JURONG JUNIOR COLLEGE

PRELIMINARY EXAMINATION 2008

H2 CHEMISTRY PAPER 3

9746 / 3

Monday 18th August 2008 2 hours

INSTRUCTIONS TO CANDIDATES

Do not open this question booklet until you are told to do so.

Write your name and class in the spaces provided on the cover sheet and writing papers provided.
Write in dark blue or black pen.
You may use a pencil for any diagrams, graphs, or rough working.
Do not use highlighters or correction fluid.

Answer any **four** questions.

Begin your answer to each new question on a fresh sheet of writing paper.

At the end of the examination, arrange the answers in numerical order and attach the cover sheet on top.

INFORMATION FOR CANDIDATES

A *Data Booklet* is provided. Do not write anything on the *Data Booklet*.

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

You are advised to show all workings in calculations.

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

This question booklet consists of 11 printed pages, including this page.

[Turn over

Answer any **four** questions.

1. Sulfuric acid, H_2SO_4, is a strong mineral acid which is an important chemical used in the manufacture of phosphate fertilisers. It is also used as an oxidising agent to remove rust in the iron and steel-making industry.

(a) The manufacture of sulfuric acid involves the reaction between sulfur dioxide and oxygen.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -197\ \text{kJ mol}^{-1}$$

The reaction is carried out at a temperature of 450 °C in the presence of a catalyst.

(i) Explain why a temperature of 450 °C is usually employed for the reaction.

(ii) When a 2:1 ratio of SO_2 and O_2 at a total initial pressure of 3 atm is passed over a catalyst at 450 °C, the percentage conversion of SO_2 into SO_3 was found to be 98 %.

Calculate the equilibrium partial pressures of SO_2 and O_2 and hence find the value for K_p.

(iii) State and explain the effect on K_p and the percentage conversion of SO_2 into SO_3 when the volume of the reaction vessel is reduced. [6]

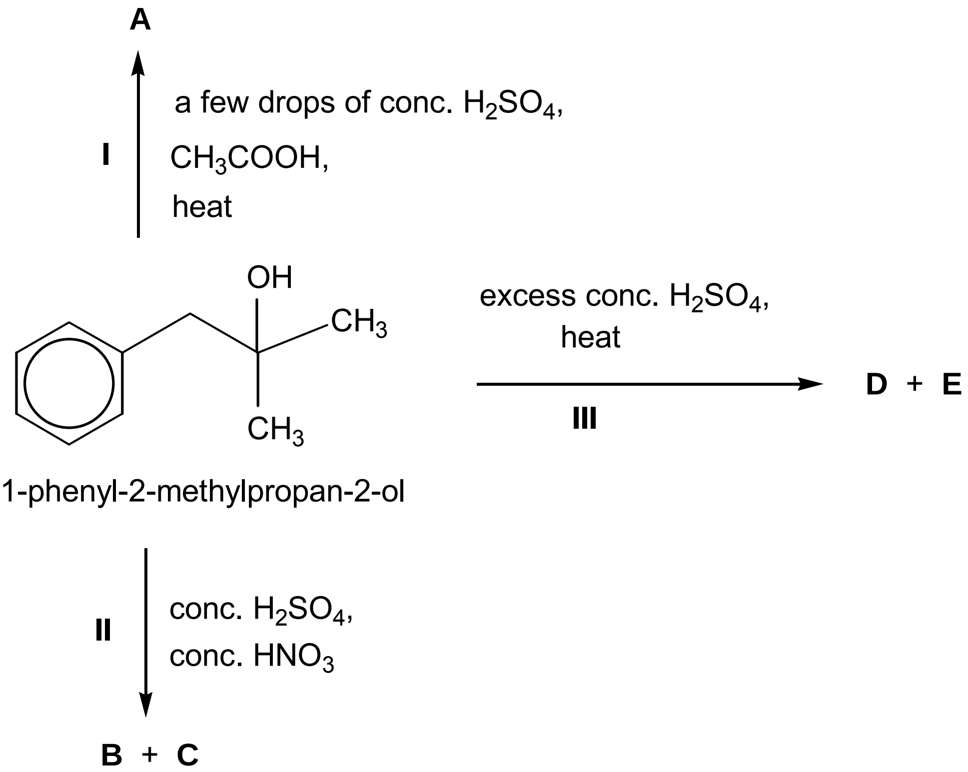
(b) SO_2, the key reactant for the manufacture of sulfuric acid, is an oxide of a Period 3 element. The table below shows the melting points of SO_2 and oxides of other Period 3 elements.

Compound	Formula	Melting point / °C
sodium oxide	Na_2O	1132
aluminium oxide	Al_2O_3	2980
sulfur dioxide	SO_2	–70

(i) Briefly relate the melting points of these oxides to their structure and bonding.

(ii) Describe the reactions, if any, of each of these oxides with water, stating the approximate pH of any solution formed, and writing a balanced equation for any reaction that takes place. [6]

1. **(c)** Concentrated sulfuric acid is also an important reagent in many organic reactions where it can perform roles such as an acid, dehydrating agent or a catalyst as illustrated in the following reaction scheme.



(i) Give the structural formulae of the compounds **A** to **E**.

(ii) The first step in reaction **II** is the generation of an *electrophile*, NO_2^+.

Using NO_2^+ as an example, explain the term *electrophile*.

(iii) With the aid of an equation, explain the role of concentrated H_2SO_4 during the generation of the electrophile, NO_2^+, for reaction **II**.

(iv) When phenol undergoes the same reaction as 1-phenyl-2-methylpropan-2-ol in reaction **II**, concentrated H_2SO_4 is not required. Explain why this is so. [8]

[Total: 20]

2. In 1727, German scientist Johann Heinrich Schulze noticed that the sun had a darkening effect on a flask of solution. He placed another flask of the same solution in a hot and dark oven and noticed that there is no change. He then concluded that light, and not heat, was responsible for this reaction. This light-sensitive compound is silver nitrate.

Silver nitrate crystals can be prepared by reacting silver metal with nitric acid, followed by evaporating the solution.

$$4Ag(s) + 6HNO_3(aq) \rightarrow 4AgNO_3(aq) + NO(g) + NO_2(g) + 3H_2O(l)$$

(a) **(i)** Write an equation, with state symbols, to represent the *standard enthalpy change of formation of $AgNO_3(aq)$*.

(ii) Using the following data, calculate the standard enthalpy change for the reaction of silver metal with nitric acid.

Species	ΔH_f° /kJ mol^{-1}
$Ag^+(aq)$	+106
$NO_3^-(aq)$	–207
$H^+(aq)$	0

Species	ΔH_f° /kJ mol^{-1}
$NO(g)$	+90
$NO_2(g)$	+33
$H_2O(l)$	–286

(iii) The enthalpy change of solution of silver nitrate is +22.8 kJ mol^{-1}.

Explain fully why silver nitrate dissolves spontaneously in water even though the process is endothermic. [5]

(b) In an experiment, a cell containing aqueous silver nitrate is connected in series with another cell containing aqueous $\mathbf{X}Cl_3$. When a current of 10 A is applied for **t** minutes, 1.44 g of silver and 0.120 g of metal **X** were deposited.

Calculate the time **t** and the A_r of **X**. [3]

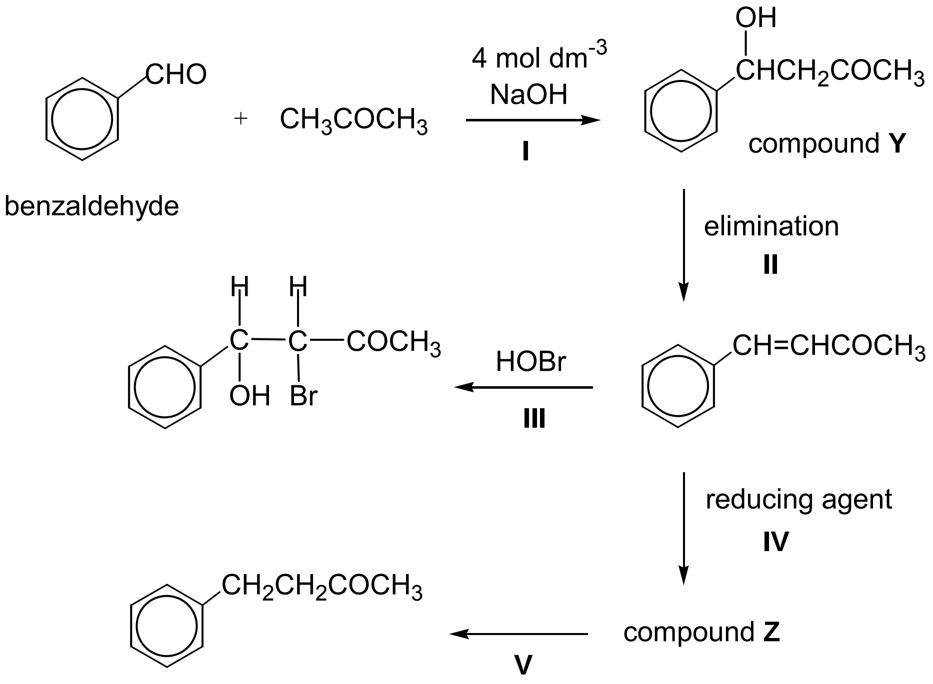
(c) Aqueous silver nitrate, followed by an excess of aqueous ammonia, can be used to identify halide ions in aqueous solution.

(i) State and explain the observations when aqueous silver nitrate is added to aqueous sodium chloride, followed by an excess of aqueous ammonia.

(ii) A precipitate is formed when sodium iodide is added to the resulting mixture in part **(c)(i)**. Identify the precipitate and explain the observation. [4]

2. **(d)** Tollens' reagent is prepared by adding aqueous ammonia to aqueous silver nitrate. It is a test reagent used to identify aldehydes. For example, when benzaldehyde is warmed with Tollens' reagent, a silver mirror is formed.

Benzaldehyde can undergo a series of reactions as follows:



(i) In reaction **I**, benzaldehyde reacts with propanone in a strongly alkaline medium to form compound **Y**. The first step is the formation of negatively charged carbanions.

$$CH_3COCH_3 + OH^- \rightarrow {}^-CH_2COCH_3 + H_2O$$

State the type of reaction for reaction **I** to form compound **Y**.

(ii) Compound **Y** exists as a pair of isomers. State the type of isomerism involved and draw the two isomers which illustrate this isomerism in **Y**.

(iii) By considering the number of bonding and non-bonding electron pairs around oxygen atom, draw the shape of HOBr.

Hence, describe the mechanism for reaction **III**.

(iv) Suggest the structural formula for compound **Z** and state the reagent and condition required for reaction **V**. [8]

[Total: 20]

3. **(a)** Blood plasma is a biological fluid that plays an important role in maintaining pH in the body.

In the blood plasma, the equilibrium between carbonic acid, $H_2CO_3(aq)$, and hydrogencarbonate ion, $HCO_3^-(aq)$, buffers pH changes.

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

The K_a value for this equilibrium is 7.90×10^{-7} mol dm^{-3}.

At body temperature, the pH of the arterial blood plasma is 7.40. If the pH falls below this normal value, a condition termed *acidosis* is produced. If the pH rises above this normal value, the condition is termed *alkalosis*.

The concentration of $H_2CO_3(aq)$ is controlled by respiration through the lungs. $H_2CO_3(aq)$ is in equilibrium with dissolved CO_2.

$$H_2CO_3(aq) \rightleftharpoons CO_2(aq) + H_2O(l)$$

In the lungs, excess dissolved $CO_2(aq)$ is exhaled as $CO_2(g)$.

$$CO_2(aq) \rightleftharpoons CO_2(g)$$

During heavy exercise, *lactic acid* is released into the blood and is buffered by the blood plasma. This eventually leads to an increase in $CO_2(aq)$ concentration and stimulates increased breathing.

(i) Explain what is meant by a *buffer solution*.

(ii) Write an expression for the acid dissociation constant, K_a, of $H_2CO_3(aq)$ and use it to determine the $[HCO_3^-(aq)]/[H_2CO_3(aq)]$ ratio in the blood plasma.

Comment on this ratio.

(iii) Write an equation to show how blood plasma can buffer the pH change when lactic acid is released into the blood.

(iv) Explain why the rate of breathing increases during the process of removing lactic acid. [7]

(b) One way to test for CO_2 gas is to bubble it into limewater, $Ca(OH)_2(aq)$. A white precipitate will be formed due to the following reaction:

$$CO_2(g) + Ca(OH)_2(aq) \rightarrow CaCO_3(s) + H_2O(l)$$

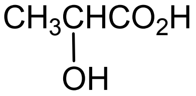
(i) Write an expression for the solubility product, K_{sp}, of calcium carbonate, $CaCO_3(s)$.

(ii) Given that the solubility of calcium carbonate at 25 °C is 9.35×10^{-5} mol dm^{-3}, determine the solubility product of calcium carbonate at 25 °C and state its unit.

3. (b) (iii) Unlike calcium carbonate, beryllium carbonate ($BeCO_3$) does not exist as a stable compound on its own. Instead, it is found in the relatively more stable compound, beryllium basic carbonate $Be_2CO_3(OH)_2$ (or $BeCO_3.Be(OH)_2$).

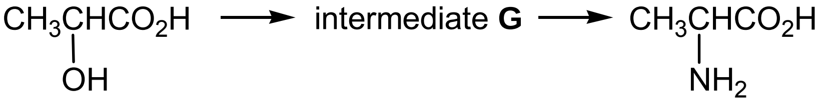
Suggest why $BeCO_3$ is not stable on its own while $Be(OH)_2$ is relatively more stable. [5]

(c) *Lactic acid* is the major acidic component of soured milk and it has the following structure:



$$\mathrm{CH_3\underset{\underset{\displaystyle OH}{|}}{C}HCO_2H}$$

(i) *Lactic acid* can be converted to 2-aminopropanoic acid in two stages.



$$\mathrm{CH_3\underset{\underset{\displaystyle OH}{|}}{C}HCO_2H} \longrightarrow \text{intermediate } \mathbf{G} \longrightarrow \mathrm{CH_3\underset{\underset{\displaystyle NH_2}{|}}{C}HCO_2H}$$

Suggest the reagents and conditions required in each stage and give the structure of the intermediate **G** involved.

(ii) On reduction, *lactic acid* is converted to compound **P** ($C_3H_8O_2$). **P**, on passing its vapour over hot Al_2O_3, gives compound **Q** (C_3H_6O).

Q gives no reaction with 2,4-dinitrophenylhydrazine but decolourises aqueous bromine. When **Q** is treated with hot concentrated acidified $KMnO_4$, it gives carbon dioxide gas as the only carbon-containing product.

Suggest a possible reducing agent to convert *lactic acid* to compound **P**.

Deduce the structures of compounds **P** and **Q**, and explain the above reactions. [8]

[Total: 20]

4. **(a)** Iron and some of its compounds are useful catalysts.

In the reaction between aqueous iodide and aqueous peroxodisulphate ($S_2O_8^{2-}$), Fe^{3+}(aq) is used as a *homogeneous catalyst*.

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

(i) Explain the term *homogeneous catalyst*.

(ii) Which property of iron allows Fe^{3+} to be a *homogeneous catalyst*?

(iii) By considering the relevant $E^{\ominus}$ values from the *Data Booklet*, explain, with the help of equations, how Fe^{3+}(aq) is able to catalyse the above reaction.

(iv) State **two** reasons why hexacyanoferrate(III), $[Fe(CN)_6]^{3-}$(aq), another complex ion of iron, does not help to increase the rate of the above reaction.

(v) Fe^{3+}(aq) is yellow and $[Fe(CN)_6]^{3-}$(aq) is orange-brown. Explain why these complexes are coloured. [10]

(b) Aqueous iodide is a relatively strong reducing agent.

By using relevant data in the *Data Booklet*, predict the outcome of mixing aqueous potassium iodide, KI with acidified potassium dichromate(VI), $K_2Cr_2O_7$.

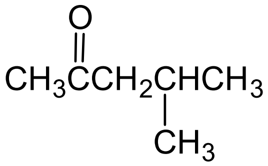
Write a balanced equation for any reaction that occurs. [2]

4. **(c)** Aqueous iodine is a relatively weak oxidising agent.

In alkaline condition, aqueous iodine is only able to oxidise specific reactive groups in organic compounds.

MIBK, used as a solvent for some adhesives, is one of the organic compounds that would react with alkaline aqueous iodine on heating.

The structure of MIBK is given below:



$$CH_3\overset{\overset{O}{\|}}{C}CH_2\underset{\underset{CH_3}{|}}{C}HCH_3$$

(i) State what you would observe and give the structure of the organic products formed when MIBK is warmed with alkaline aqueous iodine.

(ii) **R**, an isomer of MIBK, also reacts with alkaline aqueous iodine to give the same observations.

Unlike MIBK, **R** reacts with both PCl_5 and ethanoyl chloride.

On heating with concentrated $KMnO_4$ in acid solution, **R** reacts to give two products **S** (C_3H_6O) and **T** ($C_3H_4O_3$). Both **S** and **T** also react with alkaline aqueous iodine to give the same observations.

Deduce the structures of **R**, **S** and **T**, and explain the reactions involved. [8]

[Total: 20]

5. **(a)** Sucrose is the most common natural food sweetener, often known as table sugar. In acidic solution, sucrose is readily hydrolysed to a 1:1 mixture of glucose and fructose. The reaction is catalysed by aqueous H^+ ions.

$$\underset{\text{(sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+(aq)} \underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(fructose)}}{C_6H_{12}O_6}$$

A series of experiments were carried out at 25 °C to investigate the kinetics of this reaction, using 0.79 mol dm^{-3} sucrose solution and 1.25 mol dm^{-3} hydrochloric acid.

The following data were obtained:

Expt	Volume of sucrose /cm^3	Volume of HC*l* /cm^3	Volume of water /cm^3	Initial rate of reaction /mol dm^{-3} min^{-1}
1	20	20	10	0.00125
2	20	30	0	0.00188
3	10	30	10	0.000938
4	40	20	10	**?**

(i) Using the data given above, determine the orders of reaction with respect to sucrose and HC*l*.

Give the rate equation and hence, calculate the rate constant for the reaction, stating its units.

(ii) Hence or otherwise, deduce the initial rate of reaction for Experiment **4**. [6]

(b) In bacteria, sucrose is broken down into glucose and fructose by the enzyme, *invertase*. A few experiments were carried out with different initial concentrations of sucrose and the initial rates of the enzyme-catalysed hydrolysis reaction were measured.

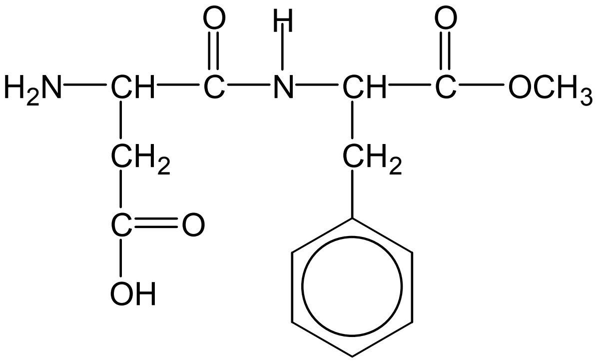
(i) Sketch a graph to show how the initial rates of this enzyme-catalysed hydrolysis reaction vary with different concentrations of sucrose. Label your graph as **Graph 1**.

(ii) Explain the shape of **Graph 1**, making reference to the order of reaction with respect to sucrose.

(iii) On the same axes in **(b)(i)**, sketch another graph to show how the initial rates will vary with the concentrations of sucrose if the reaction mixtures were contaminated with trace amount of Ag^+ ions. Label this graph as **Graph 2**.

(iv) What causes the shape of **Graph 2** to be different from **Graph 1**? Explain the chemical basis. [7]

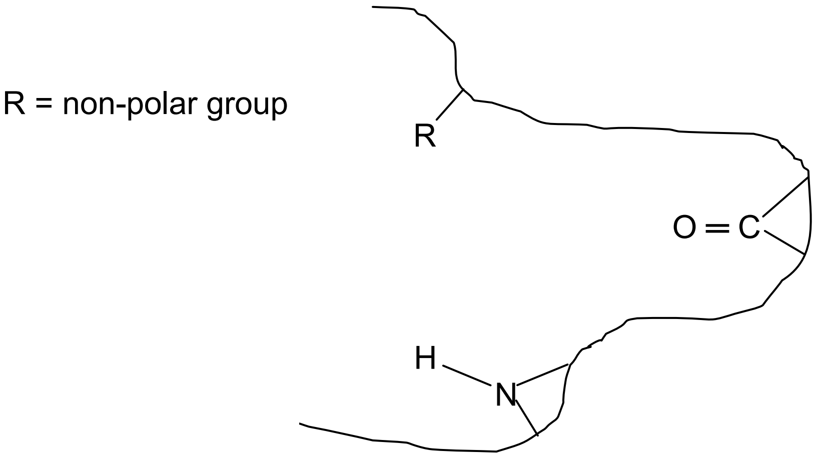
5. (c) Aspartame, an artificial sweetener, is about 200 times sweeter than sucrose. The structure of aspartame is as follows:



(i) Predict and explain whether aspartame is soluble in water, making reference to its structure and bonding.

(ii) Draw the structural formulae of all the organic products formed when aspartame is boiled with aqueous KOH, labelling with an asterisk any chiral carbon atom in each product.

(iii) Scientists believe that molecules which promote the sensation of sweetness fit into a receptor site in the taste buds on the tongue, which is essentially a protein molecule. A simplified diagram of the receptor site is shown below.



State **two** different types of interactions that can be formed between an aspartame molecule and the receptor protein. Illustrate your answer with labelled diagrams. [7]

[Total: 20]