



PRELIMINARY EXAMINATIONS
HIGHER 2

TEMASEK
JUNIOR COLLEGE

CANDIDATE
NAME

--

CIVICS
GROUP

		/	
--	--	---	--

CENTER
NUMBER

S			
---	--	--	--

INDEX
NUMBER

--	--	--	--

CHEMISTRY

9729/03

Paper 3 Free Response

13 September 2021
2 hours

Candidates answer on the Question Paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group, Centre number, index number and name in all the work you hand in.

Write in dark blue or black pen.

You may use a 2B 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.

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.

For Examiner's Use		
Paper 3 (Section A)	1	
	2	
	3	
Paper 3 (Section B)	4	
	5	
Total		

This document consists of **23** printed pages and **1** blank page.

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

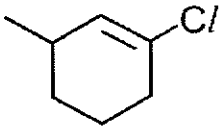
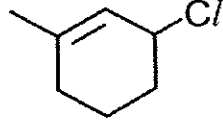
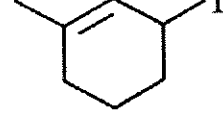
- (c) Precious metals like platinum and rhodium are fitted into car engines as catalytic converters to reduce the amount of pollutants in the exhaust.

With the aid of equations, show how the pollutants hydrocarbons, C_xH_y , and oxides of nitrogen can be removed from the exhaust. [2]

.....

.....

- (d) A student was tasked to investigate the rate of hydrolysis of compounds **A**, **B** and **C** as shown below.

Compound A	Compound B	Compound C
		

- (i) State and explain the difference in reactivity of compounds **A**, **B** and **C** towards hydrolysis. [3]
- (ii) Compound **B** reacts with bromine monochloride, $BrCl$, in the presence of an inert organic solvent.
- Name and describe the mechanism of this reaction. Show relevant lone pairs and dipoles, and use curly arrows to indicate movement of electron pairs. [3]
- (iii) Suggest the structure of another carbocation that can be formed from the mechanism drawn in (d)(ii).
- Hence, explain which carbocation is preferentially produced. [2]

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN

Area with horizontal dotted lines for writing.

[Total: 20]

(b) Similar to silver halides, silver carbonate, Ag_2CO_3 , is a sparingly soluble salt which is used in the production of microelectronics.

(i) Write an equation to represent the enthalpy change of solution of silver carbonate.

[1]

Many thermodynamic properties, such as entropy, are temperature dependent. When temperature changes, the entropy of a species varies according to the following equation,

$$\Delta S = S_{T_2} - S_{T_1} = C_p \ln \frac{T_2}{T_1}$$

where ΔS is the difference in entropy under temperatures T_2 and T_1 ;

C_p is the molar heat capacity of the species; and

T_2 and T_1 are temperatures in Kelvin.

The entropies of various species at 398 K, S_{398} , are shown below.

Species	$\text{Ag}_2\text{CO}_3(\text{s})$	$\text{Ag}^+(\text{aq})$	$\text{CO}_3^{2-}(\text{aq})$
$S_{398} / \text{J K}^{-1} \text{mol}^{-1}$	+199.9	Y	+100.7

(ii) The entropy of $\text{Ag}^+(\text{aq})$ at 298 K = $72.7 \text{ J mol}^{-1} \text{ K}^{-1}$.

Given the molar heat capacity, C_p , of $\text{Ag}^+(\text{aq}) = 35.0 \text{ J mol}^{-1} \text{ K}^{-1}$, calculate Y, the entropy of $\text{Ag}^+(\text{aq})$ at 398 K. [1]

(iii) Hence, calculate the entropy change of solution of silver carbonate at 398 K. [1]

(iv) Assuming the enthalpy change of solution of silver carbonate is a constant value of $+41.8 \text{ kJ mol}^{-1}$, calculate the Gibbs free energy change of solution of silver carbonate at 398 K. [1]

(v) The standard Gibbs free energy change of solution of silver carbonate is $+44.1 \text{ kJ mol}^{-1}$.

Comment on the effect of increasing temperature on the solubility of silver carbonate. [2]

.....

.....

.....

.....

.....

.....

.....

.....

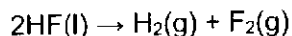
.....

.....

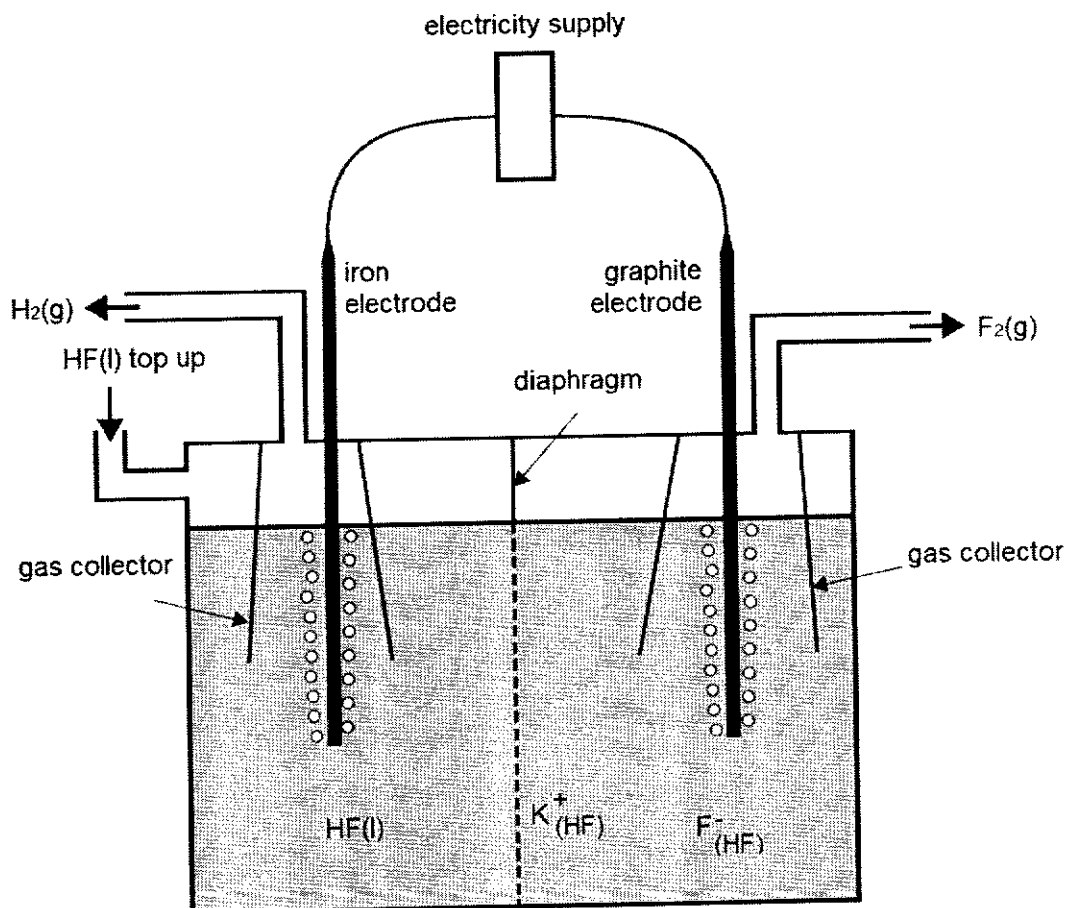
Section B

Answer **one** question from this section.

- 4 (a) Fluorine gas is the most reactive of all non-metals. It can be produced by the electrolysis of liquid hydrogen fluoride using the following set-up.



Potassium fluoride is added to increase electrical conductivity and can be dissolved in hydrogen fluoride.



- (i) Suggest which of the electrode is the cathode and state its polarity. [1]
- (ii) Write an equation for the reaction occurring at the anode. [1]
- (iii) Suggest how a diaphragm was used to ensure the safe operation of the cell. [1]
- (iv) A student considered using iron for both the electrodes but decided against it. Suggest and explain if you agree with his decision using relevant data from the Data Booklet. [2]
- (v) If some water was added to the above set-up, a colourless triatomic gas was formed at the anode instead of fluorine. [1]
- Given that the M_r of the gas is 54, suggest its identity.

.....

.....

.....

.....

.....

.....

.....

.....

- (b) (i) State how the reactivity of Mg and Ca as reducing agents is different, and relate this difference to relevant E^\ominus values. [2]
- (ii) Apart from the basic nature of magnesium hydroxide, suggest another reason why magnesium hydroxide is suitable for the role as an antacid. [1]

.....

.....

.....

.....

.....

.....

.....

.....

- (c) Fluorine gas deviates from an ideal gas and the following equation proposed by J. D. van der Waals can account for the differences.

$$\left(P + \frac{n^2 a}{V^2}\right) (V - nb) = nRT$$

where P : actual pressure
 V : volume of the container
 T : temperature
 n : amount of gas
 R : molar gas constant
 a and b : van der Waals constants

The values of a and b account for the deviation from ideality for a real gas and are dependent on certain molecular properties of the gas.

The values of a and b for fluorine and the other halogens are given in table 5.1 below.

Table 5.1

Gas	$a / \text{Pa m}^6 \text{ mol}^{-2}$	$b / \text{m}^3 \text{ mol}^{-1}$
Fluorine	0.117	2.90×10^{-5}
Chlorine	0.634	5.42×10^{-5}
Bromine	0.975	5.91×10^{-5}

- (i) For each of the constants a and b , suggest a molecular property of the gas that will directly affect its value. [2]
- (ii) Explain the differences in the values of a for the halogens. [2]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

- (d) Halogens form many interhalogen compounds. One such compound is bromine monochloride, BrCl , which have similar properties to the halogens. [1]
- Suggest an equation for the reaction between BrCl and KI .

- (e) Halogens are also found in organic compounds which can be used to synthesise amino acids.

Table 5.2 shows some naturally occurring α -amino acids found in the body. The isoelectric point is the pH at which an amino acid exists as a zwitterion.

Table 5.2

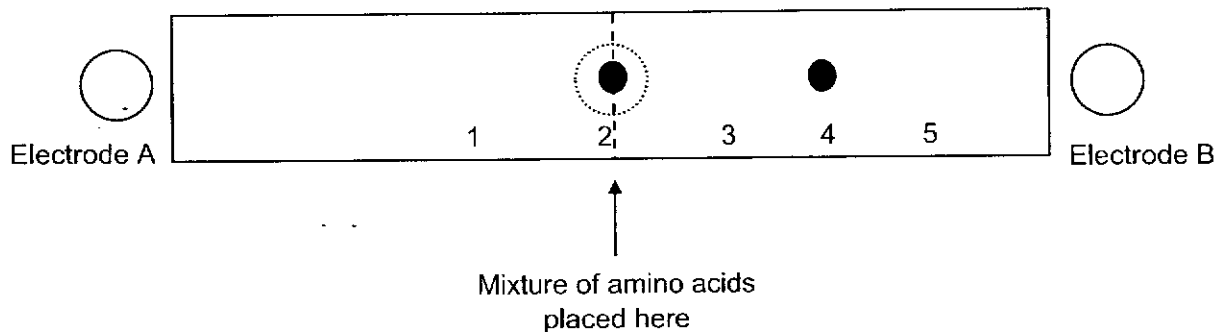
Amino acid	Abbreviation	R group	M_r	Isoelectric point
Serine	Ser	$-\text{CH}_2\text{OH}$	105	5.68
Asparagine	Asn	$-\text{CH}_2\text{CONH}_2$	132	5.43
Lysine	Lys	$-(\text{CH}_2)_4\text{NH}_2$	146	9.74

- (i) Draw the dipeptide Asn-Ser, showing the peptide bonds in displayed formula. [1]

Electrophoresis is a technique used to separate mixtures of amino acids. Ions of higher charge to mass ratio will migrate towards the electrode of opposite charge at a faster rate.

A mixture of the three amino acids in table 5.2 were placed at position 2 and subjected to electrophoresis in a buffer at pH 9.74.

The positions of two of the amino acids, serine and lysine, relative to the electrodes were as follows:



- (ii) Draw the structure of the species at positions 2 and 4. [2]
- (iii) State the number which correspond to the likely position of asparagine and explain your answer. [2]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

[Total: 20]

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN

BLANK PAGE

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN



PRELIMINARY EXAMINATIONS
HIGHER 2

TEMASEK
JUNIOR COLLEGE

CANDIDATE
NAME

--

CIVICS
GROUP

		/		
--	--	---	--	--

CENTER
NUMBER

S				
---	--	--	--	--

INDEX
NUMBER

--	--	--	--

CHEMISTRY
9729/03

Paper 3 Free Response

13 September 2021
2 hours

Candidates answer on the Question Paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group, Centre number, index number and name in all the work you hand in.
Write in dark blue or black pen.
You may use a 2B 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.

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.

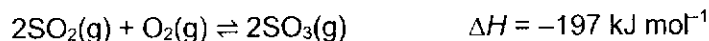
For Examiner's Use		
Paper 3 (Section A)	1	
	2	
	3	
Paper 3 (Section B)	4	
	5	
Total		

This document consists of **23** printed pages and **1** blank page.

SECTION A

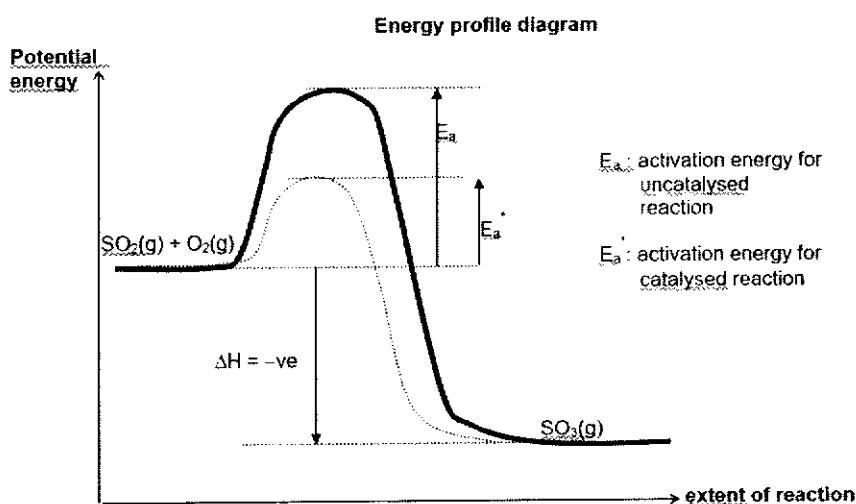
Answer all the questions in this section.

- 1 (a) The Contact Process is an industrial process for manufacturing sulfuric acid. The key stage in this process is the reaction between sulfur dioxide and oxygen.



Vanadium(V) oxide, V_2O_5 , is used as a heterogeneous catalyst for this process.

With the aid of an energy profile diagram, explain using collision theory why the addition of the catalyst speeds up the reaction. [3]



• Well-labelled diagram

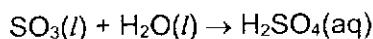
The \checkmark catalyst provides an alternative pathway, one which involves a lower E_a than that of an uncatalysed reaction.

\checkmark Number of molecules having energy greater than or equal to E_a' increases significantly. The \checkmark frequency of effective collisions increases, \checkmark rate constant, k increases and thus rate increase.

2 \checkmark : 1m

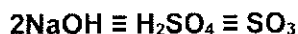
- (b) In an experiment to determine the K_p of the Contact Process in (a), a mixture containing 0.200 mol of SO_2 and 0.100 mol of O_2 was heated in a closed flask and allowed to reach equilibrium at 550 °C and 3.5 atm.

The flask was then rapidly cooled to liquefy the SO_3 so that it can be separated from the gaseous SO_2 and O_2 . Excess water was carefully added to the liquid SO_3 , causing the following reaction to occur:



The resulting solution was made up to 250 cm^3 in a standard volumetric flask. 25.0 cm^3 of this solution was titrated with 1.00 mol dm^{-3} NaOH and required 36.00 cm^3 for complete neutralisation.

- (i) Calculate the equilibrium amounts of SO_2 , O_2 and SO_3 at 550 °C. [3]



$$\text{Amt of SO}_3 \text{ at eqm} = \frac{1}{2} \times 36.00 / 1000 \times 1.00 \times (250/25) = \bullet 0.180 \text{ mol}$$

	2SO ₂ (g)	O ₂ (g)	2SO ₃ (g)
Initial / mol	0.200	0.100	0
Change / mol	-0.180	-0.09	+0.180
Eqm / mol	<u>• 0.020</u>	<u>• 0.01</u>	0.180

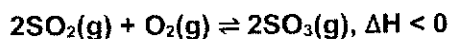
- (ii) Write the expression for K_p and calculate the value of K_p at 550°C and 3.5 atm, including its units. [2]

$$\text{Total number of moles} = 0.020 + 0.010 + 0.180 = 0.210 \text{ mol}$$

$$\bullet K_p = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 \times P_{\text{O}_2}}$$

$$= \frac{\left(\frac{0.180}{0.210} \times 3.5\right)^2}{\left(\frac{0.020}{0.210} \times 3.5\right)^2 \left(\frac{0.010}{0.210} \times 3.5\right)} = \bullet 486 \text{ atm}^{-1} \text{ or } 0.00480 \text{ Pa}^{-1} \text{ (answer + correct units)}$$

- (iii) In liquefying the SO₃, it was mentioned that the cooling was performed rapidly. Explain how the titre volume would be affected if the cooling had been performed slowly. [2]



Temperature falls when cooling happens.

- By Le Chatelier's Principle, equilibrium position will shift to the right to release more heat to increase the temperature.
- More SO₃ is formed, and titre volume increases.

- (c) Precious metals like platinum and rhodium are fitted into car engines as catalytic converters to reduce the amount of pollutants in the exhaust.

With the aid of equations, show how the pollutants hydrocarbons, C_xH_y, and oxides of nitrogen can be removed from the exhaust. [2]

- $\text{CO} + \text{NO} \rightarrow \text{CO}_2 + \frac{1}{2}\text{N}_2$
- OR $2\text{CO} + 2\text{NO} \rightarrow 2\text{CO}_2 + \text{N}_2$
- OR $2x\text{CO} + 2\text{NO}_x \rightarrow 2x\text{CO}_2 + \text{N}_2$
- $\text{C}_x\text{H}_y + (x + y/4)\text{O}_2 \rightarrow x\text{CO}_2 + y/2 \text{H}_2\text{O}$

- (d) A student was tasked to investigate the rate of hydrolysis of compounds A, B and C as shown below.

Compound A	Compound B	Compound C

- (i) State and explain the difference in reactivity of compounds A, B and C towards hydrolysis. [3]

• Reactivity: C > B > A (least reactive)

Compound A is the least reactive towards hydrolysis as the C-Cl bond is strengthened (stronger) by the delocalization of the lone pair of electrons from Cl to the double bond (or overlapping of the p orbital of Cl with the π orbital of C=C bond).

Compound C is more reactive than B as the C-I bond is weaker than C-Cl bond, due to I atom being larger than Cl atom, causing less effective orbital overlap, less energy is needed to break the C-I bond.

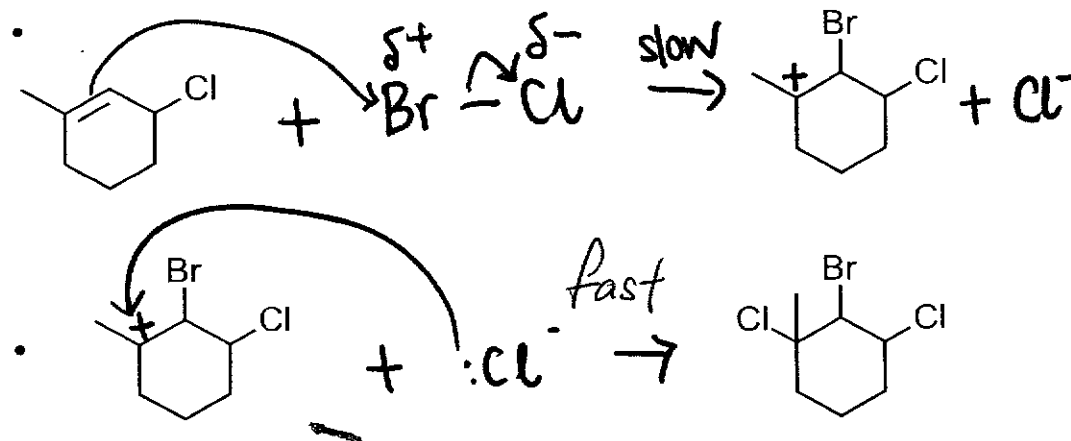
2√: 1m

- (ii) Compound B reacts with bromine monochloride, BrCl, in the presence of an inert organic solvent.

Name and describe the mechanism of this reaction. Show relevant lone pairs and dipoles, and use curly arrows to indicate movement of electron pairs. [3]

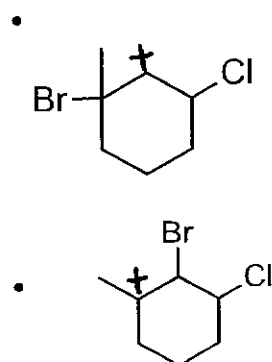
• Electrophilic addition

Note: Award 1m (out of 2m) if minor product is drawn.



- (iii) Suggest the structure of another carbocation that can be formed from the mechanism drawn in (d)(ii).

Hence, explain which carbocation is preferentially produced. [2]

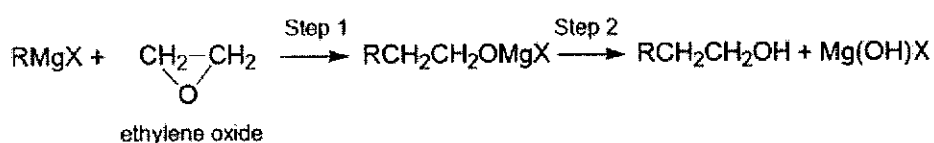


is preferentially produced as it is a tertiary carbocation which is more stable than the secondary carbocation intermediate. Tertiary carbocations are more stable due to the presence of more electron donating alkyl groups that disperse the positive charge and stabilise the electron deficient carbocation.

[Total: 20]

- 2 (a) Organometallic compounds are compounds that contain carbon-metal covalent bonds. Organometallic compounds of lithium and magnesium are strong bases and are of great importance in organic synthesis.

Organomagnesium halides are also known as Grignard reagents. The reaction between an organomagnesium halide and ethylene oxide is shown below.



- (i) Suggest the types of reaction for steps 1 and 2. [2]

- **Step 1: Nucleophilic substitution**
- **Step 2: Hydrolysis**

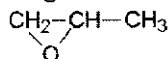
- (ii) Explain why the ring opening process in step 1 is favourable. [1]

- **In ethylene oxide, there is significant ring/angle strain (which resulted from C-C-C bond angle as 60° instead of 109.5° for a sp³ hybridised C). Opening of the ring removes the ring/angle strain.**

- (iii) Suggest why organomagnesium and organolithium compounds are more reactive than organomercury or organolead compounds. [1]

- **Since there is larger electronegativity difference between C and Li/Mg, the C-Li and C-Mg bonds are more ionic in nature, leading to stronger R nucleophiles.**

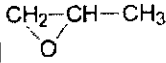
- (b) A student prepared a Grignard reagent, CH₃CH₂MgBr, from bromoethane and magnesium metal in ether solvent. He subsequently reacted the Grignard reagent with

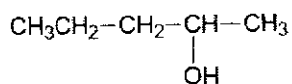


- (i) Water cannot be used as a solvent as it will react with the Grignard reagent prepared.

Explain how CH₃CH₂MgBr reacts with water, and hence suggest an organic product from the reaction. [2]

- **Grignard reagents are strong bases and will undergo neutralisation with water/abstract a proton from water.**
- **CH₃CH₃**

- (ii) Suggest the structure of the major organic product formed between $\text{CH}_3\text{CH}_2\text{MgBr}$ and . Explain your answer. [2]



- **The Grignard reagent will attack the less substituted ring carbon atom due to lesser steric hindrance.**

- (iii) Describe a simple chemical test you would carry out to confirm the presence of the functional group present in the product in (b)(ii). State what you would observe. [2]

- Test: $\text{PCl}_5(\text{s})$, rtp
 - Observations: White fumes of HCl
- OR
- Test: $\text{Na}(\text{s})$
 - Observations: Effervescence of hydrogen gas
- OR
- Test: Alkaline aqueous iodine, heat
 - Observations: Yellow precipitate of CHI_3

OR

- Test: KMnO_4 , dilute H_2SO_4 , heat
- Observations: Decolorisation of purple KMnO_4

OR

- Test: $\text{K}_2\text{Cr}_2\text{O}_7$, dilute H_2SO_4 , heat
- Observations: Solution changes from orange to green

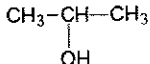
- (iv) Use the table of characteristic infra-red absorption frequencies in the Data Booklet to answer this question.

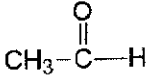
The student suggested testing for the presence of the product in (b)(ii) via infra-red spectroscopy, and observing for strong and very broad absorption at $2500\text{--}3000\text{ cm}^{-1}$.

Explain if you agree with the student's suggestion. [1]

- **Disagree. Strong absorption should be observed for O-H bond from 3200 to 3650 cm^{-1} .**

Alcohols can also be produced from a reaction between a Grignard reagent and a carbonyl compound.

- (v) Suggest the Grignard reagent and carbonyl compound needed to form . [1]

- CH_3MgBr and 

- (c) LiFePO_4 can be used in lithium-ion rechargeable batteries which are commonly used in cell phones and laptops.

When the cell is charging, lithium reacts with the graphite electrode to form LiC_6 .

- (i) Suggest the type of bonding between lithium and carbon in LiC_6 . Explain how the bonds are formed during the charging process. [2]

- **Ionic bonds**
- **The lithium atom is able to transfer its valence electron to the carbon atoms in the graphite, forming positive Li^+ cation and anionic carbon.**

When the cell is discharging, the following processes are observed:

- carbon atoms and lithium ions are formed from solid LiC_6 ;
- solid LiFePO_4 is formed from FePO_4 .

- (ii) Write equations for the reactions at the anode and cathode. [2]

- **Anode: $\text{LiC}_6 \rightarrow 6\text{C} + \text{Li}^+ + \text{e}^-$ or $\text{LiC}_6 \rightarrow \text{C}_6 + \text{Li}^+ + \text{e}^-$**
- **Cathode: $\text{Li}^+ + \text{FePO}_4 + \text{e}^- \rightarrow \text{LiFePO}_4$**

- (iii) The cell voltage of LiFePO_4 battery is 3.20 V.

Calculate ΔG for the discharging process. [1]

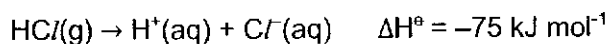
- **$\Delta G = -nFE_{\text{cell}} = -(1)(96500)(3.20) = -309 \text{ kJ mol}^{-1}$**

- (iv) State one possible advantage of using the lithium-ion rechargeable batteries. [1]

- **Low cost/low toxicity (does not contain nickel or cobalt) or long-term stability or small size/low mass or environmentally friendly (since rechargeable)**

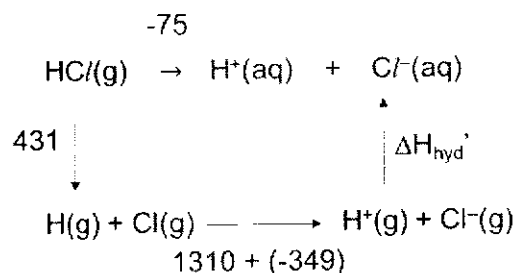
[Total: 18]

- 3 (a) Hydrogen chloride exists as white fumes under room conditions and dissolves readily in water to form a strongly acidic solution.



The first electron affinity of $\text{Cl}(\text{g})$ is given as -349 kJ mol^{-1} .

- (i) Using suitable values from the *Data Booklet* and with the aid of an energy cycle, determine $\Delta H_{\text{hyd}}^\ominus$, the sum of standard enthalpy change of hydration of gaseous proton and chloride. [3]



• By Hess' Law, $-75 = 431 + 1310 - 349 + \Delta H_{\text{hyd, sum}}^{\circ}$

$$\Delta H_{\text{hyd}}^{\circ} = \bullet \underline{-1467 \text{ kJ mol}^{-1}}$$

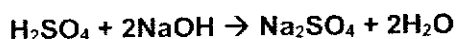
- (ii) The standard enthalpy change of reaction when 1 mole of each of the following acids reacts with excess aqueous sodium hydroxide is shown below.

Acid	$\Delta H_r^{\circ} / \text{kJ mol}^{-1}$
Nitric acid	-57.3
Sulfuric acid	-114.6
Ethanoic acid	-55.2

Explain the ΔH_r° values for the different acids above.

[2]

H_2SO_4 : 1 mol of H_2SO_4 reacts with excess NaOH to \checkmark give twice the amount of water as HNO_3 . Hence the \checkmark amount of heat given out is double and the ΔH_r is doubled.

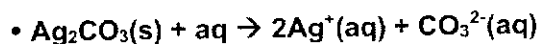


CH_3COOH : \checkmark weak acid which dissociates partially, so \checkmark some heat evolved is absorbed to dissociate the acid fully, ΔH_r is less exothermic / less negative.

Every 2 \checkmark = 1 mark

- (b) Similar to silver halides, silver carbonate, Ag_2CO_3 , is a sparingly soluble salt which is used in the production of microelectronics.

- (i) Write an equation to represent the enthalpy change of solution of silver carbonate. [1]



Many thermodynamic properties, such as entropy, are temperature dependent. When temperature changes, the entropy of a species varies according to the following equation,

$$\Delta S = S_{T_2} - S_{T_1} = C_p \ln \frac{T_2}{T_1}$$

where ΔS is the difference in entropy under temperatures T_2 and T_1 ;

C_p is the molar heat capacity of the species; and

T_2 and T_1 are temperatures in Kelvin.

The entropies of various species at 398 K, S_{398} , are shown below.

Species	$\text{Ag}_2\text{CO}_3(\text{s})$	$\text{Ag}^+(\text{aq})$	$\text{CO}_3^{2-}(\text{aq})$
$S_{398} / \text{J K}^{-1} \text{mol}^{-1}$	+199.9	Y	+100.7

- (ii) The entropy of $\text{Ag}^+(\text{aq})$ at 298 K = $72.7 \text{ J mol}^{-1} \text{ K}^{-1}$.
 Given the molar heat capacity, C_p , of $\text{Ag}^+(\text{aq}) = 35.0 \text{ J mol}^{-1} \text{ K}^{-1}$, calculate Y, the entropy of $\text{Ag}^+(\text{aq})$ at 398 K. [1]

$$\Delta S = S_{T2} - S_{T1} = C_p \ln \frac{T_2}{T_1}$$

$$\text{Entropy of } \text{Ag}^+(\text{aq}) \text{ at } 398 \text{ K, } S_{398} = 72.7 + 35 \ln(398/298) = \underline{+82.8 \text{ J mol}^{-1} \text{ K}^{-1}}$$

- (iii) Hence, calculate the entropy change of solution of silver carbonate at 398 K. [1]

$$\Delta S_{\text{sol}} \text{ at } 398 \text{ K} = 100.7 + 2(82.8) - 199.9 = \underline{+66.4 \text{ J mol}^{-1} \text{ K}^{-1}}$$

- (iv) Assuming the enthalpy change of solution of silver carbonate is a constant value of $+41.8 \text{ kJ mol}^{-1}$, calculate the Gibbs free energy change of solution of silver carbonate at 398 K. [1]

$$\text{At } 398 \text{ K, } \Delta G_{\text{sol}} = \Delta H_{\text{sol}} - T\Delta S_{\text{sol}} = +41.8 - 398(66.4/1000) = \underline{+15.4 \text{ kJ mol}^{-1}}$$

- (v) The standard Gibbs free energy change of solution of silver carbonate is $+44.1 \text{ kJ mol}^{-1}$.

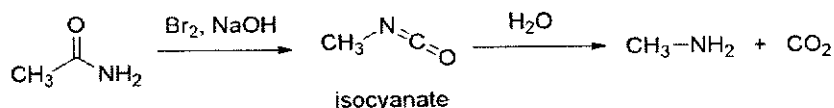
Comment on the effect of increasing temperature on the solubility of silver carbonate. [2]

As temperature increases, • ΔG value becomes less positive / decreases, implies that the dissolution of silver carbonate becomes more spontaneous and thus • solubility increases / silver carbonate becomes more soluble.

- (c) Acids and bases are often used in organic reactions, either as catalysts or to provide an acidic or basic medium.

The Hofmann Degradation reaction is one such reaction which uses an alkaline solution of aqueous bromine to convert an unsubstituted amide to a primary amine, with one less carbon atom.

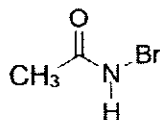
The reaction goes through the formation of an isocyanate intermediate, followed by elimination of carbon dioxide gas, as illustrated using ethanamide.



To form the isocyanate, the ethanamide first undergoes a 2-step reaction described below.

Step 1: The OH^- base abstracts an acidic N-H proton from the amide, yielding an anion.

Step 2: The anion reacts with bromine to form an N-bromoethanamide and a bromide anion.

*N*-bromoethanamide

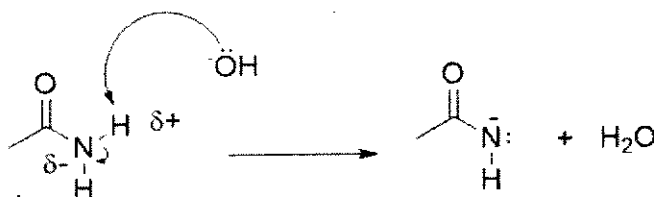
- (i) Suggest why the N-H proton on the ethanamide is acidic. [1]

After abstraction of H^+ , the \checkmark negative charge on the N atom after dissociation is dispersed due to the electron withdrawing O atom. The \checkmark anion is stabilised and the N-H proton is readily lost.

2 \checkmark = 1 mark

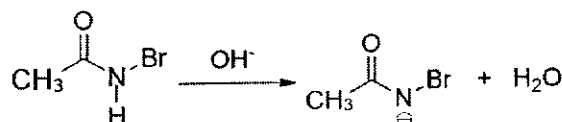
- (ii) Starting with ethanamide, illustrate the 2-step mechanism above to form *N*-bromoethanamide, using appropriate curly arrows to show the movement of electrons.

Show clearly any partial charges and lone pair of electrons on each species. [2]



1 mark for each step, with correct arrow pushing, lone pair electron and (partial) charges.

- (iii) The *N*-bromoethanamide produced in Step 2, reacts with more OH^- to form a bromoethanamide anion, which rearranges to form the isocyanate intermediate.



With reference to the strength of the conjugate acid-base pairs, explain why OH^- instead of Br^- ions abstract the acidic N-H proton on the *N*-bromoethanamide. [1]


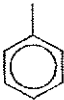
Br^- ions are less basic / weaker base than OH^- , as the corresponding acid, HBr is stronger than H_2O . Hence the OH^- ions are more likely to remove the N-H proton.

OR

OH^- ions are more basic / stronger base than Br^- , as the corresponding acid, H_2O , is weaker than HBr. Hence the OH^- ions are more likely to remove the N-H proton.

- (d) In one experiment, *N*-bromoethanamide is contaminated with bromide leftover from Step 2, in an aqueous solution. A chemist wishes to obtain pure solid *N*-bromoethanamide from the mixture.

You are provided with two solvents below. One of the solvents can be used to extract *N*-bromoethanamide from the impure mixture.

Solvent	Density / g cm ⁻³	Boiling point / °C
 chloroform	1.49	61.2
 toluene	0.87	110.6

- (i) Suggest a suitable solvent to extract *N*-bromoethanamide from the impure mixture and explain your choice. [1]

✓ **Chloroform,**

Choose 1 reason

N-bromoethanamide is ✓ more soluble in a polar solvent.

OR

✓ Chloroform is more volatile / lower boiling point than toluene and be easily removed by evaporation.

- (ii) Hence, using information from the table above, plan an experiment to purify *N*-bromoethanamide from the impure mixture, using the solvent identified in (d)(i). [3]

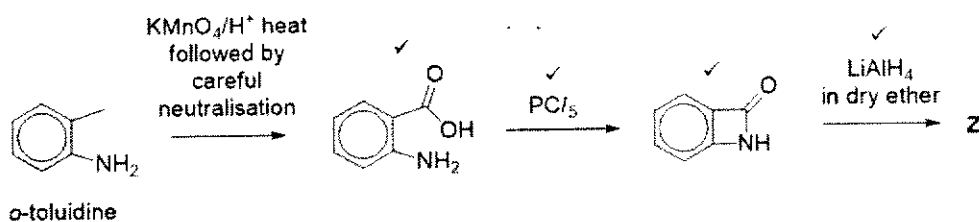
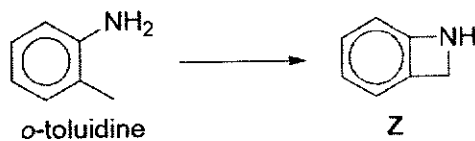
Your plan should include details of:

- how *N*-bromoethanamide is obtained in its dry solid form;
- suitable apparatus used; and
- how the purity of the product is determined.

Pour the mixture from step 2 into a separatory funnel and add an equal volume of chloroform. ✓ Stopper and shake the separatory funnel, occasionally opening the tap to prevent pressure build-up. ✓ Transfer the lower organic layer (containing *N*-bromoethanamide) from the separatory funnel into a conical flask. ✓ Add anhydrous MgSO₄ / Na₂SO₄ / CaCl₂ / CaSO₄, with stirring, to dry the organic layer. Filter the suspension into a dry conical flask. ✓ Evaporate the solvent to obtain pure and dry *N*-bromoethanamide. ✓ Conduct a melting point experiment using a small sample of product. The product is pure if it has a sharp and definite melting point.

Every 2 ✓ = 1 mark

- (iii) Starting from *o*-toluidine, suggest a synthesis route to produce **Z**, in the absence of UV light. Show clearly the reagent and conditions for each step as well as the structures of intermediates. [3]

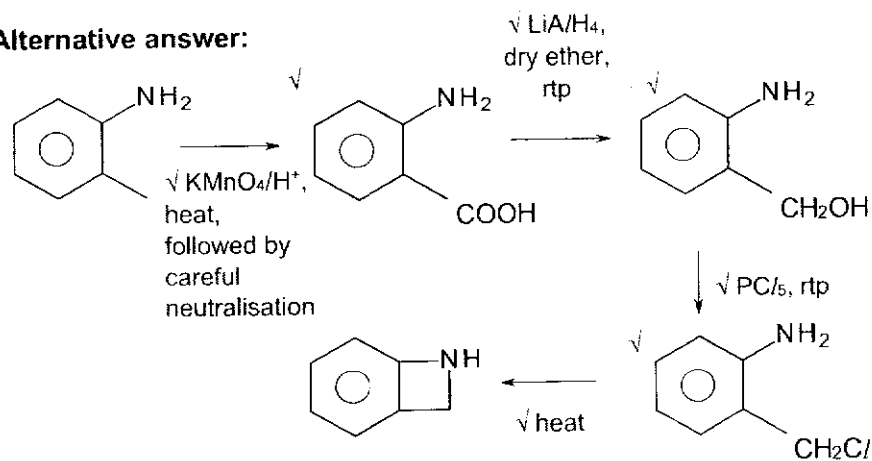


5 ✓ = 3 marks

3 to 4 ✓ = 2 marks

1 to 2 ✓ = 1 mark

Alternative answer:



7 ✓ = 3 marks

4 to 6 ✓ = 2 marks

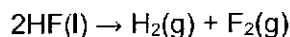
1 to 3 ✓ = 1 mark

[Total: 22]

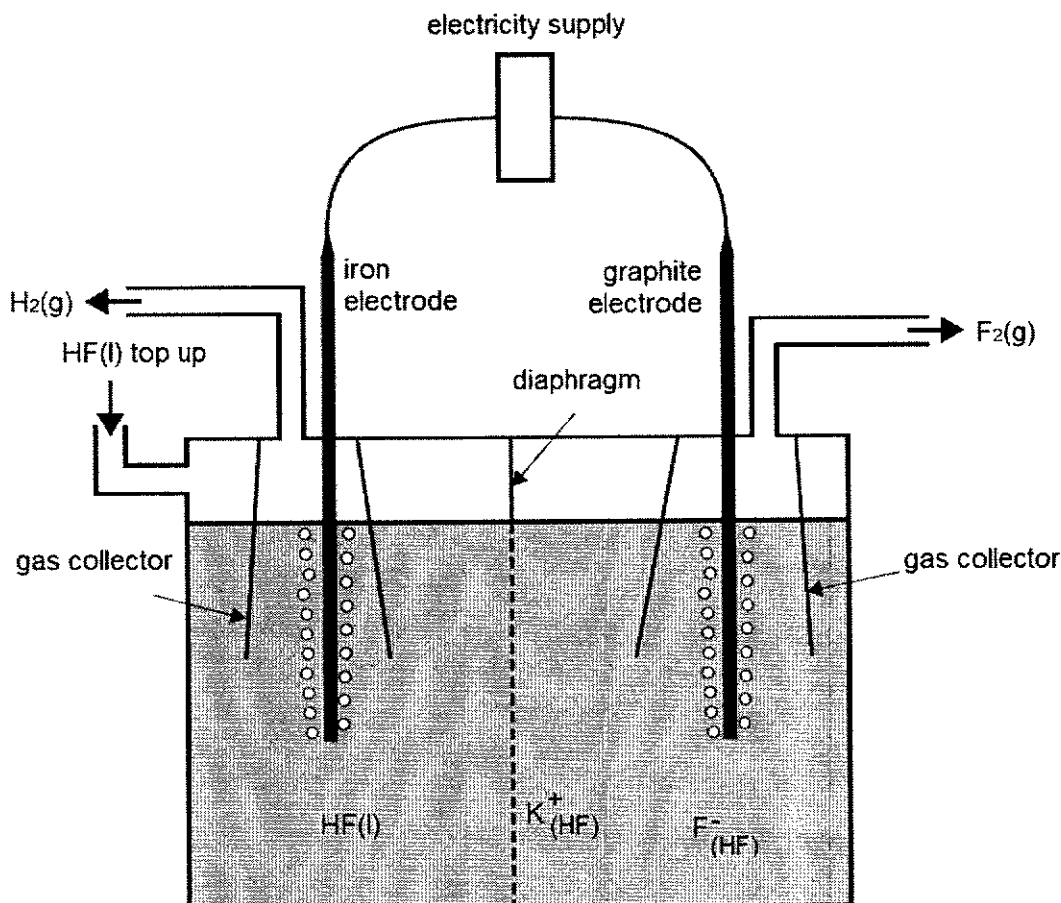
Section B

Answer **one** question from this section.

- 4 (a) Fluorine gas is the most reactive of all non-metals. It can be produced by the electrolysis of liquid hydrogen fluoride using the following set-up.



Potassium fluoride is added to increase electrical conductivity and can be dissolved in hydrogen fluoride.



- (i) Suggest which of the electrode is the cathode and state its polarity. [1]
- The cathode is the iron electrode as HF is reduced to H₂. Hence, it is negatively charged.
- (ii) Write an equation for the reaction occurring at the anode. [1]
- $2\text{HF} \rightarrow \text{F}_2 + 2\text{H}^+ + 2\text{e}^-$
 - Also accept: $2\text{F}^- \rightarrow \text{F}_2 + 2\text{e}^-$
- (iii) Suggest how a diaphragm was used to ensure the safe operation of the cell. [1]
- It prevents the mixing of the products, hydrogen and fluorine. Otherwise, they would react explosively upon contact.

- (iv) A student considered using iron for both the electrodes but decided against it. Suggest and explain if you agree with his decision using relevant data from the Data Booklet. [2]

$$\sqrt{E^{\circ}_{\text{Fe}^{2+}/\text{Fe}} = -0.44\text{V}, E^{\circ}_{\text{F}_2/\text{F}^-} = +2.87\text{V}}$$

Yes, I \checkmark agree with his decision.

If iron was used instead, it would be \checkmark preferentially oxidised instead of the fluoride ion as $E^{\circ}_{\text{Fe}^{2+}/\text{Fe}}$ is \checkmark less positive/more negative than $E^{\circ}_{\text{F}_2/\text{F}^-}$. Hence, fluorine would not be formed.

Or

$$\begin{aligned}\sqrt{E^{\circ}_{\text{cell}} &= +2.87 - (-0.44)} \\ &= +3.31 \text{ V}\end{aligned}$$

\checkmark As $E^{\circ}_{\text{cell}} > 0$, F_2 produced could react with Fe.

2 \checkmark : 1m

- (v) If some water was added to the above set-up, a colourless triatomic gas was formed at the anode instead of fluorine.

Given that the M_r of the gas is 54, suggest its identity. [1]

- F_2O

- (vi) Calculate the time needed to produce 1 dm^3 of fluorine gas using the above set-up where the current was 2.5 A, given that the temperature and pressure in the laboratory was 30°C and 101 kPa. [2]

$$\text{No. of moles of } \text{F}_2 = \frac{101000 \times 0.001}{8.31 \times (30+273)} = \bullet 0.0401 \text{ mol}$$

$$\begin{aligned}\text{No. of moles of } e^- &= 2 \times 0.0401 \\ &= 0.0802 \text{ mol}\end{aligned}$$

$$\text{Charge} = It = nF$$

$$t = \frac{(0.0802 \times 96500)}{2.5} = \bullet 3100 \text{ s}$$

- (b) The halogens are oxidising agents.

State and explain the trend in their oxidising ability down the group. [2]

- The oxidising power decreases down the group.

$$E^{\circ}_{\text{Cl}_2/\text{Cl}^-} = +1.36 \text{ V}, E^{\circ}_{\text{Br}_2/\text{Br}^-} = +1.07 \text{ V}, E^{\circ}_{\text{I}_2/\text{I}^-} = +0.54 \text{ V}$$

- As the electrode potential values become less positive, it is less likely for the halogen to be reduced.

(c) When a Group 2 metal nitrate is heated strongly, it evolves oxygen and nitrogen dioxide, leaving the metal oxide, MO (M = Group 2 metal).

(i) Write a balanced equation for this reaction. [1]



(ii) When a particular Group 2 metal nitrate was heated in this way until no further change occurred, it lost 65.8% of its mass. Calculate the A_r of the metal and hence identify it. [2]

100 g of $M(NO_3)_2$ produces $100 - 65.8 = 34.2$ g of MO

Since amount of $M(NO_3)_2$ heated = amount of MO produced

$$\frac{100}{A_r(M) + 124.0} = \frac{34.2}{A_r(M) + 16.0}$$

• $A_r = 40.1$

• Metal is calcium

(iii) Group 2 nitrates decompose in a similar manner to Group 2 carbonates.

Describe and explain how the thermal stabilities of the Group 2 nitrates vary down the group. [3]

Thermal stability \checkmark increases down the group.

This is because charge remains constant but ionic radius increases, hence \checkmark charge density of cation decreases. \checkmark Polarising power of cation decreases resulting in \checkmark less distortion of the electron cloud of NO_3^- ion, \checkmark weakening the N-O covalent bond less. \checkmark More energy/ higher temperature is needed to decompose the nitrate.

2 \checkmark 1 mark

(d) (i) Explain why the melting point of magnesium chloride is lower than that of aluminium oxide. [2]

$MgCl_2$ and Al_2O_3 have \checkmark giant ionic lattice structure or \checkmark $LSE \propto \frac{q_+q_-}{r_+ + r_-}$

Mg^{2+} has a \checkmark larger ionic radius and smaller charge than Al^{3+} . Cl^- has a \checkmark larger ionic radius and smaller charge than O^{2-} . This results in $MgCl_2$ having a smaller magnitude for its lattice energy. \checkmark Less energy is required to overcome the weaker ionic bond between Mg^{2+} and Cl^- , hence $MgCl_2$ has a lower melting point.

Every 2 \checkmark 1 mark

(ii) State whether:

- MgSO_4 or BaSO_4 would have the more exothermic lattice energy and
- Mg^{2+} or Ba^{2+} would have the more exothermic enthalpy change of hydration.

Hence, suggest why the solubility of MgSO_4 is higher compared to that of BaSO_4 . [2]

Due to the smaller ionic radius of Mg^{2+} , the $\sqrt{\text{lattice energy of MgSO}_4}$ is more exothermic than that of BaSO_4 , and the $\sqrt{\Delta H_{\text{hyd}}}$ of Mg^{2+} is more exothermic than that of Ba^{2+} .

$$\Delta H_{\text{sol}}(\text{MSO}_4) = \Delta H_{\text{hyd}}(\text{M}^{2+}) + \Delta H_{\text{hyd}}(\text{SO}_4^{2-}) - \text{LE}(\text{MSO}_4)$$

$\sqrt{\Delta H_{\text{hyd}}}$ is more dominant (or increase in $|\Delta H_{\text{hyd}}| > \text{increase in } |\text{LE}|$), hence $\sqrt{\Delta H_{\text{sol}}}$ of MgSO_4 is more exothermic than that of BaSO_4 . (accept if overall more exothermic)

2 $\sqrt{1}$ mark

[Total: 20]

5 Heartburn occurs when an excess amount of acid is produced in the stomach, leading to pain. Antacids are substances used to relieve heartburn. A common antacid used is magnesium hydroxide. Although antacids are generally safe, high antacid level in the blood may cause toxicity.

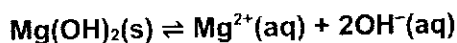
(a) 2 g of solid magnesium hydroxide is shaken in 250 cm^3 of water to reach equilibrium at 25°C and then filtered. The mass of the residue is 1.998 g.

(i) Write an expression for the solubility product, K_{sp} , of magnesium hydroxide, stating its units. [1]

$$K_{\text{sp}} = [\text{Mg}^{2+}] [\text{OH}^-]^2 \text{ mol}^3 \text{ dm}^{-9}$$

(ii) Calculate the solubility product of magnesium hydroxide. [2]

$$\begin{aligned} \bullet \text{ amount of Mg(OH)}_2 \text{ dissolved in 1 dm}^3 \text{ water} &= \frac{2 - 1.998}{(24.3 + 2(16.0 + 1.0))} \times \frac{1000}{250} \\ &= 1.372 \times 10^{-4} \text{ mol} \end{aligned}$$



$$\begin{aligned} \bullet K_{\text{sp}} &= [\text{Mg}^{2+}] [\text{OH}^-]^2 \\ &= (1.372 \times 10^{-4}) (2 \times 1.372 \times 10^{-4})^2 \\ &= 1.03 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9} \end{aligned}$$

(iii) Calculate the pH of the filtrate. [1]

$$[\text{OH}^-] = 2.744 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{pOH} = -\lg [\text{OH}^-] = 3.56$$

$$\bullet \text{ pH} = 10.4$$

(iv) 2 g of solid magnesium hydroxide is shaken in 250 cm^3 of 0.1 mol dm^{-3} magnesium nitrate to reach equilibrium at 25°C. Calculate the pH of the resulting solution. [1]

$$K_{\text{sp}} = [\text{Mg}^{2+}] [\text{OH}^-]^2$$

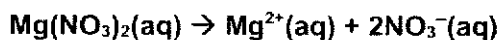
$$1.03 \times 10^{-11} = (0.1) [\text{OH}^-]^2$$

$$[\text{OH}^-] = 1.015 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\text{pOH} = -\lg [\text{OH}^-] = 4.99$$

- $\text{pH} = 9.01$

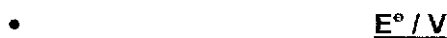
- (v) Explain the difference between your calculated values in a(iii) and a(iv). [2]



- In the presence of $\text{Mg}(\text{NO}_3)_2$, $\sqrt{[\text{Mg}^{2+}]}$ increases. By Le Chatelier's Principle, the presence of this common ion shifts the position of equilibrium to the left and decreases the solubility of $\text{Mg}(\text{OH})_2$. $\sqrt{[\text{OH}^-]}$ decreases and so $\sqrt{\text{pH}}$ decreases.

2√ 1 mark

- (b) (i) State how the reactivity of Mg and Ca as reducing agents is different, and relate this difference to relevant E^\ominus values. [2]



$E^\ominus_{\text{Ca}^{2+}/\text{Ca}}$ is more negative than $E^\ominus_{\text{Mg}^{2+}/\text{Mg}}$.

- Hence Ca has a higher tendency to be oxidised to Ca^{2+} , and the Ca is a stronger reducing agent than Mg.

- (ii) Apart from the basic nature of magnesium hydroxide, suggest another reason why magnesium hydroxide is suitable for the role as an antacid. [1]

- Magnesium hydroxide is barely soluble in water, so it can pass through the body without being absorbed, making it non-toxic.

- (c) Fluorine gas deviates from an ideal gas and the following equation proposed by J. D. van der Waals can account for the differences.

$$\left(P + \frac{n^2 a}{V^2}\right) (V - nb) = nRT$$

where P : actual pressure

V : volume of the container

T : temperature

n : amount of gas

R : molar gas constant

a and b : van der Waals constants

The values of a and b account for the deviation from ideality for a real gas and are dependent on certain molecular properties of the gas.

The values of a and b for fluorine and the other halogens are given in table 5.1 below.

Table 5.1

Gas	$a / \text{Pa m}^6 \text{ mol}^{-2}$	$b / \text{m}^3 \text{ mol}^{-1}$
Fluorine	0.117	2.90×10^{-5}
Chlorine	0.634	5.42×10^{-5}
Bromine	0.975	5.91×10^{-5}

- (i) For each of the constants a and b , suggest a molecular property of the gas that will directly affect its value. [2]

- a is dependent on the strength of intermolecular forces of attraction while
- b is dependent on the volume/size of the molecules.

- (ii) Explain the differences in the values of a for the halogens. [2]

All the three halogens have instantaneous dipole-induced dipole attractions between its molecules.

Bromine has the largest electron cloud size, followed by chlorine and fluorine.

This leads to the greatest extent of distortion of electron cloud for bromine and the strongest and more extensive instantaneous dipole-induced dipole interactions between its molecules.

Hence, bromine deviates the most from ideality and has the largest value of a .

$2\sqrt{-1m}$

- (d) Halogens form many interhalogen compounds. One such compound is bromine monochloride, BrCl , which have similar properties to the halogens.

Suggest an equation for the reaction between BrCl and KI . [1]



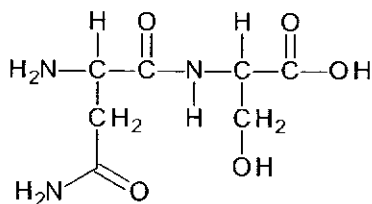
- (e) Halogens are also found in organic compounds which can be used to synthesise amino acids.

Table 5.2 shows some naturally occurring α -amino acids found in the body. The isoelectric point is the pH at which an amino acid exists as a zwitterion.

Table 5.2

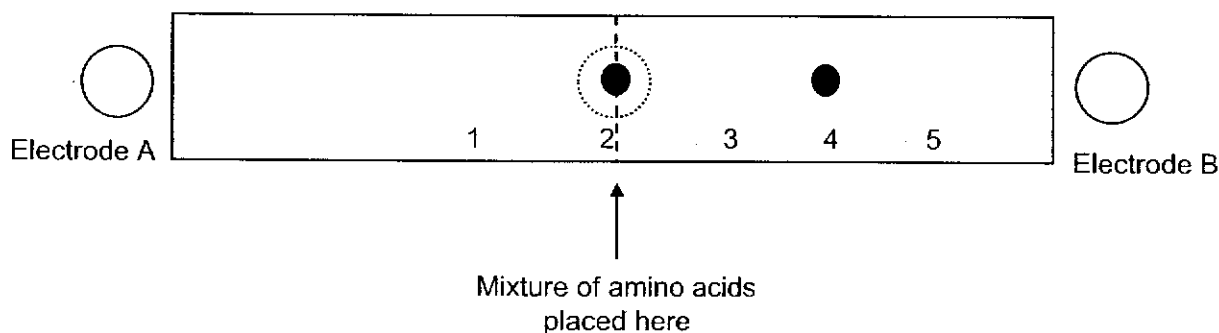
Amino acid	Abbreviation	R group	M_r	Isoelectric point
Serine	Ser	$-\text{CH}_2\text{OH}$	105	5.68
Asparagine	Asn	$-\text{CH}_2\text{CONH}_2$	132	5.43
Lysine	Lys	$-(\text{CH}_2)_4\text{NH}_2$	146	9.74

- (i) Draw the dipeptide Asn-Ser, showing the peptide bonds in displayed formula. [1]



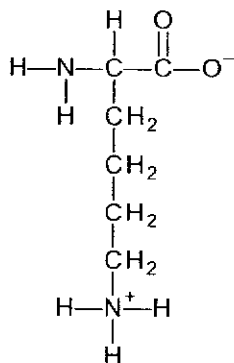
Electrophoresis is a technique used to separate mixtures of amino acids. Ions of higher charge to mass ratio will migrate towards the electrode of opposite charge at a faster rate. A mixture of the three amino acids in table 5.2 were placed at position 2 and subjected to electrophoresis in a buffer at pH 9.74.

The positions of two of the amino acids, serine and lysine, relative to the electrodes were as follows:

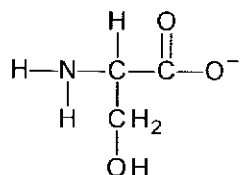


- (ii) Draw the structure of the species at positions 2 and 4. [2]

- Position 2: zwitterion of Lysine (pH = isoelectric point)



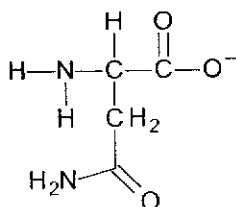
- At position 4: Serine (Since pH > pI, deprotonation of the -COOH occurs)



(iii) State the number which correspond to the likely position of asparagine and explain your answer. [2]

- **Position: 3.**
- **Both Serine and Asparagine have the same charge but Asparagine is bigger. Hence, it will migrate slower and would be closer to where the mixture of amino acids were first placed.**

Structure of Asparagine at pH = 9.74 (Since pH > pI, deprotonation of the -COOH occurs)



[Total: 20]