CATHOLIC JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATIONS
Higher 2

CHEMISTRY

9647/03

Paper 3 Free Response

Wednesday 27 August 2014
2 hours

Additional Materials: Data Booklet
Answer 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. **[PILOT FRIXION ERASABLE PENS ARE NOT ALLOWED]**
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. Write your answers on the answer paper 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.

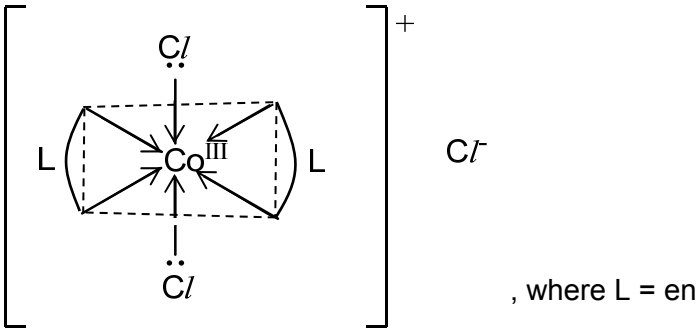
At the end of the examination, fasten all your work securely together.

This document consists of **12** printed pages and **0** blank page.

[Turn over

Answer any **four** questions.

1 **(a)** When an aqueous solution of Co^{2+} is reacted with hydrochloric acid and ethane-1,2-diamine (en) under oxidising conditions, a green mixed-ligand cobalt(III) complex, $[Co(en)_2Cl_2]^+Cl^-$, with the following structure is formed:



, where L = en

(i) State the coordination number of the above complex.

(ii) Explain why the above complex is green in colour.

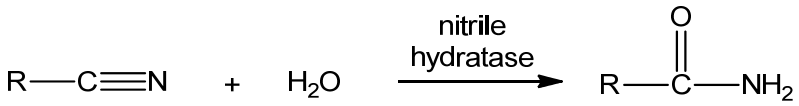
(iii) When 0.03 mol of aqueous silver nitrate is added to 0.01 mol of the above aqueous complex, a white precipitate weighing 1.44 g is formed.

Identify and calculate the amount of precipitate formed. With reference to the structure of the above complex, explain the above observations fully.

(iv) The formula $[Co(en)_2Cl_2]^+Cl^-$ may refer to a structure that is different from what is shown above.
Draw this other structure of $[Co(en)_2Cl_2]^+Cl^-$ and state its relationship with the above structure.

[9]

(b) Cobalt is also found in nitrile hydratase, a bacterial enzyme which catalyses the conversion of nitriles to their corresponding amides:



Nitrile hydratase has a quaternary structure with four subunits. Each pair of subunits binds a cobalt atom, which serves as a catalytic centre for the above reaction.

(i) Identify the type of reaction performed by nitrile hydratase, and propose a three-step synthesis pathway to perform the same conversion, stating clearly all intermediates, reagents and conditions.

(ii) One way to obtain nitriles is to synthesize them from chloroalkanes. State the reagents and conditions required to carry out this synthesis.

(iii) Haemoglobin, like nitrile hydratase, has a quaternary structure.

With reference to the **haemoglobin** (Hb) molecule, describe and explain what is meant by the terms *secondary, tertiary* and *quaternary* structures of proteins. You should state the type of bonding or interaction involved in each case.

[11]

[Total: 20]

[Turn over

2 Most commercial chlorine is produced by the electrolysis of a concentrated aqueous sodium chloride solution in a *chloralkali cell*. An example of a *chloralkali cell* is the membrane cell as shown below:

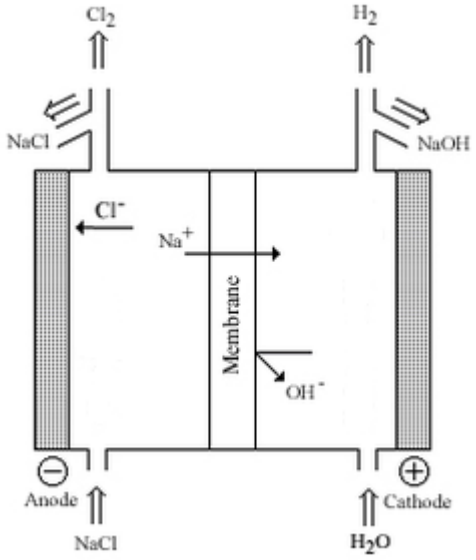


Diagram of a membrane cell

(a) (i) Write the ion-electron half-equations, with state symbols, for the reactions taking place at the anode and cathode.

(ii) Hence, deduce the overall reaction for the electrolysis of concentrated aqueous sodium chloride solution.

(iii) In the membrane cell, current was passed through the concentrated aqueous sodium chloride for 20 minutes. At room temperature and pressure, 450 dm^3 of chlorine gas was liberated at the anode.

Calculate the current used in the electrolysis.

(iv) The anode and cathode compartments are separated by a polymeric ion-exchange membrane. The membrane can exchange cations, and only permits Na^+ ions to migrate from the anode to the cathode compartment.

With the aid of a balanced equation, state the reaction that occurs when the membrane is removed and the products are allowed to mix at the high temperature of the cell.

[7]

In the laboratory, chlorine can also be prepared by reacting concentrated hydrochloric acid with manganese(IV) oxide. The half-equation involving manganese(IV) oxide is shown below:

$$MnO_2(s) + 4\ H^+(aq) + 2\ e^- \rightleftharpoons Mn^{2+}(aq) + 2\ H_2O(l) \qquad E^\ominus = +1.23\ V$$

(b) (i) Define the term *standard electrode potential*, $E^\ominus$.

(ii) Describe with the aid of a labelled diagram, the set-up used to measure the standard electrode potential of manganese(IV) oxide and the reactions occurring at each electrode.

(iii) By selecting an appropriate $E^\ominus$ value from the *Data Booklet*, explain why the reaction between hydrochloric acid and manganese(IV) oxide would **not** be expected to occur.

(iv) Suggest a possible reason why the reaction does in fact occur.

[6]

(c) The composition of a mixture of **two** solid sodium halides was investigated in two separate experiments.

Experiment 1

When a large excess of chlorine gas was bubbled through a concentrated solution of the mixture, reddish brown fumes and a black precipitate were produced.

Experiment 2

0.545 g of the solid mixture was dissolved in water and a large excess of silver nitrate solution was added. The mass of the mixture of silver halide precipitates formed was 0.902 g. After washing the mixture of precipitates with an excess of concentrated ammonia, the mass of the final precipitate was reduced to 0.564 g.

(i) With reference to **Experiment 1**, identify the two halides present in the mixture and explain why the reactions occur.

(ii) *Use of the Data Booklet is required for this question.*

The atomisation of the reddish brown substance produced in **Experiment 1** involves the vaporisation of the liquid, followed by the breaking of covalent bonds.

By constructing an energy cycle, calculate the standard enthalpy change of vaporisation of the reddish brown liquid.
[Given: $\Delta H_{atm}^\ominus$ (reddish brown liquid) = +112 kJ mol^{-1}]

[Turn over

(iii) Using data given in **Experiment 2**, calculate the mass of each halide ion present in the mixture.

[7]

[Total: 20]

3 (a) *Use of the Data Booklet is relevant to this question.*

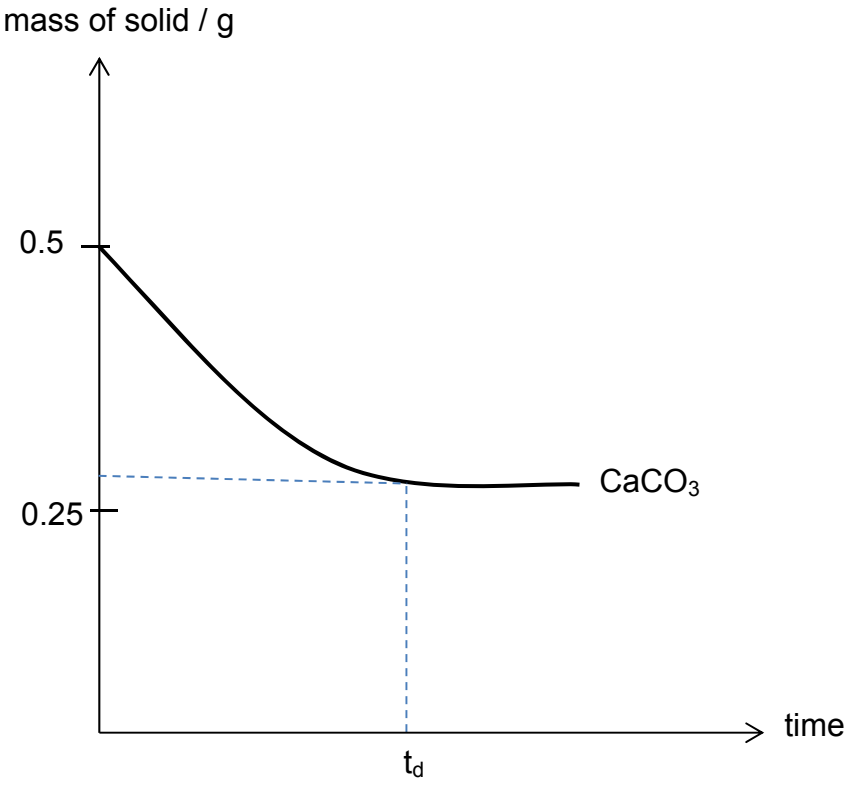
Lead(II) carbonate and zinc carbonate decompose on heating in the same way as calcium carbonate.

(i) Write an ionic equation for the thermal decomposition of the carbonate anions.

(ii) By listing the ionic radii of Zn^{2+}, Ca^{2+} and Pb^{2+}, suggest and explain the order of decomposition temperature of these three carbonates.

(iii) The graph below shows the decomposition of $CaCO_3$. Copy the graph and on the same axes, sketch the graph when the same number of moles of $ZnCO_3$ was heated under the same conditions.

t_d is the time taken for the complete decomposition of $CaCO_3$.



[6]

(b) Methanoic acid occurs naturally in ants. Ants secrete methanoic acid for attack and defense purposes. To treat ant stings, bicarbonate of soda (sodium hydrogencarbonate) is often used.

(i) Write the equation for the reaction between sodium hydrogencarbonate and methanoic acid.

[Turn over

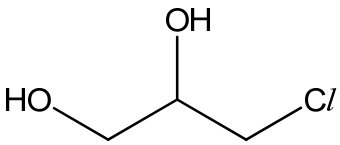
When an ant bites, it injects a solution containing 50% by volume of methanoic acid. A typical ant may inject around 6.0×10^{-3} cm^3 of this solution.

(ii) Given that the density of methanoic acid is 1.2 g cm^{-3}, calculate the number of moles of methanoic acid a 'typical ant' injects.

(iii) As soon as the methanoic acid is injected, it dissolves immediately in 1.0 cm^3 of water in the body to produce an aqueous solution of methanoic acid. The pH of the methanoic acid solution produced is 2.43. Calculate the acid dissociation constant, K_a for methanoic acid.

[5]

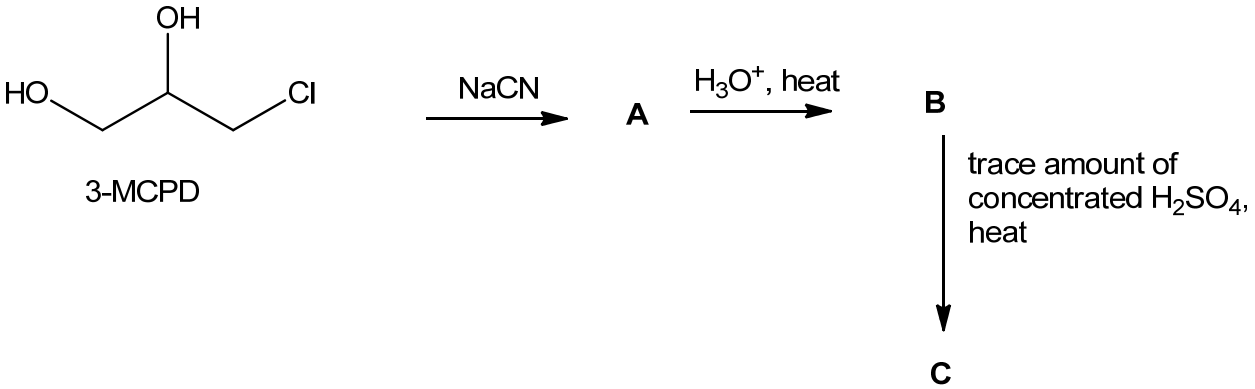
(c) 3-monochloro-1,2-propanediol (3-MCPD) is used as a raw material for the synthesis of several drugs such as guaifenesin and atorvastatin.



3-MCPD

(i) State and explain how the acidities of 3-MCPD and methanoic acid would compare with each other.

The following shows a reaction scheme involving 3-MCPD.



(ii) Suggest the structures of compounds **A** – **C**.

[5]

(d) An organic compound **E** is used as a flavouring and has the molecular formula $C_7H_{14}O_2$. **E** reacts with hot aqueous sodium hydroxide to form sodium ethanoate and compound **F**, $C_5H_{12}O$, which contains a chiral carbon. Compound **F** can be oxidised to $C_5H_{10}O_2$ by heating under reflux with acidified potassium dichromate(VI). Draw the structures of **E** and **F** and explain the reactions involved.

[4]

[Total: 20]

4 Methylbutane is an extremely volatile and flammable liquid at room temperature and pressure. When mixed with other compounds, methylbutane is often used in applications such as gasoline additives and cosmetics.

	pentane	methylbutane	cyclopentane	hydrogen
M_r	72	72	70	2
boiling point / ^oC	36.0	27.7	49.2	-252.9
standard molar entropy / J K^{-1} mol^{-1}	263	260	205	131

(a) (i) Explain the difference in boiling points between methylbutane and pentane.

(ii) Methylbutane can undergo a process of catalytic reforming at 500 ^oC in the presence of platinum catalyst to form cyclopentane. By displaying the structural formula, show a balanced equation for the reaction and use bond energy values from the *Data Booklet* to calculate the enthalpy change for this reaction.

(iii) Calculate the standard entropy change, $\Delta S^{\ominus}$, for the reaction in **(ii)** and explain the significance of the sign of $\Delta S^{\ominus}$ at the conditions where the reaction is taking place.

[6]

(b) Cyclopentane is a highly flammable alicyclic hydrocarbon and occurs as a colourless liquid with a petrol-like odour. When yellow-green chlorine gas is passed through excess cyclopentane in ultraviolet light, the mixture slowly becomes pale yellow and steamy white fumes appear above the liquid.

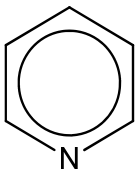
(i) Explain these observations and write a balanced equation, showing the structural formulae for relevant compounds in the overall reaction.

(ii) Name and describe the mechanism involved in the reaction.

[6]

[Turn over

(c) Pyridine is a heterocyclic aromatic compound structurally and chemically similar to benzene. It is used as a precursor to agrochemicals and pharmaceuticals and is an important solvent for many organic compounds. Pyridine is a colourless liquid that is miscible in water and boils at 115.2 °C and freezes at −41.6 °C.



pyridine

(i) Explain why pyridine is miscible in water.

(ii) Name and describe the mechanism that pyridine undergoes with a mixture of concentrated nitric acid and concentrated sulfuric acid.

(iii) Explain why pyridine does not undergo the reaction in **(ii)** as readily as benzene.

(iv) Excess pyridine reacts with chlorocyclopentane to form cyclopentene and another compound **A** with M_r 115.5, which is ionic in nature.

I. Suggest the structure of **A**.
II. State the role of pyridine in the reaction.
III. Name the type of reaction that has occurred to form cyclopentene.

[8]

[Total: 20]

5 The mechanism of the Haber Process for the manufacture of ammonia is imperfectly understood. A complete understanding of this process might lead to the development of catalysts which could operate at room temperature and pressure instead of the existing industrial conditions of 450 – 500 ^{o}C and 250 – 300 atm.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = \text{negative}$$

(a) Explain clearly the reasons why the Haber Process is operated at the stated conditions of temperature and pressure.

[2]

(b) Another contributing factor to the cost of producing ammonia is the cost incurred in the synthesis of hydrogen. Natural gas is a common starting material for the production of hydrogen and the overall reaction is summarised by the equation:

$$CH_4(g) + 2H_2O(g) \rightarrow CO_2(g) + 4H_2(g)$$

[ΔH_f /kJ mol^{-1}: CH_4 = -75 ; $H_2O(g)$ = -242 ; CO_2 = -394]

By making use of the enthalpy change of formation data given, calculate the enthalpy change for the above reaction and hence explain why the cost of the synthesis of hydrogen is high.

[2]

(c) The rate of catalytic decomposition of ammonia on tungsten to nitrogen and hydrogen has been studied at 1400 K. From an initial pressure of ammonia at 40 kPa, the total pressure, **p** of the reaction mixture, rose as the decomposition takes place over a period of time, as follows.

Time, t/s	0	250	500	750
Total pressure, **p**/kPa	40	50	60	70
Partial pressure of NH_3, p_{NH3}/kPa				

(i) Show that the partial pressure of NH_3, p_{NH3} at time, t is given by the expression, p_{NH3} = (80 – **p**) kPa and hence insert the values of p_{NH3} in the empty spaces above. Copy these values on your writing paper.

(ii) From the values of p_{NH3}, derived above, determine graphically or otherwise, the order of reaction with respect to ammonia. Explain how you arrived at your answer.

(iii) Hence, calculate the rate constant for the reaction, stating the units.

(iv) Explain why the pressure would not be exactly 80 kPa after 1000 s.

[8]

[Turn over

(d) ***Citral***, a constituent of lemon-grass oil, is a naturally occurring compound. It gives a silver mirror with Tollens' reagent.

When 0.100 g of ***citral*** is catalytically hydrogenated at 0 ^{o}C and 1 atm, 44.2 cm^3 of hydrogen react to give $(CH_3)_2CH(CH_2)_3CH(CH_3)CH_2CH_2OH$, with a relative molecular mass of 158.

Oxidation of ***citral*** with hot acidified potassium manganate(VII) gives initially three compounds, **F**, $C_2H_2O_4$, **G**, C_3H_6O, and **H**, $C_5H_8O_3$.

Suggest structures for **citral** and compounds **F**, **G** and **H** from the information given above. Explain your reasoning.

[High marks can be scored for appropriate chemistry in this part of the question without a complete structure for ***citral***.]

[8]

[Total: 20]