TEMASEK
JUNIOR COLLEGE

CHEMISTRY (H2) **9647/03**

Paper 3 Free Response

Friday **20^{th} September 2013** **2 hours**

Candidates answer on separate paper.

Additional materials: Answer paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, Civics Group and Index number in the spaces provided on the cover page and 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.

This question paper consists of 11 printed pages.

Answer any **four** questions.

1 **(a)** Describe and explain the trend observed in the ease of thermal decomposition of the nitrates of the Group II elements magnesium to barium. Write an equation for any reaction that occurs.

[3]

(b) An alloy of aluminium and magnesium is used in boat-building. A 1.75 g sample of the alloy was dissolved in the minimum volume of 4 mol dm^{-3} hydrochloric acid and the solution was then made alkaline by the addition of aqueous sodium hydroxide until no further reaction occurred. The resultant mixture was filtered and the residue, **A**, rinsed with distilled water, all washings being added to the filtrate, **B**. After drying, 0.18 g of **A** was obtained. Carbon dioxide was passed into **B** and a white solid, **C**, which contained aluminium, was collected. Heating **C** to constant mass gave a residue of mass 3.16 g.

(i) Write ionic equations for the reactions that occur when sodium hydroxide is added to the solution as described above.

(ii) Explain, using relevant equation(s), the formation of **C** when carbon dioxide is passed into **B**.

(iii) Determine the percentage composition by mass of the alloy. [7]

(c) Ozone mixed with oxygen is fairly stable but rapidly decomposes in the presence of a silver catalyst as shown in the equation below.

$$2O_3 \longrightarrow 3O_2$$

Silver was added to a 800 cm^3 sample of a mixture of oxygen and ozone. Below is a table showing the increase in volume of the mixture and volume of ozone at the respective time intervals.

Time/s	0	200	440	900	1500	1800
Volume of mixture/cm^3	800	805	810	815	818	819
Volume of ozone/cm^3	38	28	18	8		0

(i) Given that the bond angle of ozone is 116.8^0, draw the dot and cross diagram of the ozone molecule.

(ii) Calculate the volume of ozone in the mixture at t = 1500 s.

(iii) By means of a suitable graph, determine the order for the decomposition of ozone.

(iv) Calculate a value for the rate constant and write the rate equation.

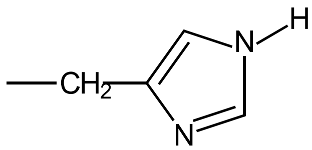
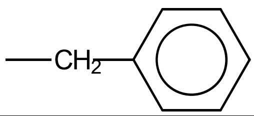
(v) Use the concept of activation energy, together with an appropriate sketch of the Boltzmann distribution, to explain how silver affects the rate of decomposition.

[10]

[Total: 20]

2 **(a)** Haemoglobin is the iron-containing oxygen-transport metalloprotein in the red blood cells of all vertebrates. Structurally, haemoglobin consists of 4 polypeptide sub-units fitted together to form a compact, globular structure which is soluble in water. Each sub-unit is bonded to a haem group. Approximately 70% of each sub-unit is incorporated into α-helices.

The α-sub-unit of haemoglobin is made up of 141 amino acids, 8 of which are listed below.

Amino acid	Formula of side chain (R in $RCH(NH_2)CO_2H$)	Number of amino acid residue per α-sub-unit.
leucine	$-CH_2-CH(CH_3)-CH_3$	18
valine	$-CH(CH_3)-CH_3$	13
lysine	$-CH_2-CH_2-CH_2-CH_2-NH_2$	11
serine	$-CH_2-OH$	11
histidine		10
phenylalanine		7
glutamic acid	$-CH_2-CH_2-C(=O)-OH$	4
cysteine	$-CH_2-SH$	1

(i) Explain what is meant by the term *primary structure* of a protein, clearly stating the types of interactions involved.

(ii) With the aid of a diagram, describe the secondary structure of the sub-units in haemoglobin, showing clearly how the structure is held in place.

(iii) Explain why there is an absence of disulfide bonds within the α-sub-unit.

(iv) The affinity of haemoglobin for oxygen decreases when the pH of the solution is decreased. This is due to the presence of the histidine residue in the sub-units. Suggest a reason for this.

Haemoglobin binds to oxygen as shown in the equation below:

$$Hb + 4O_2 \rightleftharpoons Hb(O_2)_4$$

(v) Using this equation, explain why haemoglobin binds to oxygen in the lungs and releases oxygen in the tissues in the body.

[10]

(b) Lysine is an amino acid found in haemoglobin. It is not synthesised by the human body and hence must be ingested as lysine or lysine-containing proteins.

There are three pK_a values associated with lysine: 2.15, 9.16 and 10.67.

(i) Assign each of the pK_a values to the specific functional groups in lysine, explaining the reasons for your choice.

(ii) Given that the isoelectric point is the average of two relevant pK_a values, calculate the isoelectric point for lysine and draw the structure of the major species present in a solution of lysine at that point.

[5]

(c) Carbon monoxide displaces oxygen from oxyhaemoglobin to produce carboxyhaemoglobin. The reaction of carbon monoxide with oxyhaemoglobin can be represented by the equation below.

$$Hb(O_2)(aq) + CO(aq) \rightleftharpoons Hb(CO)(aq) + O_2(aq)$$

The concentration of a gas **A** in an aqueous solution depends on the partial pressure of the gas in contact with the solution. This can be obtained from Henry's Law given as:

$$P_{\boldsymbol{A}} = k_H \text{ x } C$$

Where $P_{\boldsymbol{A}}$ = partial pressure of gas ***A***
k_H = Henry's Constant for gas ***A***
C = Concentration of gas ***A*** in water

The Henry's Constant for oxygen and carbon monoxide are given below

Gas	Henry's Constant / dm^3 atm mol^{-1}
O_2	769
CO	1052

To determine the equilibrium constant of the reaction between oxyhaemoglobin and carbon monoxide, a small amount of oxyhaemoglobin in water is exposed to air at 1 atmospheric pressure containing 3% carbon monoxide. After some time, the concentration of oxyhaemoglobin decreased to $\frac{1}{24}$ of the original concentration.

The concentration of carbon monoxide and oxygen in the air remains constant.

(i) Using Henry's Law, calculate the concentrations of oxygen and carbon monoxide in the solution.

(You may assume that air contains 20% oxygen)

(ii) Write an expression for the equilibrium constant, K_c, for the reaction between oxyhaemoglobin and carbon monoxide. Calculate the value of K_c.

(iii) The toxic effects of carbon monoxide poisoning begin to show when 10% of the oxyhaemoglobin has been converted to carboxyhaemoglobin.

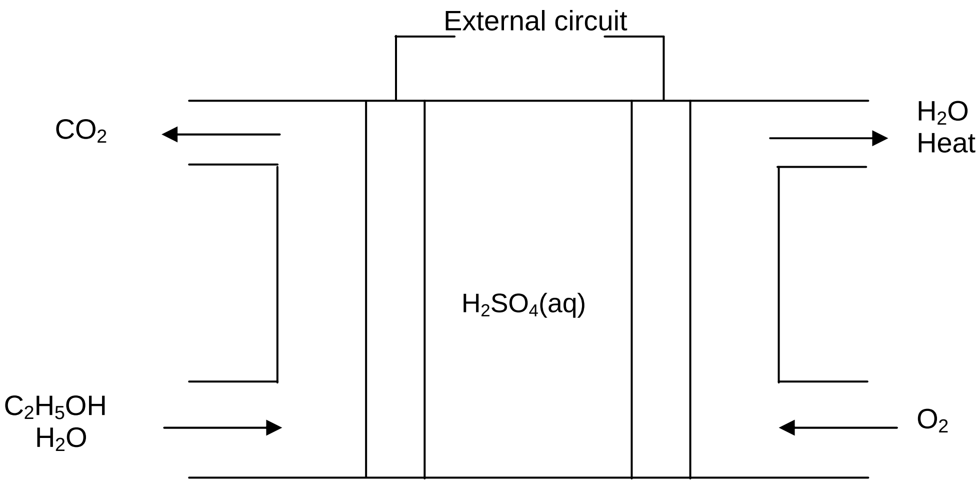
Calculate the percentage of carbon monoxide in air at atmospheric pressure that will cause this to happen.

[5]

[Total: 20]

3 A fuel cell is an electrochemical cell that converts a fuel into an electrical current. The direct oxidation of alcohols in a fuel cell has been proven to be an efficient method of obtaining electrical energy.

(a) The diagram below illustrates the functional parts of a direct-ethanol fuel cell (DEFC).



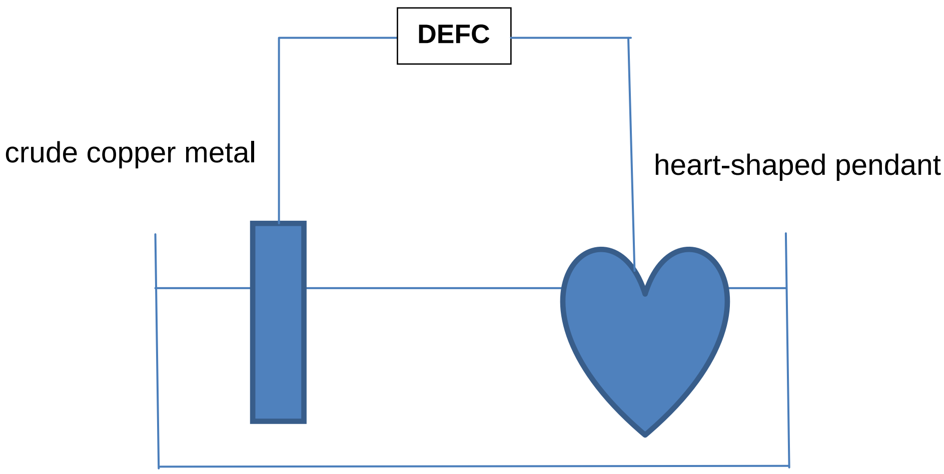
(i) Write the ion-electron half-equations for the reactions which take place at the electrodes of the DEFC, and hence an overall equation for the cell reaction.

(ii) The cell is capable of producing an e.m.f. of 1.61 V. By using suitable data from the *Data Booklet*, suggest a value for the E^θ of the CO_2/C_2H_5OH electrode reaction.

(iii) The first alcohol to be used successfully in a fuel cell was not ethanol but methanol. Suggest a possible advantage of using ethanol compared to methanol as fuel.

[5]

(b) In an attempt to coat a heart-shaped pendant with copper in the laboratory, a researcher connected the DEFC to an electrolytic cell as shown below.



1.00 mol dm^{-3} $CuSO_4$(aq)

(i) Calculate the volume of CO_2(g) produced by the DEFC when 31.75 g of copper metal was plated onto the pendant at room conditions.

(ii) The total time taken for the 31.75 g of copper to be plated was 8 hours. Calculate the current produced by the DEFC.

[4]

(c) The carbon dioxide produced by DEFC is collected to produce carbonated drinks after purification. Carbon dioxide can be collected in metal cylinders. One such cylinder has an internal volume of 2.5 dm^3, and contains 2.3 kg of carbon dioxide.

(i) Calculate the amount of carbon dioxide (in moles) in the cylinder.

(ii) Calculate the pressure (in pascals) the carbon dioxide would exert inside the cylinder at room temperature (298 K).

(iii) In fact, the pressure inside the cylinder is 4.8×10^7 Pa under these conditions. Explain why this value differs from the pressure you calculated in **(ii)**.

[4]

(d) Research was done on an organic compound, **D**, which is believed to be a better fuel than ethanol. **D** has a molecular formula of $C_3H_6O_3N_2$. **D** is a neutral compound and displays geometric isomerism. **D** did not react with Br_2 but produced white fumes when treated with PCl_5. When **D** was refluxed with NaOH(aq), it produced **E**, $C_2H_8O_2N_2$. **E** has two chiral centres, but **E** does not display optical isomerism. **E** readily dissolves in HC*l*(aq). When **E** was first warmed with acidified potassium dichromate(VI), and then warmed with NaOH(aq), NH_3(g) and **F** were produced. When **F**, $Na_2C_2O_4$, was treated with hot acidified $KMnO_4$, **F** produced CO_2 and H_2O.

(i) Identify and draw the structural formulae of compounds **D, E** and **F,** and explain the reactions involved.

(ii) Explain why **D** can exhibit geometric isomerism and draw the pair of geometric isomers.

(iii) Draw a three-dimensional structure of **E**, label each of the two chiral carbon atoms with an asterisk and explain why **E** does not display optical isomerism.

[7]

[Total: 20]

4 **(a)** Describe one physical property of transition metals in which they differ from a typical s–block metal such as calcium.

[1]

(b) Explain the following observations with relevant information from the *Data Booklet*:

I A yellow-green gas is observed when MnO_2 is added to concentrated HC*l*.

II Chromium dissolves in dilute sulfuric acid to give a gas and a blue solution which turns green upon standing.

Identify all coloured compounds and write balanced equations for all reactions. [5]

(c) **(i)** Write a balanced equation to illustrate the overall ligand exchange process when excess dilute aqueous ammonia is added to a solution containing Cu^{2+}(aq) to give a deep blue solution.

State the co-ordination number of the complex responsible for the deep blue colour.

Two possible mechanisms used for describing ligand exchange reactions involving transition metal complexes are *dissociative* and *associative*.

Some characteristics of *dissociative* and *associative* mechanisms are as described:

Dissociative

- An intermediate is formed.
- Coordination number of the intermediate is lower than that of the initial complex.
- Example:

Step 1: $ML_5X \longrightarrow ML_5 + X$

Step 2: $ML_5 + Y \longrightarrow ML_5Y$

Associative

- Example:

$$ML_5X + Y \longrightarrow ML_5XY \longrightarrow ML_5Y + X$$

where M represents a transition metal ion; X and Y represent ligands

(ii) The *dissociative* and *associative* mechanisms are often described to be analogous to typical organic mechanisms.

Suggest an organic mechanism that *dissociative* and *associative* mechanisms each resemble.

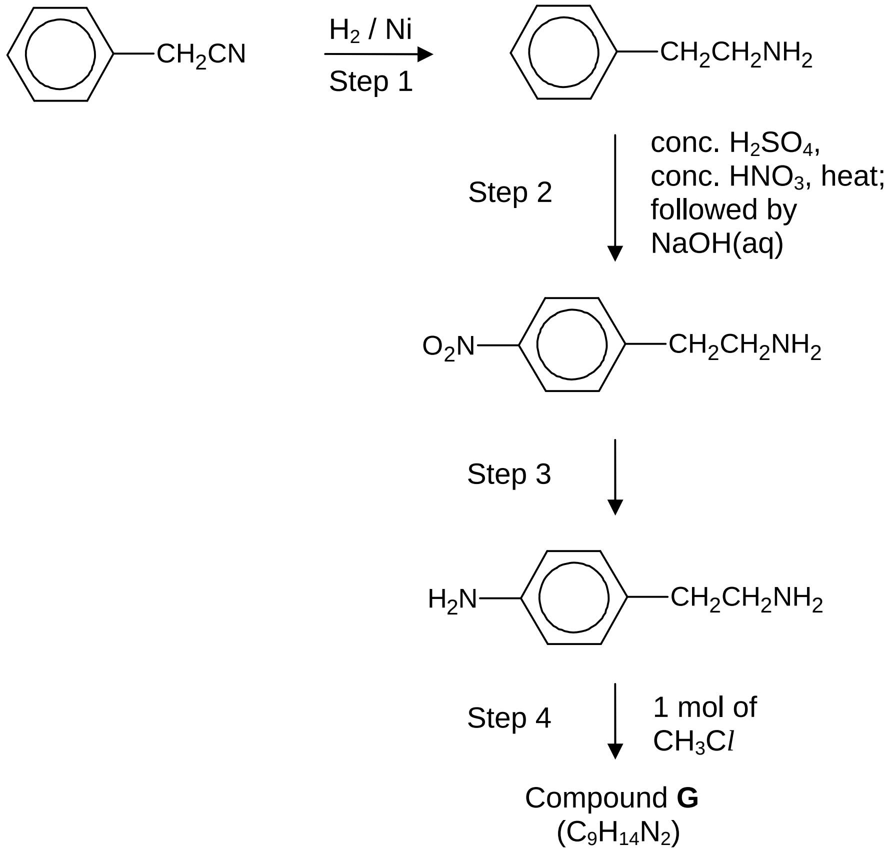
(iii) The ligand exchange process described in **(c)(i)** is believed to occur with the stepwise replacement by ammonia ligands following the *dissociative* mechanism.

Describe the mechanism when one molecule of ammonia ligand reacts with one Cu^{2+}(aq) ion. In your answer, show all ligands present, relevant lone pairs of electrons and curly arrows showing the movement of electrons.

[5]

(d) Compound **G** has been used as a monomer for obtaining ordered structures of polyamides in the mimicry of protein synthesis in living organisms.

Consider the synthesis of Compound **G**:



(i) The starting material can be synthesised from $C_6H_5CH_2OH$.
Suggest a synthesis route from $C_6H_5CH_2OH$ to $C_6H_5CH_2CN$.

(ii) Suggest the reagents and conditions you would use in step **3**.

(iii) State the role of the transition metal, nickel, in step **1** and briefly explain why it is able to perform this role.

(iv) Draw the displayed formula of compound **G** and explain its formation.

(v) Compound **G** is chiral. Illustrate the enantiomers of compound **G** using a suitable diagram.

[9]

[Total: 20]

5 **(a)** **(i)** Suggest a reagent needed to prepare hydrogen chloride from sodium chloride crystals.

Write an equation and state the observation for the reaction.

(ii) Explain the suitability of synthesizing hydrogen iodide from sodium iodide crystals using the method in **(i),** writing relevant equation(s), if any.

[4]

(b) **(i)** Propene reacts readily with hydrogen iodide.

Name the type of reaction and describe the mechanism of the reaction, including curly arrows to show the movement of electrons, and all charges.

(ii) 1-chloropropene also reacts with hydrogen iodide. However, it is less reactive compared to propene.

Suggest two possible reasons for this observation. Give the structural formula of the product formed.

[6]

(c) Two aromatic halogen-containing organic compounds, both with the molecular formula $C_{10}H_{13}OCl$, undergo chemical reactions to identify their structures. The results of the tests are shown below:

		Compound **J**	Compound **K**
		2 chiral centres	1 chiral centre
		Observations	
	Reagent	Compound **J**	Compound **K**
I	Sodium metal	Effervescence	Effervescence
II	Aqueous bromine	White ppt formed	No reaction
III	Heat with aqueous alkaline iodine	No reaction	No reaction
IV	Heat with sodium hydroxide,	Forms $C_{10}H_{14}O_2$	No reaction
	followed by acidified potassium dichromate(VI).	Solution turns green	Solution remains orange
V	Aqueous alkaline iodine with the organic product formed from (**IV**).	Yellow precipitate formed	No reaction

Deduce the structures of compounds **J** and **K**. [6]

(d) When iodic acid, HIO_3, was heated to 240 ^{o}C, the acid dehydrated with no change in oxidation state to form a white crystalline solid of iodine pentoxide, I_2O_5. When steam was passed through white-hot carbon, a mixture of two gaseous products was formed.

$$H_2O(g) + C(s) \rightarrow CO(g) + H_2(g)$$

The gaseous mixture was cooled to room temperature and an excess of I_2O_5 crystals was placed in **V** cm^3 of the gaseous mixture. Black crystals were formed and the volume of gas remained the same. The black crystals reacted with 16.60 cm^3 of 0.05 mol dm^{-3} sodium thiosulfate.

(i) Explain why the volume of gas remained the same.

(ii) Calculate the total volume, **V** cm^3, of the gaseous mixture used for the reaction. [4]

[Total: 20]