Class Adm No

Candidate Name: _____

H

millennia institute

2023 Preliminary Examination
Pre-University 3

H2 CHEMISTRY **9729/03**

Paper 3 Free Response **18 September 2023**

2 hours

Candidates answer on the Question Paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so.

Write your name, class and admission number in the spaces at the top of this page.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the page at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** questions.

Section B
Answer **one** question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

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.

Question	A			B	**Total**
	1	2	3	4 / 5	
Marks	24	19	17	20	**80**

Section A

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

1 Aluminium is the most abundant metal in the Earth's crust. It has a great affinity towards oxygen, forming a protective layer of oxide on the surface when exposed to air.

(a) Aluminium is protected from corrosion by a protective oxide layer. The thickness of the aluminium oxide layer on the surface of aluminium can be increased by anodising the aluminium. H_2SO_4 is used as an electrolyte in the anodising of aluminium.

(i) Draw a well-labelled diagram to illustrate the electrolysis set-up for the anodisation of aluminium. [2]

(ii) Write chemical equations to show the reactions at the anode and cathode during anodising. Include the overall equation in your answer. [3]

(iii) The aluminium piece to be anodised has a surface area of 29.2 cm^2. Determine the current required to pass through the set-up for 1.8 hours to form a 0.2 mm-thick protective layer of Al_2O_3 on the aluminium piece.

[Density of Al_2O_3 is 3.95 g cm^{-3}] [4]

(iv) Give one example of an anodised aluminium object, and explain the advantages of anodising it. [1]

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(b) Aluminium sulfate, $Al_2(SO_4)_3$, decomposes upon heating, forming aluminium oxide, sulfur dioxide gas and oxygen gas.

In an experiment, a 150 g sample of impure aluminium sulfate was heated until the sample reached a constant mass of 83.6 g.

(i) Write a balanced equation, with state symbols, for the decomposition of solid aluminium sulfate. [1]

(ii) Determine the percentage purity of the sample, assuming the impurities remained inert during the decomposition. [4]

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(c) Aluminium chloride is an active ingredient used in skin medication to control excessive sweating.

In the vapour phase, a dynamic equilibrium is established between aluminium chloride and its dimer as follows:

$$2AlCl_3(g) \rightleftharpoons Al_2Cl_6(g)$$

(i) Aluminium chloride is often described as *electron deficient*. Explain what is meant by *electron deficient*. [1]

(ii) With the aid of a diagram, explain how the dimer is formed. [2]

(iii) Explain what is meant by *dynamic equilibrium*. [1]

(iv) Write an expression for the equilibrium constant, K_p, for the dimerisation. [1]

(v) In an experiment, 10 atm of $AlCl_3(g)$ was allowed to reach equilibrium in a sealed vessel. At equilibrium it was found that the total pressure was 6.8 atm.

Calculate the value of K_p, stating its units. [3]

(vi) Suggest a reason why the dimerisation would not take place readily if the $AlCl_3$ is placed in an aqueous system. [1]

[Total: 24]

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2 (a) Compound **P** has a molecular formula $C_8H_9O_3N$. Treating **P** with hot acidified potassium manganate(VII) gives **Q**, $C_7H_5O_4N$, which produces effervescence with sodium hydrogencarbonate.

Heating **P** under reflux with acidified potassium dichromate(VI) gives **R**, $C_8H_7O_4N$. When **R** is treated with tin and concentrated hydrochloric acid, followed by careful neutralisation using an aqueous alkali, **S**, $C_8H_9O_2N$, is obtained.

1 mol of **S** reacts with 2 mol of aqueous bromine. Treatment of **S** with anhydrous phosphorus pentachloride produces **T**, C_8H_7ON.

(i) Deduce the structures of compounds **P** – **T** and explain the chemistry of the reactions involved. [10]

(ii) Compound **T** can be separated from any unreacted compound **S** that is left in the product mixture. This can be done by shaking the product mixture with cold dilute hydrochloric acid. The two layers (organic and aqueous layers) formed are then allowed to stand.

State and explain which compound, **S** or **T**, will be present in the aqueous layer. [2]

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(b) PCl_5 reacts with ketones in a 1 : 1 molar ratio to give gem-dichlorides. A gem-dichloride contains two chlorine atoms bonded to the same carbon atom.

For example, when butanone is treated with PCl_5, a gem-dichloride, 2,2-dichlorobutane, is obtained.

$$CH_3CH_2COCH_3 \rightarrow CH_3CH_2CCl_2CH_3$$

(i) Suggest the phosphorus-containing by-product of this reaction. [1]

(ii) Heating 2,2-dichlorobutane with alcoholic NaOH produces compounds **U** and **V**. **U** and **V** are constitutional isomers with the formula C_4H_6. Treating **U** and **V** with hydrogen over a suitable catalyst procures butane.

Suggest the displayed formula of **U** and **V** and clearly indicate on your structures, the type of hybridisation for each C atom in the two structures. [4]

(iii) If 1,1-dichlorocyclobutane is similarly heated with an excess of alcoholic NaOH, a product **W**, C_4H_5Cl, is obtained and no further loss of chlorine atoms occurs. **W** decolourises aqueous bromine.

Suggest the structure of **W**, and suggest why the expected loss of both chlorine atoms do not occur. [2]

[Total: 19]

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3 Chlorine is a yellowish-green gas with a choking smell. It has many uses, including in the treatment of drinking water.

(a) **(i)** Write balanced chemical equations for the reactions that occur when separate samples of magnesium and phosphorus are heated in excess chlorine. [2]

(ii) Describe the reaction of each of the resulting chloride with excess water, stating the approximate pH of the solution formed, and writing a balanced equation for any reaction that takes place. [3]

(b) Sulfur and chlorine can react together to form S_2Cl_2.

S_2Cl_2 can further react with Cl_2 to form SCl_2, as shown in the equation below.

$$S_2Cl_2(l) + Cl_2(g) \rightarrow 2SCl_2(l) \qquad \Delta H_1$$

(i) Draw 'dot-and-cross' diagrams to illustrate the bonding in S_2Cl_2 and SCl_2 respectively.

State the bond angle about the S atom in SCl_2. [3]

(ii) Using relevant bond energy data from the *Data Booklet*, determine the enthalpy change for the reaction, ΔH_1. [2]

(iii) The actual value of ΔH_1 is less endothermic compared to your answer in **(b)(ii)**.

Suggest two reasons for the discrepancy between the actual value and your answer in **(b)(ii)**. [2]

(iv) Define the term *entropy*. [1]

(v) State the sign of the entropy change for the reaction between $S_2Cl_2(l)$ and $Cl_2(g)$. Explain your answer. [2]

(vi) OCl_2 is a compound analogous to SCl_2.

State and explain how the bond angle in OCl_2 would differ from that in SCl_2. [2]

[Total: 17m]

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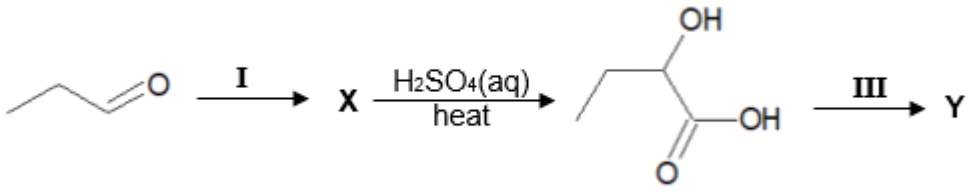
Section B

Answer **one** question from this section.

4 **(a)** Propanal is an aldehyde which exists as a colourless liquid with a fruity smell.

A cyclic diester, **Y**, can be formed from propanal as shown in the synthetic pathway below.

Y has a molecular mass of 172 g mol^{-1}.



(i) State the reagents and conditions for steps **I** and **III**. [2]

(ii) Draw the structure of **X** and **Y**. [2]

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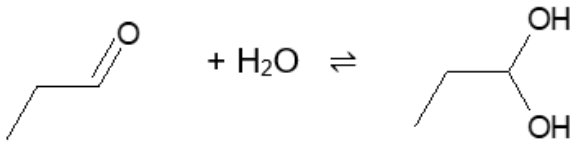
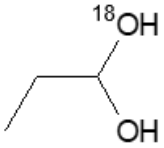
(b) Propanal undergoes reaction with water to yield a gem-diol. The reaction is reversible and a water molecule can be eliminated from the gem-diol to regenerate propanal.



(i) State the type of reaction for the above reaction. [1]

(ii) The reaction is slow but the rate is increased by the addition of a small amount of NaOH as catalyst. Suggest why NaOH is needed to initiate the reaction in the mechanism. [1]

(iii) The oxygen in water is primarily ^{16}O but water enriched with the heavy isotope, $H_2{}^{18}O$, is also available. When propanal is dissolved in $H_2{}^{18}O$, the ^{18}O becomes incorporated into the gem-diol which regenerates propanal.



Using your answer to **(a)(ii)**, suggest how ^{18}O is incorporated into the gem-diol. [1]

(iv) Suggest a reason why the addition of water to aldehydes proceeds more rapidly than it does to ketones. [1]

(v) With the aid of a labelled Boltzmann distribution diagram, explain how the addition of NaOH catalyst increases the rate of the reaction. [3]

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(c) 2-hydroxybutanoic acid can also be formed from propanal in two steps.

(i) 2-hydroxybutanoic acid is a weak Brønsted acid.

Define the term *Brønsted acid*. [1]

(ii) Draw the structure of the conjugate base of 2-hydroxybutanoic acid. [1]

(iii) Explain whether 2-hydroxybutanoic acid has a larger or smaller K_a than butanoic acid. [2]

2-hydroxybutanoic acid has a pK_a of 3.99.

A 20.0 cm^3 sample of 2-hydroxybutanoic acid was titrated against a solution of 1 mol dm^{-3} of sodium hydroxide, using a suitable indicator. It was found that the colour change occurred when 17.20 cm^3 of sodium hydroxide was added.

A sketch (not drawn to scale) of the pH titration curve is shown in Figure 4.1.

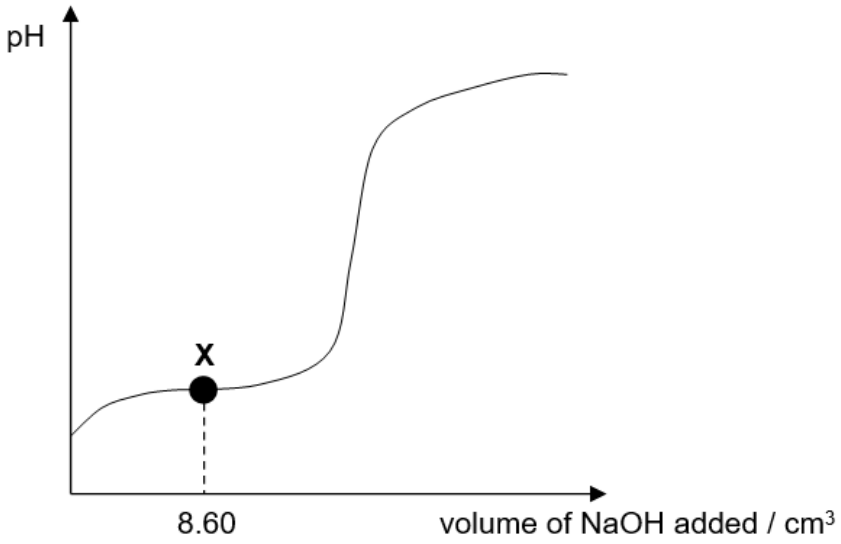

Figure 4.1

(iv) State the pH value at point **X**. [1]

(v) State whether the value of the pH at equivalence point would be 7, smaller than 7 or larger than 7.

Write an equation to support your answer. [2]

(vi) Calculate the concentration of 2-hydroxybutanoic acid in the sample. [2]

[Total: 20]

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5 Transition metal ions are often brightly coloured and can exist in a wide range of oxidation states. Vanadium was named after the Scandinavian goddess of beauty and fertility, Vanadis because of the wide range of colours found in vanadium compounds. The colours of the various vanadium ions are given in Table 5.1.

Vanadium Species	VO_2^+	VO^{2+}	V^{3+}	V^{2+}
Colour	Yellow	Blue	Green	Violet

Table 5.1

(a) V^{2+} ions are used in a redox titration to determine the concentration of Fe^{3+} ions in an unknown solution. Fe^{3+} can be reduced to Fe^{2+} and the solution is acidic throughout the entire process. The indicator used in the titration is potassium thiocyanate, KSCN. The thiocyanate ions, SCN^-, form an intense blood red complex ion with Fe^{3+} in solution while it appears colourless when complexed with Fe^{2+}. It was found that V^{2+} reacts in a 1 : 1 ratio with Fe^{3+}.

(i) State the electronic configuration of V^{3+} ion and hence explain why a solution containing V^{3+} ions is coloured. [4]

(ii) Write the oxidation and reduction half equations for the redox reaction.
Hence write the overall balanced equation. [2]

(iii) State the colour change observed at the end point of the titration. [1]

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(b) Beams of charged particles are deflected by an electric field.

In a particular experimental set-up, $^{51}V^{2+}$ ions are deflected through an angle of +4.3°.

(i) Assuming an identical set of experimental conditions, determine the angle of deflection of $^{56}Fe^{3+}$. [1]

(ii) Under identical conditions, a beam of particles, $\mathbf{Z}^{2-}$, was deflected by an angle of –3.1°.

Determine the atomic mass of **Z**. [1]

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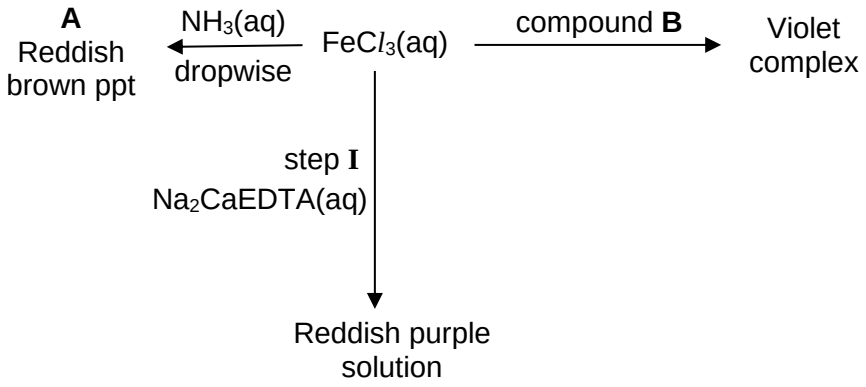
(c) The following scheme shows the reactions of iron and its compounds.



(i) Identify compounds **A** and **B**. [2]

(ii) State the type of reaction undergone in step **I** and write an ionic equation for the reaction taking place in step **I**. [2]

(iii) Another iron-containing compound, $FeCO_3$, undergoes thermal decomposition the same way as $CaCO_3$.

Using relevant data from the *Data Booklet*, state and explain which compound, $FeCO_3$ or $CaCO_3$, has higher thermal stability. [3]

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(d) Calcium hydroxide is sparingly soluble in water and has a solubility product with a numerical value of 5.50×10^{-6}.

(i) Write an expression for the solubility product, K_{sp}, of calcium hydroxide and calculate the solubility of calcium hydroxide in water. [2]

(ii) A lab technician tried to precipitate $Ca(OH)_2$ by mixing 0.20 mol dm^{-3} $Ca^{2+}(aq)$ with equal volume of 0.20 mol dm^{-3} $NH_3(aq)$.

Show through calculation why precipitation of $Ca(OH)_2$ will not occur.

[K_b of $NH_3 = 1.80 \times 10^{-5}$ mol dm^{-3}] [2]

[Total: 20]

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Additional answer space

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