Catholic Junior College

JC2 Preliminary Examinations
Higher 2

CANDIDATE NAME			
CLASS	**2T**	**INDEX NUMBER**	

CHEMISTRY **9729/03**

Paper 3 Free Response **9 September 2024**

2 hours

Candidates answer on the Question Paper.
Additional Materials: 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.
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 pages 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 examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use		
Section A	**Q1**	**/20**
	Q2	**/15**
	Q3	**/25**
Section B	**Q4** **OR** **Q5**	**/20** **/20**
TOTAL		**80**

This document consists of **29** printed pages and **1** blank page.

Section A

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

1 (a) Electrocatalysts are a specific form of catalysts that participate in electrochemical reactions. An example is the direct-methanol fuel cells (DMFCs) where methanol is oxidised over an electrocatalyst consisting of a mixture of transition metals such as platinum and rhodium to carbon dioxide.

The main reaction occurring at the anode in the DMFCs is shown below:

Anode $CH_3OH(aq) + 6OH^-(aq) \rightarrow 5H_2O(l) + CO_2(g) + 6e^-$

However, methanoic acid can also be produced at the anode and it can be further oxidised to carbon dioxide.

$$CH_3OH + 4OH^- \rightarrow HCO_2H + 3H_2O + 4e^-$$

$$HCO_2H + 2OH^- \rightarrow 2H_2O + CO_2 + 2e^-$$

Some standard electrode potentials are shown in Table 1.1.

Table 1.1

	$E^\ominus$ / V
HCO_2H / CH_3OH	+0.03
CO_2 / HCO_2H	+0.61

(i) Deduce the type of catalysis in DMFCs. Explain your answer. [1]

(ii) Explain how transition metals such as platinum and rhodium can act as catalysts. [1]

(iii) Draw a fully labelled diagram of the experimental set-up used to measure the standard electrode potential of the CO_2 / CH_3OH half-cell. [3]

(iv) State the relationship between the standard Gibbs free energy change, $\Delta G^\ominus$, and standard cell potential, $E^\ominus_{cell}$.

Use this relationship, the data in Table 1.1 and an energy cycle to calculate the standard electrode potential for the CO_2 / CH_3OH half-cell. $\Delta G^\ominus$ can be used in the same manner as $\Delta H^\ominus$ in a Hess' law cycle but $E^\ominus$ cannot. [3]

(v) Platinum(II) complexes are often coloured. Explain why complexes of transition metals are usually coloured. [3]

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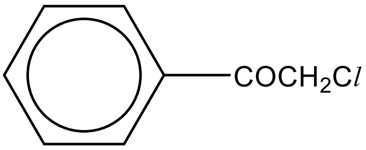
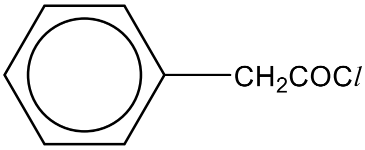
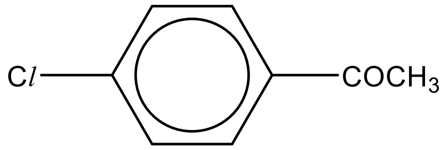
(b) Chloroacetophenone was formerly used as a tear agent and is a potent eye, throat and skin irritant. Compounds **A** and **B** are isomers of chloroacetophenone.



chloroacetophenone

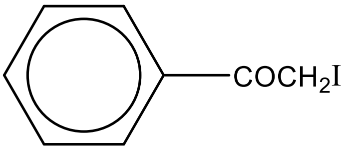


A



B

(i) Suggest a reason why iodoacetophenone is more reactive than chloroacetophenone towards hydrolysis. [1]



iodoacetophenone

(ii) Arrange chloroacetophenone, **A** and **B**, in order of increasing ease of hydrolysis. Explain your answer fully. [4]

(c) Ethanedioic acid, $H_2C_2O_4$, is the simplest dicarboxylic acid and its conjugate base, $C_2O_4^{2-}$, is a chelating agent for transition metal cations.

(i) Suggest a two-step synthesis for the formation of ethanedioic acid from ethene. Indicate clearly all reagents and conditions used in the two steps. [3]

(ii) Each ethanedioate ion $C_2O_4^{2-}$ can form two co-ordinate bonds, and under certain conditions, copper forms the complex ion $[Cu(C_2O_4)_2]^{2-}$.

Draw the structure of the complex $[Cu(C_2O_4)_2]^{2-}$. [1]

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[Total: 20]

2 **(a)** **(i)** Explain what is meant by the term *entropy* of a chemical system. [2]

(ii) Carbon monoxide, CO, has a melting point of 68 K and boiling point of 82 K.

Sketch a graph to show how the entropy of CO changes between 0 to 100 K.

Explain your reasoning. [2]

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(b) The Fischer-Tropsch process is one method of manufacturing methane through the reaction between carbon monoxide and hydrogen.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g) \qquad \Delta H^{\ominus} = -206\ \text{kJ mol}^{-1}$$
$$\Delta G^{\ominus} = -156\ \text{kJ mol}^{-1}$$

(i) Use the data to calculate the entropy change for this reaction at 298 K and comment on its sign with respect to the equation for the reaction. [2]

(ii) A mixture of CO and H_2 in the molar ratio 1 : 3 is added into a sealed vessel and heated to 800 ^{o}C. At equilibrium, the total pressure is 32 atm and 40% of CO has reacted.

Write the expression for the equilibrium constant, K_p, for this reaction. Use your expression to calculate the value of K_p for this reaction. Include its units. [4]

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(c) The Fischer-Tropsch process can be used to form many different types of hydrocarbons.

Alkynes are a series of non-cyclic hydrocarbons containing one carbon-carbon triple bond per molecule. A five-carbon alkyne has the formula, C_5H_8, and exhibits constitutional isomerism.

(i) Explain what is meant by *constitutional isomerism*. [1]

(ii) Carbon-carbon triple bonds are formed between carbons that are sp hybridised. Explain how sp hybridisation of the carbon atom arises. [2]

(iii) Draw the structures of all alkynes with the formula C_5H_8. [2]

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[Total: 15]

3 **(a)** Describe how the behaviour of beams of the ions of $^{1}H^{+}$, $^{2}H^{+}$ and the electron, e^{-}, differ in an electric field. [2]

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(b) Calcium is a Group 2 element. It has five stable isotopes as shown in Table 3.1.

Table 3.1

Relative isotopic mass of Ca	Percentage abundance / %
39.96	96.93
41.96	0.65
42.96	0.14
43.96	2.09
47.96	0.19

Use the data in Table 3.1 to calculate the relative atomic mass of calcium to two decimal places. [1]

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(c) The mineral dolomite is a double carbonate of magnesium and calcium, with the formula written as $CaMg(CO_3)_2$. When one mole of dolomite was heated at 315 °C, one mole of gas was collected which produced white precipitate with limewater. When another sample of the same amount of dolomite was heated at 530 °C, two moles of gas were collected.

(i) Write an equation for the thermal decomposition of a Group 2 carbonate, XCO_3. [1]

(ii) By considering the thermal stability of Group 2 carbonates, account for the different moles of gas collected at 315 °C and 530 °C. [3]

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(d) Iodine reacts readily with propanone, CH_3COCH_3, to form 1-iodopropanone, in the presence of an acid catalyst. The rate of this reaction is known to be zero order with respect to iodine and first order with respect to CH_3COCH_3.

(i) Define the term *order of reaction.* [1]

(ii) A series of six separate experiments is carried out, each with a different initial concentration of CH_3COCH_3, but same initial concentration of iodine and acid, and the volume of the reaction mixtures were kept the same. The amount of iodine used is much lower than the amount of CH_3COCH_3, and the time taken for the iodine to decolourise was noted for each experiment.

Describe:

- how the results can be used to calculate the relative rate for each experiment and
- how to graphically show that the reaction is first order with respect to the concentration of CH_3COCH_3. Include a sketch of the graph to be used. [3]

(iii) For a certain concentration of acid used, the rate constant, k, was found to be 2.16×10^{-3} min^{-1} for the simplified rate equation of rate = k [CH_3COCH_3].

Use the given data to calculate the half-life for this reaction. [1]

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(e) Nobel laureate Ronald Norrish studied the photodecomposition of propanone with UV light. He showed that the mechanism consists of three steps.

- The first step involves the homolytic fission of the C–C bond of propanone, forming a methyl radical, $\bullet CH_3$ and another free radical intermediate, **X**.

- The second step involves **X** undergoing further decomposition to produce carbon monoxide and another methyl radical, $\bullet CH_3$. This involves homolytic fission and formation of a dative bond.

- In the last step, free radicals combine to form ethane.

(i) Draw the 'dot-and-cross' diagram for carbon monoxide. [1]

(ii) Suggest the mechanism for the photodecomposition of propanone, taking note of the formation of carbon monoxide. Use curly arrows to show movement of electrons. [3]

(iii) When Ronald Norrish performed the photodecomposition of butanone to further study the mechanism, he discovered a mixture of three different alkanes was formed.

Draw the three possible structures of these alkanes. [1]

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(f) Compound **D**, $C_4H_7NO_2$, contains two different functional groups and one chiral carbon atom. Samples of compound **D** are tested separately with

- 2,4-DNPH forming an orange precipitate **E**
- Fehling's reagent in strongly alkaline NaOH solution in the presence of heat to form a red precipitate **F** and organic compound **G**, $C_4H_4O_4Na_2$
- aqueous sodium hydroxide in the presence of heat to form ammonia gas and an organic compound **H,** $C_4H_5O_3Na$.

(i) Suggest possible identities for **D**, **E**, **F**, **G**, and **H**.
For each test, state the type of reaction described. [7]

(ii) Suggest the structure of the organic product when **D** reacts with excess $LiAlH_4$. [1]

[Total: 25]

Section B

Answer **one** question in this section.

4 1,4-dibromobutane is a halogenoalkane. It can undergo controlled hydrolysis to form 4-bromobutan-1-ol.

For this reaction, the rate equation is rate = k[$CH_2BrCH_2CH_2CH_2Br$][OH^-].

$$\underset{\text{1,4-dibromobutane}}{CH_2BrCH_2CH_2CH_2Br} \xrightarrow{OH^-} \underset{\text{4-bromobutan-1-ol}}{CH_2BrCH_2CH_2CH_2OH} + Br^-$$

(a) Name and describe the mechanism involved in the above hydrolysis. [3]

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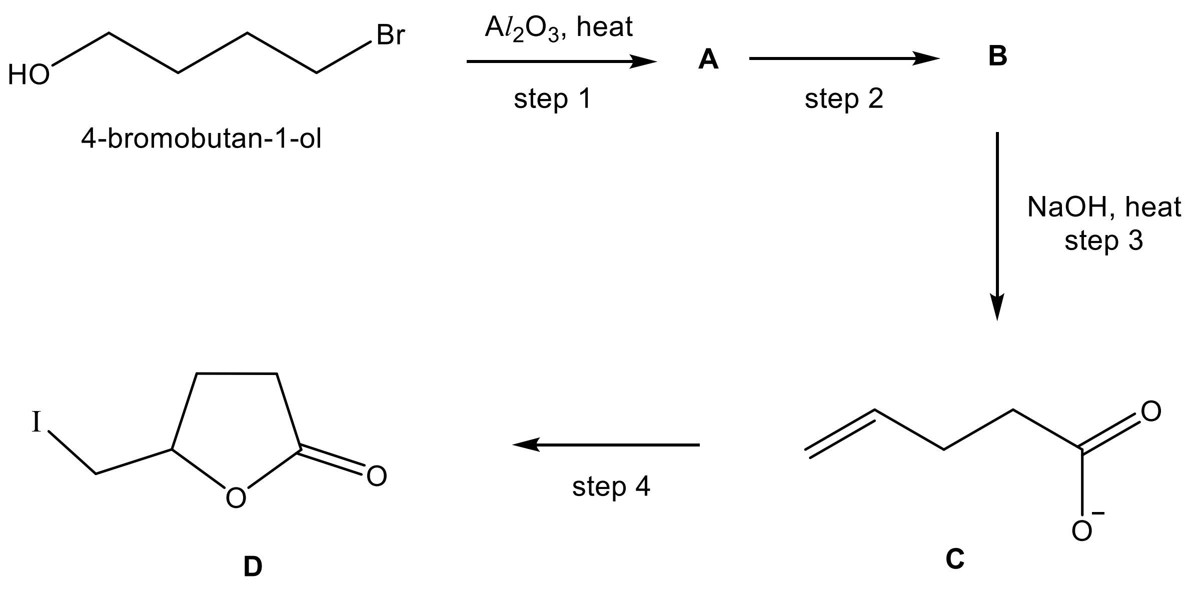
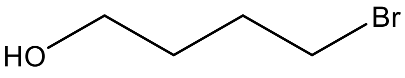
(b) **C** and **D** can be synthesised from 4-bromobutan-1-ol using the reaction scheme proposed below.



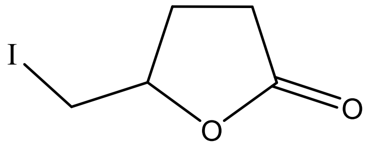
(i) Suggest the structures of compounds **A** and **B**. [2]

(ii) In step 4, a carbocation intermediate is formed. Suggest the reagent used. [1]

(iii) Suggest a simple chemical test to distinguish 4-bromobutan-1-ol from compound **D**. [2]



4-bromobutan-1-ol



D

(c) Aluminum chloride, $AlCl_3$, is commonly employed as a catalyst in halogenation reactions involving aromatic compounds. It is important that $AlCl_3$ is anhydrous when used in such reactions.

Describe the reaction of $AlCl_3$ with water and write equations for any reactions that occur. [2]

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(d) As compared to $AlCl_3$, the oxide of aluminum, Al_2O_3, does not react with water.

(i) Explain why Al_2O_3 is insoluble in water. [1]

(ii) Anodising is an electrolytic process used to increase the thickness of natural oxide layer on the surface of metal parts. Aluminum can be anodised to make it more resistant to corrosion.

Draw a fully labelled diagram, indicating the direction of electron flow in the circuit, and write the equations for both the cathode and anode reactions for the anodising of aluminium. [3]

(iii) Aluminum chloride, $AlCl_3$ can react with nitrogen compounds such as trimethylamine, $N(CH_3)_3$, as shown by the following equation:

$$N(CH_3)_3 + AlCl_3 \longrightarrow (CH_3)_3NAlCl_3$$

Name the type of bond formed between N and Al in $(CH_3)_3NAlCl_3$ and draw the structure of the compound, $(CH_3)_3NAlCl_3$. [2]

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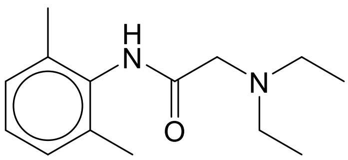
(e) Lidocaine is commonly used as local anaesthetic for dental surgeries and minor operations.



Lidocaine

$pK_b = 6.1$

(i) Lidocaine is a basic compound. Calculate the pH of a 0.025 mol dm^{-3} solution of Lidocaine. [2]

(ii) Hydrochloric acid is added to 1 dm^3 of the Lidocaine solution in **(i)** to produce a buffer solution. Determine the volume of 0.500 mol dm^{-3} HC*l* required to form a buffer solution of pH 7. [2]

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[Total: 20]

5 **(a)** Hydrazine, N_2H_4, is used in various rocket fuels. In the engine, hydrazine is passed over a suitable catalyst and decompose to its constituent elements, making hydrazine an efficient propellant. Hydrazine can be synthesised from the reaction between ammonia and hydrogen peroxide.

$$2NH_3(g) + H_2O_2(l) \longrightarrow N_2H_4(l) + 2H_2O(l) \qquad \Delta H^{\ominus} = -241.0 \text{ kJ mol}^{-1}$$

Relevant standard enthalpy change of formation data are shown in Table 5.1.

Table 5.1

	$NH_3(g)$	$H_2O_2(l)$	$H_2O(l)$
$\Delta H_f^{\ominus}$ / kJ mol^{-1}	–46.1	–187.8	–285.8

(i) Write a balanced equation for the decomposition of hydrazine to its elements. [1]

(ii) Calculate the standard enthalpy change for the decomposition of hydrazine to its elements and explain why this reaction makes hydrazine an efficient propellant. [3]

(iii) Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for the reaction between ammonia and hydrogen peroxide, given the standard entropy change of the reaction is –233.6 J mol^{-1} K^{-1}. [1]

(iv) Suggest a reason, in terms of structure and bonding, why ammonia is a gas but hydrazine, N_2H_4, is a liquid under standard conditions. [2]

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(b) Hydrazine, N_2H_4, is a weak base. It dissociates according to the equation shown.

$$N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH^-$$

Fig. 5.1 shows the change in pH when 0.10 mol of aqueous hydrazine is titrated with HC*l*(aq).

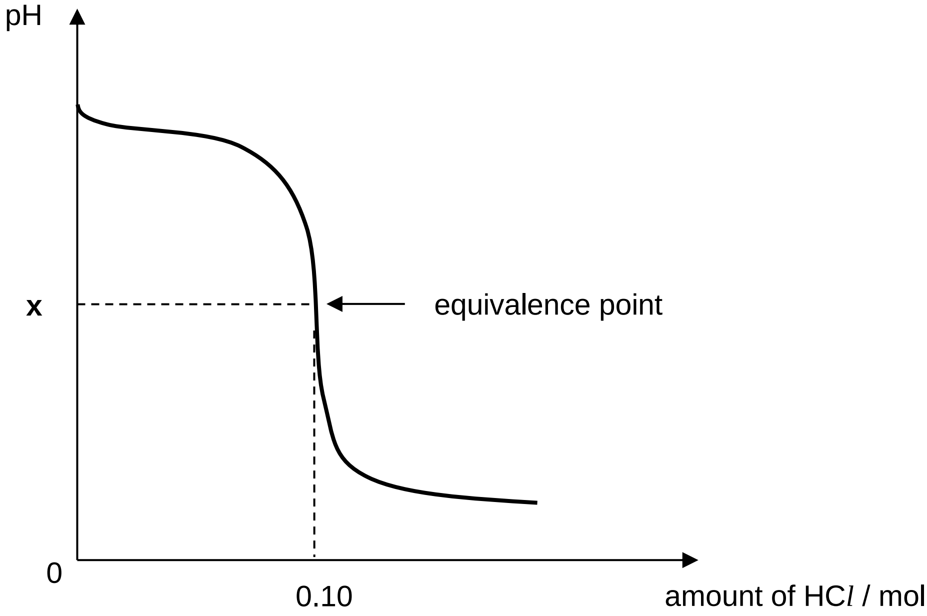

Fig. 5.1

(i) Describe and explain the relative basicities of hydrazine and ammonia. [2]

(ii) Show clearly on the graph in Fig. 5.1 the region where the mixture is acting as a buffer solution. [1]

(iii) Identify the two major species in this buffer solution and write two equations to show how the mixture can act as a buffer solution on the addition of acid and alkali. [2]

(iv) Suggest and explain, with the aid of an equation, whether the pH at the equivalence point is more or less than pH 7 in this titration. [2]

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(c) Hydrazine is used in Wolff-Kishner reduction, a reaction that converts carbonyl compounds to alkanes as shown in Fig. 5.2.

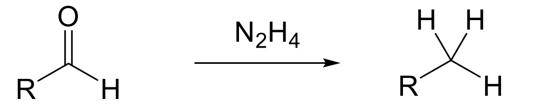


Fig. 5.2

In the first step of the Wolff-Kishner reduction mechanism, hydrazine reacts with a carbonyl compound to form a hydrazone as shown in Fig. 5.3.

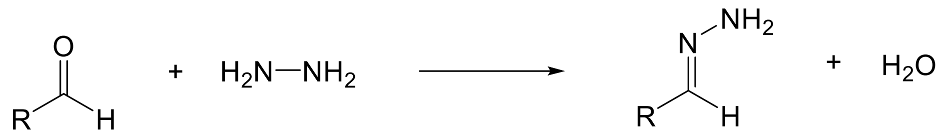


Fig. 5.3

In the second last step of the mechanism, an azo compound formed from the hydrazone undergoes deprotonation of the N–H group to produce N_2 gas and a carbanion as shown in Fig. 5.4. The carbanion is then protonated in the last step to form an alkane product.

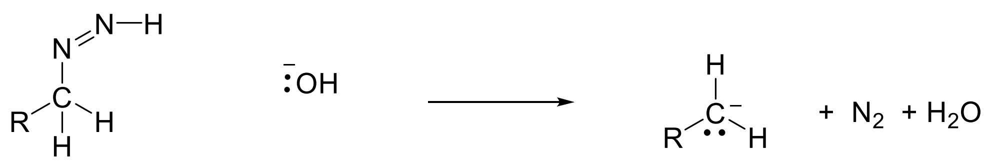
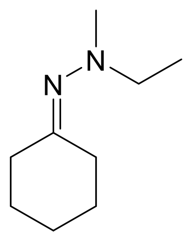


Fig. 5.4

(i) On Fig. 5.4, draw three curly arrows to show the mechanism for this step. [1]

(ii) Suggest the structure of a carbonyl compound and the derivative of hydrazine that would form the following hydrazone by a similar reaction to that shown in Fig. 5.3. [1]



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(d) Singapore competed at the 2012 Summer Olympics in London and won two bronze medals in table tennis. Bronze medals contain copper. A redox titration is used to determine the percentage by mass of copper in the bronze medal.

- A 0.800 g sample of a bronze medal is dissolved in hot concentrated nitric acid. After cooling, an excess of potassium iodide solution was added to form iodine and the solution was made up to 250 cm^3 in a volumetric flask.

$$2Cu^{2+}(aq) + 4I^-(aq) \longrightarrow 2CuI(s) + I_2(aq)$$

- 25.0 cm^3 of this solution was then titrated with aqueous sodium thiosulfate solution. 12.20 cm^3 of 0.100 mol dm^{-3} sodium thiosulfate was required for complete reaction, as shown.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

(i) Calculate the percentage by mass of copper in the bronze metal. [2]

(ii) All medals had a radius of 42.5 mm and thickness of 7 mm. The silver medal was made up of 92.5% silver and 7.5% copper, by mass. Given the density of silver is 10.49 g cm^{-3} and copper is 8.96 g cm^{-3}, calculate the mass of a silver medal, assuming that the density of the alloy varies proportionally to its composition by mass.

The equation for the volume of a medal, V, is given below:

$$V = \pi \times (\text{radius})^2 \times \text{thickness}$$

[2]

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[Total: 20]

Additional answer space

If you use the following pages to complete the answer to any questions, the question number must be clearly shown.