NAME _____ CLASS **21S**

JURONG PIONEER JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2022

CHEMISTRY **9729/02**

Higher 2

Paper 2 Structured Questions

14 September 2022
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and exam index number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a HB pencil for any diagrams, graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
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	
1	**/ 10**
2	**/ 10**
3	**/ 17**
4	**/ 10**
5	**/ 11**
6	**/ 12**
7	**/ 5**
Penalty (delete accordingly)	
Bond linkages	**–1 / NA**
Significant figures & units	**–1 / NA**
Total	**/ 75**

This document consists of **21** printed pages inclusive of **1** blank page.

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

For Examiner's Use

1 **(a)** Figure 1.1 shows the **third** ionisation energies of eight consecutive elements **A** to **H,** in the Periodic Table.
[Note that letters **A** to **H** are not the atomic symbols of the elements concerned.]

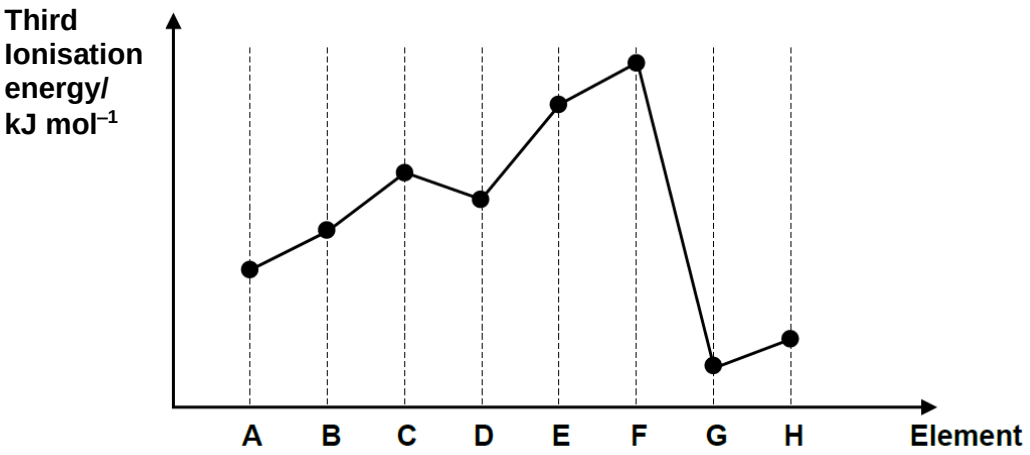

Figure 1.1

(i) Write an equation, including state symbols, to represent the *third ionisation energy* of element **A**.

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…… [1]

(ii) From Figure 1.1, suggest the identity of **B**. Explain how you arrived at your answer.

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…… [2]

(iii) Explain why the third ionisation energy of element **D** is slightly lower than that of element **C**.

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…… [1]

For Examiner's Use

(b) Nitrogen and phosphorus are elements of Group 15 in the Periodic Table.
Nitrogen exists naturally as gaseous diatomic N≡N molecules whereas phosphorus is a solid and exists as P_4 molecules comprising of P-P single bonds.

(i) Account for the difference in their physical states in terms of structure and bonding.

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…… [2]

(ii) Suggest why phosphorus does **not** occur naturally as P≡P molecules.

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…… [1]

(iii) Nitrate, NO_3^-, and phosphate, PO_4^{3-}, are oxoanions of nitrogen and phosphorus respectively.

Draw a dot-and-cross diagram to show the bonding PO_4^{3-}, deducing the shape and the bond angle around the phosphorous atom.

Hence explain why it is not possible for nitrogen to form an oxoanion with formula of NO_4^{3-}.

[3]

[Total: 10]

For Examiner's Use

2 Iron oxides are chemical compounds composed of iron and oxygen. Most iron ores are oxides, making them important precursors to iron metal and its many alloys.

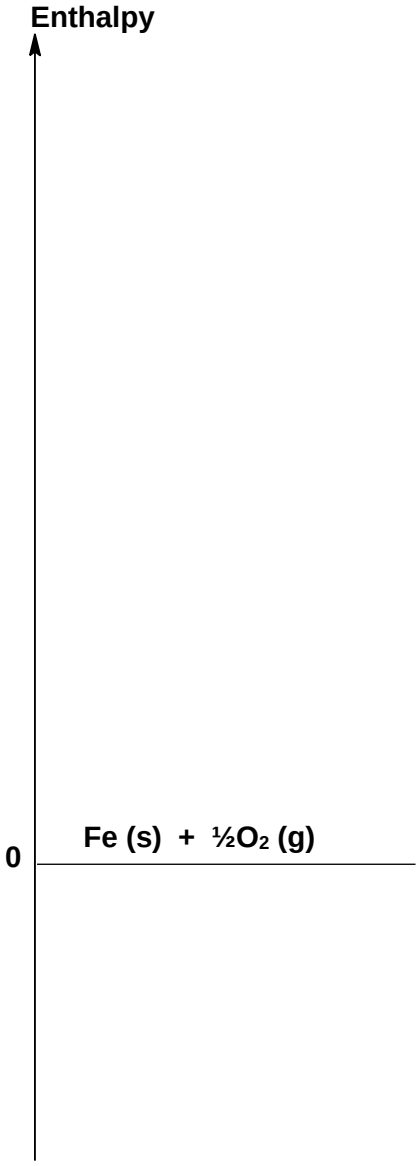
(a) Iron (II) compounds are only stable in neutral, non-oxidising conditions.

It is difficult to determine the lattice energy of FeO experimentally.

(i) Given the following data in Table 2.1 and data from the *Data Booklet*, draw and complete the energy diagram below to calculate the lattice energy of FeO(s) in kJ mol^{-1}.

standard enthalpy change of atomisation of Fe(s)	+416 kJ mol^{-1}
standard enthalpy change of formation of FeO(s)	–272 kJ mol^{-1}
Sum of 1st and 2nd electron affinity of oxygen	+157 kJ mol^{-1}

Table 2.1



[3]

(ii) Most naturally occurring samples of iron(II) oxides are found as the mineral Wüstite.

Wüstite has the formula $Fe_{20}O_x$. It contains both Fe^{2+} and Fe^{3+} ions. 90% of the iron is present as Fe^{2+} and the remaining as Fe^{3+}.

By means of calculations, deduce the value of x.

[1]

(iii) State and explain how the lattice energy of FeO compares with the lattice energy of Fe_2O_3.

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…… [2]

(b) Another common iron oxide as hematite, Fe_2O_3 is the main source of iron for the steel industry. Fe_2O_3 will readily react with acids to form soluble salts such as the following reaction.

$$Fe_2O_3(s) + 6HI(aq) \rightarrow 2FeI_2(aq) + I_2(aq) + 3H_2O(l)$$

(i) Define standard enthalpy change of solution.

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…… [1]

For Examiner's Use

(ii) Use the data in Table 2.2 to calculate the enthalpy change of solution of iron (II) iodide, FeI_2.

ΔH_{latt} (FeI_2(s))	– 2440 kJ mol^{-1}
ΔH_{hyd} (Fe^{2+} (g))	– 1950 kJ mol^{-1}
ΔH_{hyd} (I^- (g))	– 308 kJ mol^{-1}

Table 2.2

[1]

(iii) A yellow precipitate of PbI_2 forms when 25 cm^3 of x mol dm^{-3} Pb^{2+} ions are added to 10 cm^3 of 0.100 moldm^{-3} FeI_2 (aq).

Given that the solubility product, K_{sp}, of PbI_2 = 9.8 x 10^{-9} mol^3 dm^{-9}, find the minimium value for x, concentration of Pb^{2+} for precipitation to occur.

[2]

[Total: 10]

For Examiner's Use

3 Carboxylic acids and their derivatives are classes of organic compounds that play important roles in our everyday lives. Some of their uses include the manufacturing of polymers, production of pharmaceutical drugs, as food additives and industrial solvents.

This question deals with some of the properties of acidic organic compounds, including carboxylic acids and their derivatives.

(a) Table 3.1 below shows three organic compounds that can be found in nature.

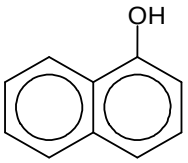
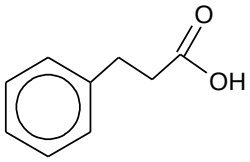
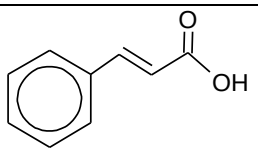
name	**1-naphthol**	**hydrocinnamic acid**	**cinnamic acid**
where it can be found	*selaginella sinensis* tree	cowberries	cinnamon
structural formula			
pK_a	9.51	4.70	4.37

Table 3.1

(i) By reference to the structures, explain why cinnamic acid will be the first to react when aqueous KOH is added dropwise to a mixture containing both cinnamic acid and hydrocinnamic acid.

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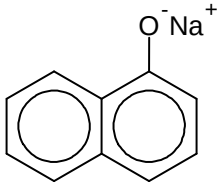
…… [2]

(ii) With the aid of balanced equation(s), explain any reaction(s) that occurs when a solution containing sodium 1-naphtholate is added to a solution containing hydrocinnamic acid.



sodium 1-naphtholate

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…… [2]

A laboratory technician was tasked to prepare a buffer solution by mixing hydrocinnamic acid and aqueous potassium hydroxide.

For Examiner's Use

(iii) What is a buffer solution?

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…… [1]

(iv) Write equations to show how a mixture of hydrocinnamic acid and its salt can function as a buffer.

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…… [2]

(v) Using appropriate data from Table 3.1 in **(a)**, determine the volume of 0.100 mol dm^{-3} KOH(aq) the student needs to add to 0.100 dm^3 of 0.100 mol dm^{-3} hydrocinnamic acid to form a buffer of pH 5.50.

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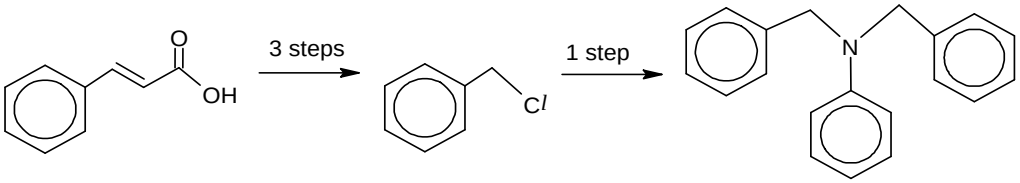
[2]

For Examiner's Use

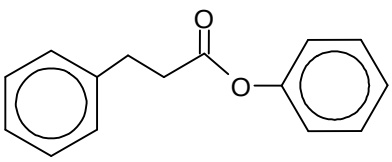
(b) The diagram below shows a reaction scheme involving cinnamic acid.

Suggest a possible synthetic pathway involving 4 steps, stating clearly the reagents and conditions required, and the intermediate organic compounds formed for every step.

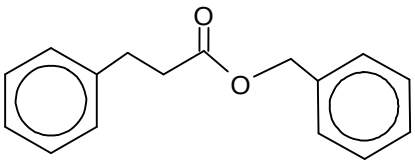


[3]

(c) Hydrocinnamic acid form many different types of esters that have great commercial uses. Two such esters are shown below:



ester P



ester Q

(i) Suggest a simple chemical test that would enable the laboratory technician to distinguish between the two esters.

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…… [2]

(ii) State the type of reaction that occurred when hydrocinnamic acid forms these esters.

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…… [1]

(d) Describe and explain the trend observed in the thermal stability of the carbonates of the Group 2 elements, MCO_3.

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…… [2]

[Total: 17]

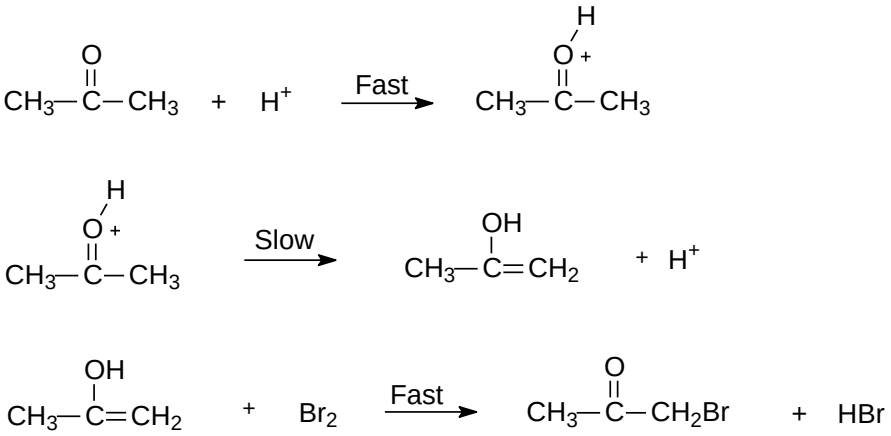
For Examiner's Use

4 Carbonyl compounds can react with halogens in acidic or alkaline medium to form different products. Kinetic studies are conducted to investigate the orders of reaction and the mechanisms of these reactions.

In acidic medium, propanone reacts with bromine to form bromopropanone as shown in the equation below:

$$CH_3COCH_3 + Br_2 \xrightarrow{H^+} CH_3COCH_2Br + HBr$$

The kinetic studies of the above reaction have shown that the reaction is second order overall, and a three-step mechanism is involved in this reaction.



(a) From the mechanism above, construct the rate equation for the above reaction.

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…… [1]

(b) From the mechanism above, how can you deduce that H^+ is acting as a catalyst?

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…… [1]

(c) Sketch, in the space below, the graph of $[Br_2]$ against time in minutes, given that the initial concentration of Br_2 is 0.008 mol dm^{-3} and initial concentration of propanone, CH_3COCH_3, is 0.80 mol dm^{-3}.

[1]

(d) Explain what will happen to the rate of reaction if chlorine is used in place of bromine, assuming that the mechanism remains unchanged?

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…… [1]

(e) The kinetics data for the experiment may be collected using a continuous sampling method, which requires a sample of the chemical reaction to be extracted at various time intervals from a reaction mixture followed by titration.

Briefly describe a physical property that allows you to determine the $[Br_2]$ at various times.

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…… [1]

(f) The reaction between CH_3COCH_3 and Br_2 was carried out in experiments **1** and **2**, and the following results were obtained:

Experiment	Initial $[CH_3COCH_3]$/ mol dm^{-3}	Initial $[H^+]$ / mol dm^{-3}	Initial $[Br_2]$ / mol dm^{-3}	Half-life / min
1	0.40	0.30	0.20	22.5
2	0.60	0.10	0.20	**s**

The half-life of CH_3COCH_3 in experiment **1** was found to be constant at 22.5 minutes. Predict the value of half-life of CH_3COCH_3 in experiment **2**, **s**, giving your reasoning.

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…… [2]

(g) With the aid of a labelled Boltzmann distribution diagram, explain how the presence of a catalyst affects the rate of a chemical reaction.

[3]
[Total:10]

For Examiner's Use

5 **(a)** Compound **P**, $C_5H_{10}O_2$ is optically active. It reacts with 2,4–dinitrophenylhydrazine to give an orange precipitate. However, **P** does not react with Tollens' reagent.

Upon reaction with sodium metal, **P** produces effervescence that extinguishes a lighted splint with pop sound. **P** forms gave a yellow precipitate when treated with alkaline aqueous iodine, and upon acidification, **Q**, $C_3H_4O_4$ is formed as the resulting compound.

Q reacts with Na_2CO_3(aq) to produce effervescence that forms white precipitate with limewater.

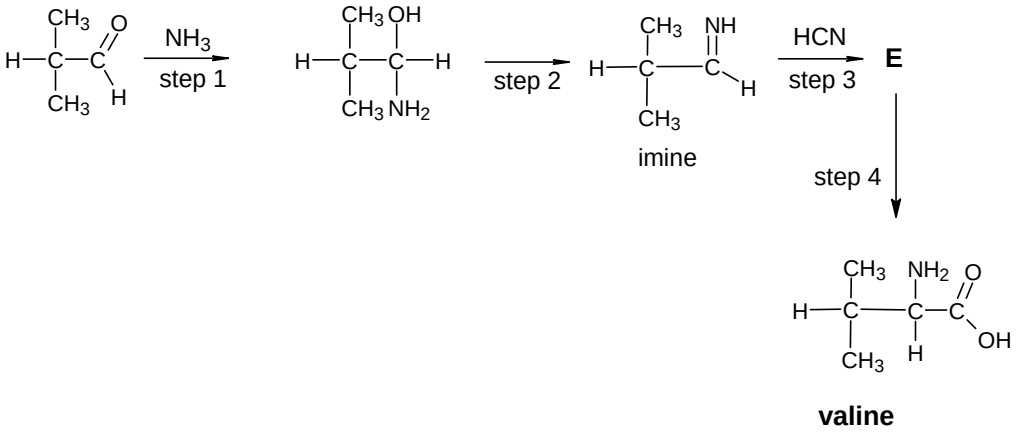
(i) Suggest the structure of compound **Q**.

[1]

(ii) Suggest a structure of **P** that is consistent with the information provided, giving your reasoning.

[3]

(b) The Strecker synthesis is a method to prepare ∝-amino acids. The amino acid valine can be prepared from 2-methylpropanal via Strecker synthesis as shown below.



(i) Suggest the type of reaction occurring in step 2.

[1]

(ii) Given that the reaction of the imine in step 3 with HCN is similar to the reaction of a carbonyl compound with HCN, suggest the structure of **E**.

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…… [1]

(iii) Valine can exist as a pair of stereoisomers. Draw the 2 stereoisomers of valine.

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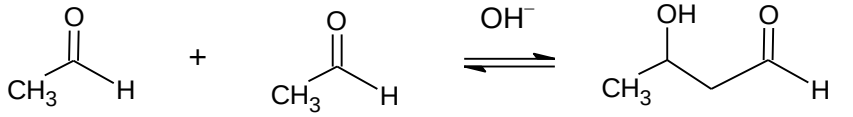
……..

…….. [2]

For Examiner's Use

(c) The aldol reaction is a useful method of making new carbon–carbon bonds in organic chemistry. It involves combining two molecules of the same aldehyde to form a product which contains both an aldehyde and alcohol functional groups. Thus, it is also known as the **aldol** reaction.

Ethanal undergoes base-catalysed aldol reaction as shown below.



3-hydroxybutanal

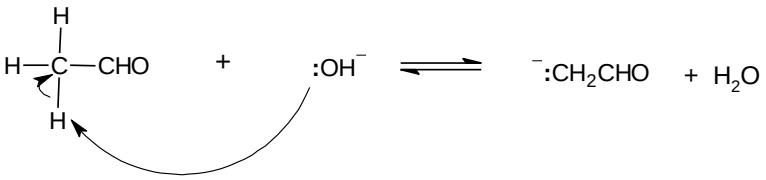
(an aldol)

The aldol synthesis involved the following reactions in two stages**:**

Stage 1**:**

An acid-base reaction takes place between the OH^- base and the acidic H atom bonded to alpha C of an ethanal molecule, forming a carbanion.

The first stage is drawn below.



Stage 2:

The carbanion formed in stage 1 attacks the delta positive carbon of another ethanal molecule, forming a tetrahedral intermediate which is negatively charged. The tetrahedral intermediate rapidly reacts with H_2O to form the aldol product and regenerates back the OH^- catalyst.

Name and outline the mechanism for stage 2.

[3]

[Total:11]

For Examiner's Use

6 **(a)** The value of the equilibrium constant is 4.0 for the reaction below:

$$CH_3CO_2H(l) + C_2H_5OH(l) \rightleftharpoons CH_3CO_2C_2H_5(l) + H_2O(l)$$

(i) Write an expression for the equilibrium constant, K_c, of the **reverse** reaction, i.e. the hydrolysis of ethyl ethanoate, stating its numerical value.

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…… [2]

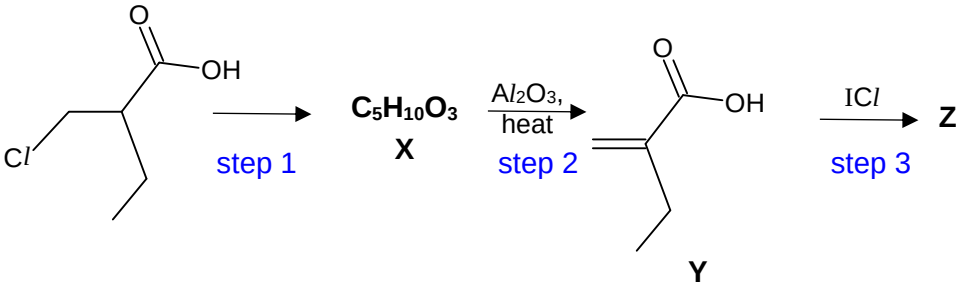
(ii) In an experiment, 2 mol of ethyl ethanoate and 2 mol of water are mixed.

Calculate the number of moles of each substance present when equilibrium is reached.

[2]

For Examiner's Use

(b) The following shows a flow scheme involving a chlorocarboxylic acid to form compounds **X**, **Y** and **Z**.



(i) Suggest the structure of compound **X**.

[1]

(ii) Give the reagents and conditions for step 1.

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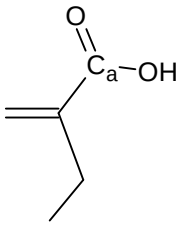
…… [1]

(iii) State the hybridisation of C_a labelled in the structure of **Y** below.



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…… [1]

(iv) Give the structure of compound **Z**.

[1]

(v) Give the structure of the product formed when compound **Y** is reacted with hydrogen with nickel, upon heating.

[1]

Aluminium objects that have had the aluminium oxide layer removed may then be oxidised.

(c) (i) State why aluminium objects are anodised.

……

…… [1]

(ii) Complete Table 6.1 below to show the type of reaction occurring, with the relevant half-equations, during the anodising of an aluminium object.

	type of reaction	half-equation(s)
anode		
cathode		

Table 6.1

[2]

[Total:12]

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For Examiner's Use

7 **(a)** Baryta water, barium hydroxide, $Ba(OH)_2(aq)$ is a Bronsted base.

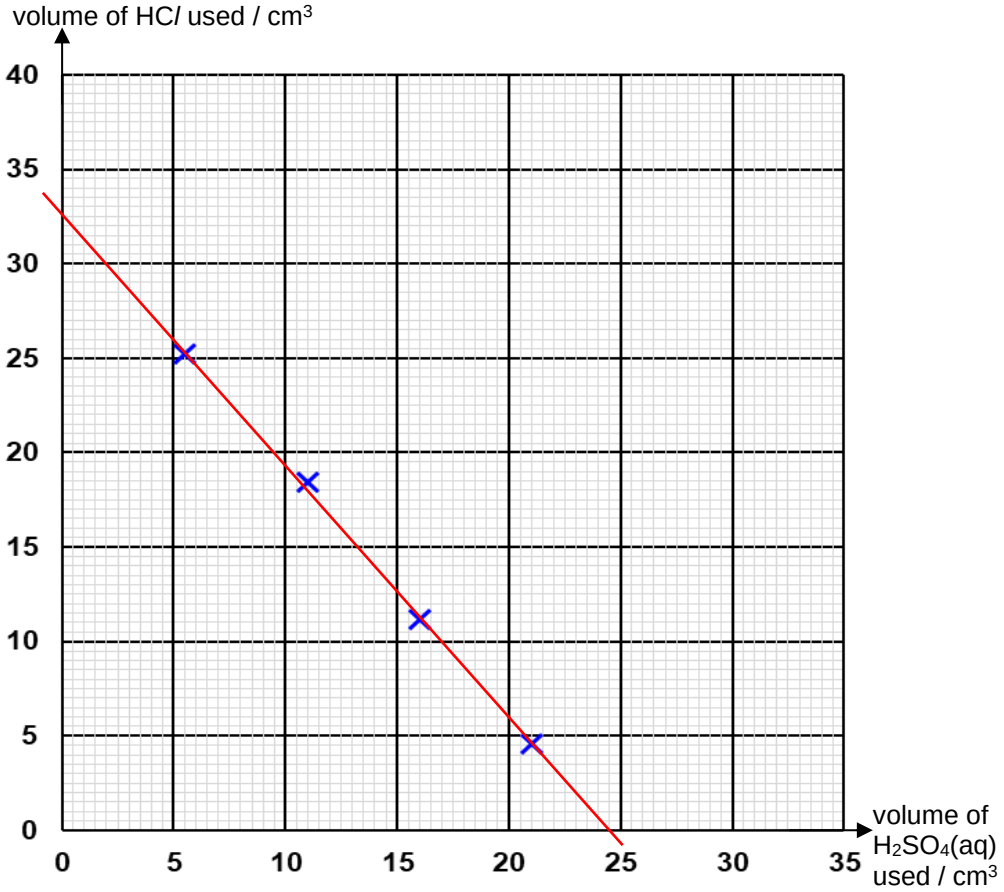
Define what is meant by a Bronsted base.

……

…… [1]

(b) $Ba(OH)_2(aq)$ neutralises both H_2SO_4 and HC*l* acid. In an experiment, a student prepared 4 mixtures, each containing the same volume of 25.0 cm^3 of $Ba(OH)_2$ solution, but with different volumes of sulfuric acid added.

In each mixture, neutralisation has not been completed, the solution remains alkaline and is neutralised by titration with 0.150 mol dm^{-3} HC*l* acid. A graph of volume of HC*l* on the y-axis was plotted against volume of H_2SO_4 for each of the 4 mixtures. The graph is extrapolated until it touches both axes.



(i) Read from the graph, and record the volume of HC*l* (Vol.HC*l* (max), required to exactly neutralise 25.0 cm^3 of $Ba(OH)_2$.

……

…… [1]

For Examiner's Use

(ii) Calculate the concentration of $Ba(OH)_2$.

[2]

(iii) Explain in terms of the chemistry involved, why the direction of the slope of the graph is negative.

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…… [1]

[Total:5]

End of paper