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CATHOLIC JUNIOR COLLE	GE
CHEMISTRY Higher 1	8872/02
Paper 2 Pr	eliminary Examination 2009
	2 hours
Candidates answer Section A on the Question Paper and Section B on separate paper. Additional Materials: Paper Data Booklet	
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 paper clips, highlighters, glue or correction fluid.	Э.
Section A Answer all questions.	
Section B Answer any two questions on separate answer paper.	
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 ques	stion or part question.
	For Examiner's Use
	Section A
	B6
	B7
	Total

There are a total of <u>10</u> printed pages including this cover page.

Section A

Answer **all** the questions in this section in the spaces provided.

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

 $H_2O_2 \rightleftharpoons H_2O + \frac{1}{2}O_2$

The activation energy of the forward reaction is 180 kJ mol^{-1} and that for the reverse reaction is 282 kJ mol^{-1} . The rate of the reaction can be increased by the addition of platinum catalyst.

(i) Use the data provided to construct a reaction pathway diagram for the uncatalysed reaction, indicating the activation energy of the forward reaction.

(ii) Calculate the enthalpy change for the decomposition of hydrogen peroxide.

ΔH = _____

- (iii) State how the reaction pathway diagram will change with the addition of platinum catalyst.
- (iv) Use the bond energies given in the *Data Booklet* to calculate another value for the enthalpy change for the decomposition of hydrogen peroxide. (The structure of H_2O_2 can be taken as: H-O-O-H)

(v) Suggest a reason for the discrepancy between the values in (a)(ii) and that in (a)(iv).

(b) Wine contains a small amount of sulfur dioxide that is added as a preservative. The sulfur dioxide content of the wine can be determined by the following method.

A 50 cm³ sample of wine is reacted with 40 cm³ of 0.01 mol dm⁻³ of aqueous iodine which is present in excess.

The unreacted iodine requires 23.60 cm³ of 0.02 mol dm⁻³ sodium thiosulfate, $Na_2S_2O_3$ for complete reaction. This reaction follows the equation given:

$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^{-}$$

(i) What is the amount of unreacted iodine that reacted with sodium thiosulfate?

(ii) What is the amount of iodine that reacted with sulfur dioxide in the sample of wine?

(iii) The sulfur dioxide in the wine is oxidised by I_2 to sulfate, $SO_4^{2^2}$, according to the half equation:

$$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$$

With reference to the *Data Booklet*, construct a balanced equation for the reaction between SO_2 and I_2 . Hence, find the amount of sulfur dioxide present in the wine.

(iv) Determine the concentration of sulfur dioxide, in mol dm⁻³, in the wine.

2 The following diagram represents the first ionisation energies of the elements in Period 2 and in Period 3 of the Periodic Table.



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3(a) Complete the reaction scheme below by writing the structural formula of the products A - D in the spaces provided.



Give the reagents and conditions for the reactions E and F.

E		
F	₽ <u>.</u>	
		[6]

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(b) Three compounds J, K and L are given below:



Describe briefly how you would **positively** identify the three compounds using simple chemical tests.



(c) Give the reagents, conditions and intermediates to synthesise 3-chlorobenzoic acid from methylbenzene.

CH₃ CO₂H

methylbenzene

3-chlorobenzoic acid

(Note that the synthesis requires more than one step.)

4. In the Age of Exploration, scurvy was a very serious problem among sailors. This resulted in their high death tolls. Sufferers of this disease often appear pale, are likely to have spots on their skins, and will also experience bleeding. When vitamin C was introduced to the diet of these sailors in that era, their fatality rates dropped significantly.

Vitamin C has the following structure:



In more recent times, vitamin C can be synthesised in the laboratory that involves biological and organic chemistry. A global health-care company from Switzerland called Hoffmann-LaRouche was the first to manufacture vitamin C synthetically from glucose.

Vitamin C tablets are now readily available in the market. The common doses are 100 mg, 250 mg, 500 mg and 1000 mg tablets. These tablets can come in chewable form or in effervescent form. The amount of vitamin C in a tablet can be determined by titration with a complex of iodine called triiodide.

The soluble triiodide is formed when the relatively insoluble iodine is present in a solution of iodide ions:

$$I_2 + I^- \rightleftharpoons I_3^-$$

Triiodide oxidises vitamin C (C₆H₈O₆) to form dehydroascorbic acid:

$$C_6H_8O_6 + I_3^- + H_2O \rightarrow C_6H_6O_6 + 3I^- + 2H^+$$

Howevever, when the all the vitamin C is oxidised, iodine and triiodide will be present, which react with starch to form a blue-black complex. The blue-black color is the endpoint of the titration.

- (a) Suggest a possible method by which the sailors managed to introduce vitamin C into their diets.
- (b) On the Vitamin C structure given above, circle the functional group that can be easily oxidised to form a carboxylic acid group. [1]
- (c) Based on the description given in the above passage, what is the indicator used for the titration?

[1]

[1]

(d) A vitamin C tablet is crushed and made into a 100 cm³ solution. 25.0 cm³ of the vitamin C solution was titrated with 22.60 cm³ of 0.031 mol dm⁻³ triiodide solution. Which of the four common doses of vitamin C did the tablet contain? (Given: M_r of vitamin C = 176)

Section B

Answer **two** of the following questions. Answer these questions on separate answer paper.

5 (a) 40 cm³ of 3.0 mol dm⁻³ CH₃CO₂H were added to 60 cm³ of 1.4 mol dm⁻³ KOH in a polystyrene cup.

The reaction follows this equation:

$$CH_3CO_2H + KOH \rightarrow CH_3CO_2K^+ + H_2O$$

The maximum temperature rise was recorded as 10.5 $^{\circ}$ C. (Assume that the specific heat capacity of the solution is 4.2 J g⁻¹ K⁻¹.)

- (i) Define the term *enthalpy change of neutralisation*.
- (ii) Calculate the enthalpy change of neutralisation of CH_3CO_2H with KOH.
- (iii) Explain how would you expect the value in **(a)**(ii) to compare with the enthalpy change of neutralisation of HCl with KOH.

[5]

- (b) (i) State Le Chatelier's Principle.
 - (ii) Both carbon dioxide and carbon monoxide are present in the exhaust gases of cars. The following equilibrium between the two gases can be set up:

 $2 \operatorname{CO}_2(g) \rightleftharpoons 2 \operatorname{CO}(g) + \operatorname{O}_2(g) \Delta H > 0$

State and explain whether the production of carbon dioxide (CO₂) is favoured by

- High or low temperature
- Good or poor air flow
- (iii) State and explain what the effect on the production of sulfur trioxide (SO₃) will be if the same conditions chosen in **(b)**(ii) were employed.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
 $\Delta H < 0$

- (iv) Write an expression for the equilibrium constant, K_c, for the reaction given in **(b)**(iii).
- (v) 2 moles of SO₂ and 1 mole of O₂ were contained in a volume of 2 dm³ and passed over a catalyst at 430°C. The SO₃ formed at equilibrium is 1.9 moles. Calculate the equilibrium concentrations of SO₂ and O₂, and hence find the value of K_c at 430 °C. [11]
- (c) (i) Identify the type of reaction that occurs when ammonia reacts with chloromethane.
 - (ii) Ammonia, in the presence of excess chloromethane, forms compound **Y**, $(CH_3)_4N^+CI^-$. Explain why compound **Y** has a high boiling point and is also soluble in water.

[4]

[Total: 20]

6 (a) A neutral liquid **A**, C₁₀H₁₂O₂ when heated with aqueous hydrochloric acid gave two products, **B** and **C**.

B, $C_8H_{10}O$, gave a yellow precipitate when warmed with aqueous alkaline iodine. When heated with acidified sodium dichromate (VI), **B** gave **D**, C_8H_8O .

D reacts with 2,4-dinitrophenylhydrazine to give orange crystals, **E**.

Deduce the possible structures of compounds A to E. Explain the chemistry of the reactions involved. Write an equation for A when it is heated with aqueous hydrochloric acid. [8]

(b) The kinetics of the reaction of peroxodisulfate (VI) ions $(S_2O_8^{2-})$ and iodide ions (I) can be investigated experimentally by using different concentrations of the two reactants involved and determining the time taken for the brown iodine colour to first appear.

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

The following results were obtained in such an investigation:

Expt	Vol of S ₂ O ₈ ²⁻ /cm ³	Vol of I ⁻ /cm ³	Vol of water /cm ³	Time /s
1	10	20	20	90
2	20	30	0	30
3	10	30	10	60

- (i) Suggest a reason why the reaction is slow.
- (ii) Deduce the order of reaction with respect to $S_2O_8^{2-}$ and I^{\cdot}. Explain your reasoning.
- (iii) Write the rate equation for the reaction between $S_2O_8^{2-}$ and Γ .

(c) Aqueous solutions of AICl₃ and PCl₃ give acidic solutions. Explain how these acidic solutions are formed and write equations to illustrate your answer. [4]

- (d) Selenium dioxide, SeO₂, is often present in red-coloured glass and the compound is also used as a toner in photographic developing. SeO₂ vapour can burn the nose and throat on inhalation.
 - (i) Is SeO₂ expected to be an acidic or basic oxide?
 - (ii) SeO₂ is able to undergo a neutralisation reaction to form a salt containing the anion selenite, SeO₃²⁻. Write a balanced equation for the neutralisation reaction.
 - (iii) Suggest the shape of SeO_2 in the vapour phase.

[3]

[5]

[Total: 20]

7 (a) Cinnamic acid has the following structure:

cinnamic acid

- (i) Cinnamic acid can exhibit geometric isomerism. Draw clearly the two isomers.
- (ii) The methyl ester of cinnamic acid is methyl cinnamate. This ester is found naturally in a variety of plants. Draw the structure for methyl cinnamate, showing all the bonds in the functional group.

Cinnamic acid can react with HCI(g) at room temperature to form X.

- (iii) What is the hybridisation of the carbon marked with an asterisk (*)?
- (iv) Arrange the three compounds, $C_6H_5CH_2CO_2H$, $C_6H_5CH_2CH_2CH_2OH$ and **X** in order of increasing acidity. Hence, explain the difference in acidity between **X** and $C_6H_5CH_2CH_2CO_2H$.
- (v) Suggest a simple chemical test to distinguish **X** from **Y**.

$$\mathbf{Y} \qquad \underbrace{\bigcirc}_{\mathbf{I}} \mathbf{C} \mathbf{H}_{2} \mathbf{C} \mathbf{H} \mathbf{C} \mathbf{O}_{2} \mathbf{H} \\ \overset{|}{\mathbf{I}} \qquad [8]$$

(b) The ionisation of water can be written as follows:

 $H_2O(I) \rightleftharpoons H^+(aq) + OH^-(aq)$

- (i) Write an expression for the ionic product of water, K_w, stating the units clearly.
- (ii) The reverse reaction, $H^+ + OH^- \rightarrow H_2O$, is very common. What is the name given to this reaction?
- (iii) State and explain whether the reaction in **(b)**(ii) is expected to be endothermic or exothermic.

The following data show the temperature dependence of the pH values of pure water.

рН	7.51	7.28	7.00	6.97	6.54
Temp / °C	5.1	10.8	25.0	41.0	62.0

- (iv) The pH of water is below 7.00 at temperatures above 25.0 °C. Explain briefly why water is not acidic at temperatures above 25.0 °C.
- (v) From the data shown above, find the value of K_w at 62 °C.
- (vi) Find the pH of 1×10^{-8} mol dm⁻³ HCl at 62 °C.

(c) "Free" H^+ ions in an aqueous environment form H_3O^+ with water molecules.

- (i) Draw the dot-and-cross diagram of the H_3O^+ ion, showing clearly the type of bond between H^+ and H_2O .
- (ii) Draw clearly the shape of the H_3O^+ ion.

[3]

[9]