CATHOLIC JUNIOR COLLEGE



PRELIMINARY EXAM 2008

CHEMISTRY Higher 2

9746/03

Paper 3 Free Response

8 September 2008

2 hours

Additional Materials: Data Booklet Answer Paper

READ THESE INSTRUCTIONS FIRST

Write in dark blue or black pen.

You may use a soft pencil for any diagrams, graphs or rough working.

Do not use correction fluid.

Answer any four questions.

A Data Booklet is provided.

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

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.

This document consists of <u>8</u> printed pages and <u>0</u> blank page.

Answer any **four** questions.

1 Grignard reagents are organo-magnesium halides, commonly used in synthesis to prepare a variety of organic compounds.

The reaction scheme for the synthesis of 3-methylpentan-2-ol, **B**, using a Grignard reagent is shown below. The Grignard reagent is prepared from the alkylhalide **A** and subsequently acts as a nucleophile before forming the product **B**.

 $CH_{3}CH_{2}CH=CH_{2} \xrightarrow{HCl} C_{4}H_{9}Cl \xrightarrow{Mg} CH_{3}CH_{2}CHCH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{C} C_{6}H_{14}O$

- (a) (i) Describe the mechanism for the reaction in step I.
 - (ii) Hence explain why compound **A** may be found as an equimolar mixture of two isomers.

[6]

- (b) An alternative method of preparing 3-methylpentan-2-ol is through the use of 3-methylpentane as a starting material.
 - Suggest an alternative two-step method of preparing 3-methylpentan-2-ol from 3-methylpentane, stating clearly the reagents and conditions required for each step.
 - (ii) Suggest a reason why the synthetic method stated in (b)(i) is **not** preferred to that of using Grignard reagents.

[3]

- (c) 3-methylpentan-2-ol is easily converted to other useful organic compounds such as 2-methylbutanoic acid, which is widely used in perfumery. Outline how 3-methylpentan-2-ol may be converted to 2-methylbutanoic acid, giving the structure of any intermediate product(s) formed.
- (d) There are certain practical issues with the use of Grignard reagents, notably slow formation of the Grignard reagent and susceptibility to water in air.
 - (i) The slow starting rate may be offset by cutting the magnesium into smaller pieces or scraping the sides of the metal before use. Using a balanced equation, explain why the magnesium may not react as quickly as expected.
 - (ii) The Grignard reagents have similar properties to that of magnesium chloride. Using balanced equations, show the reaction of magnesium chloride in water and state the pH of the resultant solution. Hence, suggest why effort is required to ensure only anhydrous chemicals are used during synthesis involving Grignard reagents.

[5]

(e) Compare the structure and bonding of the oxides of magnesium in contrast to the oxides of silicon and sulphur. [3]

[Total: 20]

2 (a) Nitrogen and oxygen react in a hot car engine to form nitrogen monoxide which is a serious pollutant of the atmosphere. Nitrogen monoxide may be removed from the car exhaust by using a catalytic converter. In this process, nitrogen monoxide reacts with carbon monoxide (a product of combustion of gasoline) in the presence of platinum catalyst as follows:

NO (g) + CO (g)
$$\rightarrow \frac{1}{2} N_2(g) + CO_2(g)$$

By using the following values of enthalpy change of formation, calculate the relevant enthalpy changes of reactions and explain why this reaction is more efficient as a method of removing nitrogen monoxide than decomposing it to its elements. [ΔH_f / kJ mol⁻¹ : NO = +90; CO = -111; CO₂ = -394]

[3]

(b) In heavily polluted air, a brown haze is often seen due to the formation of nitrogen dioxide from nitrogen monoxide that passes into the atmosphere.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \qquad \Delta H < 0$$

In a series of experiments carried out to investigate this reaction, the following results were obtained.

Experiment	concentration / mol dm ⁻³		initial rate /
	NO (g)	O ₂ (g)	mol dm ^{−3} s ^{−1}
1	0.001	0.1	0.70×10^{-3}
2	0.002	0.1	2.80×10^{-3}
3	0.003	0.2	12.60×10^{-3}

- (i) Deduce the order of reaction with respect to each reactant, and hence write the rate equation for the reaction.
- (ii) Calculate a value for the rate constant *k*, giving its units.
- (iii) Suggest, with explanation, how the value of the rate constant k is affected (if at all) as the gases get cooler in the upper part of the atmosphere.

[5]

(c) The first step in a possible mechanism for the reaction in (b) is

 $2NO(g) \rightarrow N_2O_2(g)$ fast (step 1)

- (i) Draw dot-and-cross diagrams to show the electronic structures of the two molecules, NO and N_2O_2 . What feature in the electronic structure of NO would suggest that this is a likely first step in the reaction?
- (ii) Suggest an equation for the *slow* rate-determining step (step 2).
- (iii) Sketch and clearly label the energy profile diagram for the proposed mechanism represented by steps 1 and 2.

[6]

- (d) (i) When 2-bromocyclohexanol reacts with NaOH in hot ethanolic solution, two isomeric products are formed. Draw the structures of the two isomers.
 - (ii) A different reaction occurs when 2-bromocyclohexanol reacts with aqueous NaOH. Draw the structural formula of the product formed.
 - (iii) The kinetics of the reaction in (d)(ii) is given by the rate equation

rate = k [2-bromocyclohexanol]

Outline a mechanism which is consistent with the observed kinetics, using curly arrows to denote any electron transfer.

[6] [Total : 20]

- **3** Use of the *Data Booklet* is relevant to this question.
 - (a) Explain the following observations with the aid of equations.
 - (i) When sodium hydroxide was added to a solution of iron(II) ions, a green precipitate was observed. On standing, in the presence of air, the precipitate turned brown.
 - (ii) When iodide ions were added to aqueous iron(III) chloride, a brown solution was obtained. However, no such observation was seen when the experiment was repeated in the presence of cyanide ions.

[6]

- (b) One method for powering a heart pacemaker comprises zinc and platinum electrodes implanted within the body tissues. These electrodes in the oxygen-containing body fluid at a *pH* of 7.4 form a 'biogalvanic' cell in which zinc is oxidised and oxygen is reduced.
 - (i) Write a balanced equation for the overall chemical reaction and calculate the E^{θ}_{cell} of this cell.
 - (ii) Explain how the E_{cell}^{θ} value would change if the *pH* of the body fluid decreases.
 - (iii) If a current of 4×10^{-5} A was drawn from the cell, calculate how long a zinc electrode weighing 5 g will last before it needs to be replaced. Give your answer correct to the nearest day.

[7]

- (c) Explain why a solution of Zn^{2+} ions is colourless but a solution of Fe^{2+} is coloured. [3]
- (d) An aqueous solution of Co^{2+} is able to catalyse the reaction between iodide and peroxodisulphate, $S_2O_8^{2-}$.
 - (i) State the type of catalysis involved and explain why Co²⁺ is suitable as such a catalyst.
 - (ii) Explain, with the help of equations, how Co²⁺ is able to catalyse the above reaction.

[4] [Total: 20] 4 (a) Compound A has molecular formula C₇H₁₄O₂ and can exhibit both geometrical isomerism and optical isomerism. When one mole of A is heated with acidified potassium manganate(VII), one mole of B, C₅H₈O₂, is produced together with two moles of carbon dioxide. Subsequently, when one mole of B is warmed with an alkaline solution of iodine, one mole of C is produced together with two moles of a yellow precipitate D. Upon treatment of C with dilute sulphuric acid, compound E, C₃H₄O₄, is produced which can undergo reaction with ethane-1,2-diol to form the cyclic compound F shown below.



- (i) Identify the structures of **A**, **B**, **C**, **D**, and **E** using appropriate balanced equations to explain the reactions they undergo.
- (ii) Give the structure of the organic product formed when compound **B** reacts with excess 2,4-dinitrophenylhydrazine.

[12]

(b) (i) The formulae of four amino acids are given:



Draw the structure of the tripeptide Ala – Pro – His.

- (ii) Briefly describe the interactions that give rise to the different levels of protein structures found in haemoglobin.
- (iii) Chemical analysis shows that haemoglobin contains 0.34 % iron by mass. What is the minimum possible molar mass of haemoglobin? The actual molar mass is four times this minimum value. What conclusion can you draw from these data about the haemoglobin molecule?
- (iv) In sickle cell anaemia, which is a hereditary disease that restricts the flow of blood to vital organs in the human body, a valine molecule replaces a glutamic acid molecule on two polypeptide chains in haemoglobin. Suggest the type of intermolecular forces that arise due to this substitution.

[8] [Total: 20]

- 5 Use of the *Data Booklet* is relevant to this question.
- (a) You are provided with the following thermochemical data:

Reactions	∆ <i>H^θ</i> / kJmol ⁻¹
Ba (s) 🛛 Ba (g)	+176
Ba (s) + aq → Ba ²⁺ (aq) +2e	+286
NO_3 (g) + aq \rightarrow NO_3 (aq)	-325
$Ba^{2+}(g) + 2NO_3(g) \longrightarrow Ba(NO_3)_2(s)$	-1395

- (i) Calculate the enthalpy change of hydration of barium ion and hence, the enthalpy change of solution of Ba(NO₃)₂.
- By using your answer from (a)(i), and given the entropy change of solution of Ba(NO₃)₂ is positive, predict whether Ba(NO₃)₂ is soluble in water. Give your reasoning.

[3]

- (b) The hydroxides and nitrates of Group II elements undergo thermal decomposition.
 - (i) Write a balanced equation, including state symbols, for the decomposition of barium nitrate.
 - (ii) The decomposition temperatures of the hydroxides of some Group II elements are given in the table below:

Hydroxides	Decomposition Temperature / °C
Ca(OH) ₂	129
Sr(OH) ₂	560
Ba(OH) ₂	832

The following equation shows the decomposition of a Group II hydroxide.

 $Ba(OH)_2$ (s) \rightarrow BaO (s) + H_2O (l)

By using your knowledge and understanding of the thermal stability of Group II nitrates, explain the trend shown by the data given in the table above.

[3]

- (c) A solution containing chloric(I) acid, HCIO, and potassium chlorate(I), KCIO, can act as an acidic buffer system.
 - (i) Explain how the above solution acts as a buffer system. Support your answer by using relevant equations.
 - (ii) Calculate the *pH* of an aqueous solution of 0.01 mol dm⁻³ potassium chlorate(I), given the pK_a value of chloric(I) acid is 7.4.
 - (iii) Calculate the *pH* of the solution formed when 250 cm³ of 0.1 mol dm⁻³ chloric(I) acid is mixed with 300 cm³ of 0.2 mol dm⁻³ potassium chlorate(I).
 - (iv) Suggest how potassium chlorate(I) may be prepared using Cl₂, stating clearly the reagents and conditions. Write a balanced equation and state the type of reaction that has occurred.

(d) Interpret the following as fully as you can.

When 1 cm³ of 1 mol dm⁻³ aqueous silver nitrate is added separately to two beakers containing 1 dm³ of 1 mol dm⁻³ of carbonate ions and 1 dm³ of 1 mol dm⁻³ of ethanoate ions respectively, silver carbonate but not silver ethanoate is precipitated. [K_{sp} (silver carbonate) = 8 x 10⁻¹² mol³ dm⁻⁹; K_{sp} (silver ethanoate) = 2 x 10⁻³ mol² dm⁻⁶.]

[4]

[Total: 20]

END OF PAPER