHOLIC JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATIONS
Higher 2

CANDIDATE
NAME

CLASS

CHEMISTRY

Paper 3 Free Response

9647/03

THURSDAY 25 AUGUST 2011

2 Hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.

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 any **four** questions.

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.

At the end of the examination, fasten all work securely together.

For Examiner's Use		
Paper 3	Q 1	20
	Q 2	20
	Q 3	20
	Q 4	20
	Q 5	20
Total	80	

This document consists of **11** printed pages and **1** blank page.

[Turn over]

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Answer any **four** questions.

- 1** Nanochemistry is an important field of science that explores the use of extremely small particles that have diameters about thousand times thinner than the width of a human hair. Transition metals and its compounds are often the subject of interest in nanochemistry, as many useful properties are improved at this ultra small scale.

(a) Nano-sized iron(III) hydroxide, $\text{Fe}(\text{OH})_3$ exists as a precipitate and can be used as a catalyst to remove aqueous arsenate(V) ions, AsO_4^{3-} from contaminated water. The $\text{Fe}(\text{OH})_3$ with the adsorbed arsenate(V) ions are filtered off, and undergoes an ion-exchange with the arsenate(V) ions removed and $\text{Fe}(\text{OH})_3$ precipitate recovered unchanged.

- (i)** State the electronic configuration of iron in $\text{Fe}(\text{OH})_3$.
- (ii)** State the type of catalysis and briefly explain why transition metal compounds are suitable for such catalysis.
- (iii)** Suggest why the use of nano-sized particles will improve this catalytic property.

[4]

(b) Nano-sized iron(II) hydroxide exists as a complex solid with the formula $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2$ and has no net dipole moment.

- (i)** State the colour and coordination number of the complex iron(II) hydroxide.
- (ii)** Suggest the structure of the complex solid, given that it is a non-polar species.

[4]

(c) Nano-sized iron(II) hydroxide, $\text{Fe}(\text{OH})_2$ is often unstable, due to oxidation by water even though oxygen is not present. The pH of the solution remains largely unchanged, a reddish-brown precipitate and effervescence are observed.

- (i)** Identify the reddish-brown precipitate and suggest an equation for this reaction.
- (ii)** The reaction is not expected to occur under standard conditions and can be considered reversible. Suggest a possible reason why it does in fact occur for an opened bottle of $\text{Fe}(\text{OH})_2$ suspended in water.

[3]

(d) Nano-sized iron(II) hydroxide, $\text{Fe}(\text{OH})_2$ is used for the purpose of removal of toxic selenite(IV) ions, SeO_3^{2-} from water, by reducing selenite(IV) ions to selenium, Se.

- (i)** Construct a half-equation for the reduction of SeO_3^{2-} to Se in an alkaline solution.
- (ii)** In water that is heavily contaminated with CN^- ions, iron(II) hydroxide appears to dissolve. State the type of reaction that is occurring and construct a balanced chemical equation for it.
- (iii)** By selecting $E^\ominus$ values from the *Data Booklet*, and given that the redox potential of the reaction in **(i)** is -0.37 V , explain and justify if SeO_3^{2-} can be removed from water contaminated with CN^- ions.

[5]

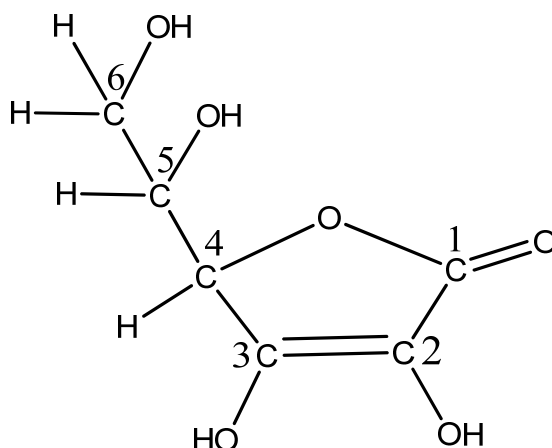
- (e) Electrochemistry is also widely used in the synthesis of nano-sized materials. For instance, anodising of aluminium can be conducted to produce extremely small aluminium oxide.

Describe with the aid of a labelled diagram, the set-up used during anodising of aluminium, and the reactions occurring at each electrode. [4]

[Total: 20]

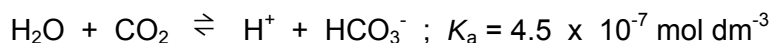
- 2 (a) **Vitamin C**, $C_6H_8O_6$, is also known as ascorbic acid. It is a monobasic acid and has a pK_a of 4.10. When a 500 mg tablet of **Vitamin C** is swallowed, it dissolves in the stomach before being absorbed into the bloodstream. The stomach may be assumed to contain 1.0 dm^3 of 0.10 mol dm^{-3} hydrochloric acid

- (i) Estimate the percentage of **Vitamin C** that is ionised in the stomach under these conditions. State the assumptions made during the calculation.
 (ii) The structure of **Vitamin C** is



State which hydrogen atom in the molecule is likely to be acidic, and justify your choice.

- (iii) Blood has a pH of 7.35 and is saturated with carbon dioxide of concentration $3.2 \times 10^{-3} \text{ mol dm}^{-3}$. The equilibrium reaction,

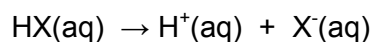


acts as a buffer.

- (I) Explain clearly how this buffering action minimizes the change in pH on the addition of either acid or alkali.
 (II) Calculate the concentration of HCO_3^- ions in blood.
 (III) Explain **qualitatively** how the extent of ionisation of **Vitamin C** changes as it moves from the stomach to the bloodstream.

[8]

- (b) The acid strength of the hydrogen halides in aqueous solution may be related to the enthalpy change for the process,



where X is a halogen.

- (i) By constructing a suitable energy cycle and using the data in the following table, calculate the enthalpy change of this process for hydrofluoric acid.

Reaction	$\Delta H^\ominus / \text{kJ mol}^{-1}$	
	X = F	X = Cl
$\text{HX(aq)} \rightarrow \text{HX(g)}$	+48	+18
$\text{HX(g)} \rightarrow \text{H(g)} + \text{X(g)}$	+568	+432
$\text{H(g)} \rightarrow \text{H}^+(\text{g}) + \text{e}^-$	+1312	+1312
$\text{X(g)} + \text{e}^- \rightarrow \text{X}^-(\text{g})$	-328	-349
$\text{H}^+(\text{g)} \rightarrow \text{H}^+(\text{aq})$	-1091	-1091
$\text{X}^-(\text{g)} \rightarrow \text{X}^-(\text{aq})$	-515	-381

- (ii) Hence calculate the enthalpy change of this process for hydrochloric acid.
 (iii) Comment on your answers in relation to the strength of hydrofluoric acid ($K_a = 6.7 \times 10^{-4} \text{ mol dm}^{-3}$) and hydrochloric acid.

[4]

(c) Each Group II element forms an iodate(V) with the formula $M(\text{IO}_3)_2$. The iodates(V) have many uses, for example, calcium iodate is an oxidant added to lotions and ointments as an antiseptic and deodorant.

- (i) Draw the structural formula of the iodate(V) ion, indicating the likely bond angle.
- (ii) Draw a dot-and-cross diagram corresponding to this structure.
- (iii) The iodates(V) readily decompose on heating giving oxygen gas as one of the two products formed.
 - (I) Write a likely equation for the decomposition of $M(\text{IO}_3)_2$.
 - (II) Predict and explain how the thermal decomposition of these iodates(V) varies down the group. The decomposition of the iodates(V) is similar to the decomposition of the nitrates(V).
- (iv) The percentage purity of a sample of barium iodate(V), $\text{Ba}(\text{IO}_3)_2$ can be determined by the following method.

0.105 g of $\text{Ba}(\text{IO}_3)_2$ ($M_r = 487$) is added to excess aqueous potassium iodide, KI in acidic medium. The iodine liberated is then titrated against aqueous sodium thiosulfate pentahydrate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ($M_r = 248.2$) of concentration, 24.8 g dm^{-3} .

25.00 cm^3 of the thiosulfate is used for the titration. By using the reactions given below, and the information described above, calculate the percentage purity of the sample of barium iodate(V).

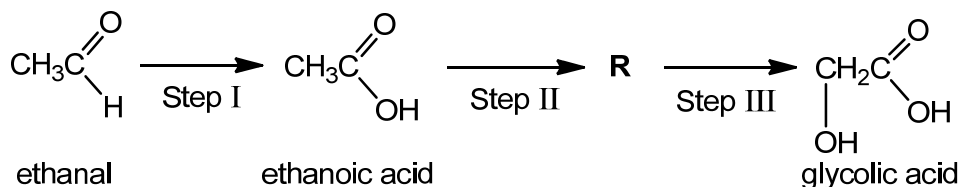
[In the presence of acid and the iodide ions, the following reaction takes place quantitatively: $\text{IO}_3^- + 5 \text{I}^- + 6 \text{H}^+ \rightarrow 3 \text{I}_2 + 3 \text{H}_2\text{O}$. The reaction between iodine and thiosulfate is given by the equation: $\text{I}_2 + 2 \text{S}_2\text{O}_3^{2-} \rightarrow 2 \text{I}^- + 2 \text{S}_4\text{O}_6^{2-}$].

[8]

[Total: 20]

- 3 Ethanal occurs commonly in coffee and fruits. In humans, ethanal is formed by oxidation of ethanol consumed from alcoholic drinks and is believed to cause hangovers. Ethanal can be used as precursors of other important organic compounds. In addition, ethanal can also be used to synthesize glycolic acid, which is used in various skin-care products.

(a) In the synthesis of glycolic acid as shown below,



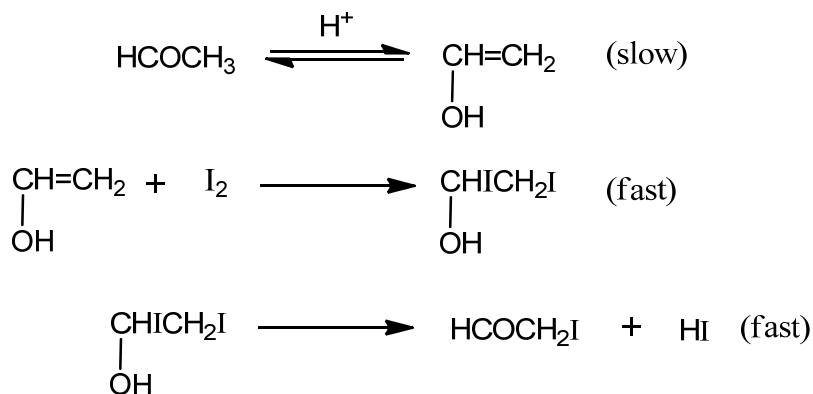
- (i) state the reagents and conditions for Step II and Step III, and identify the intermediate **R**, and
 (ii) explain the difference in acidity between glycolic acid and ethanoic acid.

Two molecules of glycolic acid can react with one another under suitable conditions with the loss of two water molecules.

- (iii) Suggest a possible structure for the compound formed.

[6]

(b) Ethanal and iodine reacts in an acidic medium according to the mechanism as shown.



- (i) State the type of reaction that occurs in each of the fast step.
- (ii) Suggest the rate equation for the reaction, and hence the units of the rate constant.
- (iii) Suggest how the rate of reaction between ethanal and iodine can be determined experimentally.
- (iv) Sketch an appropriate graph and show how the order of reaction with respect to ethanal can be obtained experimentally.
- (v) Explain how the rate of reaction would change if bromine is used instead of iodine.

[9]

(c) Ethanol can first be oxidised to ethanal by the mild oxidising agent formed when iodine reacts with the hydroxide ions in the alkaline medium. The ethanal formed then reacts with iodine in an alkaline medium via a different mechanism.

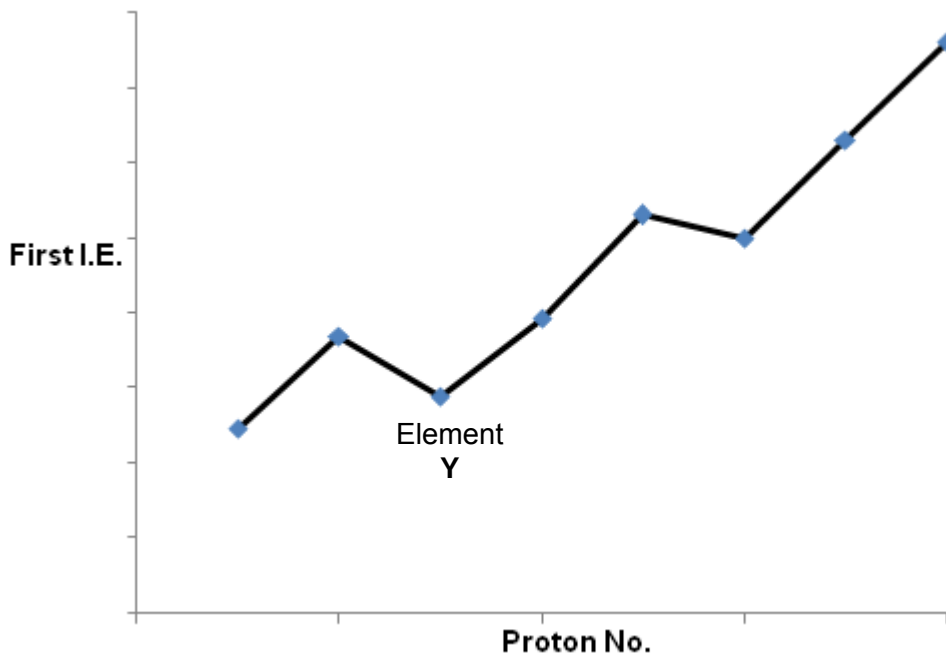
- (i) Draw the structure of all organic compounds formed in the reaction when ethanal reacts with iodine in an alkaline medium.
- (ii) Write an ionic equation to show how iodine reacts with the hydroxide ions and state the type of reaction that is occurring. Hence, suggest the identity of the oxidising agent.

[5]

[Total: 20]

- 4 (a) The elements **Y** and **Z** are in Period 3 and can be one of the following: Mg, Al, Si and P.

The following graph depicts the variation in first ionization energy (I.E.) of the elements across Period 3.



- (i) Based on the above data, identify element **Y**. Explain why the first ionization energy of **Y** is lower than that of the element preceding it.

When NaOH is added to a solution containing ions of **Y**, a white precipitate is formed initially. When an excess of NaOH is added, the precipitate dissolves to give a colorless solution.

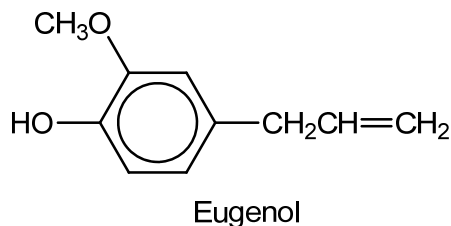
The oxide of **Y** reacts with both aqueous hydrochloric acid and sodium hydroxide.

Element **Z** has a chloride and an oxide and both react vigorously with water to form a solution of pH = 2.

- (ii) By identifying the white precipitate, construct ionic equations for the formation of this precipitate and its subsequent dissolving in NaOH.
- (iii) State the identity the element **Z** and hence give the equation for the reaction between the chloride of **Z** and water.

[7]

- (b) **Eugenol** is an important compound in spices like cinnamon and cloves.
[The CH_3O group is inert and can be disregarded in this question.]



- (i) Explain why **Eugenol** is more soluble in aqueous sodium hydroxide than in water.
- (ii) Draw the structures of **all** the possible organic products formed when **Eugenol** reacts with each of the following reagents.
 - (I) cold, dilute manganate(VII) ions
 - (II) aqueous bromine

[4]

- (c) A hydrocarbon **A** has the molecular formula of $\text{C}_{10}\text{H}_{14}$. When **A** is treated with hot aqueous acidified KMnO_4 , benzoic acid is formed. When reacted with bromine in the presence of ultraviolet light, **A** produced **four** isomeric monobromo compounds with the formula $\text{C}_{10}\text{H}_{13}\text{Br}$. Upon heating with alcoholic NaOH , two of the monobromo compounds **B** and **C** gave the **same** compound which can exist as a pair of geometric isomers, **D** and **E**. Heating **B** with aqueous NaOH produces compound **F** which does not react with acidified potassium dichromate(VI). Suggest the structures of **A-F**, explaining your reasoning.

[9]

[Total: 20]

- 5 Proteins are found in every living organism and are made up of many amino acids linked together in a long chain.

Below are some of the naturally occurring amino acids.

Amino Acid	Abbreviated name	Structure
Aspartic acid	Asp	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CO}_2\text{H} \\ \\ \text{CH}_2\text{CO}_2\text{H} \end{array}$
Leucine	Leu	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CO}_2\text{H} \\ \\ \text{CH}_2\text{CH}(\text{CH}_3)_2 \end{array}$
Tyrosine	Tyr	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CO}_2\text{H} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{OH} \end{array}$
Lysine	Lys	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CO}_2\text{H} \\ \\ (\text{CH}_2)_4\text{NH}_2 \end{array}$
Cysteine	Cys	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CO}_2\text{H} \\ \\ \text{CH}_2\text{SH} \end{array}$
Methionine	Met	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CO}_2\text{H} \\ \\ (\text{CH}_2)_2\text{SCH}_3 \end{array}$
Serine	Ser	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CO}_2\text{H} \\ \\ \text{CH}_2\text{OH} \end{array}$

- (a) Draw the structural formula of the tripeptide *leu-met-lys*, stating clearly the type of linkage formed. [2]
- (b) Proteins structures can be classified into primary, secondary, tertiary and quaternary structures. The tertiary structure of proteins enables it to adopt a 3-dimensional shape which allows it to be soluble in water and be mobile within the cell.
- (i) Identify 2 amino acids from the list above which would be present in proteins enabling it to dissolve in water.
- (ii) Hence, state the interactions between the selected amino acids and water molecules.

[2]

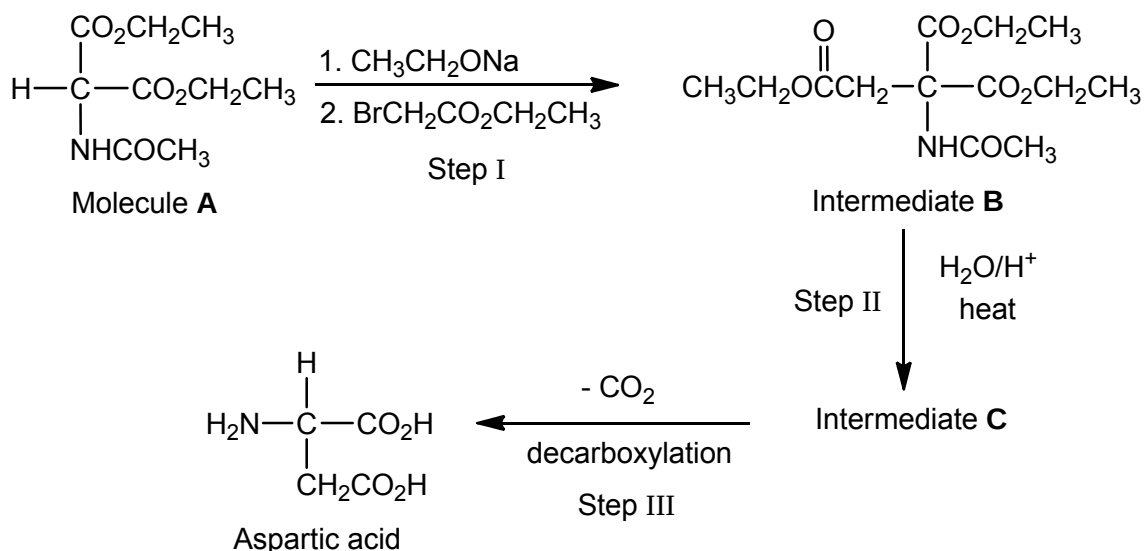
(c) Compound **X** is one of the amino acids shown in the table. 1 mol of **X** reacts with solid sodium to form 1 mol of hydrogen gas. In addition, 1 mol of **X** only react with 1 mol of aqueous NaOH. Compound **X** has pK_a values of 2.21 and 9.15. When acidified potassium dichromate(VI) is added to compound **X** and distilled, the product formed gives an orange precipitate, compound **Y** with 2,4-DNPH.

- Explain, with the aid of an equation if applicable, why the amino acid **CANNOT** be cysteine.
- Deduce the structures of compound **X** and **Y**, explaining the reactions involved by writing appropriate equations.
- Draw the two forms of compound **X** which exist at pH 2.21.

[8]

(d) A general method for the preparation of α -amino acids is the amidomalonate synthesis.

Below is an example of the synthesis of aspartic acid using this method:



In Step I, the reaction begins with a treatment of molecule **A** with a base, followed by the attack of a primary alkyl halide by a nucleophile. Step II is an acid hydrolysis to form intermediate **C**, followed by decarboxylation in Step III.

- Identify the base used to attack molecule **A** in Step I, explaining its property as a base.
- By determining the nucleophile, suggest the type of reaction undergone in Step I.
- Draw the structure of intermediate **C**.
- By using the amidomalonate method described above, the amino acid, methionine can also be produced. State the appropriate intermediate formed after Step I and the halogenoalkane which can be used to form methionine.
- This method usually yields an optically inactive mixture. Explain why the mixture is optically inactive.

[8]

[Total: 20]