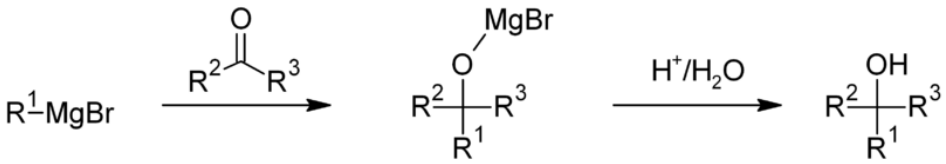
1

1 The Grignard reagent, R^1-MgBr, can be made by reaction between alkyl bromide and magnesium. In a Grignard reaction, the Grignard reagent may be added to a carbonyl compound for the formation of an alcohol. This reaction is useful for the formation of carbon–carbon bonds.

$$R^1Br + Mg \rightarrow R^1\text{-}MgBr$$



(a) The above reaction between the Grignard reagent and ketone can give a yield of about 80 %. You are required to prepare 4 g of 2-methylpropan-2-ol.

(i) Identify the alkyl bromide and ketone required to synthesise 2-methylpropan-2-ol. **[1]**

Bromomethane/ Methylbromide and propanone

(ii) Assuming that the alkyl bromide can be completely converted into the Grignard reagent, determine the mass of each reactant in **(a)(i)** needed to prepare the desired amount of the pure organic product. **[2]**

Mass of product based on 100% yield = $\frac{100}{80}$ x 4 = 5 g

$n_{product} = \frac{5}{(3\times15+12+16+1)}$ = 0.0676 mol

[Assuming both are limiting reagents]

Mass of methyl bromide = 0.0676 x 94.9 = <u>6.41 g</u>
Mass of propanone = 0.0676 x 58.0 = <u>3.92 g</u>

(iii) Similar to the lithium aluminium hydride, the Grignard reagent is rapidly **destroyed by water and air**. **[1]**

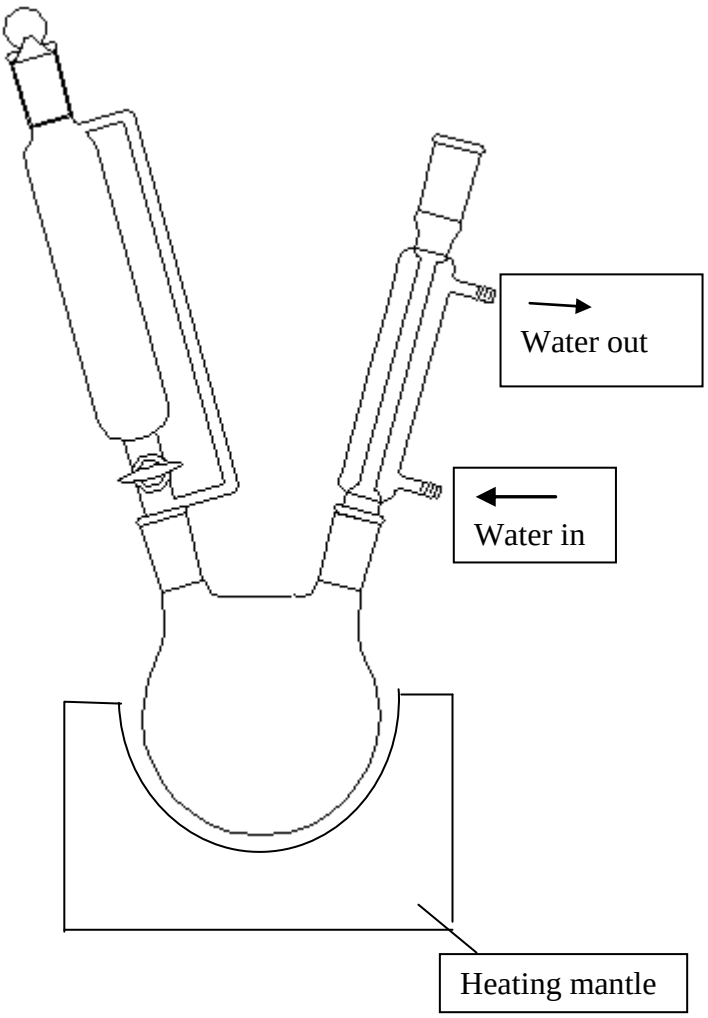
Give a suitable solvent and the condition required for the solvent in the synthesis of the Grignard reagent.

Anhydrous/Dry diethyl ether

(b) The Grignard reagent was first prepared by adding an appropriate mass of magnesium to an appropriate mass of alkyl bromide dissolved in an appropriate volume of solvent. The mixture was then heated under reflux for about 30 minutes.

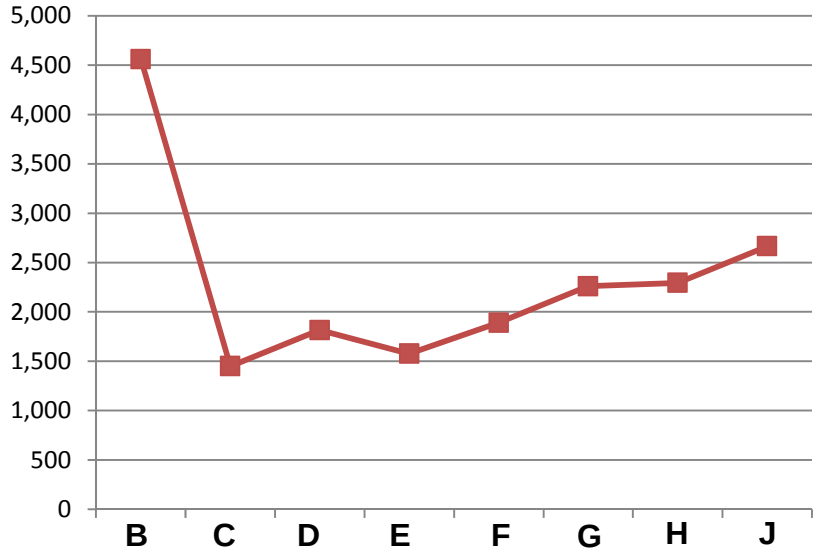
After cooling the reaction mixture which now contains the prepared Grignard reagent, a fixed amount of ketone was then slowly added dropwise to it with intermittent swirling and warming.

2

		(i)	You are provided with the following apparatus: two-necked round bottom flask, condenser, heating mantle and dropping funnel. Draw a suitable set-up using the glassware provided for conducting the above experiment.	**[2]**
			The drawing should include: + A two-necked round bottom flask with a condenser and dropping funnel; The condenser should be connected to a water supply with correct connection. + A heating mantle should be placed under the round bottomed flask.  	

		(ii)	Write a step-by-step procedure on how you would prepare 4 g of the pure 2-methylpropan-2-ol using provided magnesium as well as the suggested alkyl bromide and ketone from your answers in **(a)(i)** bearing in mind that the yield in such a procedure is about 80 %. Your plan should: • show how the quantities of reactants calculated in **a(ii)** are used; • show that the mass of magnesium used is in excess for complete conversion of the alkyl bromide to the Grignard reagent; • use an appropriate volume of the solvent from your answer in **a(iii)**; • ensure that the reactions are conducted under the appropriate condition.	**[5]**
			Mass of magnesium required = 0.0676 x 24.3 = 1.64 g Step 1: Weigh, using a weighing balance, 6.41 g of methyl bromide, 3.92 g of propanone and 2 g of magnesium (excess). Step 2: **Add** both 6.41 g of methyl bromide and 2 g of magnesium reagents **to the 50 ml of anhydrous diethyl ether** in the two-necked round bottom flask. Step 3: **Heat** the reaction mixture and allow the mixture to reflux gently for **30 minutes**. Cool the reaction mixture to room temperature. Step 4: Add the 3.92 g of propanone **dropwise** to the Grignard reagent at room temperature **from the dropping funnel**. Warm and swirl the mixture intermittently. (Students were not expected to give details on the follow-up reaction of adding dilute acid to form the 2-methyl-propan-2-ol, the extraction with diethyl ether and purification by recrystallization after extraction.)	
	(c)	Excess unreacted magnesium in the reaction mixture could be destroyed by addition of sulfuric acid. Give a safety precaution, with reason, which you would take to perform the above step.		**[1]**
		Add the dilute acid drop wise. The mixture will foam out of the flask if the acid is added too quickly.		
			[Total: 12 marks]	

2 The graph for the second ionisation energies of Period 3 elements is given below:



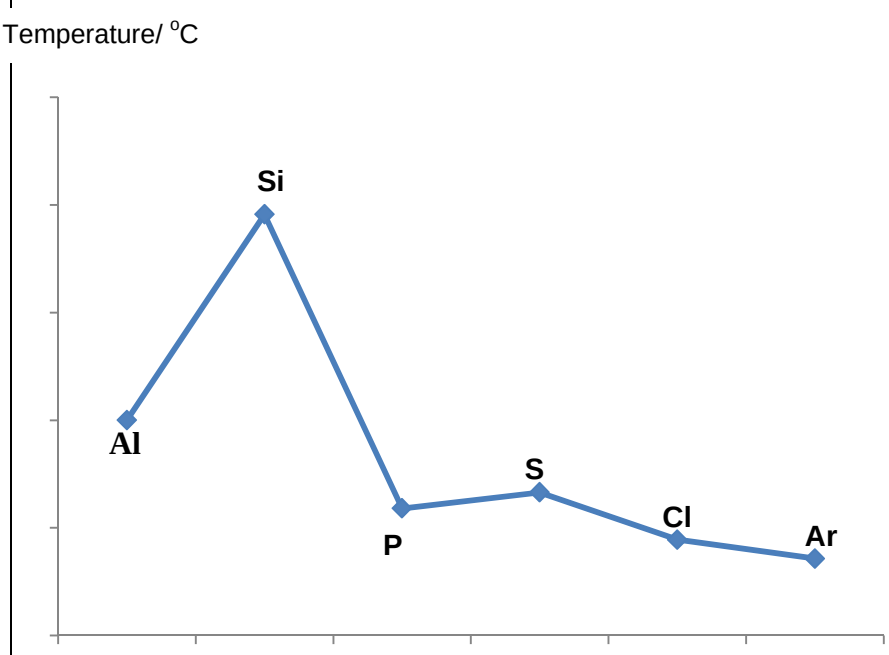
(a) (i) State the electronic configuration of element **D** and deduce the group which element **D** belongs to. **[2]**

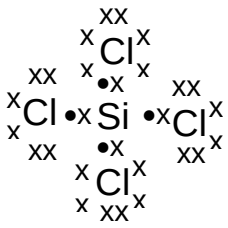
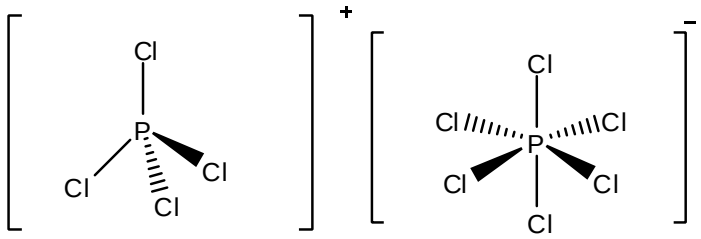
$1s^2 2s^2 2p^6 3s^2 3p^1$

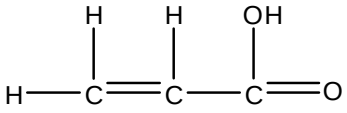
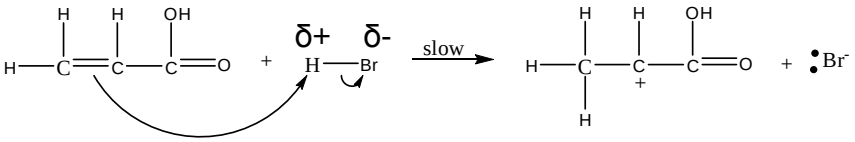
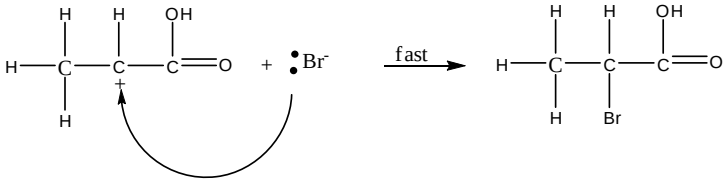
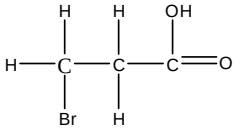
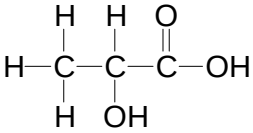
D belongs to group III.

(ii) The figure below shows the melting points of six consecutive elements in the periodic table. **[4]**

Explain in terms of structure and bonding the variation in melting points of the elements.

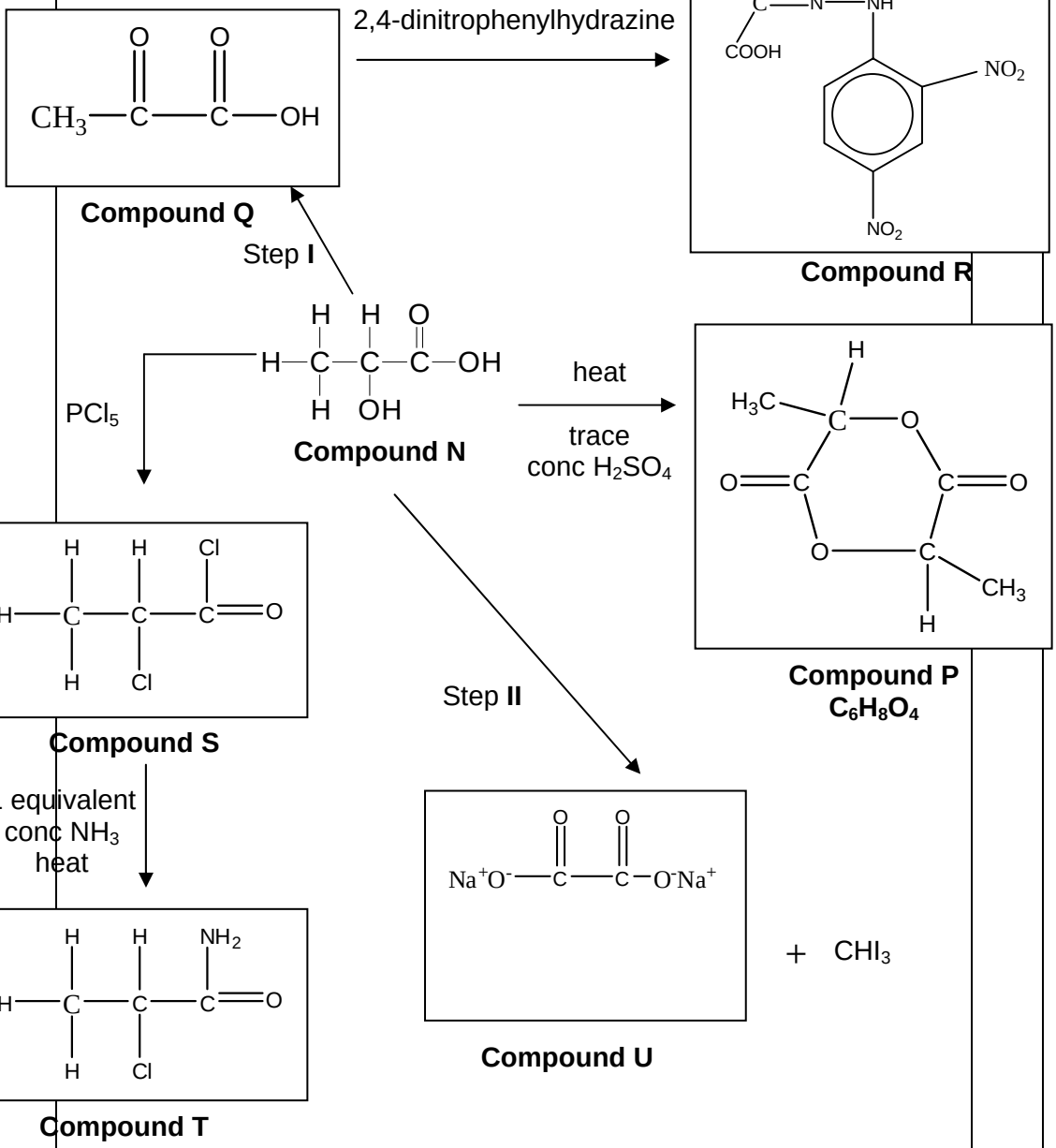


			- Aluminium has <u>giant metallic structure</u>, <u>Large amount of energy</u> is required to overcome the <u>strong electrostatic attraction between the positive metal cations and free electron cloud</u> in the <u>giant metallic lattice</u>. - Silicon has <u>giant covalent structure</u>, <u>Large amount of energy</u> is required to break the <u>strong covalent bonds between the Si atoms</u> in the <u>giant molecular structure</u>. - P_4,S_8 and Cl_2 has <u>simple covalent structures</u>, <u>Lesser energy</u> is required to break the <u>weaker Van der Waals' (VDW) forces</u> <u>between the discrete molecules</u> (for P_4, S_8 and Cl_2) <u>or atoms</u> (for Ar) in the <u>simple molecular (or atomic) structure</u>. <u>- Strength of VDW forces increases</u> with size of the molecule or atom, <u>therefore melting points of S_8 > P_4 >Cl_2. Larger molecules have more electrons in the electron cloud</u> and this electron cloud is more easily distorted.	
	(b)	Draw the dot and cross diagram for the compound $SiCl_4$.		**[1]**
				
	(c)	Silicon tetrachloride is a liquid at room temperature, phosphorous (V) chloride, however exist as an ionic solid due to the presence of the ions $[PCl_4]^+$ and $[PCl_6]^-$.		
		(i)	Draw the structures of the cation, $[PCl_4]^+$ and anion, $[PCl_6]^-$. State the shapes of the two ions.  Tetrahedral octahedral	**[3]**
		(ii)	Silicon tetrachloride reacts readily with water but carbon tetrachloride does not hydrolyse readily. Explain. <u>Si</u> has <u>low-lying, vacant 3d-orbitals available</u> for <u>dative bonding with water molecules</u>.	**[1]**
		(iii)	Suggest another physical property that is different between silicon tetrachloride and phosphorous (V) chloride. <u>PCl_5 is able to conduct electricity</u> when dissolved in polar solvents where it does not react <u>but not $SiCl_4$</u>.	**[1]**
				[Total: 12 marks]

3	**(a)**	**(i)**	Compound **M**, shown below, reacts with hydrogen bromide. Describe the mechanism for the reaction.  Electrophilic Addition   Or  was accepted as the product.	
		(ii)	Compound **M** can be chemically converted into compound **N**, shown below:  Compound **N**, is found in muscle tissues as lactic acid and is optically active whereas when it is chemically synthesised it is optically inactive. Explain. Lactic acid contains a chiral carbon: $CH_3C^*H(OH)COOH$ and exists as two optical isomers. Only **one optical isomer** of lactic acid is found naturally in muscle tissues which rotates plane-polarised light and is optically active. When lactic acid is chemically synthesised, **a racemic mixture** is obtained	**[4]**

7

(b) **(i)** The flow scheme below concerns the reactions of compound **N**. Draw the structures of the organic compounds **P** to **U** in the boxes provided.



(ii) State the reagents and conditions for Step **I** and Step **II**.

Step **I**: $K_2Cr_2O_7$, dilute H_2SO_4, heat

Step **II**: I_2, NaOH(aq) & warm

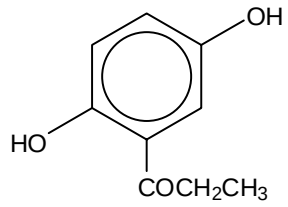
[8]

[Total: 12 marks]

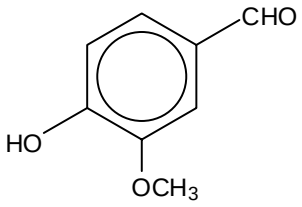
8

4	Suggest how the following compounds could be distinguished from each other by chemical tests. For each test, state the reagents and conditions you would use, the observations you would make with **each** compound undergoing the test and write balanced equations for the reactions.	**[6]**

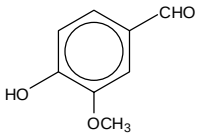
(a)



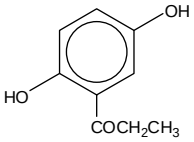
and

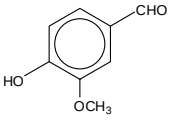


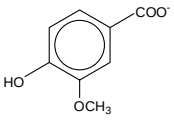
Reagents: aq. soln of diamminesilver(I) ion, $[Ag(NH_3)_2]^+$ / Tollen's Reagent
Condition: warm

Silver mirror obtained for 

and no silver mirror for

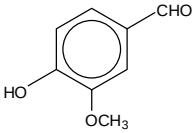




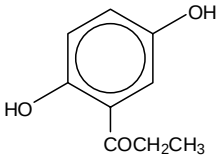
$+ \ 2[Ag(NH_3)_2]^+ + 3OH^- \rightarrow$ 

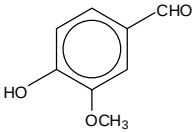
$+ \ 2Ag + 4NH_3 \ + \ 2H_2O$

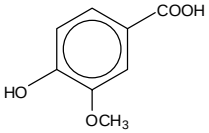
OR Acidified $Cr_2O_7^{2-}$ or acidified MnO_4^- and heat



Orange $Cr_2O_7^{2-}$ turns green or Purple MnO_4^- decolorises for
Orange dichromate remains or purple manganate remains for

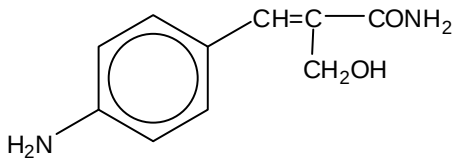


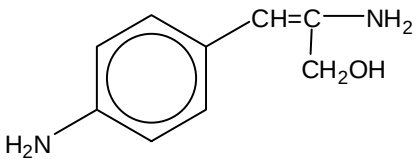


$+ \ [O] \rightarrow$ 

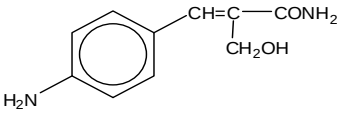
9

(b)

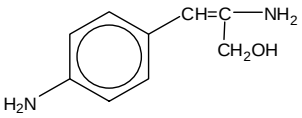




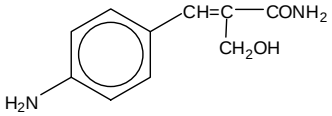
Reagent: NaOH(aq)
Condition: heat

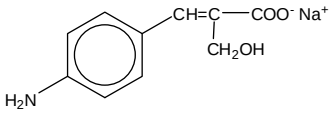


With compound , $NH_3(g)$ is evolved which turns moist red litmus blue.



No $NH_3(g)$ is evolved with compound .





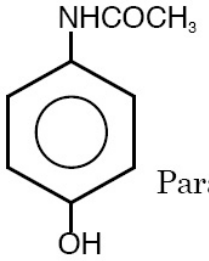
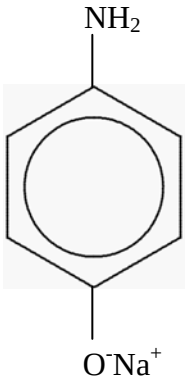
+ NaOH → + NH_3

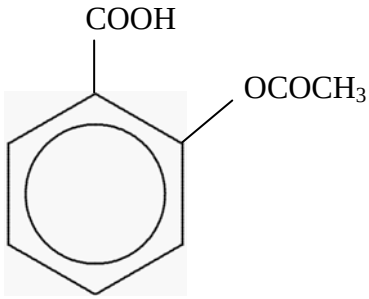
[Total: 6 marks]

5	**(a)**	**(i)**	Explain why magnesium gives the nitride Mg_3N_2 in addition to its oxide when burned in air. The **large amount of energy released** from the reaction between Mg and O_2 helps to **break the strong N≡N triple bond**. This facilitates the formation of Mg_3N_2.	**[1]**
		(ii)	A 1.00 g sample of the powder obtained from burning magnesium in air was boiled with water. It produced a hydroxide and ammonia. The ammonia that was evolved neutralised 12.0 cm^3 of 0.5 mol dm^{-3} hydrochloric acid. Write an equation for the action of water on magnesium nitride. Hence calculate the percentage of magnesium nitride in the sample. $Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$ $NH_3 + HCl \rightarrow NH_4Cl$ Amount of NH_3 liberated = Amount of HCl used = (0.012)(0.5) = 0.006 mol Amount of Mg_3N_2 = 0.006 ÷ 2 = 0.003 mol Mass of Mg_3N_2 = (0.003)((100.9) = 0.303g Percentage by mass of Mg_3N_2 in sample = 0.303 ÷ 1 x 100% = 30.3%	**[3]**
		(iii)	Suggest a suitable indicator to use for the titration of NH_3(aq) with HCl(aq) in **(a)(ii)**. (Screened) Methyl Orange / Methyl Red	**[1]**
	(b)	**(i)**	Two glass bulbs are connected by a glass tube with a valve. One bulb has a volume of 600 cm^3 and contains NH_3(g) at 41.3 kPa. The other bulb has a volume of 400 cm^3 and contains HCl(g) at 31.0 kPa. After opening the valve, what will be the equilibrium pressure if temperature is kept constant at 25°C throughout the whole process? For Bulb 1, PV = nRT (41,300)(600 / 1,000,000) = (n)(8.31)(298) n = 0.0100 For Bulb 2, PV = nRT (31,000)(400 / 1,000,000) = (n)(8.31)(298) n = 0.00500 $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$ Amount of Excess NH_3(g) = 0.0100 – 0.005 = 0.005 mol PV = nRT P (600 + 400) / 1,000,000 = (0.005)(8.31)(298) P = 12.4 kPa	**[3]**

		(ii)	Predict whether the actual pressure will be higher or lower than the calculated value in **(b)(i)**. Explain. Actual pressure will be **lower** than calculated one, because there is significant **hydrogen bond between NH_3(g) molecules**.	**[1]**
	(c)		Describe and explain the trend in the thermal stabilities of the nitrates of Group II elements from Mg to Ba. Write a general equation for the reaction that occurs on heating. $M(NO_3)_2(s) \rightarrow MO(s) + 2NO_2(g) + ½O_2(g)$ where M is Mg, Ca, Sr or Ba. Down Group II, **thermal stability increases**. Down Group II, cationic size increases though they have same charge of +2. Hence **charge density** and polarising power **decrease**. Electron cloud of nitrate ion is less polarised. The N–O bond is less weakened. It requires more energy to decompose nitrate down the group.	**[3]**
	(d)		Explain why beryllium oxide is amphoteric. The oxide has **ionic bond with covalent character**.	**[1]**
				[Total: 13 marks]

6	**(a)**		When a person exercises, the process known as "cell respiration" provides the body with the energy needed. During this process, glucose is 'burnt' in the reaction which is similar to the following complete combustion of glucose. $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$	**[6]**
		(i)	The ignition temperature of glucose is approximately 800 ^oC. Suggest how the combustion of glucose occurs inside our bodies, where the average body temperature is only 37 ^oC. There are biological catalysts/enzymes in our body that provides an alternative reaction pathway which lowers activation energy of the reaction and allows the oxidation of glucose to occur at a lower temperature.	

		(ii)	A person exercising uses energy at an average rate of 240 kJ per hour. Using the data given below, construct **an energy cycle** to calculate the enthalpy change of combustion of glucose. Hence, calculate the mass of glucose that has to undergo combustion to provide this energy for one hour. ΔH_f^o CO_2 (g) = -393 kJ mol^{-1} ΔH_f^o H_2O (l) = -285 kJ mol^{-1} ΔH_f^o $C_6H_{12}O_6$ (s) = -1248 kJ mol^{-1} **$C_6H_{12}O_6$ (s) + $6O_2$ (g) → $6CO_2$ (g) + $6H_2O$(l)** **6C (s) + 9 O_2 (g) + $6H_2$ (g)** **ΔH = -393 x 6 + (-285) x 6 – (-1248)** **= -2820 kJ mol^{-1}** **No. of moles of glucose that undergoes complete combustion = 240 / 2820 = 0.0851** **Mass of glucose = 0.0851 x (6x12+12+6x16) = 15.3g**	
	(b)	 Paracetamol Paracetamol is used as pain killer.		**[4]**
		(i)	After paracetamol is refluxed with aqueous sodium hydroxide, draw the products of the resulting mixture. $CH_3COO^-Na^+$  	

		(ii)	Aspirin which has the following structure  is also used to relieve pain. Boiling point of aspirin is lower than paracetamol. Suggest why this is so. Intramolecular hydrogen bonds exist between –COOH and –$OCOCH_3$ group due to proximity in distance. Hence, intermolecular hydrogen bonding between aspirin molecules is less extensive as compared to between paracetamol molecules. Less energy is needed to overcome the hydrogen bonding between aspirin molecules and therefore lower boiling point.	
				[Total: 10 marks]

7	Read through the account of the experiment below and answer the questions that follow. Test I: **X** is a white salt. It decomposes readily on heating to give a colourless odourless gas, which gives white precipitate with limewater, and a white residue. Test II: A saturated solution of **X** (sparingly soluble) gives a yellow precipitate with aqueous silver nitrate, which dissolves in dilute aqueous ammonia to give a colourless solution. Test III: When solution **X** is treated with dilute nitric acid, followed by aqueous silver nitrate, it gives no precipitate. Test IV: A solution of **X** gives a white precipitate with aqueous sodium hydroxide, which remains insoluble in excess aqueous sodium hydroxide. Test V: When solution **X** is treated with aqueous ammonia, it gives no precipitate.		
	(a)	Identify the cation and anion in salt **X**.	**[2]**
		Ca^{2+} and CO_3^{2-}	

	(b)	Write equations, with state symbols, for **all** the reactions in Test I and Test II.	**[4]**
		Expt I: $CaCO_3$ (s) → CO_2 (g) + CaO (s) CO_2 (g) + $Ca(OH)_2$ (aq) → $CaCO_3$ (s) + H_2O (l) Expt II: CO_3^{2-} (aq) + $2Ag^+$ (aq) → Ag_2CO_3 (s) Ag^+ (aq) + $2NH_3$ (aq) ⇌ $[Ag(NH_3)_2]^+$ (aq)	
	(c)	Why is there no precipitate in Test III?	**[1]**
		The nitric acid **reacted with the carbonate** in solution X such that the Ionic Product of Ag_2CO_3 is lower than the K_{sp} of Ag_2CO_3 and no precipitate is formed.	
			[Total: 7 marks]