Candidate Name: _____

Class	Adm No

H

millennia institute

2014 Preliminary Examination II
Pre-university 3

H2 CHEMISTRY

9647/03

Paper 3 Free Response

Tuesday, 23 Sep 2014

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet
Graph Paper

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
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 question.
At the end of the examination, fasten all your work securely together.

Begin each question on a fresh sheet of paper.

1. Lactic acid (2-hydroxypropanoic acid), also known as milk acid, is a chemical compound that plays a role in several biochemical processes.

(a) **(i)** **A** is an isomer of lactic acid. It rotates plane-polarised light and reacts with Fehling's solution to give a reddish brown precipitate. 0.01 mol of **A** reacts with sodium to give 0.24 dm^3 of hydrogen gas under room temperature and pressure conditions. Suggest a structural formula of **A**, giving reasons for your answer.

(ii) Compare the acidity of isomer **A** and lactic acid. Explain your answer.

[7]

(b) Lactic acid can undergo a condensation reaction in the presence of hot concentrated sulfuric acid to form a cyclic diester **B**, $C_6H_8O_4$.

$$2 \text{ Lactic acid } (l) \underset{\text{heat}}{\overset{\text{conc } H_2SO_4}{\rightleftharpoons}} \text{Diester } \mathbf{B} \ (l) + 2\ H_2O\ (l)$$

The system exists in *dynamic equilibrium*.

(i) Draw the structure of diester **B**.

(ii) Explain what is meant by the term *dynamic equilibrium*.

(iii) Write an expression for the equilibrium constant, K_C, for the reaction, stating its units.

(iv) In an experiment, 2.0 mol of lactic acid was allowed to reach equilibrium. Given that 95% of lactic acid has reacted at equilibrium and the total volume of the mixture remained constant at 200 cm^3, calculate the K_C for this reaction.

(v) In the reverse reaction, i.e. the hydrolysis of the diester **B**,

$$\text{Diester } \mathbf{B} \ (l) + 2\ H_2O\ (l) \longrightarrow 2 \text{ Lactic acid } (l)$$

the rate of reaction gradually increases at first, but subsequently it decreases. Explain why this is so.

[8]

(c) Lactic acid, along with ammonium hydrogen carbonate, $(NH_4)HCO_3$, is used in mosquito attractant.

Ammonium hydrogen carbonate is a solid which can decompose into ammonia, carbon dioxide and water.

(i) Write an equation, with state symbols, for the decomposition of ammonium hydrogen carbonate.

(ii) Using the enthalpy changes given in the table below, calculate the enthalpy change of reaction for the decomposition of $(NH_4)HCO_3$.

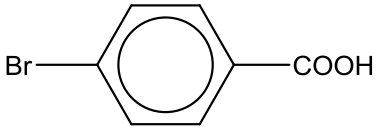
Compound	**Enthalpy change of formation / kJ mol^{-1}**
$(NH_4)HCO_3$ (s)	-853
NH_3 (g)	-46.0
CO_2 (g)	-394
H_2O (*l*)	-286

(iii) Predict, with a reason, the sign of ΔS for the decomposition of ammonium hydrogen carbonate.

[5]

[Total: 20]

2. (a) Compound **P** is a halogen derivative with molecular formula $C_9H_{10}Br_2$. Reaction of **P** with ethanolic KOH gives rise to a mixture of two isomeric products, **Q** and **R**, with the molecular formula C_9H_9Br. Both **Q** and **R** decolourise hot acidified $KMnO_4$ and the reaction produces **S** (structure given below) and ethanoic acid, CH_3COOH. On treatment with excess ethanolic ammonia, **P** produces **T** ($C_9H_{12}NBr$) as the major product.



S

(i) Draw all possible structural isomers of **S** that have the same chemical properties.

(ii) Deduce the structures of **P**, **Q**, **R** and **T**. Explain your reasoning.

[8]

(b) Bromocyclohexane ($C_6H_{11}Br$) and benzoyl bromide (C_6H_5COBr) differ in their reactivity with aqueous sodium hydroxide. Describe and explain the differences.

[2]

(c) The kinetics of the reaction between bromocyclohexane and hot aqueous sodium hydroxide was investigated.

1.0 mol dm^{-3} of bromocyclohexane was reacted with 0.01 mol dm^{-3} of aqueous sodium hydroxide. The pH of the reaction mixture was measured at regular time intervals using a data-logger. The data in the following table was obtained.

Time / min	**pH**	**$[OH^-]$ / mol dm^{-3}**
0	13.0	
2	12.9	
4	12.8	
6	12.6	
8	12.4	
10	11.9	

(i) Copy the table and fill in the $[OH^-]$ for each set of readings.

(ii) Using a graphical method, prove that the reaction is zero order with respect to $[OH^-]$.

(iii) Given that the reaction is first order with respect to [bromocyclohexane], give the rate equation for the reaction.

(iv) The half-life of bromocyclohexane was found to be 75.3 min when 1.0 mol dm^{-3} of bromocyclohexane was reacted with 0.01 mol dm^{-3} of aqueous sodium hydroxide.

Deduce the half-life of bromocyclohexane when 2.0 mol dm^{-3} of bromocyclohexane was reacted with 0.02 mol dm^{-3} of aqueous sodium hydroxide. Explain your reasoning.

(v) Determine the rate constant of the reaction when 1.0 mol dm^{-3} of bromocyclohexane was reacted with 0.01 mol dm^{-3} of aqueous sodium hydroxide.

(vi) Using your answer in **(c)(iii)**, propose the reaction mechanism for this reaction.

[10]

[Total: 20]

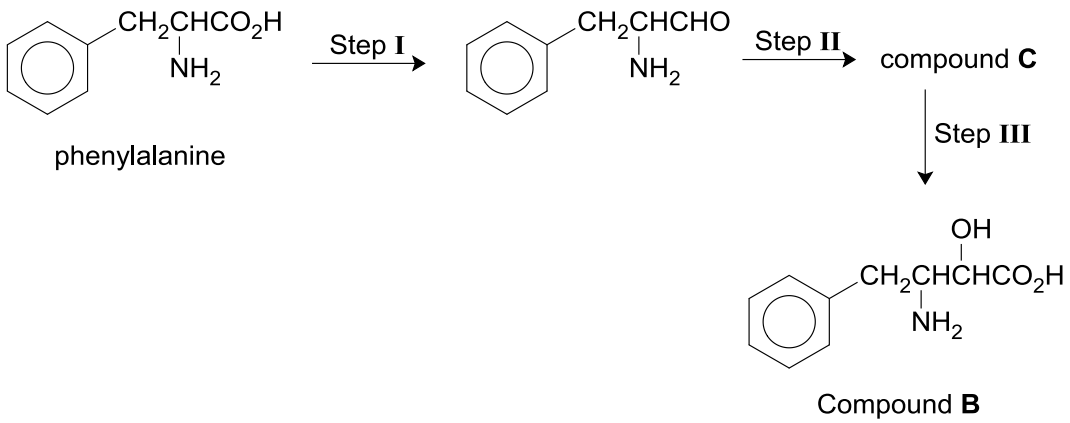
3. **(a)** Haemoglobin is a water soluble globular protein which is composed of two *α* polypeptide chains, two *β* polypeptide chains and an inorganic prosthetic haem group. Its function is to carry oxygen around in the blood and it is facilitated in doing so by the presence of the haem group.

(i) State the transition metal cation present in the haem group.

(ii) Describe what is meant by the terms *primary*, *secondary*, *tertiary* and *quaternary* structures of proteins. In each case, you should state the type of bonding or interaction involved.

[8]

(b) Compound **B** can be synthesised from the naturally occurring amino acid phenylalanine by the following route:



phenylalanine

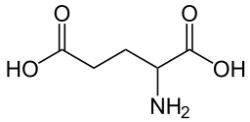
Compound **B**

(i) State the reagents and conditions for Steps **I**, **II** and **III** and draw the structure of compound **C**.

(ii) Compound **B** is an amino acid that is not involved in the building of proteins in the body. Explain why this is so.

[5]

(c) Glutamic acid is a non-essential amino acid. All meats, poultry, fish, eggs and dairy products are excellent sources of glutamic acid. The structure of glutamic acid is shown below.



Glutamic acid

(i) Explain what is meant by the term pK_a as applied to a weak acid, H**A**. Hence, state the relationship between the pK_a value and the acidity of a compound.

(ii) There are three pK_a values associated with glutamic acid: 2.1, 4.1 and 9.5. Make use of these pK_a values to draw the structures of the major species present in solutions of glutamic acid at the following pH values.

I. pH 1

II. pH 7

III. pH 11

(iii) When two oppositely-charged electrodes are placed into an aqueous solution of glutamic acid at a particular pH, the glutamic acid migrates towards neither the anode nor the cathode.

Draw the structure of glutamic acid under this condition and give the term used to describe chemical species that behave in this way.

[7]

[Total: 20]

4. **(a)** Transition metals are often alloyed with one another to enhance their properties. For example, titanium can be alloyed with copper to form a strong and corrosion resistant material used in the aerospace and automobile industries.

(i) Explain what is meant by the term *transition metal*.

(ii) State the electronic configuration of copper.

(iii) When 50 g of the titanium-copper alloy is completely oxidised, 34.4 g of CuO and a violet oxide of titanium, compound **D**, is obtained. The mass of oxygen measured in compound **D** is found to be 11.3 g. Determine the molecular formula of this oxide. Hence calculate the oxidation number of titanium in **D**.

(iv) On strong heating, compound **D** undergoes disproportionation to form two oxides. One of the oxides is a yellow solid and the other oxide is a white solid, compound **E.**

Write a balanced equation for the disproportionation reaction.

(v) State the full electronic configuration of Ti in compound **E**. Hence, explain why compound **E** is a white solid.

(vi) A solution of $[Ti(H_2O)_6]^{3+}$ is violet while a solution of $[TiF_6]^{3-}$ is pale green. Explain the difference in colour. [12]

(b) Pure copper can be obtained from copper ore by chemical reduction. The impure copper obtained can be purified using electrolysis.

(i) Draw a labelled diagram to show how an impure sample of copper can be purified by electrolysis.

(ii) A 1.20 kg of impure copper sample was electrolysed using a current of 12 A. Calculate the time (in days) required for 850 g of pure copper to be deposited at the cathode.

(iii) The impure copper sample contains other metals alloyed with it, one of which is zinc.

Explain, using data from the *Data Booklet*, why zinc is not deposited at the cathode. [6]

(c) Like aluminium oxide, copper(II) oxide, CuO, is an amphoteric oxide. Write two equations to show how CuO reacts with separate solutions of dilute HC*l* and aqueous NaOH. [2]

[Total: 20]

5. Nitrogen is a chemical element with a proton number of 7. Many industrially important compounds such as ammonia, nitric acid and cyanides contain nitrogen.

(a) Explain the following observations clearly.

(i) The third ionisation energy of nitrogen is lower than that of carbon.

(ii) The bond angle of NH_3 is smaller than that of CH_4.

(iii) The melting point of $H_2NCH_2CONH_2$ is lower than that of H_2NCH_2COOH.

[7]

(b) Group II nitrates undergo thermal decomposition to form the metal oxide, nitrogen dioxide and oxygen. Magnesium nitrate decomposes at 330°C whereas barium nitrate decomposes at 600°C.

(i) Explain why, going down Group II, the thermal stability of the nitrates increases.

(ii) A sample containing 20 g of a mixture of magnesium nitrate and barium nitrate was heated at 350°C until no further change occurred. The remaining solid weighed 10.9 g. Calculate the percentage composition by mass of magnesium nitrate in the sample.

[5]

(c) A hydrocarbon **R**, C_5H_8, reacts with aqueous bromine in a mole ratio of 1 : 2. When **R** undergoes oxidation with hot acidified $KMnO_4$, **S**, $C_3H_4O_4$, is formed.

1 mole of **S** reacts with 1 mole of solid sodium carbonate to give effervescence. When **S** reacts with thionyl chloride, **T**, is formed along with the evolution of white fumes.

When **T** reacts with $CH_2(NH_2)_2$, a cyclic neutral compound **U**, $C_4H_6O_2N_2$, is formed.

Deduce the structures of compounds **R** – **U**, explaining the chemistry involved.

[8]

[Total: 20]

END OF PAPER

BLANK PAGE