Class Adm No

Candidate Name: _____

H

millennia institute

2019 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/02**

Paper 2 Structured Questions **16 Sept 2019**

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 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.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

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	1	2	3	4	5	Total
Marks	/7	/23	/16	/14	/15	/75

1	**(a)**	Zinc-air batteries worked by oxidising zinc with oxygen from the air. At the cathode, oxygen converts to hydroxide ions. At the anode, zinc reacts with the hydroxide ions to form zincate, $[Zn(OH)_4]^{2-}$.		
		(i)	Construct an ion-electron equation for the reaction that takes place at each electrode under alkaline conditions. [2]	
			Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ Anode: $Zn + 4OH^- \rightarrow [Zn(OH)_4]^{2-} + 2e^-$	
		(ii)	At 298K, the standard electrode potential of the $[Zn(OH)_4]^{2-}(aq)\|Zn(s)$ half-cell is -1.25 V. Calculate the cell voltage using relevant data from the *Data Booklet*. [1]	
			$E_{cell} = 0.40 – (-1.25) = +1.65$ V	
		(iii)	Using relevant data from the *Data Booklet*, deduce if oxygen gas can be replaced with chlorine gas. [2]	
			$E_{cell} = 1.36 – (-1.25) = +2.61$ V Since the E_{cell} value is more positive when oxygen gas is replaced with chlorine gas, the reaction is feasible.	
	(b)	Another type of battery known as the nickel-cadmium battery is a type of rechargeable battery using nickel oxide hydroxide and metallic cadmium as electrodes. The electrode reaction equations for the **discharging** process under alkaline conditions is given below. Cathode: $Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$ Anode: $2NiO(OH) + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^-$		
		(i)	Construct the overall equation for the reaction that takes place during **charging**. [1]	
			$2Ni(OH)_2 + Cd(OH)_2 \rightarrow 2NiO(OH) + Cd + 2H_2O$	
		(ii)	Suggest a disadvantage of using nickel-cadmium battery. [1]	
			Cadmium is a toxic heavy metal which can result in pollution if discarded in landfill or incinerated.	
			[Total: 7]	

2 Paramagnetism and diamagnetism are different forms of magnetism. Paramagnetic materials are weakly attracted by an externally applied magnetic field and form magnetic fields in the direction of the applied magnetic field. In contrast, diamagnetic materials are repelled from magnetic fields and form magnetic fields in the direction opposite to that of the applied magnetic field.

Transition metals are mostly paramagnetic or diamagnetic. The magnetic property is characterised by the presence of unpaired electrons in paramagnetic compounds and absence of unpaired electrons in diamagnetic compounds.

The table below shows the magnetic property of metal complexes.

Formula of complex	**Magnetic property of complex**
$Fe(CO)_5$	Paramagnetic
$[Fe(H_2O)_6]^{2+}$	Paramagnetic
$[Fe(H_2O)_6]^{3+}$	Paramagnetic
$[ZnCl_4]^{2-}$	Diamagnetic
$[V(H_2O)_6]^{3+}$	
$[Sc(H_2O)_3(OH)_3]$	

(a) (i) Write the electronic configurations of V in $[V(H_2O)_6]^{3+}$ and Sc in $[Sc(H_2O)_3(OH)_3]$. [2]

Sc^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

V^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2$

(ii) State the magnetic property of $[V(H_2O)_6]^{3+}$ and $[Sc(H_2O)_3(OH)_3]$ in the above table. [1]

$[V(H_2O)_6]^{3+}$: paramagnetic

$[Sc(H_2O)_3(OH)_3]$: diamagnetic

(iii) Draw labelled diagrams to show the shapes of the d orbitals of the metal ion in $[V(H_2O)_6]^{3+}$. Include the relative energy of the d-orbitals in the complex. [3]

Draw d_{xy}, d_{xz} and d_{yz}, stating that it is of lower energy and $d_{x^2-y^2}$ and d_{z^2} at higher energy

(iv) Explain why transition metal can show variable oxidation states. [1]

The electrons in the 3d and 4s subshells are similar in energy, thus different number of these electrons are available for use in bond formation / ions formed by using different number of electrons for bonding are of similar stability.

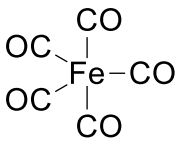
(b) Sodium reacts with iron pentacarbonyl to produce a salt known as sodium tetracarbonylferrate, $Na_2Fe(CO)_4$.

$$2Na + Fe(CO)_5 \longrightarrow Na_2Fe(CO)_4 + CO \quad \text{------- eqn (1)}$$

(i) Explain what is meant by the coordination number of a complex using $Fe(CO)_5$ as an example. [1]

Co–ordination number is the number of dative bonds attached to the central atom or ion in a complex. In the case of $Fe(CO)_5$, there are 5 dative bonds formed between Fe atom and C of CO, thus, the coordination number of $Fe(CO)_5$ is 5.

(ii) Draw the structure of $Fe(CO)_5$ and state its shape. [2]



Shape: trigonal bipyramidal

(iii) Deduce the oxidising and reducing agent in eqn (1). [2]

Na is the reducing agent since itself is oxidised from Na to Na^+ in $Na_2Fe(CO)_4$, with an increase in oxidation number from 0 to +1.

$Fe(CO)_5$ is the oxidising agent since Fe is reduced with a decrease in oxidation number from 0 in $Fe(CO)_5$ to -2 in $Na_2Fe(CO)_4$.

(iv) Explain why carbon monoxide, CO, is poisonous. [2]

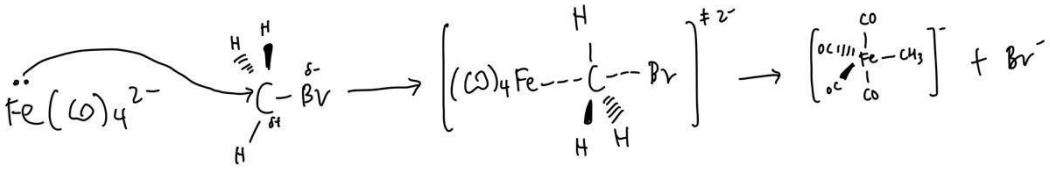
CO competes with O_2 for bonding with haemoglobin as it enters into the bloodstream. Being a stronger ligand than O_2, CO will displace the weaker O_2 ligand in oxyhaemoglobin by forming a stronger dative bond with iron in haemoglobin, resulting in a more stable carboxyhaemoglobin complex. The formation of carboxyhaemoglobin complex is not readily reversible due to its stability, and this reduces the availability of haemoglobin for oxygen transport. Deprivation of oxygen causes damage to living organs and tissues, resulting in death. Hence, Co is poisonous.

(v) The tetracarbonylferrate dianion acts as a nucleophile and react with alkyl halide by the S_N2 mechanism to form a new C-Fe bond.

$$[Fe(CO)_4]^{2-} + CH_3Br \longrightarrow [Fe(CH_3)(CO)_4]^- + Br^- \quad \text{------- eqn (2)}$$

Suggest a mechanism between $Fe(CO)_4^{2-}$ and CH_3Br. State clearly any intermediates that may be formed and use curly arrows to indicate the movement of electron pairs. [3]

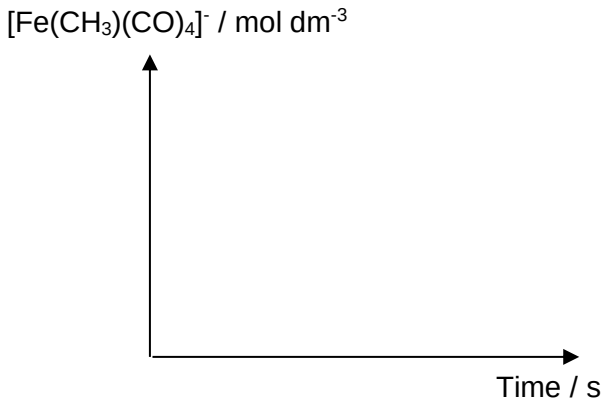
S_N2 Nucleophilic Substitution (not included in marking point as question already states S_N2)



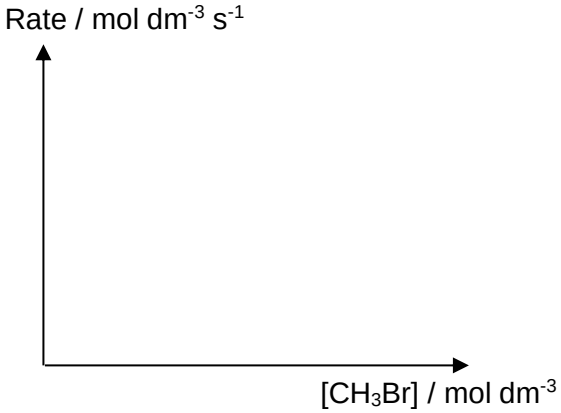
(vi) State the rate equation for the reaction in eqn 2. [1]

Rate = k $[CH_3Br][Fe(CO)_4^{2-}]$

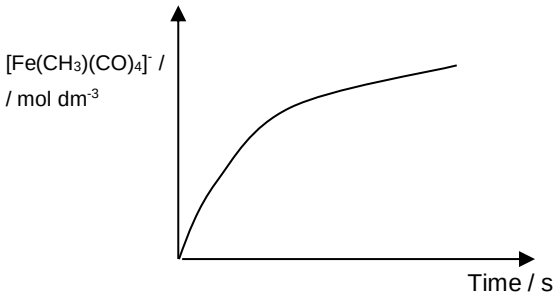
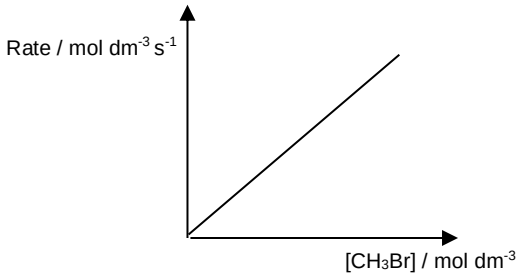
(vii) **I** Sketch the graph of $[Fe(CH_3)(CO)_4]^-$ against time.



II Sketch the graph of rate against $[CH_3Br]$ given that $[Fe(CO)_4]^{2-}$ is in excess.



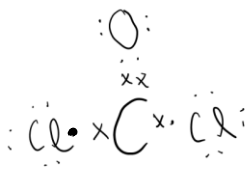
[2]

			I:  II: 
	(c)	The melting point of sodium tetracarbonylferrate, $Na_2Fe(CO)_4$ is lower than that of sodium oxide. With reference to the structure and bonding, explain the difference in melting point.[3]	
		Both sodium oxide and $Na_2Fe(CO)_4$ have giant ionic lattice structure with strong electrostatic forces of attraction between oppositely charged ions. Both compounds have Na^+ as the cation. Since $L.E \propto \left\|\frac{q^+q^-}{r^+ + r^-}\right\|$ and $[Fe(CO)_4]^{2-}$ anion is larger than O^{2-} anion, the lattice energy of Na_2O is more exothermic than that of $Na_2Fe(CO)_4$. Thus, more energy is needed to overcome the stronger ionic bonds in Na_2O than $Na_2Fe(CO)_4$, thus $Na_2Fe(CO)_4$ has a lower melting point.	
			[Total: 23]

3 **(a)** Phosgene, $COCl_2$, is essential in the manufacturing of everyday products, including medical products and footwear. Phosgene is produced by combining carbon monoxide and chlorine with a catalyst.

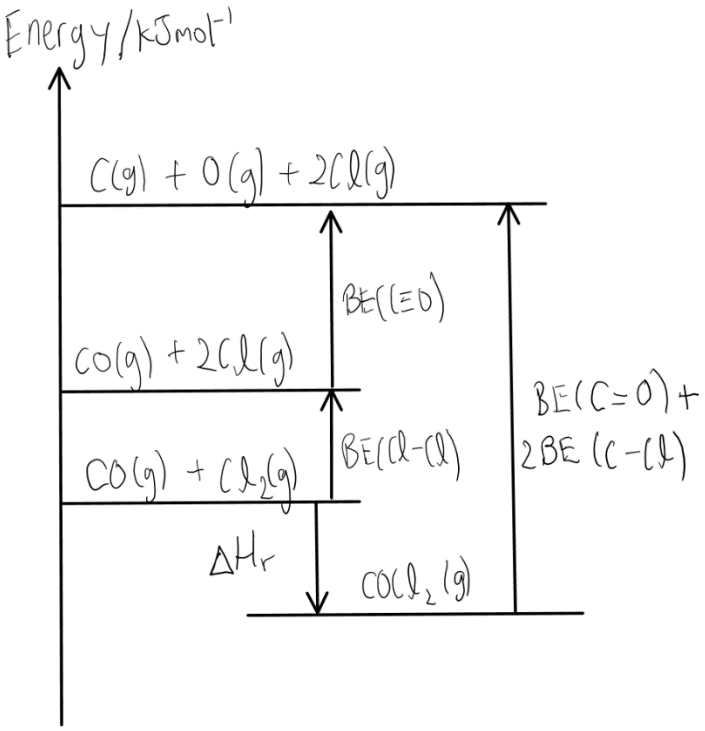
$$CO(g) + Cl_2(g) \rightarrow COCl_2(g)$$

(i) Draw a 'dot-and-cross' diagram of $COCl_2$ and state the bond angle about the central atom. [2]



Bond angle: 120°

(ii) Using relevant data from the *Data Booklet*, construct a fully labelled energy level diagram to calculate the enthalpy change of the above reaction. [3]



$\Delta H_r = 244 + 1077 - (740 + 2(340)) = -99$ kJ mol^{-1}

(iii) Explain what is meant by the term entropy of a chemical system. [1]

Entropy measures the amount of disorderliness in a system.

(iv) Predict, with reasons, the sign of the entropy change of the reaction between CO(g) and Cl_2(g) to form $COCl_2$. [2]

Entropy change of the reaction should be negative, as the number of moles of gas decreases from 2 moles to 1 mole, there are less ways of arranging the particles, hence the system decreases in disorderness.

(v) Hence, state and explain the significance of the sign of the standard Gibbs free energy change when temperature is low. [2]

$\Delta G = \Delta H - T\Delta S$, standard Gibbs free energy change should be negative at low temperature, since the enthalpy change is negative, and entropy change is negative. $|T\Delta S| < |\Delta H|$. Thus, the reaction is spontaneous at low temperature.

(b) Above 200°C, a 2.0 dm^3 cylinder containing gaseous phosgene decomposes to carbon monoxide and chlorine in a dynamic equilibrium according to the following equation:

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$$

(i) Predict and explain the effect of a catalyst on the position of the above equilibrium. [1]

No change in the position of equilibrium since the catalyst increases the rate of both the forward and backward reaction to the same extent.

(ii) At 350°C, the percentage dissociation of $COCl_2$ is found to be 45% and the total pressure at equilibrium is 3.5 atm. Calculate the value of K_p at 350 °C. [3]

	$COCl_2(g)$	$\rightleftharpoons$	$CO(g)$	+	$Cl_2(g)$
Initial pressure/ atm	a		0		0
Change in pressure / atm	-0.45a		+0.45a		+0.45a
Equilibrium pressure / atm	0.55a		0.45a		0.45a

0.55a + 0.45a + 0.45a = 3.5 atm
a = 2.414
$K_p = \frac{(2.414\times0.45)^2}{(2.414\times0.55)}$ = 0.889 atm

(iii) Calculate the mass of the carbon monoxide gas that exists inside the cylinder at 350°C. [2]

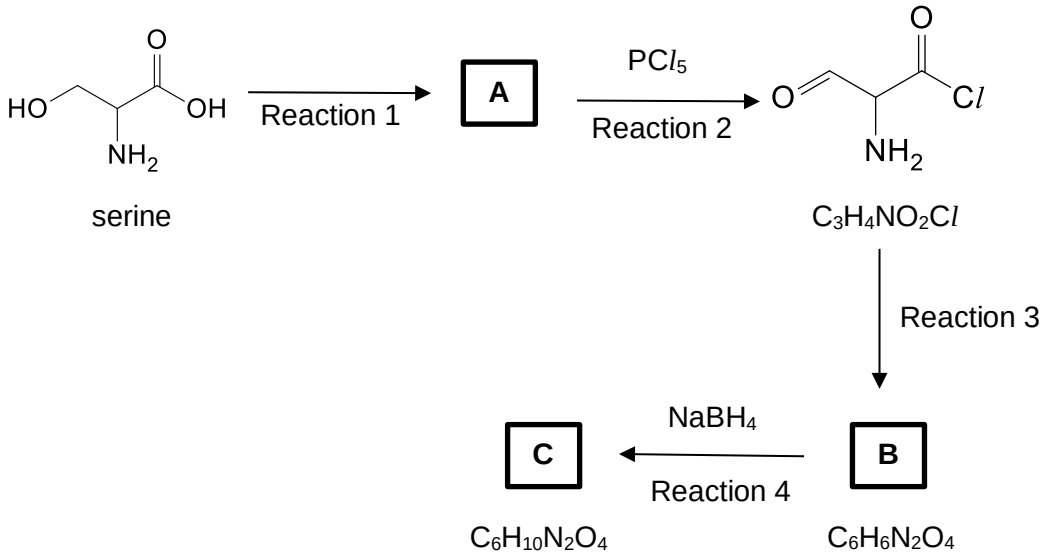
pV = m/Mr RT

(2.41 x 0.45) x 101325 x 2.0 x 10^{-3} = (m / 28) (8.31) (350 + 273)

M = 1.19 g

[Total: 16]

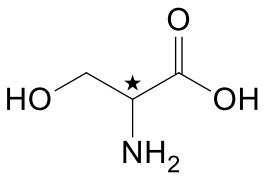
4 Spider silk is a protein fibre. Major amino acids in the silk protein are alanine, serine and glycine. The following reaction scheme involves serine as a starting material.



(a) Explain what is meant by a chiral centre.
Label with an asterisk (*) for any chiral centre that is present in serine. [2]

A chiral centre exists when a molecule has at least one asymmetric carbon atom where the carbon atom is bonded to 4 different substituents.

Serine has a chiral carbon.

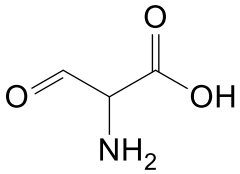


(b) Name the functional group common to compounds **B** and **C**. [1]

Secondary Amide

(c) Draw the structure of compound **A** in the box and state the reagents and conditions for reaction 1. [2]

A:



Dilute $K_2Cr_2O_7$, H_2SO_4(aq), heat with immediate distillation

(d) Name the type of reaction for reactions 2, 3 and 4. [3]

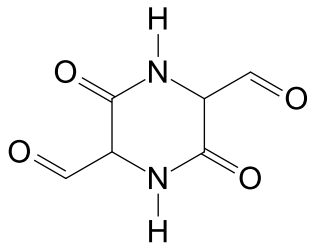
Reaction 2: nucleophilic substitution

Reaction 3: condensation / nucleophilic substitution

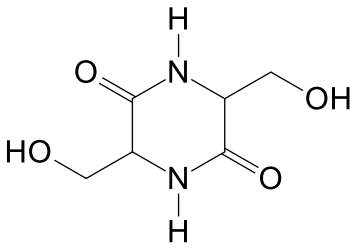
Reaction 4: Reduction

(e) Draw the structures of compound **B** and **C** in the box. [2]

B:



C:



(f) The following table contains the pK_a values of different compounds.

Compound	**pK_a**
Serine	2.21
Propanoic acid	4.87
Phenol	9.95

(i) Suggest a reason why pK_a of propanoic acid is higher than serine. [2]

The NH_2 group in serine exerts an electron-withdrawing effect, pulling electrons away from the O atom of the carboxylate salt, dispersing the negative charge and making the carboxylate ion more stable. Thus, serine is more acidic than propanoic acid and has a lower pK_a value.

(ii) Suggest a reason why pK_a of propanoic acid is lower than phenol. [2]

For the propanoate ion, there is a delocalisation of the negative charge over the two oxygen atoms. This disperses the negative charge and stabilises the anion. For the phenoxide ion, the p-orbital of oxygen overlaps with the π orbital of the benzene ring and this delocalises the negative charge on the oxygen atom into the benzene ring. However, this delocalisation is not as effective as that of the carboxylate ion as the carbon atoms are not very electronegative compared to oxygen atoms. Hence phenol is less acidic than propanoic acid.

[Total: 14]

5	**(a)**	**X** and **Y** are two different elements in Period 3. The following are some of their properties: - Oxide of **X** is insoluble in water while the aqueous solution of chloride of **X** is weakly acidic. - Element **Y** conducts electricity and has a lower melting point than element **X**. - The first ionisation energy of element **X** is lower than that of element **Y**.	
		(i)	Identify the elements, **X** and **Y**. [2]
			X: aluminium **Y**: Magnesium
		(ii)	Write the balanced equation(s) for the reaction when chloride of **X** dissolves in water and state the pH of the solution. [2]
			$AlCl_3$ (s) + 6 $H_2O(l)$ → $[Al(H_2O)_6]^{3+}$ (aq) + 3Cl^- (aq) $[Al(H_2O)_6]^{3+}$(aq) → $[Al(H_2O)_5(OH)]^{2+}$ (aq) + H^+ (aq) pH = 3
		(iii)	Explain why oxide of **X** is insoluble in water. [1]
			Energy released from the ion-dipole interaction between Al^{3+} and O^{2-} and water is insufficient to overcome the high strong electrostatic forces of attraction between oppositely charged ions in Al_2O_3.
		(iv)	Explain why element **Y** has a lower melting point than element **X**. [2]
			Both X and Y has giant metallic lattice structure with strong electrostatic forces of attraction between the positively charged ions and sea of delocalised electrons. Since Al has more delocalised electrons than Mg (or Al^{3+} has a higher charge density than Mg^{2+}), more energy is needed to overome the stronger electrostatic forces of attraction in Al than in Mg. Thus, Mg (element Y) has a lower melting point.
		(v)	Explain why the first ionisation energy of element **X** is lower than that of element **Y**. [2]
			Less energy is required to remove an electron from the 3p orbital in Al than to remove an electron from the 3s orbital in Mg as the 3p electron is further away from the nucleus and experiences greater screening than 3s electron.

(b) Sulfur is another period 3 element with a relative atomic mass of 32.09.

There are three naturally occurring isotopes. The relative abundances of the isotopes of sulfur are found to be the following.

Isotope	% Abundance
^{32}S	95.0
^{33}S	*a*
^{34}S	*b*

(i) Define the term *relative atomic mass*. [1]

Relative atomic mass (A_r) is defined as the weighted average mass of the isotopes of an element compared to $\frac{1}{12}$ of the mass of one atom of ^{12}C.

(ii) Calculate the percentage abundances of isotopes ^{33}S and ^{34}S. [2]

32.09 = 0.95(32) + 33(a/100) + 34(100-95-a/100)

a = 1.0 %

b = 4.0 %

(c) A 2.00 g sample of food additive containing magnesium carbonate is allowed to react with 50 cm^3 of 0.200 mol dm^{-3} aqueous hydrochloric acid. The excess acid required 19.30 cm^3 of 0.100 mol dm^{-3} aqueous potassium hydroxide for complete reaction.

Calculate the percentage of magnesium carbonate that is present in the food additive. [3]

$MgCO_3 + 2HCl \rightarrow MgCl_2 + H_2O + CO_2$

$KOH + HCl \rightarrow NaCl + H_2O$

Amount of initial HCl = 50/1000 x 0.2 = 0.01 mol

Amount of HCl in excess = 19.3/1000 x 0.1 = 0.00193 mol

Amount of reacted HCl = 0.01 - 0.00193 = 0.00807 mol

Amount of $MgCO_3$ = 0.00807/2 = 0.004035 mol

Mass of $MgCO_3$ = 0.004035 x (24.3 + 12 + 48) = 0.340 g

Percentage of magnesium carbonate = 0.34/2 x 100 = 17.0 %

[Total: 15]

END OF PAPER 2

BLANK PAGE

BLANK PAGE