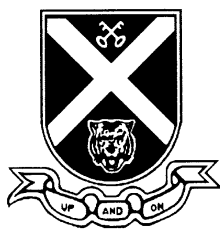


ST ANDREW'S JUNIOR COLLEGE**JC2 Preliminary Examinations****Chemistry****Higher 2****9647/03****Paper 3****12 September 2011****2 hours**

Candidates answer on separate paper.

Additional Materials: Writing paper, Data Booklet

READ THESE INSTRUCTIONS FIRST:

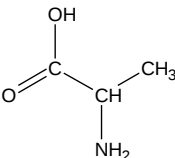
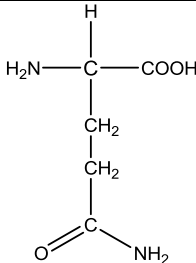
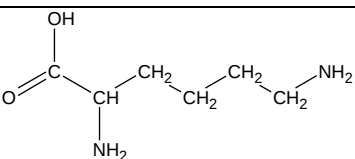
Write your name and civics group on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.

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.

Answer any **four** questions

- 1** Deoxyribonucleic acid, DNA, is a nucleic acid that contains the genetic instructions used in the development and functioning of all known living organisms. The main role of DNA molecules is the long-term storage of information. DNA is often compared to a set of blueprints, like a recipe or a code, since it contains the instructions needed to construct other components of cells, such as proteins. Part of human DNA is formed using alanine, glutamine and lysine (which are listed in the following table).

Amino Acid	Structure	Isoelectric point
Alanine (Ala)		6.01
Glutamine (Gln)		5.65
Lysine (Lys)		9.74

- (a)** With reference to these three different types of amino acids only,
- describe and explain with the aid of a diagram what is meant by the *primary* structure of proteins given that the pH of the bloodstream is 7.3.
 - describe how an excess amount of ethanol in the bloodstream would affect the function of proteins.

[5]

- (b)** Ethanol, which is a commonly used organic solvent, has been used as the starting component in the synthesis of a variety of organic by-products. State the reagents and conditions needed to convert ethanol into:

- 2-hydroxypropanoic acid
- methanoic acid

[5]

[Turn Over

- 1 (c) Drink driving is the act of driving a motor vehicle with blood levels of alcohol in excess of a specified limit. Hence, with drink driving becoming an increasingly prevalent issue, the breathalyser technology has become more precise and one of the cruder initial prototype was based on the oxidation process of ethanol using acidified potassium dichromate (VI).

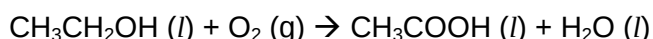
- (i) Derive the ion electron half equation for the oxidation of ethanol to ethanoic acid. Hence, using relevant information from the *Data Booklet*, write a balanced equation for the oxidation of ethanol using acidified potassium dichromate (VI).
- (ii) When potassium dichromate (VI) is reacted with sodium hydroxide, a colour change from orange to yellow was observed. Suggest the identity of the yellow solution.
- (iii) Explain why compounds of chromium are usually coloured.

The driver would be asked to exhale a deep breath of air at a volume of 1 dm^3 , 36.9°C and 101325 Pa into the breathalyser. If the colour of the dichromate (VI) ions changes, the driver would then be sent to the hospital for further testing, before being charged with drink driving.

- (iv) Given that the breathalyser contains 15.0 cm^3 of $0.017 \text{ mol dm}^{-3}$ acidified potassium dichromate (VI), calculate the minimum volume of vaporised ethanol needed to turn all the potassium dichromate (VI) green.

[8]

- (d) Ethanol, upon prolonged exposure to the atmosphere, would eventually oxidise to form ethanoic acid according to the following equation.



Use the following data, to construct an energy cycle to calculate the standard enthalpy change for the oxidation of ethanol.

	$\Delta H^\theta / \text{kJ mol}^{-1}$
Enthalpy change of combustion of ethanol	-1371
Enthalpy change of combustion of ethanoic acid	-876

[2]

[Total: 20]

[Turn Over]

2 (a) Explain the following observations.

- (i) The fifth ionisation energy of chlorine is a smaller numerical value than the fifth ionisation energy of sulfur.
- (ii) 1 mole of hydrogen fluoride gas occupies a smaller volume than 1 mole of hydrogen chloride gas at low temperature and pressure.
- (iii) The different relative rate of formation of precipitate upon reacting chloromethane and bromomethane with aqueous sodium hydroxide, followed by acidified silver nitrate.

[7]

- (b) During the catalytic cracking of long chain and branched alkane molecules, fragments of chained or branched molecules could be formed. An example of these fragments is 2-methylpropene.

Outline the mechanism for the reaction of 2-methylpropene and liquid iodine monochloride, ICl .

[2]

- (c) 2-chloro-2-methylpropan-1-ol, can also be formed when aqueous chlorine is used in place of liquid iodine monochloride. It is then reacted with acidified potassium manganate (VII) solution to form compound **HA**.

- (i) Write out the displayed formula of compound **HA**.

FA1 was made by dissolving 1.0×10^{-3} mol of **HA** into 1 dm^3 of deionised water. At 40°C , **FA1** was found to have a 14.1% degree of dissociation. ($K_w = 2.92 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$)

- (ii) Calculate the concentration of **HA** after dissociation. Hence, calculate the acid dissociation constant of **HA** at 40°C .

- (iii) 10.0 cm^3 of **FA1** was titrated against a solution of $5 \times 10^{-4} \text{ mol dm}^{-3}$ NaOH .

Calculate the pH of the resulting solution, named **FA2**, after 10.00 cm^3 of NaOH solution was added.

- (iv) When 10.00 cm^3 of $2.5 \times 10^{-4} \text{ mol dm}^{-3}$ $\text{Ca}(\text{OH})_2$ was added to 20.0 cm^3 of **FA2**, a salt solution was formed.

(1) Calculate the concentration of the salt solution formed.

(2) Write a balanced equation to show why the salt solution is alkaline.

(3) Hence, calculate the pH of the resulting solution taking into account the dissociation of water.

[11]

[Total: 20]

[Turn Over]

- 3 (a) Compound **B** has the molecular formula $C_{11}H_{14}O_2$. It is sparingly soluble in water. It does not decolourise aqueous bromine. Upon heating with acidified potassium manganate (VII) solution, it does not decolourise the purple solution, but forms two organic products, compounds **C** and **D**.

Compound **C** forms a violet colouration when neutral iron (III) chloride solution is added. Upon reaction of **C** with aqueous bromine (in a stoichiometric ratio of 1:3), it forms a white precipitate and copious white fumes which turn moist blue litmus paper red.

Compound **D** is able to rotate plane-polarised light. Upon combustion with excess oxygen, 0.1 mol of compound **D** produces 34.7 dm^3 of gas at 150°C and 101325 Pa. The volume is halved when the gaseous products was passed through anhydrous calcium chloride. Compound **D** also reacts with sodium carbonate powder, in a ratio of 2:1, to give effervescence. It is then reacted with lithium aluminium hydride in dry ether to form compound **E**.

Compound **E** is then reacted with excess concentrated sulfuric acid, and subsequently decolourises acidified potassium manganate (VII) to form compound **F** with the evolution of a gas. Compound **F** has also been found to give orange crystals with 2, 4 dinitrophenylhydrazine.

Deduce the structures of compounds **B**, **C**, **D**, **E**, and **F**. Explain the chemistry of the reactions described, writing balanced equations where appropriate.

[14]

- (b) (i) Sketch a labelled diagram to show how the standard cell potential of the electrode systems between iodide and acidified potassium manganate (VII) is measured. Hence, calculate the standard cell potential using relevant information from the *Data Booklet*.
- (ii) By considering appropriate E° values, explain how Fe^{2+} acts as a homogeneous catalyst for the reaction in **b(i)**.

[6]

[Total: 20]

[Turn Over]

- 4 (a) An experiment was set up to determine the mechanism of 2-bromo-3-methylpentane, **FA3**, of concentration 0.01 mol dm^{-3} and sodium hydroxide, **FA4**, of concentration 0.01 mol dm^{-3} .

The results were tabulated in the following table:

Experiment number	Vol. of FA3 used / cm^3	Vol. of FA4 used / cm^3	Vol. of ether used / cm^3	Rate / $\text{mol dm}^{-3} \text{ s}^{-1}$
1	1.00	29.00	20.00	8.17×10^{-7}
2	1.00	35.00	14.00	9.86×10^{-7}
3	7.50	2.50	40.00	5.28×10^{-7}

- (i) Use the data in the table to deduce the order of reaction with respect to 2-bromo-3-methylpentane and sodium hydroxide.
- (ii) Write an overall rate equation for the reaction between 2-bromo-3-methylpentane and sodium hydroxide.
- (iii) Hence, outline the mechanism between 2-bromo-3-methylpentane and sodium hydroxide.
- (iv) Calculate the rate constant for the reaction, including the units.
- (v) By using the collision theory of reaction kinetics, describe with the aid of a suitable diagram, the effect on the rate when a catalyst is added into the reaction mixture.

[10]

- (b) 2-bromo-3-methylpentane reacts with hot aqueous sodium hydroxide to give alcohol **G**.
 0.04 mol of **G** and 0.02 mol of ethanoic acid were dissolved in 100 cm^3 of ether and allowed to react in the presence of concentrated sulphuric acid.
 At equilibrium, 10.0 cm^3 of the mixture required 24.80 cm^3 of 0.08 mol dm^{-3} potassium hydroxide for complete neutralisation.

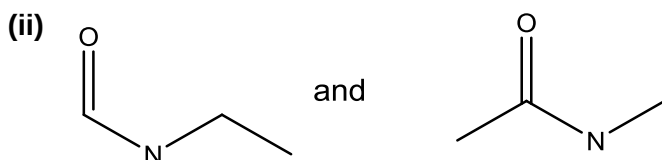
- (i) Write a balanced equation between **G** and ethanoic acid.
- (ii) Hence, calculate the value of K_c .
- (iii) Given that the reaction is favourable at high temperatures only, deduce if the reaction is exothermic or endothermic. Hence, explain the effect on the position of the equilibrium with increasing temperature.

[6]

[Turn Over

4. (c) Suggest methods by which the following pairs of compounds could be distinguished from each other by chemical tests. The distinguishing may rely on a preliminary breaking-up of compounds, and subsequent testing of the reaction products.

(i) 2-bromo-3-methylpentane and 3-bromo-2-methylpentane



[4]

[Total: 20]

5. (a) Group II carbonates are unstable to heat.

Describe and explain the trend in the thermal decomposition of the carbonates of the Group II elements Mg to Ba, writing an equation for any reaction that occurs.

[3]

- (b) The following table lists some of the K_{sp} values for barium salts.

Anion	K_{sp}
Carbonate	2.58×10^{-9}
Hydroxide	2.55×10^{-4}
Sulfate	1.08×10^{-10}

- (i) Write an expression for the K_{sp} of BaCO_3 .
- (ii) Calculate the pH of **FA5**, which is a saturated solution of Ba(OH)_2 .
- (iii) Given that 100 cm^3 of $0.001 \text{ mol dm}^{-3}$ barium nitrate and 100 cm^3 of $0.001 \text{ mol dm}^{-3}$ sulfuric acid was mixed, calculate the mass of precipitate formed.

[5]

[Turn Over]

5. (c) (i) What do you understand by the term *lattice energy*?
- (ii) Using the following data, together with appropriate data from the *Data Booklet*, construct an energy cycle to calculate the lattice energy of BaO.

	$\Delta H^\theta / \text{kJ mol}^{-1}$
Enthalpy change of 1 st electron affinity of oxygen	-140
Enthalpy change of 2 nd electron affinity of oxygen	+798
Enthalpy change of atomisation of barium	+182
Enthalpy change of formation of barium oxide	-548

[4]

- (d) Compound **H** has a molecular formula C_8H_{14} . It decolourises bromine solution in the dark. Upon reacting with hot acidified potassium manganate (VII) solution, it forms compounds **I**, **J** and **K**.

Compound **I** forms an orange precipitate with 2,4-dinitrophenylhydrazine. After reacting **I** with alkaline iodine solution and acidifying the resulting mixture, it forms **K** and a yellow precipitate. **K** can also be formed by boiling ethanitrile with sulfuric acid. 0.104 g of compound **J**, a dicarboxylic acid, neutralises 25.0 cm^3 of **FA5** in (b)(ii).

Deduce the structures of compounds **H**, **I**, **J**, and **K**. Explain the chemistry of the reactions described, writing equations where appropriate.

[8]

[Total: 20]

~~~ END OF PAPER ~~~