Class	Adm No

Candidate Name: ____________________

H

millennia institute

2020 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/02**

Paper 2 Structured Questions **14 Sep 2020**

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	**11**	**23**	**15**	**15**	**11**	**75**

Answer all questions in the spaces provided.

1 **(a)** Describe the structure of a ^{31}P atom, in terms of the number and type of subatomic particles.

For Examiner's use

……………………………………………………………………………………………………[1]

There are 15 electrons, 15 protons and 16 neutrons. ;

(b) State and explain how the atomic radius and anionic radius of phosphorus differ.

The number of protons in both the atom and anion are the same, hence nuclear charge remains the same. When it gains electrons the inter-electron repulsion is increased as there are more electrons. Hence the anionic radius is larger than the atomic radius.

……………………………………………………………………………………………………

……………………………………………………………………………………………………[1]

(c) **(i)** Solid PCl_5 can be prepared by the chlorination of liquid PCl_3. Write an equation, with state symbols, to represent this chlorination.

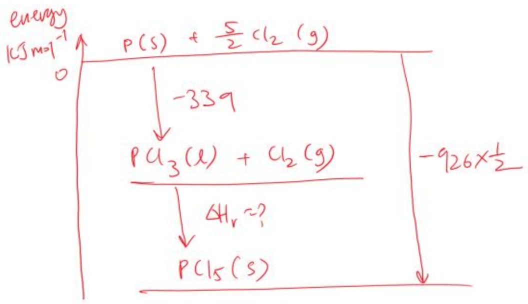
$PCl_3(l) + Cl_2(g) \longrightarrow PCl_5(s)$

……………………………………………………………………………………………………[1]

(ii) By means of an energy cycle and the information given below, calculate the standard enthalpy change of chlorination of PCl_5.

$P(s) + \frac{3}{2}Cl_2(g) \longrightarrow PCl_3(l)$ ΔH = -339 kJ mol^{-1}

$2P(s) + 5Cl_2(g) \longrightarrow 2PCl_5(s)$ ΔH = -926 kJ mol^{-1}



By Hess' Law,

$\Delta H_r = -(-339) + (-463)$

$= -124$ kJ mol^{-1}

2m for diagram
1m for Hess' law calculations

[3]

(iii) Write an equation, including state symbols to illustrate the reaction of PCl_5 with water.

Suggest the approximate pH of the solution formed.

$PCl_5 (s) + 4H_2O (l) \rightarrow H_3PO_4 (aq) + 5HCl (aq)$;
pH = 2.0 ;
Also accepted:
$PCl_3 (s) + H_2O (l) \rightarrow POCl_3 (aq) + HCl (aq)$;

……………………………………………………………………………………………………

……………………………………………………………………………………………………[2]

(d) PCl_5 reacts with hydrazine, N_2H_4, to give a molecular compound **X** with composition by mass shown below and a molecular formula of 303.0.

P, 20.5 % ; N, 9.2%; Cl, 70.3%

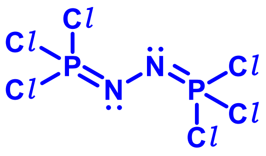
(i) Calculate the empirical formula of **X** and hence, state its molecular formula.

	P	N	Cl
mass / g	20.5	9.2	70.3
Amount / mol	20.5 / 31 = 0.661	9.2 / 14.0 = 0.657	70.3 / 35.5 = 1.98
simplest mole ratio	1	1	3

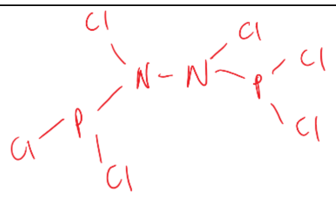
Empirical formula: $PNCl_3$;
Molecular formula: $P_2N_2Cl_6$;

[2]

(ii) Given that **X** contains a N–N single bond, suggest the structure of **X.**



or



[1]

[Total: 11]

2 Volcanoes can contribute to air pollution through the release of toxic gases when volcanoes erupt. The most abundant volcanic gas is water vapour. However, significant amounts of carbon dioxide, sulfur dioxide, hydrogen sulfide and hydrogen halides are also emitted.

Table 1: Volcanic gas composition in town **A**

Gas	Volume Percentage
Water vapour, H_2O	87.1
Carbon dioxide, CO_2	unknown
Sulfur dioxide, SO_2	0.5
Hydrogen, H_2	0.7
Carbon monoxide, CO	0.01
Hydrogen sulfide, H_2S	0.23
Hydrogen halides	unknown

The composition of the volcanic gases are expressed in terms of volume percentage, which can be calculated using the formula below.

$$\text{volume percentage} = \frac{\text{volume of gas}}{\text{total volume}} \times 100\%$$

(a) When carbon dioxide is emitted from volcanoes, it becomes diluted to low concentrations quickly and is not a harmful gas. However, the carbon dioxide gas when cooled, can flow into low-lying areas where it can reach higher concentrations.

(i) Suggest why at low temperatures, carbon dioxide would accumulate to high concentrations. Explain your answer.

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……………………………………………………………………………………………[2]

At low temperatures, there is insufficient energy to overcome the strong instantaneous dipole-induced dipole (id-id) interactions between CO_2 molecules. ;

Hence, there are more CO_2 molecules in a given volume leading to high concentrations. ;

People living in town **A** had to be evacuated as the levels of carbon dioxide gas was increasing rapidly. Breathing air with more than 3% CO_2 can lead to headaches, increased heart rate and difficulty breathing. At about 15%, unconsciousness and death can result.

For Examiner's use

(ii) Given that 0.35 g of CO_2 was present in 1 dm^3 of gas mixture at r.t.p, determine the volume percentage of carbon dioxide present.

Amount of CO_2 = $\frac{0.35}{44.0} = 0.00795\ mol$

Vol of CO_2 = $0.00795\ (24) = 190.9$ cm^3 ;

volume percentage of CO_2 = (190.9 / 1000) x 100% = 19.1% ;

[2]

(iii) Hence, comment on the possible danger if people remained in the town.

Unconsciousness and death can result.

…………………………………………………………………………………………….[1]

(b) Further analysis of the hydrogen halides composition of the volcanic gases revealed that the hydrogen halides were mostly made up of HC*l*(g) and HBr(g).

(i) **Table 2:** Bond energies of hydrogen halides

Bond	**Bond energy / kJ mol^{-1}**
H–C*l*	432
H–Br	366

State the trends of **two** chemical properties of hydrogen halides that can be explained by the data given in **table 2**.

- Thermal stability decreases from HC*l*(g) > HBr(g) > HI(g)
- Reducing power increases from HC*l*(g) < HBr(g) < HI(g)
- Acid strength increases from HC*l*(g) < HBr(g) < HI(g)

Any two ;;

……………………………………………………………………………………………….

…………………………………………………………………………………………….[2]

(ii) Explain why HBr(g) deviates more from ideality as compared to HC*l*(g).

……………………………………………………………………………………………….

…………………………………………………………………………………………….[1]

The permanent dipole-permanent dipole forces of attraction between HBr molecules are more significant due to the larger electron cloud size in each molecule of HBr. ;

(iii) Hydrogen halides can be used in the reaction with alkenes to synthesise halogenoalkanes.

Draw the **displayed formula** of **both** the major and minor products of the reaction of HC*l*(g) with 2-methylbut-2-ene. Label the major and minor products clearly.

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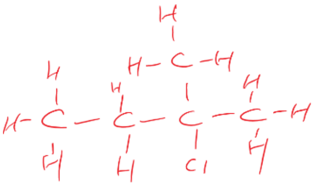
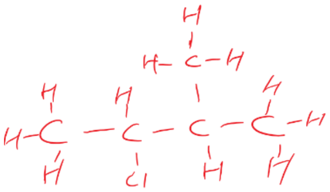


(major)

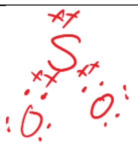


(minor)

[2]

(c) Another volcanic gas, sulfur dioxide, also has harmful effects on human health.

(i) Draw the 'dot-and-cross' diagram of one molecule of SO_2 and state its bond angle.



; 118° ;

[2]

(ii) SO_2 can be converted SO_3 in the presence of atmospheric oxygen. By using appropriate values from the data booklet, write an equation for the conversion of SO_2 to SO_3 and calculate the enthalpy change of this reaction.

$2SO_2 (g) + O_2 (g) \rightarrow 2SO_3(g)$;

$\Delta H = [(2x2x500) + 496] – (2x3x500) = - 504 \text{ kJ mol}^{-1}$; ;

(also accept ½(-504) depending on the equation that students have written)

[3]

(iii) SO_2 can be used to produce H_2SO_4 in a multi-step reaction. In one such reaction, 100 cm^3 of H_2SO_4 was produced. The H_2SO_4 produced was tested for its concentration where 25.0 cm^3 of the resultant solution required 23.50 cm^3 of 2.00 mol dm^{-3} NaOH for complete titration.

Calculate the amount of H_2SO_4 produced in the method above.

No. of moles of NaOH = (23.50/1000) x 2 = 0.047

No. of moles of H_2SO_4 (25 cm^3) = 0.047 / 2 = 0.0235 ;

No. of moles of H_2SO_4 (100 cm^3) = 0.0235 x 4 = 0.094 ;

[2]

(d) Student **A** suggested that one possible method to remove harmful SO_2 from volcanic gases is to react the gaseous SO_2 with magnesium oxide.

For Examiner's use

(i) Explain the Chemistry behind why this method is possible.

Magnesium oxide is basic and can undergo acid-base reaction with acidic sulfur dioxide.

……………………………………………………………………………………………[1]

Student **B** suggested that besides magnesium oxide, other metal oxides like sodium oxide and calcium oxide can also be used to remove sulfur dioxide.

(ii) The pH of the resulting solutions when one mole of MgO and Na_2O are added to 1 dm^3 of water separately are shown in **table 3** below.

Table 3: pH of metal oxides

Metal Oxide	pH of resulting solution
MgO	9
Na_2O	13
CaO	**?**

Predict and suggest an explanation for the pH of a solution containing 1 mol dm^{-3} of CaO.

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……………………………………………………………………………………………[3]

pH of MgO < pH of CaO < pH of Na_2O (accept between 9-13) ;

CaO has a lower magnitude of lattice energy than MgO due to a larger cationic radii. Thus, CaO should be more soluble than MgO and so giving a higher concentration of OH^- ions when CaO is added to water. ;

Na_2O is very soluble in water (lowest magnitude of lattice energy), thus it will give the highest concentration of OH^- in solution, thus most basic. ;

Student **C** suggested that seawater can also be used to absorb and remove SO_2. The main substance in seawater that is responsible for removing SO_2 is the HCO_3^- ions. When SO_2 is absorbed in water, the following two equilibria reactions take place:

$$SO_2(g) + H_2O(l) + \tfrac{1}{2}O_2(g) \rightleftharpoons SO_4^{2-}(aq) + 2H^+(aq) \quad \text{— (1)}$$

$$HCO_3^-(aq) + H^+(aq) \rightleftharpoons H_2O(l) + CO_2(g) \quad \text{— (2)}$$

(from seawater)

(iii) Explain how the use of seawater would allow the removal of sulfur dioxide.

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……………………………………………………………………………………………………

……………………………………………………………………………………………[2]

For Examiner's use

When SO_2 is absorbed in the water, it will react with water and oxygen to from sulfate and H^+ ions. The presence of HCO_3^- in the seawater will remove H^+ ions as CO_2, which will escape into the atmosphere. ;

This will shift the position of equilibrium (2) forward, which in turn shifts the position of equilibrium (1) to the right , removing SO_2. ;

[Total: 23]

3 **(a)** The Kolbe electrolysis is an electrochemical method used to synthesise alkanes. Carbon dioxide and ethane was produced during the Kolbe electrolysis of an aqueous solution of potassium ethanoate.

The reaction mechanism involves a three-stage process.

In step I, the ethanoate ion CH_3COO^- is first converted into an ethoxy radical intermediate $CH_3COO\bullet$.
This intermediate then undergoes decarboxylation to form a methyl radical intermediate.

step II $CH_3COO\bullet \rightarrow \bullet CH_3 + CO_2$

Finally two methyl radical intermediates dimerises to form the alkane product.

step III $2\ \bullet CH_3 \rightarrow CH_3\text{-}CH_3$

(i) Given that the reaction in step I takes place at the anode, write a half-equation for the reaction.

……………………………………………………………………………………………[1]

$CH_3COO^- \rightarrow CH_3COO\bullet + e^-$

(ii) Write another half-equation to illustrate the formation of a gaseous product at the cathode.

……………………………………………………………………………………………[1]

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

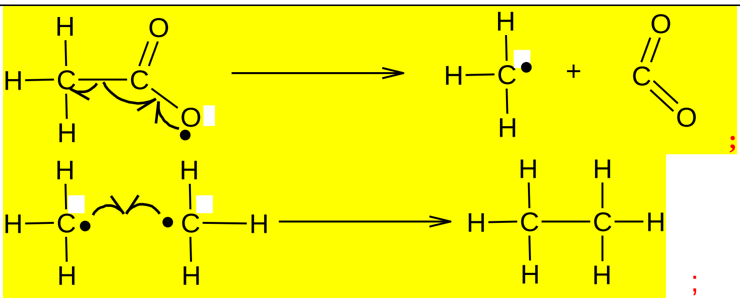
(iii) Calculate the volume of gas produced at the cathode at room temperature and pressure when a current of 500 mA is passed for 20 minutes through a solution of potassium ethanoate.

For Examiner's use

$Q = It = 500 \times 10^{-3} \times 20 \times 60 = 600$ C ;
$Q = n_eF$
$\Rightarrow 600 = n_e (96500)$
$n_e = 0.00622$ mol ;
$n(H_2) = n_e / 2 = 3.11 \times 10^{-3}$ mol
$v(H_2) = 3.11 \times 10^{-3} \times 24 = 0.0746$ dm^3 (or 74.6 cm^3) ;

[3]

(iv) Use the information given above to draw out the full mechanism for steps II and III. Use appropriate curly arrows to indicate which bonds are broken and which bonds are formed.



;

;

[2]

(v) In a separate Kolbe electrolysis experiment, an alkane **X** was produced when a mixture of an ethanoate salt and the salt of a carboxylic acid was electrolysed.

A gaseous sample of 0.30 g of **X** occupied 168 cm^3 at 300 K and 1 atm. Calculate the M_r of **X** and hence deduce its molecular formula.

$$PV = \frac{m}{Mr}RT$$

$$Mr = \frac{mRT}{PV}$$

$$= \frac{(0.30)(8.31)(300)}{(101325) \times (168 \times 10^{-6})}$$

$= 43.9$; ;

Alkanes have the formula C_nH_{2n+2}

$12(n) + 2n + 2 \approx 44$
$n = 3$
$\Rightarrow$ **X** is C_3H_8 ;

[3]

For Examiner's use

(b) Galvanic cells are electrochemical cells that contain a spontaneous reaction. An example of a galvanic cell include the zinc-carbon battery. Ammonium chloride is used as electrolyte in zinc–carbon batteries, where the outer zinc casing is the negatively charged terminal and is oxidised during discharge.

The following reaction also takes place in the cell.

$2MnO_2(s) + 2e^- + 2NH_4Cl(aq) \rightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l) + 2Cl^-(aq)$ --- $E^\ominus = +0.5$ V

(i) Write a half-equation for the reaction occurring at the negatively charged terminal. Hence, write an overall equation for the reaction that occurs in the cell.

……………………………………………………………………………………………[2]

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$;

$Zn(s) + 2MnO_2(s) + 2NH_4Cl(aq) \rightarrow Mn_2O_3(s) + ZnCl_2(aq) + 2NH_3(aq) + H_2O(l)$;

(ii) Calculate the voltage that is generated by this cell.

$E^\circ_{cell} = (+0.5) - (-0.76) = +1.26$V

[1]

(iii) Calculate a value of $\Delta G^\ominus$ for the cell reaction, and explain the significance of its sign.

$\Delta G^o = -nFE^o = -2 \times 96500 \times 1.26 = -243\,000$ J mol^{-1}

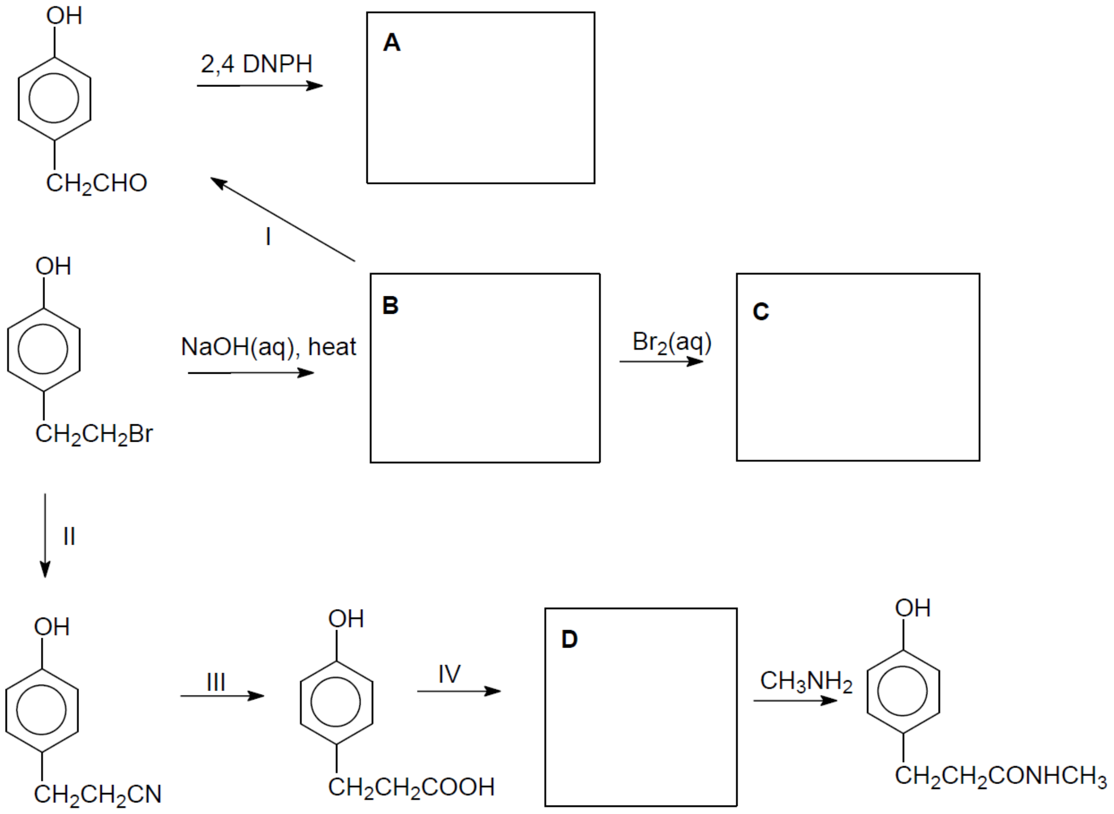
$= -243$ kJ mol^{-1} ;

The sign of ΔG^o is negative and hence the reaction is spontaneous. ;

[2]

[Total: 15]

4 **(a)** A reaction scheme is shown below.



(i) Draw the structures of **A**, **B**, **C** & **D** in the boxes provided.

[4]

(ii) State the reagents and conditions for steps I, II, III, IV.

Step I: ……………………………………………………………………………………………

Step II: …………………………………………………………………………………………...

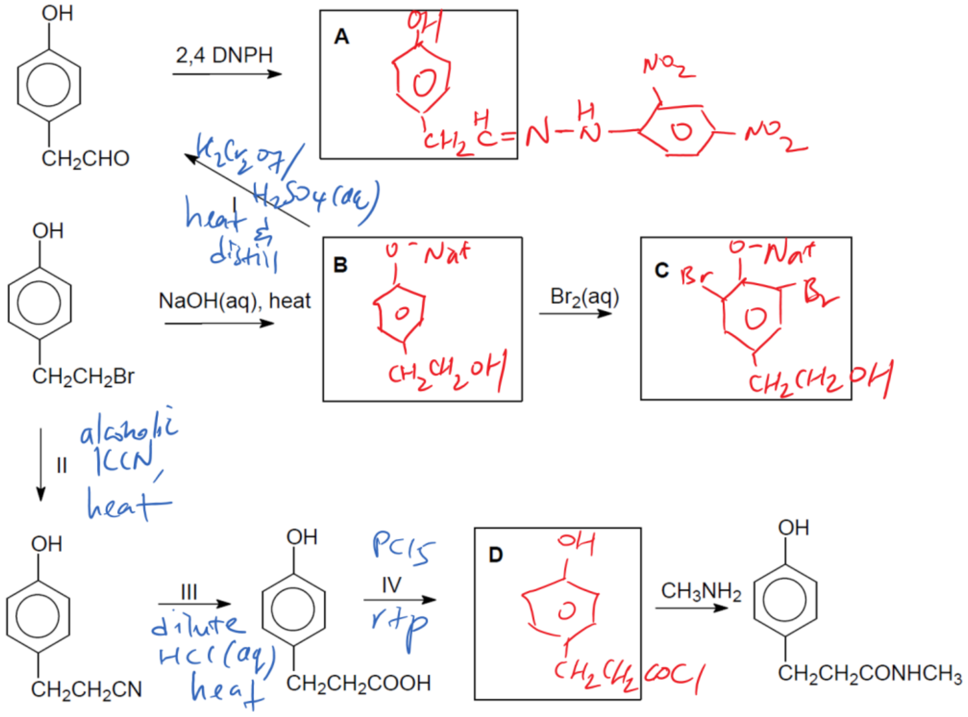
Step III: …………………………………………………………………………………………

Step IV: …………………………………………………………………………………………

[4]

[Turn over

For Examiner's use



(b) Compare the acidicity between phenol and 2,4,6-trinitrophenol. State and explain which of the two compounds is more acidic.

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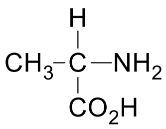
....

....[2]

2,4,6-trinitrophenol is more acidic. NO_2 groups are electron withdrawing groups which disperses the negative charge on O of the phenoxide ion. ; Thus, the phenoxide ion is more stable, resulting in a more acidic solution. ;

(c) The amino acid, alanine, has the structure shown below.



$$CH_3-\overset{\displaystyle H}{\underset{\displaystyle CO_2H}{C}}-NH_2$$

alanine

(i) By drawing an appropriate structure, explain why alanine has a surprisingly high melting point considering its relatively small molecular mass.

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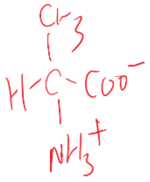
…………………………………………………………………………………………………[2]

For Examiner's use



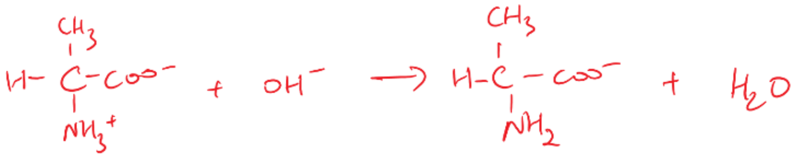
$H-C(CH_3)(NH_3^+)-COO^-$;

Alanine exist as a zwitterion in solid state, with strong electrostatic forces of attraction between oppositely charged ions. Thus, a large amount of energy is required to overcome these strong forces of attraction, resulting in a high melting point. ;

(ii) Solutions of amino acids are buffers important in maintaining optimal pH in our body.

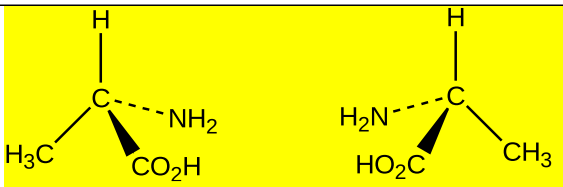
With the aid of an equation, show how alanine behaves as a buffer when small amount of base is added.

…………………………………………………………………………………………………[1]



$H-C(CH_3)(NH_3^+)-COO^- + OH^- \longrightarrow H-C(CH_3)(NH_2)-COO^- + H_2O$

(iii) By drawing suitable structures, state the type of isomerism displayed by alanine.



;

Enantiomerism ;

[2]

[Total: 15]

5 **(a)** Aqueous magnesium chloride can act as a weak monobasic acid. In an experiment, 50.0 cm^3 of an aqueous solution of magnesium chloride at an initial pH of 6 was titrated with 1.00 mol dm^{-3} sodium hydroxide. 20 cm^3 of NaOH(aq) was required for complete neutralisation.

(i) By writing suitable equations, illustrate how aqueous magnesium chloride can act as a weak monobasic acid.

$MgCl_2 + 6H_2O \rightarrow [Mg(H_2O)_6]^{2+} + 2Cl^-$

$[Mg(H_2O)_6]^{2+} \rightleftharpoons [Mg(H_2O)_5OH]^{2+} + H^+$

……………………………………………………………………………………………[2]

(ii) Calculate the initial concentration of magnesium ions.

$$[Mg^{2+}]\text{ initial} = \frac{\frac{20.00}{1000}\times 1}{\frac{50.00}{1000}} = 0.4\text{ mol dm}^{-3}$$

[1]

For Examiner's use

(iii) Calculate the K_a value for a solution of aqueous magnesium chloride.

initial pH = 6 $\Rightarrow [H^+] = 1 \times 10^{-6}$;

$$K_a = \frac{[Mg(H_2O)_5OH]^+\,[H^+]}{[Mg^{2+}]}$$

$$= \frac{(10^{-6})^2}{(0.4)}$$

$$= 2.5 \times 10^{-12}\text{ mol dm}^{-3}\ ;$$

[2]

(b) In a different experiment, a solution containing 0.100 mol dm^{-3} magnesium chloride and 0.100 mol dm^{-3} barium chloride was prepared. Solid sodium carbonate was added slowly to 1 dm^3 of this solution in an attempt to separate the two metal cations.

[Given, K_{sp} of $MgCO_3 = 3.5 \times 10^{-8}$ mol^2 dm^{-6}; K_{sp} of $BaCO_3 = 5.1 \times 10^{-9}$ mol^2 dm^{-6}]

(i) Calculate the concentration of carbonate in the solution, needed for the first trace of precipitate to be seen, stating which metal ion is precipitated first.

Ba^{2+} is precipitated first. ;

When $BaCO_3$ precipitates; $[CO_3^{2-}]_{min} = 5.1 \times 10^{-8}$ mol dm^{-3} ;

[2]

(ii) Determine the concentration of the metal ion in **(b)(i)** remaining in the solution when the other metal ion just starts to precipitate.

As $Mg(OH)_2$ starts to precipitate, $[CO_3^{2-}] = 3.5 \times 10^{-7}$ mol dm^{-3} ;

$$[Ba^{2+}]\text{ remaining in solution} = \frac{5.1\times10^{-9}}{3.5\times10^{-7}} = 0.0146\text{ mol dm}^{-3}\ ;$$

[2]

		(iii)	Given that an effective separation means that less than 1% of a metal ion should remain in solution, deduce if the separation of the metal ion in **(b)(i)** has been effective.	
			% of Ba^{2+} remained in solution = $\frac{0.0146}{010} \times 100 = 14.6\ \% >> 1\%$; ⇒ separation is not effective ;	
			[2]	
			[Total: 11]	

End of Paper 2

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