TEMASEK JUNIOR COLLEGE

PRELIMINARY EXAMINATIONS
HIGHER 2

CANDIDATE NAME										
CIVICS GROUP			/							
CENTER NUMBER	S					INDEX NUMBER				

CHEMISTRY
9647/02

Paper 2 Structured Questions **14th September 2011**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group and name 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 **all** questions.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/12
2	/18
3	/10
4	/16
5	/16
Total	

This document consists of **23** printed pages including **1** blank page.

For Examiner's Use

1 The literature value of standard enthalpy change of reaction between solid copper and aqueous hydrochloric acid is +64.8 kJ mol^{-1}.

$Cu(s) + HCl(aq) \rightarrow CuCl_2(aq) + H_2(g)$ $\quad \Delta H^{\ominus}_{reaction} = +64.8$ kJ mol^{-1}

$\Delta H^{\ominus}_{reaction} = +64.8$ kJ mol^{-1} is a hypothetical value as copper does not react with hydrochloric acid under normal room conditions. Hence, to determine the hypothetical value for the enthalpy change, a suitable Hess cycle needs to be constructed.

To construct a suitable Hess cycle, the enthalpy change of the following two reactions needs to be determined experimentally.

Reaction 1: $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$ $\quad \Delta H^{\ominus}_1 = x$ kJ mol^{-1}

Reaction 2: $Mg(s) + CuCl_2(aq) \rightarrow Cu(s) + MgCl_2(aq)$ $\quad \Delta H^{\ominus}_2 = y$ kJ mol^{-1}

(a) Draw an enthalpy cycle diagram that shows the relationship between $\Delta H^{\ominus}_{reaction}$, $\Delta H^{\ominus}_1$ and $\Delta H^{\ominus}_2$. Hence, show how $\Delta H^{\ominus}_{reaction}$ can be calculated.

[2]

For Examiner's Use

(b) An online website reported that the enthalpy change of **Reaction 1**, $\Delta H^{\ominus}_1$, is about -460 kJ mol^{-1}.

Write a plan to verify if the enthalpy change of **Reaction 1**, $\Delta H^{\ominus}_1$, is -460 kJ mol^{-1}.

Reaction 1: $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$ $\quad \Delta H^{\ominus}_1 = x$ kJ mol^{-1}

You may use the apparatus normally found in the school laboratory and the following apparatus and chemical reagents.

- 200 cm^3 Styrofoam cup
- Magnesium powder
- $HCl(aq)$ of concentration 5 mol dm^{-3}

Note: 4.2 J of heat energy raise the temperature of 1 cm^3 of water or aqueous solution by 1 ^oC

Density of HCl = 1 g cm^{-3}

In your plan you should give the essential details of the procedures, including quantities used, for the determination of $\Delta H^{\ominus}_1$.

For Examiner's Use

[5]

(c) Draw up tables with appropriate headings to show the data you would record in **(b)**.

[1]

For Examiner's Use

(d) Outline how you would use the data collected to determine enthalpy change of **Reaction 1**, $\Delta H^{\ominus}_{1}$.

You may use letters such as **a**, **b**, **c** and the like to represent the various data collected.

[2]

(e) Identify one potential safety hazard in this experiment and state how you would minimize this risk.

[1]

For Examiner's Use

(f) Copper does not react with hydrochloric acid under normal room conditions. In thermodynamic terms, explain if copper is able to react with hydrochloric acid at high temperature.

.....

.....

.....

.....

[1]

[Total: 12]

BLANK PAGE

For Examiner's Use

For Examiner's Use

2 Iodine can be produced through various processes.

(a) In the laboratory, a common method of obtaining iodine is to react sodium iodide with concentrated sulfuric acid. Sample procedures could be as follows:

Procedures

A1. Add about 15 g of sodium iodide into a 250 cm^3 beaker.

A2. Add enough deionised water to just dissolve all the sodium iodide.

A3. Place the beaker in an ice bath.

A4. Using a 50 cm^3 measuring cylinder, add 50 cm^3 of concentrated sulfuric acid to the sodium iodide solution and stir for 5 minutes.

A5. Scrape off the black crystalline solid iodine formed on the inside of the beaker, and transfer to a tall glass jar.

A6. Heat the iodine crystals with a gentle flame and collect the purified iodine at the top of the jar.

(i) Write a balanced equation for the reaction of the iodide with concentrated sulfuric acid to form iodine.

.....

(ii) Describe what you would observe during the 5 minutes of stirring in procedure **A4**.

.....

.....

(iii) Suggest why an ice bath is necessary.

.....

.....

(iv) When the iodine crystals came into contact with sodium iodide, a reddish brown colouration would be observed. Explain the observation.

.....

.....

.....

For Examiner's Use

(v) Procedure **A6** is done in order to obtain a higher-purity sample of iodine. A research assistant suggested that instead of performing procedure A6, the iodine crystals could be washed with cold aqueous sodium hydroxide to remove any sulfuric acid impurity.

With the aid of a relevant chemical equation, evaluate how this suggestion might affect the yield of iodine obtained.

.....

.....

.....

.....

.....

[6]

For Examiner's Use

(b) In the 18th and 19th centuries, iodine was industrially produced from kelp, a large seaweed. Combustion of the kelp converts the organic substances to ash, and sodium halides (mainly sodium iodide) are obtained.

In the laboratory, a similar process can be done according to the following procedures.

Procedures

B1. Fill a large crucible on a tripod with the seaweed. Heat with a strong Bunsen flame until all the seaweed has been turned to ash.

B2. Boil the ash with about 20 cm^3 of purified water in a beaker, and filter while hot. Collect the clear filtrate in a second beaker and allow to cool.

B3. Add about 2 cm^3 of dilute sulfuric acid to the solution, followed by hydrogen peroxide solution.

B4. Transfer the mixture to a separating funnel and add 10 - 20 cm^3 of cyclohexane. Stopper the separating funnel and shake vigorously for about 30 s. With the separating funnel inverted, release any pressure that has built by opening the tap briefly.

B5. Clamp the funnel and allow the layers to separate. The cyclohexane will form a layer on top of the aqueous layer.

B6. Run off the lower aqueous layer into a 250 cm^3 conical flask.

B7. Run the purple cyclohexane layer into an evaporating basin, and set aside to evaporate in the fume cupboard to obtain the iodine crystals.

(i) State and explain, with the aid of a relevant equation, what you would observe during procedure **B3**.

.....

.....

(ii) With reference to the *Data Booklet*, explain why hydrochloric acid is **not** used in the acidification process in procedure **B3**.

.....

.....

.....

.....

For Examiner's Use

(iii) Explain why cyclohexane is a suitable solvent for the extraction of iodine and state what you would observe during procedure **B4**.

.....

.....

.....

.....

.....

.....

(iv) Suggest a reason why in procedure **B7**, evaporation is preferred over direct heating over a strong Bunsen flame.

.....

.....

(v) In order to check if the kelp contained significant amount of chloride anions, a student transferred 1 cm^3 of the filtrate obtained in procedure **B2** into a test tube and added acidified silver nitrate solution. A cream precipitate was obtained.

State and explain what reagent should be added to verify if there was a significant amount of chloride mixed with the iodide.

.....

.....

.....

For Examiner's Use

(vi) When the student left the test tube from **(b)(v)** in the sun, the precipitate started to darken and gave a purplish colouration. A very faint smell of chlorine gas was detected. Given the following data, explain what caused the purplish colouration when the test tube was left in the sun.

Silver metal deposits are either silvery, gray or black in large amounts. However, when a solution contains a fine suspension of silver nanoclusters, the colour varies depending on the size of the nanoclusters. A silver nanocluster is a group of silver atoms that are nanometres in diameter.

Size of silver nanocluster / nm	20	30	40	50	60	70
Colour of solution	red	green	blue	cyan	orange	violet

.....

.....

.....

.....

[11]

(c) Ultra-pure elemental iodine is often prepared for research work through the reaction of potassium iodide with copper(II) sulfate(VI). Precipitation first occurs, but the precipitate instantaneously decomposes to form a white precipitate and iodine, which turns the pale blue solution brown.

Write a balanced equation, including state symbols, for the decomposition reaction that occurs.

.....

[1]

[Total: 18]

For Examiner's Use

3 Electroplating is an important industrial process where it produces a thin coating of precious metals such as gold or silver onto other metals.

Traditionally in silver plating, the electrolytic cell consists of a silver electrode connected to one end of the battery and the object to be plated will be connected to the other end. The electrolyte used in silver plating industrially is an aqueous solution of silver cyanide.

(a) **(i)** Write the appropriate ion-electron half-equations, with state symbols, for the changes which takes place at each electrode.

Anode: .....

Cathode: .....

(ii) Explain how the electroplating process occurs and describe what you would observe during this electroplating process.

.....

.....

.....

.....

[3]

(b) Explain why the concentration of silver ions remains constant during the process of silver plating.

.....

.....

[1]

For Examiner's Use

A research student tries to plate silver onto a metal coin in his lab, changing the following laboratory procedures:

I. Electrolyte used: An aqueous solution of silver nitrate

II. Graphite electrode was used instead of silver electrode

(c) **(i)** Describe any observation by the research student as electric current was passed through the electrolytic cell.

.....

.....

.....

(ii) Construct an equation for the reaction occurring at the positive electrode, and hence construct the equation for the overall reaction, showing your working.

.....

.....

.....

(iii) Calculate the length of time in hours that a current of 5.0 A has to be passed through the above electrolysis setup in order to plate 10 g of silver onto the electrode.

(iv) Suggest a reason why the graphite electrode needs to be replaced after some time.

.....

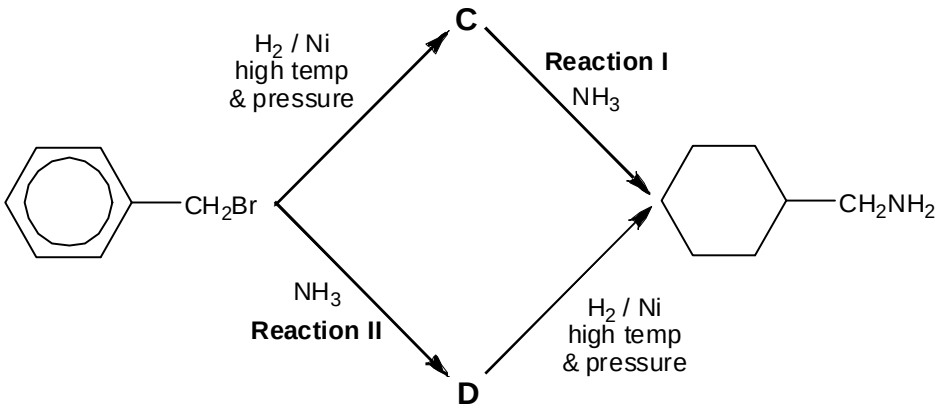
.....

[6]

[Total: 10]

For Examiner's Use

4 Bromomethylbenzene is intensely irritating to skin, mucous membranes as well as the corneal nerves in the eyes. Because of these properties, it has been used as a tear gas during World War II. Bromomethylbenzene is a colourless liquid and can be used in the formation of cyclohexylmethylamine though the following two processes.

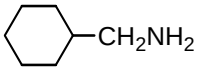


(a) Give the structural formulae of the compounds **C** and **D**.

[2]

For Examiner's Use

(b) To investigate the kinetics of **Reaction I**, the time taken for a small constant amount of cyclohexylmethylamine was measured when various concentrations of **C** and NH_3 were reacted. The results are shown in the table below:

Experiment	**[C] / mol dm^{-3}**	**[NH_3] / mol dm^{-3}**	**Time for formation of  / min**
1	0.40	4.00	18
2	0.30	4.00	24
3	0.50	4.40	13

(i) Determine the order of reaction with respect to **C** and NH_3 showing how you arrive at your answers.

(ii) Construct the rate equation for the reaction between **C** and NH_3.

.....

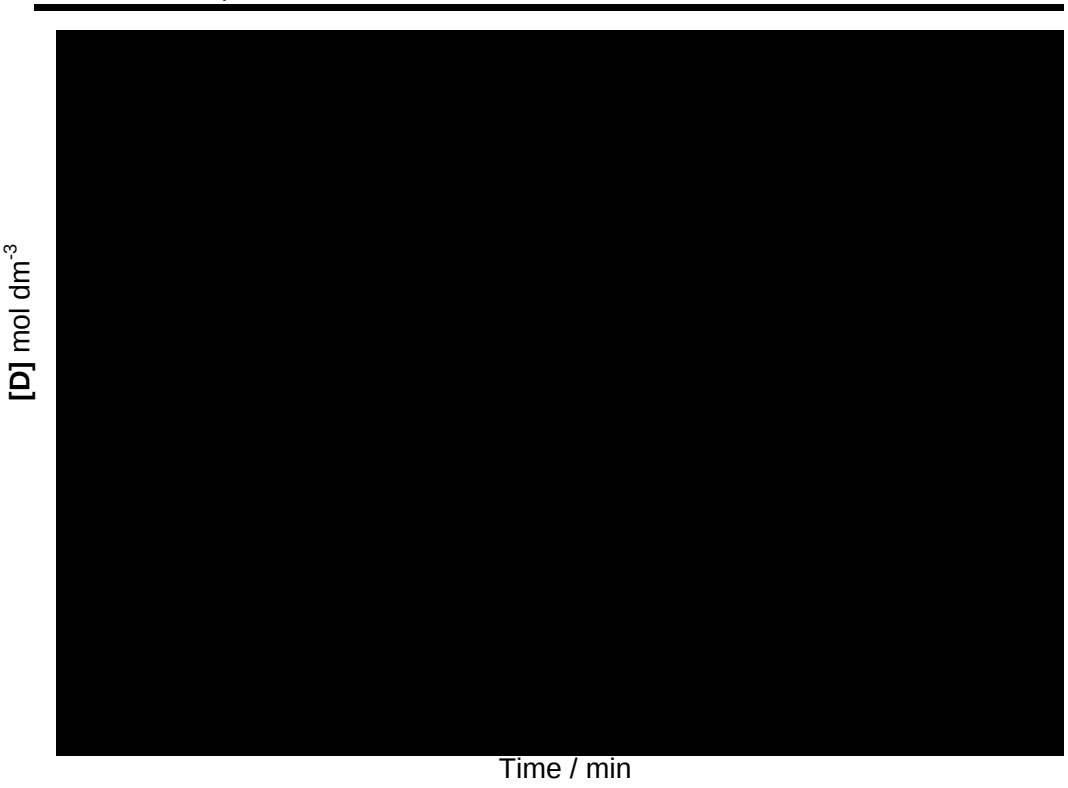
(iii) State the mechanism between **C** and NH_3.

.....

[4]

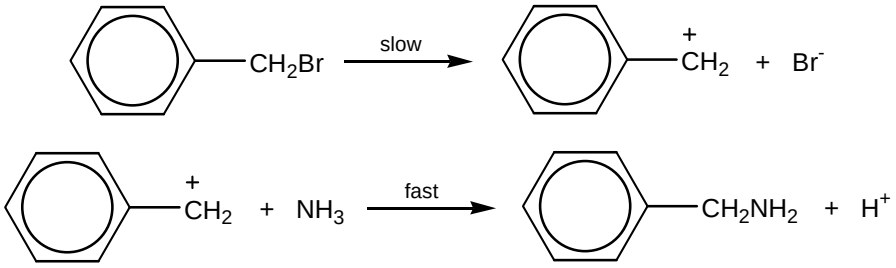
For Examiner's Use

(c) To investigate the kinetics of **Reaction II**, the concentration of **D** produced with time was obtained and plotted on a graph shown below. The initial concentrations of bromomethylbenzene and NH_3 were 0.50 mol dm^{-3} and 2.50 mol dm^{-3} respectively. When the reaction is complete, the concentration of **D** is 0.50 mol dm^{-3}.



When the initial concentration of NH_3 was doubled, the same graph was obtained.

The following mechanism is known to occur for Reaction II:



For Examiner's Use

(i) Using the graph and data above, deduce the orders of reaction with respect to NH_3 and bromomethylbenzene and explain whether the data is consistent with the mechanism given.

(ii) Determine the rate constant for the reaction, stating the units.

(iii) Unlike typical primary bromoalkanes, bromomethylbenzene undergoes unimolecular instead of bimolecular nucleophilic substitution reaction due to the stable carbocation formed. Suggest a reason for the stability of the carbocation formed.

[4]

For Examiner's Use

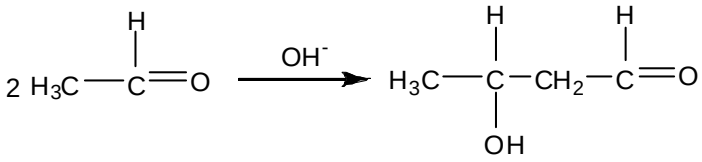
(d) Unlike bromomethylbenzene, 3-bromopropene can undergo reaction readily with HBr under room conditions to produce a dibromo-compound.

(i) Draw the possible optical isomers of the dibromo-compound produced.

(ii) Explain why the resultant mixture formed by the reaction of 3-bromopropene and HBr is optically inactive.

[4]

(e) Under the influence of a dilute base or acid, two molecules of an aldehyde or a ketone may combine in a process known as aldol condensation which involves the transfer of an α-hydrogen. An example of an aldol condensation between ethanal molecules is shown below.



Give the structural formula of the possible products formed when butanone undergoes aldol condensation.

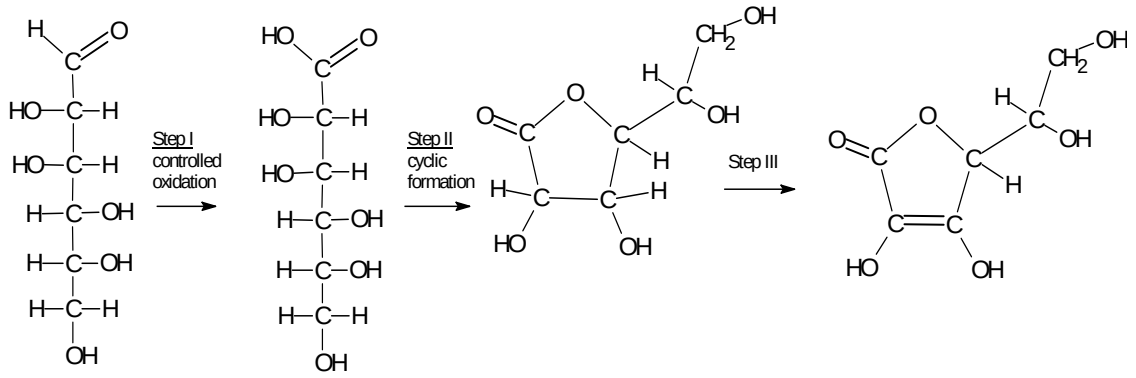
[2]

[Total: 16]

For Examiner's Use

5 Ascorbic acid, also known as Vitamin C is required for the synthesis of collagen in humans. A vitamin C deficient diet leads to a disease called scurvy. Ascorbic acid is known to be water soluble and is commonly used as food additives.

The building block for ascorbic acid is the glucose molecule. The following synthetic pathway was proposed.



Glucose **Intermediate E** **Intermediate F** **Ascorbic Acid**

(a) State the functional group(s) present in **Intermediate F**.

.....

.....

[2]

(b) **(i)** State the type of reaction found for

Step II: .....

Step III: .....

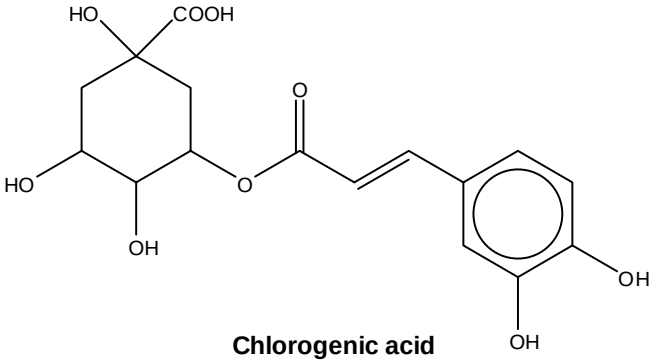
(ii) Circle the functional group(s) present in the **Intermediate E** that are involved in **Step II.**

[3]

For Examiner's Use

(c) Ascorbic acid, thiols and polyphenols are often reducing agents known as antioxidants. Antioxidants prevent the oxidation of other molecules by being oxidised themselves. In doing so, they inhibit other oxidation reactions in the body.

An example of a polyphenol is chlorogenic acid.



Chlorogenic acid

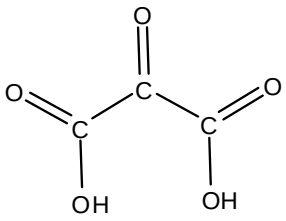
Chlorogenic acid is treated with the following reagents. Draw the structural formulae of all the organic compounds formed in the reactions.

Reagent	**Structural formula of organic compounds**
Solid Na_2CO_3	
aq NaOH, heat	
PCl_5	
aq Br_2	

[5]

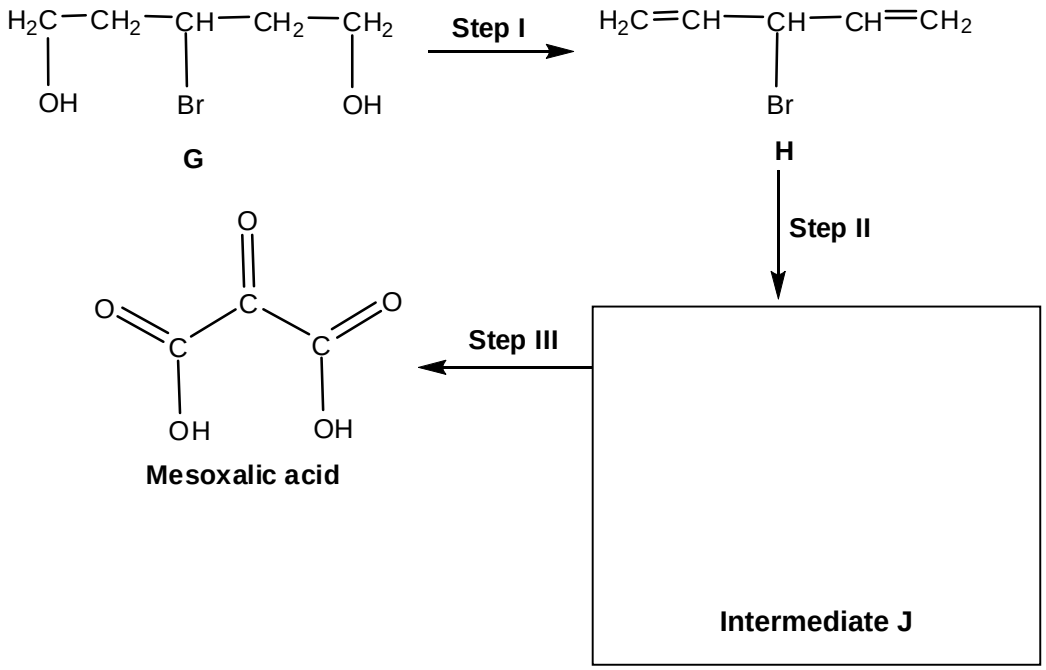
For Examiner's Use

(d) 2-oxopropanedioic acid is also known as mesoxalic acid. It has been used as an antidote to cyanide poisoning.



Mesoxalic acid

(i) State the reagents and conditions required for the conversion of compound **G** below into mesoxalic acid, and draw the structures of the intermediate **J** in the spaces provided.



Step	Reagents and conditions
I	
II	
III	

(ii) Suggest a chemical test that could be used to distinguish **G** from **H**. Write a balanced equation for the reaction that occurred.

For Examiner's Use

.....

.....

.....

.....

[6]

[Total:16]

End of Paper