Name ________________________ **Class: 13S**________ **Reg Number:** _____

MERIDIAN JUNIOR COLLEGE
JC 2 Preliminary Examination
Higher 2

Chemistry 9647/03

Paper 3 Free Response **17 September 2014**

2 hours

Additional Materials: *Data Booklet*
Writing Paper

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Answer 4 out of 5 questions in this paper.

Begin each question on a fresh page of writing paper.

Fasten the writing papers behind the given **Cover Page for Questions 1, 2 & 3** and **Cover Page for Questions 4 & 5** respectively.

Hand in Questions **1**, **2** & **3** and **4** & **5** **separately**.

You are advised to spend about 30 minutes per question only.

INFORMATION FOR CANDIDATES

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

You are reminded of the need for good English and clear presentation in your answers.

This document consists of **12** printed pages *(excluding the cover pages for answer scripts)*.

Answer any 4 out of 5 questions in this paper.

Begin each question on a ***fresh sheet*** *of writing paper.*

1 The following tables show some standard enthalpies change of solution, $\Delta H^{\ominus}_{sol}$, regarding some Group I chlorides and Group II carbonates, as well as their corresponding solubility in water under standard conditions.

Group I chlorides	NaC*l*	KC*l*	RbC*l*
$\Delta H^{\ominus}_{sol}$ / kJ mol^{-1}	+3.9	+17.2	+16.7
Solubility / mol per 100 cm^3 of water	0.615	0.481	0.781

Group II carbonates	$MgCO_3$	$CaCO_3$	$SrCO_3$
$\Delta H^{\ominus}_{sol}$ / kJ mol^{-1}	–25.3	–12.3	–3.4
Solubility / mol per 100 cm^3 of water	1.26×10^{-4}	1.30×10^{-5}	7.45×10^{-6}

Use relevant data from the tables above, if applicable, to answer the following questions.

(a) It is a well-known fact that the solubility of Group II carbonates decreases down the group.

(i) Using the $\Delta H^{\ominus}_{sol}$ data from **both** tables, comment on whether $\Delta H^{\ominus}_{sol}$ is a good predictor for the solubilities of salts in water.

(ii) Calculate the solubility product of calcium carbonate, stating its units.

[3]

(b) **(i)** Assuming a 100% efficient system, calculate the maximum temperature change that could take place when potassium chloride is dissolved in 100 cm^3 of water. State clearly whether the temperature increases or decreases.

(ii) The enthalpy change of solution assumes that an infinitely dilute solution is formed when one mole of ionic compound dissolves in water. Based on this assumption, suggest a reason to account for the maximum temperature change not being achieved in practice other than the system is not 100% efficient.

[3]

(c) The standard entropy change of solution, $\Delta S^{\ominus}_{sol}$, of sodium chloride is $+42.6 \text{ J mol}^{-1} \text{ K}^{-1}$.

(i) Calculate the standard Gibbs free energy change of solution, $\Delta G^{\ominus}_{sol}$, of sodium chloride, explaining why sodium chloride is soluble.

(ii) The standard Gibbs free energy change of solution, $\Delta G^{\ominus}_{sol}$, of magnesium chloride is $-126.3 \text{ kJ mol}^{-1}$. Some standard enthalpy change of formation, $\Delta H^{\ominus}_{f}$, related to magnesium chloride are provided below.

Substances	$MgCl_2(s)$	$Mg^{2+}(aq)$	$Cl^-(aq)$
$\Delta H^{\ominus}_{f}$ / kJ mol^{-1}	–641.6	–462.0	–167.5

Calculate the $\Delta S^{\ominus}_{sol}$ of magnesium chloride. Hence, explain with reasoning, whether the sign of $\Delta S^{\ominus}_{sol}$ obtained is as expected.

[5]

(d) The melting point of $CaCO_3$ is 825 °C and its thermal decomposition temperature is 837 °C.

(i) The melting point of $BeCO_3$ is 54 °C. Briefly explain why the melting point of $BeCO_3$ is much lower than that of $CaCO_3$.

(ii) By quoting data from the *Data Booklet*, predict whether the thermal decomposition temperature of $SrCO_3$ would be higher or lower than that of $CaCO_3$.

[5]

(e) Using relevant data from the *Data Booklet* and information given below, construct an energy cycle to calculate the lattice energy of $MgCO_3$.

enthalpy change of formation of magnesium carbonate = $-1096 \text{ kJ mol}^{-1}$
enthalpy change of formation of CO_2 (g) = -393 kJ mol^{-1}
enthalpy change of atomisation of magnesium = $+148 \text{ kJ mol}^{-1}$
sum of first and second electron affinities of oxygen = $+657 \text{ kJ mol}^{-1}$
$CO_2 (g) + O^{2-} (g) \longrightarrow CO_3^{2-} (g)$; $\Delta H_1 = -778 \text{ kJ mol}^{-1}$

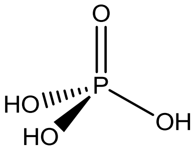
[4]

[Total: 20]

[Turn Over

2 This question is about phosphoric acid.

(a) Phosphoric acid, H_3PO_4, is a triprotic acid and its structure is given below.



phosphoric acid

The pK_a values of the two successive dissociations of H_3PO_4 at 25 °C are as shown.

	pK_{a1}	pK_{a2}
Phosphoric acid	2.1	7.2

Small quantities of H_3PO_4 are used to impart the sour taste to many soft drinks. A typical can of soft drink with density of 1.00 g cm^{-3} contains 0.05 % by mass of H_3PO_4.

(i) Briefly explain why the pK_{a2} of phosphoric acid is higher than its pK_{a1}.

(ii) Calculate the concentration, in mol dm^{-3}, of phosphoric acid in the soft drink.

(iii) Hence, by considering only the first dissociation of H_3PO_4, determine the pH of this soft drink. Assume that the acidity of the soft drink arises only from H_3PO_4.

(iv) Suggest, with reasoning, a suitable indicator that can be used to detect the first end point of the titration between H_3PO_4 and sodium hydroxide.

[5]

(b) A buffer solution was prepared by mixing 50 cm^3 of 1.00 mol dm^{-3} Na_2HPO_4 and 50 cm^3 NaH_2PO_4 of unknown concentration. When 5.00 x 10^{-3} moles of sodium hydroxide was added to the buffer solution, the pH increased to 7.38.

Determine the unknown concentration of NaH_2PO_4 used to prepare the buffer. [2]

(c) When pure H_3PO_4 undergoes dehydration, another phosphorus-containing acid **Y** is produced. The addition of calcium hydroxide to **Y** produces a white precipitate, $Ca_2P_2O_7$.

Draw the structure, clearly indicating the shape of **Y**. [1]

[Turn Over

(d) Porous ceramics containing calcium phosphate, $Ca_3(PO_4)_2$, are commonly used in the manufacture of artificial teeth.

Given: K_{sp} of $Ca_3(PO_4)_2 = 1.21 \times 10^{-26}$ mol^5 dm^{-15}.

(i) Calculate the solubility of calcium phosphate in water.

(ii) Some calcium phosphate is dissolved into a solution of 0.50 g dm^{-3} calcium hydroxide, $Ca(OH)_2$, to produce a saturated solution. Calculate the solubility of $Ca_3(PO_4)_2$ in the saturated solution.

(iii) Comment on the difference in the solubility values of calcium phosphate in **(d)(i)** and **(d)(ii)**.

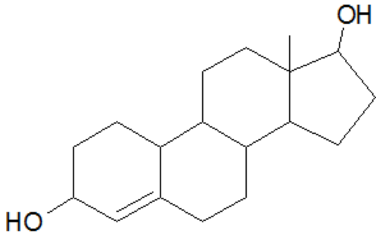
[6]

(e) When concentrated phosphoric acid and concentrated sulfuric acid are reacted separately with solid potassium bromide, different bromine-containing substances **A** and **B** are formed respectively.

When concentrated sulfuric acid is reacted with solid potassium chloride, the product formed reacted with manganese(II) oxide to give a chlorine-containing substance **C**. Substances **C** and **B** are structurally similar.

For the following questions, you need to use the actual identity of A, B and C in your answers.

(i) Bolandiol is a banned synthetic anabolic steroid.



bolandiol

Draw the structural formulae of the organic products formed when bolandiol is heated with:

1. **A**.
2. **B**.

(ii) Write the equation when **C** is reacted with hot concentrated NaOH.

(iii) By considering the reactions of **C** and I_2 with thiosulfate, $S_2O_3^{2-}$, explain the difference in the oxidising strength of **C** and I_2 in terms of their oxidation numbers. Include any relevant equations in your answers.

[6]

[Total: 20]

[Turn Over

3 In mammals including humans, nitrogen monoxide NO is an important cellular signaling molecule. It acts as a powerful vasodilator.

(a) Although elements in the same group can be said to have similar chemical properties, there are variations, e.g. in reactivity or products formed in a reaction.

For example, nitrogen is the only element in Group V that does not readily produce an oxide when burnt in oxygen or air. Nitrogen monoxide is produced only when temperatures typically found in fuel engines are reached.

Down Group V, there is also an increased tendency for the element to possess metallic properties. This is due to the changes in ionisation energies and electronegativity down the group.

(i) Suggest a reason why nitrogen monoxide is formed only when temperatures in fuel engines are reached.

(ii) State and explain how the first ionisation energy of the element changes down the group.

(iii) How does the changes in ionisation energies and electronegativity down the group account for the increasing metallic behaviour of the Group V elements?

[4]

(b) At 800 K, nitrogen monoxide reacts with hydrogen as shown below:

$$2H_2(g) + 2NO(g) \longrightarrow 2H_2O(g) + N_2(g)$$

In a series of experiments, the initial rate of the above reaction was investigated with varying partial pressures of the reactants. The following data was obtained:

Experiment	$p(H_2)$ / atm	p(NO) / atm	initial rate / atm s^{-1}
1	0.64	1.60	1.50×10^{-7}
2	0.64	0.80	3.75×10^{-8}
3	0.32	1.60	7.50×10^{-8}

(i) On the same axes, sketch suitable graphs to illustrate clearly how the rate of reaction would vary with increasing partial pressures of H_2 and NO respectively.

(ii) Write down the rate equation in terms of the partial pressures, indicating clearly the units of the rate constant.

(iii) Based on the rate equation, the following mechanism was proposed for this reaction.

Step 1 $2NO \longrightarrow N_2O + O$
Step 2 $H_2 + O \longrightarrow H_2O$
Step 3 $H_2 + N_2O \longrightarrow H_2O + N_2$

Suggest which of the steps in the mechanism is therefore the rate determining step.

[4]

[Turn Over

(c) The following reduction potentials regarding nitrogen monoxide and its related compounds are relevant in this question.

	$E^\ominus$ / V
$NO_3^- + 3H^+ + 2e \rightleftharpoons HNO_2 + H_2O$	+0.93
$HNO_2 + H^+ + e \rightleftharpoons NO + H_2O$	+0.99
$2NO + 2H^+ + 2e \rightleftharpoons N_2O + H_2O$	+1.59
$N_2O + 2H^+ + 2e \rightleftharpoons N_2 + H_2O$	+1.77

(i) An excess of iron(II) sulfate was added to a solution of nitric(V) acid. Using the information provided, state which nitrogen-containing product would be produced.

(ii) Instead of the predicted product in **(c)(i)**, a dark brown iron(II) octahedral complex is formed in the reaction, whereby one molecule of nitrogen monoxide is involved in each unit of the cation. Suggest the formula of this compound.

(iii) Hence, by considering the structure of nitrogen monoxide, relative to the other possible nitrogen compounds, suggest a reason why the reaction stops at the production of nitrogen monoxide.

[3]

(d) Compound **F**, C_4H_5NO, is a neutral compound to form a series of compounds investigated for their possible vasodilation properties. By heating **F** in dilute H_2SO_4, compound **G** $C_4H_6O_3$ is obtained. In a separate one-step reaction, **F** is able to form **H** $C_4H_{11}NO$.

Compared to their solubility in water, compound **G** is more soluble in sodium hydroxide, whereas compound **H** is more soluble in dilute acid. When **G** reacts with PCl_5 and subsequently added to **H** in a 1:1 ratio, two possible isomers **J** and **K**, with a formula $C_8H_{15}NO_3$, are produced. Of the two, **J** is a neutral compound whereas **K** is not.

All the compounds **F**, **G**, **H**, **J** and **K**, produce a yellow precipitate with alkaline aqueous iodine.

Deduce the structures of **F**, **G**, **H**, **J** and **K**, clearly stating your reasoning. Include in your answer, the possible reagents and conditions needed to convert **F** to **H**.

[9]

[Total: 20]

4 (a) (i) Describe the reactions that occur when separate samples of sodium and phosphorous are heated in excess chlorine.

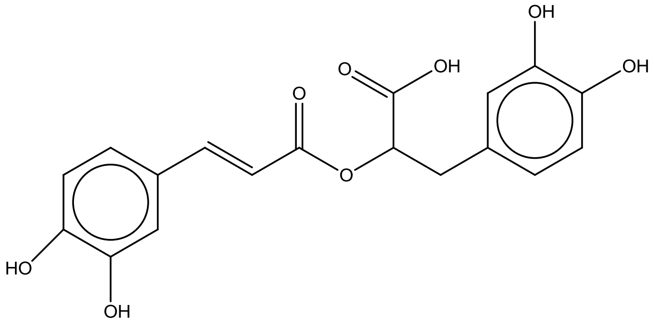
(ii) Describe the reaction of each of the resulting chloride with excess water, stating the approximate pH of the solution formed, and writing a balanced equation with state symbols for any reaction that takes place.

[4]

(b) Sulfur and chlorine can react together to form S_2Cl_2. When 1.35 g of this sulfur chloride reacted with water, a yellow solid was formed, together with a solution containing sulfurous acid and hydrochloric acid. The resulting solution required 20.00 cm^3 of 1.00 mol dm^{-3} silver nitrate for complete reaction.

Use the data above to deduce the equation for the reaction between S_2Cl_2 and water, and suggest the type of reaction. [2]

(c) Rosmarinic acid occurs in culinary herbs such as rosemary, sage and thyme



rosmarinic acid

(i) State the number of moles of HC*l* that will be formed when excess PCl_5 is added to one mole of rosmarinic acid.

(ii) Draw the structural formulae of the organic products produced when rosmarinic acid is reacted with hot KOH(aq).

(iii) Draw the structural formulae of the two compounds produced when rosmarinic acid is heated under reflux with acidified $Na_2Cr_2O_7$(aq). Suggest one test (stating reagents, conditions and observations) that would enable the two compounds to be distinguished from each other.

(iv) Rosmarinic acid produced an aromatic compound and a carbon-containing inorganic compound when heated under reflux with alkaline $KMnO_4$(aq) followed by dilute HC*l*.

Draw the displayed formula of the compound formed when the aromatic compound is treated with excess ethanoyl chloride.

[7]

[Turn Over

(d) Rosmarinic acid contains two organic groups with pK_a values lower than that of alcohol. Compare and explain the relative pK_a values of these three organic groups. [3]

(e) 1 mol of diol **P**, $C_4H_{10}O_2$, undergoes oxidation to produce 2 mol of yellow solid. **P** produces a mixture of 4 different products when heated with concentrated sulfuric acid. Three of the products, **W**, **X** and **Y** with the formula C_4H_6 are unsaturated compounds while product **Z** with formula $C_8H_{16}O_2$ is a saturated compound.

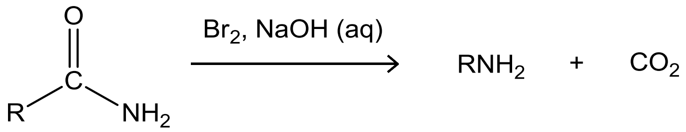
(i) State the reagents and conditions used for the oxidation reaction.

(ii) Suggest the structural formulae of **P**, **W**, **X**, **Y** and **Z**.

[4]

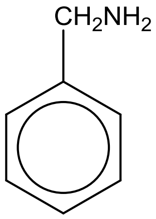
[Total: 20]

5 **(a)** An amine may be derived from an amide following a reaction known as the Hofmann rearrangement. In this reaction, a primary amide is treated with Br_2 and aqueous NaOH to yield the corresponding amine and CO_2 as a by-product.



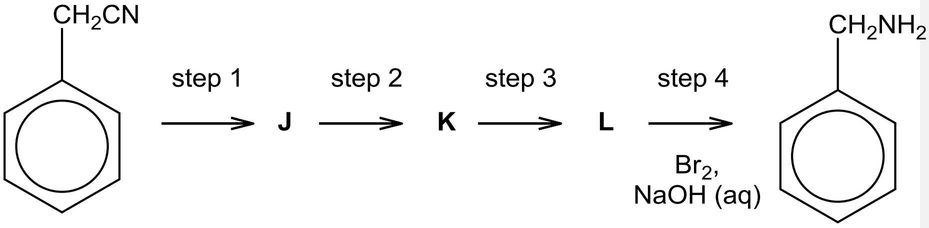
R = alkyl / phenyl

(i) Benzylamine is a compound used in topical creams and antifungal solutions.



benzylamine

Suggest reagents and conditions you would use in a four-step synthesis of benzylamine from phenylacetonitrile, using the Hofmann rearrangement as the final step. Identify the intermediates **J**, **K** and **L**.



phenylacetonitrile

(ii) In a laboratory experiment of the synthesis in **(a)(i)**, the carbon dioxide gas produced in step 4 was collected. Calculate the volume of gas collected at standard conditions when 0.468 g of phenylacetonitrile was used in the experiment.

[6]

(b) In the human body, carbon dioxide is dissolved in the bloodstream as carbonic acid, H_2CO_3. The carbonic acid is in equilibrium with hydrogen carbonate, HCO_3^-, which allows the blood to maintain the pH of the body at 7.4.

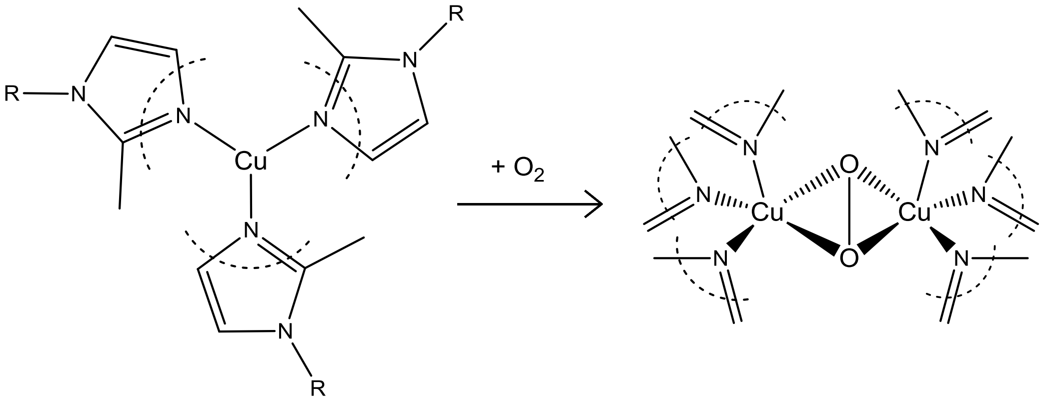
(i) Briefly describe how hydrogen carbonate, HCO_3^-, maintained relatively constant pH when the acid concentration in the bloodstream increases and decreases. Write any equations necessary to account for the observations.

(ii) Suggest another example of buffer in biological system.

[3]

(c) In the human bloodstream, the oxygen-carrying haemoglobin protein is red in colour due to iron being present. In certain crustaceans such as crabs, the oxygen-carrying protein is haemocyanin, where copper is involved.

Deoxyhaemocyanin is colourless. When it combines with oxygen as oxyhaemocyanin, the protein turns blue, giving crab's blood its characteristic blue colour.

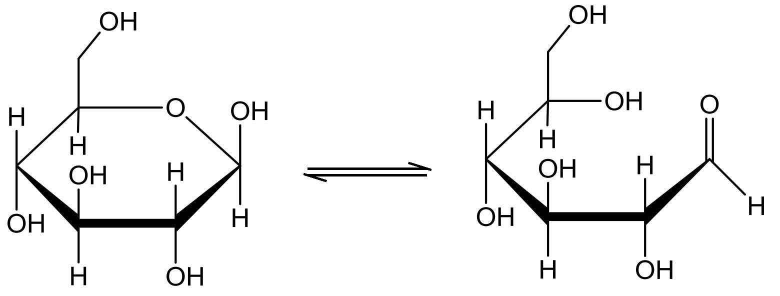


deoxyhaemocyanin - colourless

oxyhaemocyanin - blue

Suggest the oxidation states of copper in deoxyhaemocyanin and oxyhaemocyanin, and explain why oxyhaemocyanin is blue in colour whereas deoxyhaemocyanin is colourless. [4]

(d) Copper ions are present in Fehling's solution and can be used to test for "reducing sugars". Glucose, a basic form of sugar, has the following structure.



cyclic form of glucose

open-chain form of glucose

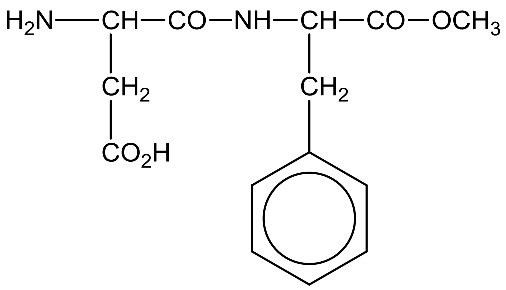
Glucose gives a positive test with Fehling's solution.

(i) Identify the functional group involved in the reaction and describe what is observed when Fehling's solution is added to glucose with heating.

(ii) Explain why glucose is classified as a "reducing sugar".

[2]

(e) *Aspartame* is a simple synthetic dipeptide used as a sweetening agent which is often sold under the trade names of *Nutrasweet* or *Equal*. It is 180 times as sweet as sugar. It is often used to sweeten soft drinks due to its relatively good solubility in water.



Aspartame

(i) Apart from the phenyl ring, name **four** different functional groups in the *aspartame* molecule.

(ii) Identify a functional group in *aspartame* which contributes to its solubility in water. Give a reason for your answer.

(iii) Aspartame is also not stable under low pH conditions. Draw the products formed when *aspartame* is reacted with hot aqueous hydrochloric acid.

Comment [M1]: Change to low pH since you are using hot acid for reaction.

[5]

[Total: 20]

End of Paper 3