ST ANDREW'S JUNIOR COLLEGE

JC2 Preliminary Examinations

Chemistry

Higher 2 **9647/03**

Paper 3 **18 September 2012**

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.

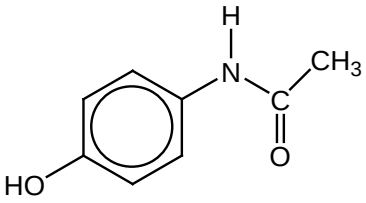
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **12** printed pages **including** this page.

Answer **any 4** questions.

1. Paracetamol and aspirin are well known drugs to treat pain and to reduce fever.

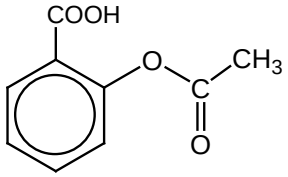
(a) The following are structures of paracetamol and aspirin:



Paracetamol

pK_a = 9.5

M*r* = 151.0



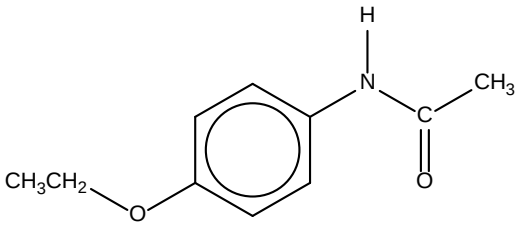
Aspirin

pK_a = 3.5

M*r* = 180.0

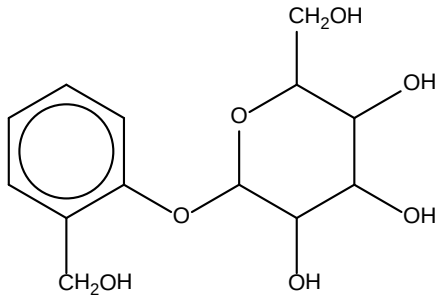
(i) Explain the difference in the pK_a values of aspirin and paracetamol.

(ii) Phenacetin is an analgesic whose use has largely declined due to its carcinogenic properties. Starting from paracetamol, show the steps involved in the synthesis of phenacetin. In your answer, include the reagents and conditions required for each step, as well as the structure of the intermediate involved.



Phenacetin

(iii) Salicin is an anti-inflammatory agent that is closely related in chemical make-up to aspirin. Suggest a chemical test that could be used to distinguish salicin from aspirin. Write a balanced equation for the reaction that occurred.



Salicin

1. **(a)** **(iv)** Aspirin is supplied as a crystalline solid. A standard solution of aspirin may be made by dissolving aspirin in an organic solvent. Explain why water is not used as a suitable solvent.

[9]

(b) **(i)** Write an expression for the acid dissociation constant, K_a, of aspirin.

(ii) A tablet of aspirin is swallowed into the stomach. Given that the pH of the stomach is 1, calculate the percentage of aspirin molecules that remain undissociated in the stomach.

[3]

(c) 0.270 g of aspirin and 0.121 g of paracetamol are dissolved in 30 cm^3 of ethanol and titrated against 0.100 mol dm^{-3} aqueous sodium hydroxide, using 1 to 2 drops of two indicators, methyl red and phenolphthalein.

x cm^3 of aqueous sodium hydroxide is required to change the colour of the methyl red and a further y cm^3 of aqueous sodium hydroxide is needed to change the colour of phenolphthalein.

(i) Explain why both indicators are added in small amounts.

(ii) Calculate the initial pH of the mixture, assuming the initial pH is from aspirin ***only***.

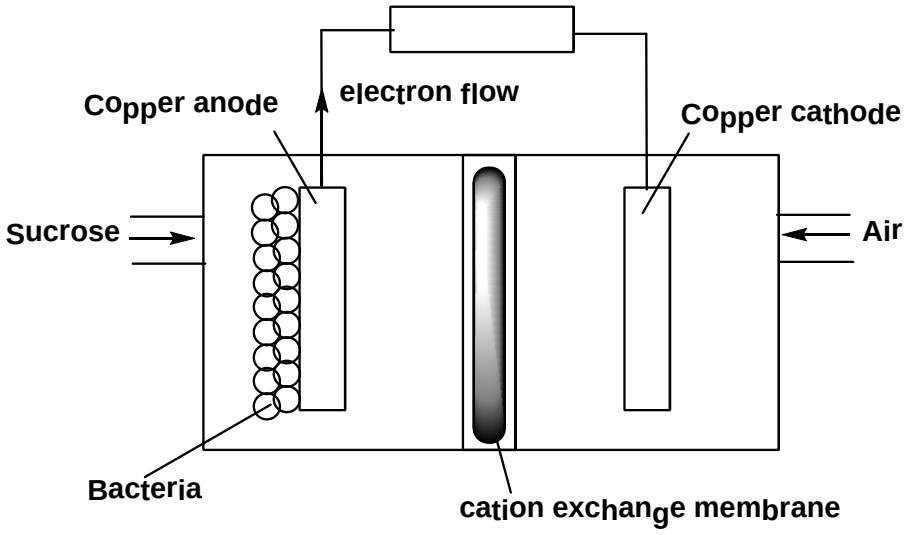
(iii) Calculate the values of x and y.

(iv) Sketch the shape of the pH curve during this titration.

[8]

[Total 20]

2. (a) In an effort to provide a sustainable system for waste treatment and energy production, scientists are currently working in the area of microbial fuel cell (MFC) technology. MFC is a device that converts chemical energy to electrical energy by the catalytic reaction of microorganisms such as bacteria. A typical microbial fuel cell consists of an anode and a cathode separated by a cation exchange membrane which only allows cations to pass through. Copper has been used extensively as electrodes in MFCs as shown in the following diagram.



On the anode side, bacteria grow and proliferate, forming a dense cell aggregate known as a biofilm that adheres to the MFC's anode. In the course of their microbial metabolism, the bacteria act as catalysts for converting the organic substrate such as sucrose, $C_{12}H_{22}O_{11}$, into carbon dioxide. At the cathode, in the presence of air, steam is produced.

(i) Write balanced half-equations, occurring at each electrode, when the MFC discharges.

(ii) Given the electromotive force of the MFC is 1.25 V, calculate the reduction potential of the carbon dioxide / sucrose half-cell.

(iii) Suggest with a reason, the effect on the standard cell potential if the pH of the electrolyte at the cathode is increased.

[5]

2. (b) Copper reacts with 50% nitric (V) acid, HNO_3, to give a blue solution, containing complex ion **A** and a brown gas **B**. If the solution containing **A** is diluted and sodium hydroxide solution added cautiously, a gelatinous blue precipitate **C** is obtained, which if heated, forms a black solid **D**.

Addition of concentrated aqueous ammonia solution to **A** gives a deep blue solution that contains the ion **E**. Addition of concentrated hydrochloric acid to **E** gives a yellow solution of the ion **F**, which on dilution with water gives a solution containing the same ion **A**.

If the brown gas **B** is passed into water, a mixture of acids **G** and **H** is formed in a disproportionation reaction.

(i) Identify **A – H**. Construct balanced equations, with state symbols, for the formation of **C**, **D**, **E** and **F**.

(ii) Draw a dot-and-cross diagram of nitric (V) acid, HNO_3. With reference to the Valence Shell Electron Repulsion theory, explain the shape about the nitrogen atom.

[15]

[Total 20]

3. Hydrazine, N_2H_4, is a colourless, volatile and corrosive liquid with an ammonia-like odour. It is well known for its use in various rocket fuels and to prepare gas precursors used in air bags.

(a) Hydrazine decomposes thermally, liberating a large amount of heat and a large volume of gaseous products in the following ways:

$3\ N_2H_4\ (l)$ à $4NH_3\ (g) + N_2\ (g)$ $\quad \Delta H_r = +111.8\ kJ\ mol^{-1}$

$N_2H_4\ (l)$ à $N_2\ (g) + 2H_2\ (g)$ $\quad \Delta H_r = z\ kJ\ mol^{-1}$

(i) Write the equation that corresponds to the enthalpy change of formation of ammonia.

(ii) Hence, using your answer to **(a)(i)**, the above reactions and relevant data from the *Data Booklet*, construct an energy cycle to calculate z.

[3]

(b) Hydrazine can be synthesised by the Raschig process, where Cl_2 gas and NH_3 gas are heated under certain conditions in the presence of sodium hydroxide.

(i) State the change in oxidation number of nitrogen atom during the Raschig process.

(ii) Predict the product of Cl_2 in the process.

(iii) Construct an ionic equation for the Raschig process.

[3]

3. **(c)** The **Wolff–Kishner reduction** is a chemical reaction that reduces a carbonyl compound (ketone or aldehyde) to its corresponding alkane. Condensation of the carbonyl compound with hydrazine forms a hydrazone intermediate, and treatment with a base induces the formation of the corresponding alkane.

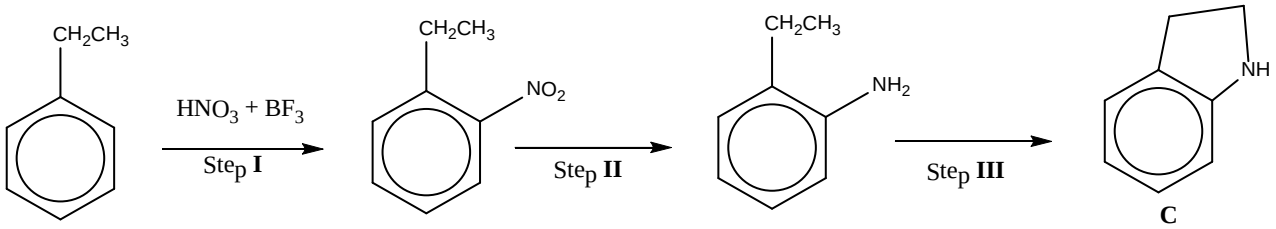
Below shows the synthesis of propane from propanone via the **Wolff-Kishner reduction**.

Carbonyl compounds **A** and **B** both undergo the **Wolff-Kishner reduction** separately forming ethylbenzene.

A is found to give a silver mirror with Tollen's reagent but **B** does not.
Draw the displayed formulae of **A**, **B** and the hydrazone intermediate formed with **A**.

[3]

3. **(d)** Ethylbenzene undergoes the following reaction scheme producing **C**.



For Step **I,**

(i) outline the mechanism of the reaction.

(ii) with reference to the structure of BF_3, explain how BF_3 helps in the mechanism.

For Step **II,**

(iii) state the reagents and conditions required.

For Step **III**,

(iv) an intermediate is involved. Draw the structure of the intermediate.

(v) state the reagents and conditions required to form the intermediate.

(vi) name the two types of reactions involved.

(vii) explain why the yield of **C** is low.

[11]

[Total 20]

4. **(a)** A 25.0 cm^3 solution containing 0.00500 mol dm^{-3} of potassium chloride, KC*l*, and 0.800 mol dm^{-3} of potassium chromate (VI), K_2CrO_4, was titrated against 0.100 mol dm^{-3} aqueous silver nitrate. White precipitate was first formed.

When $\boldsymbol{v}$ cm^{-3} of aqueous silver nitrate was added, a trace amount of red precipitate, Ag_2CrO_4, was observed.

K_{sp} for AgC*l* = 1.6 x 10^{-10} mol^2 dm^{-6}
K_{sp} for Ag_2CrO_4 = 9.0 x 10^{-12} mol^3 dm^{-9}

(i) Assuming no dilution was caused by the addition of aqueous silver nitrate, calculate the concentration of chloride present in the mixture when the first trace of red precipitate was observed.

(ii) Calculate the percentage of chloride precipitated when the first trace of red precipitate was observed.
Hence, suggest the role of potassium chromate (VI) in the solution.

[4]

Potassium chlorate (I), KC*l*O, and potassium chlorate (V), KC*l*O_3, can be easily made by the electrolysis of saturated potassium chloride solution under different conditions.

During the electrolysis, inert electrodes are used and the products at the electrodes are allowed to mix.

(b) **(i)** Using the *Data booklet,* describe and explain the reactions occurring at the cathode and the anode.

(ii) Write a balanced equation to show the formation of KC*l*O_3.

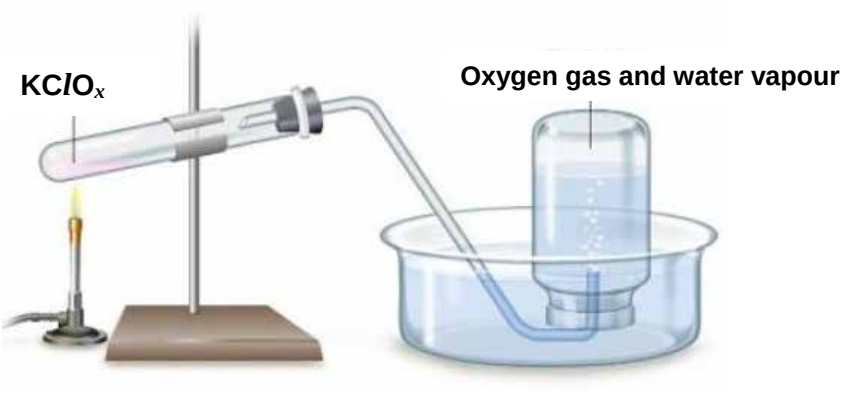
(iii) How do you ensure that potassium chlorate (I), KC*l*O, is not formed.

(iv) A current of 3 A was passed through the electrolytic cell. Calculate the time required to obtain 30 g of KC*l*O_3.

[9]

4. **(c)** 2.12 g of potassium chlorate, $KClO_x$, was heated and decomposed completely to give oxygen gas and potassium chloride as shown in the diagram below.

The oxygen gas produced was collected over water at 22 ^oC at a total pressure of 100525 Pa. The volume of gas collected was 650 cm^3, and the vapour pressure of water at 22 ^oC is 2800 Pa.



(i) Write the balanced equation, with state symbols, of the decomposition reaction of $KClO_x$.

(ii) Calculate the amount of O_2 produced. Hence, deduce the value of x in $KClO_x$.

[5]

(d) Compare and explain the ease of decomposition between $KBrO_x$ and $KClO_x$.

[2]

[Total 20]

5. The following information was taken from the side of a carton of milk.

How long does your milk keep?

30°C	½ day
18°C	1 day
5°C	4 days

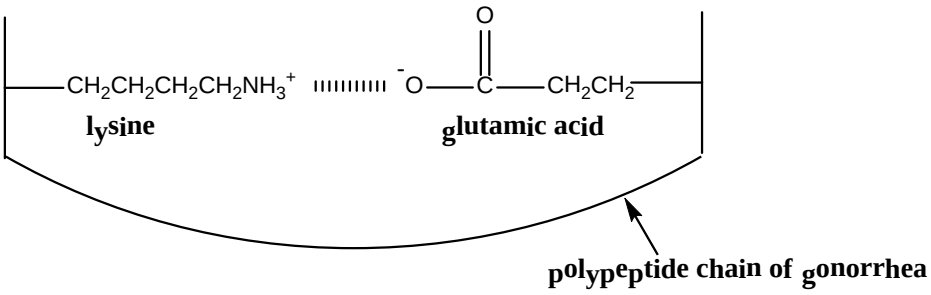
(a) (i) The souring of milk is a chemical reaction. How is the rate of this reaction related to the length of time the milk keeps?

(ii) Explain how this rate varies with temperature. Draw an energy distribution diagram to illustrate your answer.

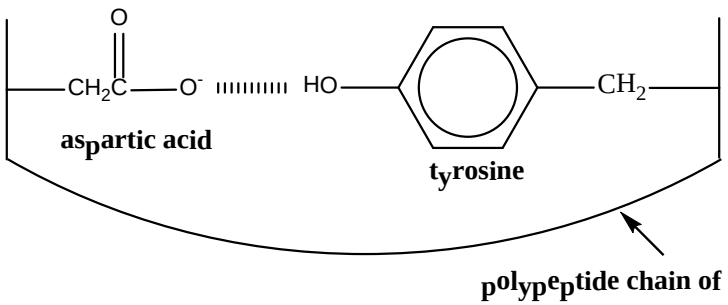
[4]

(b) (i) For each of the following cases, explain with the help of a diagram, how the following types of side chain interactions are affected during each denaturation process.

I. $AgNO_3$ is used as disinfectants to prevent gonorrhea infections in the eyes of new born infants.



II. Ethanol solutions are used as disinfectants on the skin as it can penetrate the bacterial cell wall and denature the proteins inside the cell.



5. **(b)** **(ii)** Which of the treatments, $AgNO_3$ in case **I** or ethanol in case **II**, is likely to affect the alpha helix structure? Explain.

[6]

(c) Compound **B** ($C_{10}H_{14}O_2$) is optically active and does not react with aqueous sodium carbonate. However, it dissolves slowly in aqueous sodium hydroxide.

B reacts with hydrogen bromide but will not decolourise acidified potassium dichromate (VI). **B** decolourises aqueous bromine to form white precipitate **C** ($C_{10}H_{12}O_2Br_2$), together with dense white fumes.

Upon treatment with concentrated sulfuric acid at 170°C, **B** gives compound **D** ($C_{10}H_{12}O$) which exists as a pair of geometric isomers. **D** gives compound **E** ($C_{10}H_{14}O_3$) on addition of cold, dilute alkaline potassium manganate (VII) solution.

E reacts with phosphorus pentachloride to give copious fumes and compound **F** ($C_{10}H_{12}OCl_2$).

Suggest a structure for each lettered compound, **B** – **F**, and explain the reactions involved.

[10]

[Total 20]

~~~ END ~~~