

JURONG JUNIOR COLLEGE JC 2 PRELIMINARY EXAMINATION Higher 2

CLASS

CHEMISTRY

Paper 3 Free Response

9746/03

21 August 2009

2 hours

Additional Materials:	Answer Paper	
	Data Booklet	
	Graph Paper	

READ THESE INSTRUCTIONS FIRST

Write your name and class 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.

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.

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.

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.

- 1. Phenol is a powerful disinfectant and has antiseptic properties. Hence it is found in medicinal products such as ear and nose drops, throat lozenges and mouthwashes.
 - (a) The standard enthalpy change of combustion of solid phenol is -3054 kJ mol⁻¹.
 - (i) What is meant by the term standard enthalpy change of combustion?
 - (ii) Write the equation, with state symbols, which represents the standard enthalpy change of combustion of phenol.
 - (iii) Using the following standard enthalpy changes of formation together with data given above, calculate the standard enthalpy change of formation of phenol.

 $\Delta H_{f}(CO_2) = -394 \text{ kJ mol}^{-1}$

 $\Delta H_{f}(H_{2}O) = -286 \text{ kJ mol}^{-1}$

- (iv) Given that the standard entropy change for the formation of phenol is $-384 \text{ J K}^{-1}\text{mol}^{-1}$, calculate the value of the standard free energy change, ΔG^{\cdot} , for the formation of phenol.
- (b) 2,4,6-trichlorophenol is a chlorinated phenol which is a stronger germicide than phenol.



2,4,6-trichlorophenol

- (i) Predict and explain if 2,4,6-trichlorophenol has a larger or smaller K_a value as compared to phenol.
- (ii) Suggest a suitable chemical test to distinguish between 2,4,6-trichlorophenol and phenol.

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1. (c) 1-naphthol, a derivative of phenol, can be used to synthesize compound **Q** by the following reaction scheme.



1-naphthol

Compound Q

- (i) Suggest a suitable structure for the intermediate, **P**.
- (ii) State the reagents and conditions for Steps I and II.
- (iii) 1-naphthol is less soluble in water than phenol. Explain why.

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- (d) An alkaline solution of compound **Q** from part (c) can also act as a bidentate ligand. When the alkaline solution containing **Q** is added to a blue solution of Cu^{2+} (aq), a pale blue precipitate **R** is formed. Analysis of **R** shows that the formula is $Cu(C_{10}H_8NO)_2(H_2O)_2$.
 - (i) Explain why the Cu^{2+} (aq) solution is coloured.
 - (ii) Suggest a reason why Cu^{2+} has a tendency to form complexes.
 - (iii) Draw the structural formula of **R**, showing the arrangement of the ligands in the structure.
 - (iv) When excess of concentrated aqueous ammonia is added to **R**, the precipitate dissolves to form a deep blue solution.

Identify the species that gives rise to the deep blue solution.

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[Total marks: 20]

2. An active ingredient in aspirin is a weak monobasic acid called acetylsalicylic acid. Its molecular formula is $C_8H_7O_2CO_2H$. ($K_a = 3.2 \times 10^{-4} \text{ mol dm}^{-3}$)

50 cm³ of 0.1 mol dm⁻³ acetylsalicylic acid was titrated against 0.1 mol dm⁻³ sodium hydroxide solution to obtain a titration curve as shown below:



(a) (i) Define the term "weak acid".

- (ii) Calculate the pH of the solution in the conical flask at point **A**.
- (iii) Determine the volume of NaOH required for complete neutralisation, x, and hence calculate the pH of the solution at point **B**.

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- (b) At point **C**, a buffer solution was obtained.
 - (i) Calculate the pH of the solution at point **C**.
 - (ii) Write equations to show how this solution at point **C** reacts with small amounts of hydrogen ions and hydroxide ions.
 - (iii) When 2 cm³ of 0.1 mol dm⁻³ HC*l* is added to the buffer solution at Point C, calculate the pH of the resulting solution.

2. (c) $C_6H_5CH_2Br$ can be synthesised from $C_6H_5CH_3$ through the following reaction pathways:



- (i) State the reagents and conditions required for steps I, II and III. Hence, deduce the structure of Compound D.
- (ii) Suggest reagents and conditions for Reaction Route 2 whereby the synthesis can be completed in one step.
- (iii) Comparing Reaction Route 1 and Reaction Route 2, which one is a better synthetic pathway? Explain your choice.
- (iv) Suggest a chemical test to confirm the presence of

[8]

in the synthesis.

[Total marks: 20]

CH₂Br

3. (a) Phosphorus forms 2 chlorides, PCl_3 and PCl_5 . The pentachloride is prepared by reacting PCl_3 with dry chlorine.

 $PCl_3 + Cl_2 = PCl_5$ $\Delta H = -124 \text{ kJ mol}^{-1}$

The preparation is carried out in a cooled flask under anhydrous conditions.

- (i) Suggest two reasons why a cooled flask is used.
- (ii) Give a reason for the use of anhydrous conditions. Include any relevant equations.
- (b) Describe and explain what happens in the following experiment and write balanced equations, including state symbols, for the reactions that occur.

Aqueous sodium chloride and aqueous silver nitrate are mixed and aqueous ammonia is then added.

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(c) Using your knowledge of the reactions of solid sodium chloride, bromide and iodide, predict the gaseous products that will be formed when concentrated sulphuric acid is warmed with solid sodium astatide (NaAt). Write equations, including state symbols, for **all** the reactions occurring with sodium astatide.

[2]

(d) Hydrogen chloride is another very commonly used chlorine-containing reagent in the laboratories for simple reactions as shown below:

When **P**, $C_6H_{10}O_4$, is heated with aqueous sodium hydroxide, compound **Q**, $C_2H_6O_2$, and sodium ethanoate are formed.

When 1 mol of **Q** reacts with 1 mol of hydrogen chloride, **R**, C_2H_5OCI , is formed. **R** gives **S**, C_3H_5ON on heating with ethanolic potassium cyanide.

When **S** is heated with dilute HC*l*, an optically inactive liquid **T**, $C_3H_6O_3$, is obtained. On heating **T** with Al_2O_3 , a liquid **U**, $C_3H_4O_2$, is formed. **U** rapidly decolourises aqueous bromine.

Deduce the structural formulae of compounds **P** to **U**, giving your reasoning. [11]

[Total marks: 20]

4. (a) Hydrogen peroxide reacts with iodide ions in acidic solution as shown below.

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

In a series of experiments, the reaction was carried out with different concentrations of the 3 reagents and the following results were obtained.

Expt	$[H_2O_2]$	[H⁺]	[I ⁻]	Relative initial rate
INO.	/ mol dm ⁻³	/ mol dm ⁻³	/ mol dm⁻³	/ mol dm ⁻³ s ⁻¹
1	0.020	0.060	0.060	1.00
2	0.020	0.050	0.050	0.833
3	0.020	0.050	0.060	1.00
4	0.025	0.050	0.050	1.042

- (i) Use the data to deduce the order of reaction with respect to each reagent. Explain your answers and write a rate equation.
- (ii) Two different mechanisms have been suggested for this reaction.

Mechanism A:	H ₂ O ₂ + I [−]	\rightarrow H ₂ O + IO ⁻	(Step 1)
	H⁺ + IO ⁻	\rightarrow HIO	(Step 2)
	$HIO + H^+ + I^-$	\rightarrow H ₂ O + I ₂	(Step 3)
Mechanism B:	$H_2O_2 + I^- + H^+$	\rightarrow H ₂ O + HIO	(Step 1)
	HIO + I⁻	$\rightarrow \ I_2 \ + \ OH^-$	(Step 2)
	OH⁻ + H⁺	\rightarrow H ₂ O	(Step 3)

Which mechanism is consistent with your rate equation in a(i)? Explain your answer.

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(b) The decomposition of hydrogen peroxide is a first order reaction.

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2 \quad \Delta H = -98 \text{ kJ mol}^{-1}$$

The uncatalysed reaction has an activation energy of 79 kJ mol⁻¹.

- (i) Use the data provided to sketch a fully labeled reaction pathway diagram showing all relevant energy changes.
- (ii) Define the terms activation energy and rate constant.
- (iii) How will the *activation energy* and the *rate constant* for the reaction be affected by an increase in temperature? Explain your answer with the [8] aid of the Boltzmann Distribution diagram if necessary.

4. (c) Hydrogen cyanide adds to the carbonyl group to form a cyanohydrin.



The reaction is slow, but the rate is increased by the addition of a small amount of sodium cyanide.

- (i) Give the mechanism of this reaction, showing clearly the flow of electrons.
- (ii) Identify the rate determining step in the mechanism and give a reason for your choice.
- (iii) Why is sodium cyanide needed to achieve a rapid reaction?
- (iv) Why does hydrogen cyanide not react in a similar fashion with an ester, RCO_2CH_3 ?
- (v) Give a synthetic pathway for the preparation of CH₃CH₂CH(OH)CH₂NH₂ in two steps, using a cyanohydrin as the intermediate. [7]

[Total: 20]

- 5. (a) (i) Draw a labeled diagram to show how the standard electrode potential $E(Fe^{2^+}/Fe)$ might be measured in the laboratory.
 - (ii) With the aid of the Data Booklet, predict the outcome of the reaction between iron(II) sulfate and hydrogen peroxide in aqueous solution. Write a balanced equation for any reaction that occurs.
 - (b) The variation in the electrode potential, $E(Fe^{2+}/Fe)$ with pH is shown in the diagram below.



- (i) What is the concentration of iron(II) ions at the pH range of 0 to x?
- (ii) Write an expression for the solubility product, K_{sp} , of iron(II) hydroxide.
- (iii) The numerical value of the solubility product of iron(II) hydroxide is 6.0×10^{-15} at 25 °C. Calculate the pH value, *x*, as indicated on the diagram.
- (iv) Suggest an explanation for the decreasing trend of the electrode potential, $E(Fe^{2+}/Fe)$ when pH is beyond the value of x.

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5. (c) To determine the amount of iron in compounds present in tea leaves, a student carried out the following procedure.

A 500 g sample of dry tea leaves was ignited to constant mass in a crucible. The residue was stirred into excess nitric acid and the mixture heated gently for some minutes. Excess zinc was then stirred into the mixture and after the reaction had ceased, the mixture was filtered. The filtrate was then made up to exactly 100 cm³ of solution.

A 10.0 cm³ portion of the solution was acidified with sulfuric acid and, on titration, required 26.8 cm³ of 0.0010 mol dm⁻³ potassium manganate(VII).

- (i) Explain the role of zinc in this analysis.
- (ii) Determine the mass of iron (per gram of dry tea leaves) in compounds present in tea leaves.
- (d) **E** is a magnesium compound which is insoluble in water.

The action of heat on **E** produces a gas **F**, which forms white precipitate with limewater.

E dissolves in aqueous nitric acid with the evolution of **F** and white hydrated crystals **G** can be obtained by evaporating the solution formed.

On heating \mathbf{G} , water vapour is produced along with brown fumes and another gas that relights a glowing splint.

- (i) Suggest the formulae of **E**, **F** and **G**.
- (ii) Suggest balanced equations for the three reactions described:
 - action of heat on E
 - action of acid on E
 - action of heat on **G**
- (iii) Magnesium nitrate decomposes at a lower temperature than barium nitrate. Explain why these two nitrates decompose at different temperatures.

[Total: 20]

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