

PIONEER JUNIOR COLLEGE JC2 PRELIMINARY EXAMINATION 2008

CHEMISTRY Higher 2

9746/03

Paper 3 Free Response

11 September 2008

2 hours

Additional Materials: Data Booklet Writing Paper Cover Page

READ THESE INSTRUCTIONS FIRST

Write your name, CT Group and index number in the spaces at the top of this page and every sheet of your scripts.

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.

Answer any **four** questions.

Write your answers on the writing papers provided. **Begin** each question on a **fresh** page. If there is no answer to any of the questions, a <u>blank sheet</u> of paper for each unanswered question with the question number(s) must still be submitted.

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 with the Cover Page on top. Indicate clearly on the Cover Page the questions you have attempted.

This document consists of **7** printed pages.

[Turn Over

Answer any four questions.

1 (a) When a sample containing 2 moles of SO_2Cl_2 is placed in a 2.0 dm³ vessel at $30^{\circ}C$, it decomposes to SO_2 and Cl_2 as shown in the equation below.

 $SO_2Cl_2(g) \Rightarrow SO_2(g) + Cl_2(g)$ ΔH negative

At equilibrium, the total pressure of the mixture is determined to be 38.9 atm.

- Assuming the gases behave ideally, calculate the number of moles of each gas present at equilibrium. [4]
- (ii) Hence, calculate the value of K_c, giving its units. [2]
- (iii) State Le Chatelier's principle. [1]
- (iv) State and explain how the value of K_c would change if there was an increase in temperature.
 [2]
- (b) The chlorides of sodium and silicon differ considerably in their physical and chemical properties.

State and account for **one** difference in the

- (i) physical property
- (ii) chemical property

of the two compounds, writing equations where appropriate. [6]

- (c) Propose a reaction scheme (in not more than 3 steps) for each of the following conversions. Give the reagents and conditions, as well as the structures of the intermediate compounds formed.
 - (i) CH₃CH₂CH₂NH₂ from CH₃CH₂OH
 - (ii) CH₃COCH₂OH from CH₃CH=CH₂

[Total: 20]

- **2 (a) (i)** Define the term standard enthalpy change of neutralisation. [1]
 - (ii) The table shows the standard enthalpy change of neutralisation when various acids are neutralised by sodium hydroxide.

Acid	Standard enthalpy change of neutralisation	
hydrochloric acid	-57.3 kJ mol⁻¹	
nitric acid	-57.3 kJ mol ⁻¹	
ethanoic acid	-55.2 kJ mol ⁻¹	

Explain why the standard enthalpy change of neutralisation of ethanoic acid is different from the other two acids. [1]

(iii) In an experiment to determine the enthalpy change of reaction between ethylamine and hydrochloric acid, 35.0 cm³ of 1.0 mol dm⁻³ ethylamine was mixed with 45.0 cm³ of 2.0 mol dm⁻³ hydrochloric acid. The temperature of the mixture rose by 5.2°C.

Calculate the standard enthalpy change of the above reaction. (Assume the heat capacity of all solutions to be $4.2 \text{ J K}^{-1} \text{ g}^{-1}$) [2]

- (b) Ethylamine, CH₃CH₂NH₂, is a weak base with a base dissociation constant of 4.5 x 10⁻⁴ mol dm⁻³ at 25°C. In an acid-base titration, 40.00 cm³ of 0.10 mol dm⁻³ hydrochloric acid is slowly added from a burette to 20.0 cm³ of 0.10 mol dm⁻³ of ethylamine solution.
 - (i) Calculate the pH of 0.10 mol dm⁻³ ethylamine solution. [2]
 - (ii) Calculate the volume of hydrochloric acid to be added to obtain a solution which is equally effective in resisting pH changes on addition of small amount of acid or alkali. Hence, calculate the pH of this solution.
 - (iii) Using your answers to (i) and (ii), sketch the expected acid-base titration graph to indicate the essential pH changes for the titration described. Mark clearly where the end point occurs and suggest a suitable indicator for the titration.
- (c) Arrange 4-methylphenylamine, phenylamine and ethylamine in the order of increasing basicity. Explain your answer. [3]
- (d) The common analgesic drug *Paracetamol* can be synthesised from 4-aminophenol.



- (i) Suggest the reagent and condition necessary for this synthesis. [1]
- (ii) Suggest why the corresponding ester is not formed in the synthesis. [1]
- (iii) *Paracetamol* forms different products when it is treated with aqueous sodium hydroxide under different conditions.

Give the structural formulae of the products formed and state the conditions for the reaction with aqueous sodium hydroxide. [3]

[Total: 20]

3 (a) Hydrogen peroxide reacts with acidified iodide ions to liberate iodine, according to the following equation:

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(I) + I_2(aq)$$

The rate of reaction can be measured by the increase in the concentration of iodine formed over time. The reaction was determined to be **zero order** with respect to hydrogen ions.

The following results were obtained by varying the concentrations of hydrogen peroxide and iodide ions.

Expt	Initial [H ₂ O ₂ (aq)]	Initial [I (aq)]	Initial rate
-	$/ \text{ mol dm}^{-3}$	/ mol dm ⁻³	/ mol dm ⁻³ min ⁻¹
1	0.020	0.040	1.2 x 10 ⁻⁴
2	0.020	0.050	1.5 x 10⁻⁴
3	0.050	0.040	3.0 x 10⁻⁴
4	0.020	0.500	1.5 x 10⁻³
5	0.050	1.000	7.5 x 10⁻³

- (i) Define the terms order of reaction and half-life.
- (ii) Determine the order of the reaction with respect to the two reactants and write down the rate equation. [3]

[2]

[1]

- (iii) Calculate the rate constant, stating its units.
- (iv) The half-life of hydrogen peroxide in experiment 4 was 9.2 min. Predict the half-life of hydrogen peroxide in experiment 5. [1]
- (b) An alternative method of investigating the rate of the above reaction can be conducted by titrating the iodine formed with sodium thiosulphate solution.
 - (i) Suggest how the reaction can be quenched at specified time intervals. [1]
 - (ii) Write an equation for the reaction between iodine and thiosulphate. [1]
- (c) Explain each of the following observations as fully as you can.
 - (i) The boiling points of HCl, HBr and HI increase down the group. [2]
 - (ii) The thermal stability of HC*l*, HBr and HI decrease down the group. [2]

(d) An organic compound P, C₁₀H₁₁O₂Br, does not react with aqueous sodium carbonate. P reacts slowly on heating with aqueous sodium hydroxide, followed by acidification to form an optically active compound Q, and an insoluble oil R, C₇H₈O. R gives benzoic acid on oxidation. One mole of Q reacts with two moles of phosphorus pentachloride to give steamy fumes.

Deduce the structures of compounds **P**, **Q** and **R**. Explain the chemistry of the reactions described, writing equations where appropriate. [7]

[Total: 20]

- 4 (a) Solid magnesium amide, $Mg(NH_2)_2$ decomposes when heated to form a high melting point solid, Mg_3N_2 , and ammonia gas as the only products.
 - (i) Construct a balanced equation for the decomposition of $Mg(NH_2)_2$. [1]
 - (ii) The variation in thermal stability of Group II amides parallels that of Group II carbonates. Explain qualitatively whether magnesium amide, is more or less thermally stable than barium amide. [2]
 - (iii) Magnesium produces nitride, Mg_3N_2 , in addition to its oxide when burnt in air.

A 1.00 g sample of the powder obtained from the burning of magnesium in air was boiled with water. The ammonia that was evolved neutralised 12.0 cm^3 of 0.50 mol dm⁻³ hydrochloric acid.

Calculate the percentage of magnesium nitride in the 1.00 g sample. [2]

(b) The decomposition of zinc carbonate is shown below,

$$ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$$
 $\Delta H^{\theta} = +71 \text{ kJ mol}^{-1}$

- (i) Calculate ΔG^{θ} for the reaction, given its ΔS^{θ} is +174 J mol⁻¹ K⁻¹ at 298 K and predict whether the reaction is feasible at 298 K. [2]
- (ii) Is the decomposition of ZnCO₃ feasible at higher temperature? Explain your answer. [2]
- (c) Zinc oxide occurs in nature as the mineral zincite. In recent years, it has received considerable attention because of its unique optical, semiconducting, piezoelectric, and magnetic properties.

Using the data provided and relevant data from the *Data Booklet*, construct a labelled Born-Haber cycle to calculate the lattice energy of zinc oxide. [4]

Standard enthalpy change of formation of zinc oxide / kJ mol ⁻¹	-348
Standard enthalpy change of atomisation of zinc / kJ mol ⁻¹	+130
Sum of first and second electron affinity for oxygen / kJ mol ⁻¹	+657

- (d) This question is about L, C_9H_8O .
 - Compound L is insoluble in water and aqueous sodium hydroxide.
 - With liquid bromine, **L** gives **M**, C₉H₈OBr₂.
 - L does **not** react with Fehling's solution but reacts with Tollens' reagent to give a silver mirror.
 - On heating with acidified potassium manganate(VII), **L** gives **N**, C₈H₆O₄.

Compound **N** is soluble in aqueous sodium hydroxide. Treatment of **N** with thionyl chloride followed by ethylamine gives **O**.

Deduce the structures of compounds L, M, N and O. Explain the chemistry of the reactions described. [7]

[Total: 20]

5 (a) Anodising is an important industrial process which involves increasing the thickness of the natural oxide layer on the surface of metal parts.

In one such industrial operation, an artefact made of aluminium is to be anodised. Given that the total surface area of the artefact is 800 cm², and that the density of Al_2O_3 is 4.0 g cm⁻³, calculate the total quantity (in coulombs) of electricity that will be required to increase the thickness of its oxide layer by 0.1 mm. [3]

- (b) Transition metals, such as iron, can form coloured *complex ions* in aqueous solutions.
 - (i) What do you understand by the term *complex ion*? [2]
 - (ii) Explain why the complex ions of transition elements are coloured. [3]
- (c) By using relevant data from the *Data Booklet*, explain the following observations.

A reddish brown solution is formed when an aqueous solution of iron(III) chloride is added to potassium iodide. The reddish brown solution is not observed when an aqueous solution of $K_3Fe(CN)_6$ is used. [3]

(d) Describe the quaternary structure of haemoglobin. [3]

(e) The iron atom in the haemoglobin molecule contains six 3d electrons and it is surrounded by six ligand atoms. Five of these are nitrogen atoms from the globin protein, and one is an oxygen atom from a water molecule. This molecule is replaced by an oxygen molecule in oxyhaemoglobin. This equilibrium may be expressed as shown.



- (i) Describe the bonding between oxygen and the iron atoms in haemoglobin and oxyhaemoglobin. [1]
- (ii) State and explain the change of oxidation number, if any, that occurs when haemoglobin is converted into oxyhaemoglobin. [2]
- (f) The structures of the three amino acids and their respective isoelectric points (IEP) are given.



In preparation for electrophoresis, the three amino acids were dissolved together in the same buffer solution kept at pH 6.07.

During electrophoresis, a potential difference is applied across the solution containing the three amino acids and the results are obtained as shown in the diagram.



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By drawing the corresponding forms of the three amino acids in the buffer solution, deduce the identities of the amino acids **A**, **B** and **C**. [3]

[Total: 20]

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