

<b>Name:</b>		<b>Centre/Index Number:</b>		<b>Class:</b>	
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# DUNMAN HIGH SCHOOL

## Preliminary Examination

### Year 6

## H2 CHEMISTRY

Paper 3 Free Response Questions

**9729/03**

**25 September 2025**

**2 hours**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

### READ THESE INSTRUCTIONS FIRST

Write your centre number, index number, name and class at the top of this page.

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 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.

A Data Booklet is provided.

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

The number of marks is given in brackets [ ] at the end of each question or part question.

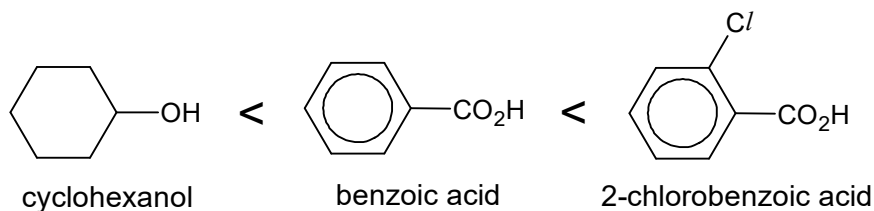
For Examiner's Use	
Section A	
1	20
2	20
3	20
Section B	
4 / 5	20
Total	80

This document consists of **31** printed pages and **1** blank page.

## Section A

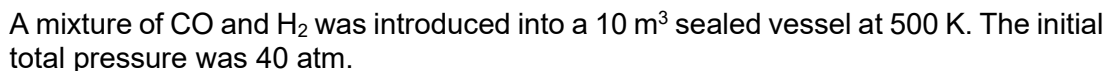
Answer **all** the questions in this section.

- 1 (a) The order of increasing Brønsted-Lowry acidity of cyclohexanol, benzoic acid and 2-chlorobenzoic acid is shown. Explain this order. [3]

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- (ii) Draw a structure for **P** to show the bonding present. [1]

[illegible]



After dynamic equilibrium was established at 500 K, the total pressure in the vessel decreased to 28 atm.

- (i) Write an expression for the equilibrium constant,  $K_p$ , for this reaction, and state its units. [1]

The amount of  $\text{CH}_3\text{OCH}_3$  at equilibrium was found to be 732 mol. Show that the equilibrium partial pressure of  $\text{CH}_3\text{OCH}_3$  in the sealed vessel is 3 atm. [1]

- (iii) At equilibrium, it was found that 60% of the CO had been converted to the products. Calculate the equilibrium partial pressures of CO and  $\text{H}_2$  in atm. Hence, determine the value of  $K_p$  for the reaction. [3]

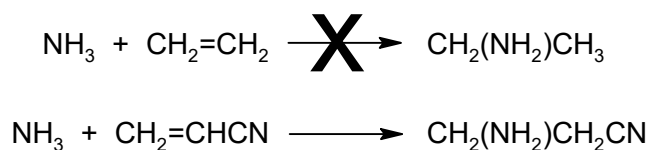
- (iv) The volume of the vessel is reduced from  $10 \text{ m}^3$  to  $5 \text{ m}^3$  and the system is allowed to reach equilibrium.

Explain the effect this will have on the partial pressures of the individual gases and the composition of the reaction mixture. [2]

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- (d)  $\text{NH}_3$  is commonly used as a nucleophile in organic chemistry. In some instances, it adds to the  $\text{C}=\text{C}$  bond as shown in Fig. 1.1.



**Fig. 1.1**

Suggest reasons to explain Fig. 1.1.

Use concepts of electronegativity and electronic effects in your answer. [2]

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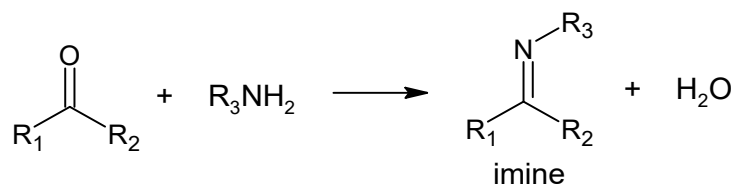
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- (e) Ammonia or primary amines react with aldehydes and ketones to produce imines as shown in Fig. 1.2.  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}_3$  represent alkyl groups or hydrogen atoms.

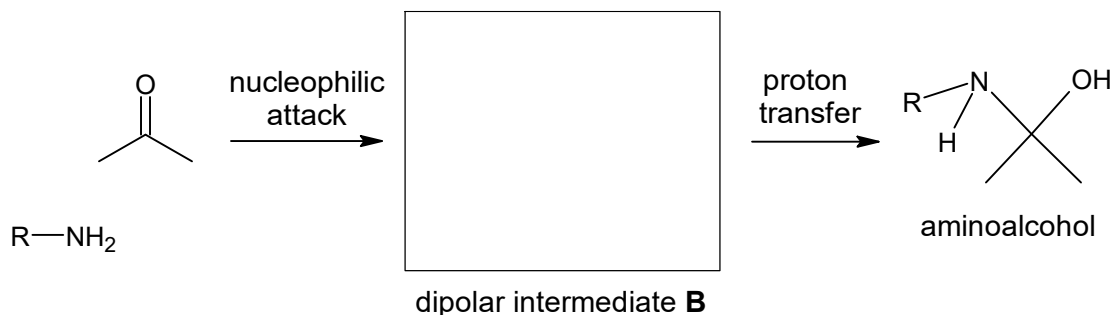


**Fig. 1.2**

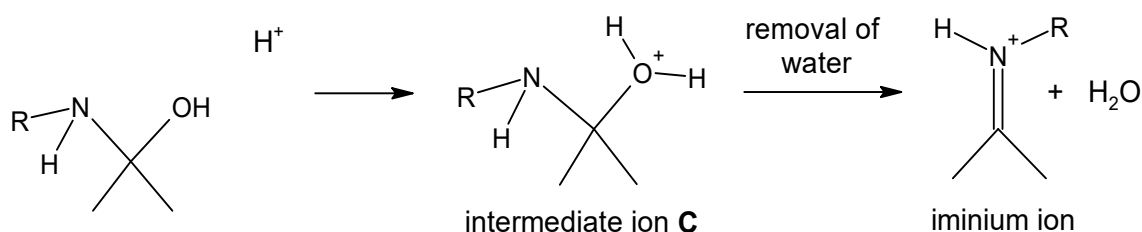
The reaction is carried out at carefully controlled pH of between 4 and 5.

The mechanism for the formation of an imine between a primary amine and propanone is shown in Fig. 1.3.

## Stage 1: Formation of aminoalcohol



## Stage 2: Formation of iminium ion intermediate



## Stage 3: Formation of imine via deprotonation

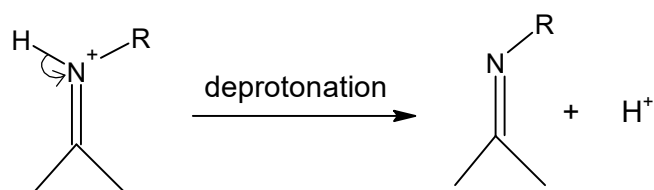


Fig. 1.3

(i) Complete the mechanism for the formation of **B** in Fig. 1.3 by

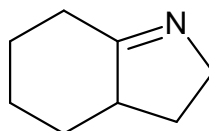
- adding curly arrows, a lone pair and a dipole to show how the nucleophilic attack occurs between the primary amine and propanone.
- drawing the structure of the dipolar intermediate **B** in the box provided. [2]

(ii) Complete the mechanism for stage 2 in Fig. 1.3 by

- adding a curly arrow and a lone pair to show protonation of the aminoalcohol.
- adding a lone pair and curly arrows on intermediate ion **C** to show how the iminium ion is formed. [2]

(iii) By considering stage 1, suggest why the reaction is slower at pH lower than 4. [1]

(iv) Suggest the reactant used to form the following product by a similar reaction to that shown in Fig. 1.2. [1]







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- 2 (a) Phenylamine can be made in the laboratory using the method given below.

Nitrobenzene is heated under reflux with a mixture of tin and concentrated hydrochloric acid.

Once the reaction mixture has cooled, concentrated sodium hydroxide solution is added until the mixture is alkaline. Pure phenylamine can be obtained from this mixture.

The reaction between tin and concentrated hydrochloric acid produces  $\text{SnCl}_2$  and  $\text{H}_2$  gas. Nitrobenzene then reacts with  $\text{SnCl}_2$ , in the presence of concentrated hydrochloric, to form  $\text{C}_6\text{H}_5\text{NH}_3^+$  and  $[\text{SnCl}_6]^{2-}$  ions.

- (i) Describe the roles of tin and concentrated hydrochloric acid when they are added together to form  $\text{SnCl}_2$  and  $\text{H}_2$  gas. Explain your answer in terms of electron transfer. [2]
- (ii) Construct a half-equation for the formation of  $\text{C}_6\text{H}_5\text{NH}_3^+$  from nitrobenzene. State symbols are **not** required. [1]
- (iii) Using the relevant theory of acids and bases, explain how the phenylamine can be recovered from the mixture by adding concentrated sodium hydroxide solution. [1]
- (iv) Describe a simple chemical test you could carry out to confirm the presence of phenylamine in the product. State what you would observe. [2]

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name	structure	p <i>K</i> <sub>b</sub>
phenylamine	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	9.40
phenylalanine	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH(NH <sub>2</sub> )CO <sub>2</sub> H	4.87 (α-amino group)
propylamine	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	3.46

(ii) Use Table 2.2 to draw the predominant species of phenylalanine at pH 8. [1]

name	structure	pK <sub>a</sub> at 25 °C	
		α-carboxyl group	α-amino group
phenylalanine	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH(NH <sub>2</sub> )CO <sub>2</sub> H	1.83	9.13

[illegible]

(c) Arecoline,  $C_8H_{13}NO_2$ , is a compound found in the Taiwanese betel nut.

Arecoline has three different functional groups, does not display cis-trans isomerism and does not contain a chiral centre. It contains a six-membered ring comprising one nitrogen and five carbon atoms.

Table 2.3 shows the organic products formed, and other information, when arecoline and compound **F**,  $C_8H_{15}NO_2$ , are added to different reagents under specific conditions.

**Table 2.3**

test	reactant	reagents and conditions	organic products formed	other information
1	arecoline	excess $H_2$ / Ni	<b>F</b> , $C_8H_{15}NO_2$	<b>F</b> contains one chiral centre.
2	arecoline	2,4-DNPH	no reaction	
3	arecoline	$Na_2CO_3(aq)$	no reaction	
4	arecoline	ethanoyl chloride	no reaction	
5	arecoline	excess $CH_3Cl$ in ethanol, heat	<b>G</b> , $C_9H_{16}NO_2Cl$	<b>G</b> is an ionic compound.
6	<b>F</b>	excess $HCl(aq)$ , heat	<b>H</b> , $C_7H_{14}NO_2^+$ , and <b>J</b>	
7	<b>F</b>	excess acidified $KMnO_4$ , heat	<b>H</b> only	effervescence observed.

For each of the seven tests, state the type of reaction occurring, if any. For each compound, state what the information in Table 2.3 tells you about the functional groups it contains. Include your reasoning.

Suggest possible structures for **F**, **G**, **H** and **J**. Hence deduce a possible structure for arecoline. [10]

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- 3 (a)** Aqua regia (a mixture of 25% nitric acid and 75% hydrochloric acid by volume) is highly corrosive. Only noble metals like iridium are inert to this solution. A 5 g sample of platinum–iridium alloy required 24.6 cm<sup>3</sup> of aqua regia for complete reaction. Platinum was completely oxidised to platinum(IV) ions by nitric acid and 0.5 g of the remaining metal was recovered.

(i) Find the percentage of each metal in the alloy. [1]

(ii) Aqua regia was prepared using 5.0 mol dm<sup>-3</sup> nitric acid. Assuming that the reaction between the sample and aqua regia is complete, calculate the number of moles of nitric acid reacted per mole of platinum. [2]

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- (b)** Gold is typically an inert metal and it does not dissolve in either hydrochloric acid or nitric acid alone. It will dissolve in aqua regia because of the unique combined action of the two acids.

In aqua regia, nitric acid converts gold to its ionic form, Au<sup>3+</sup>, and hydrochloric acid provides a source of chloride which reacts with the gold cations to form stable tetrachloroaurate(III) complex, AuCl<sub>4</sub><sup>-</sup>.

The standard reduction potential of Au<sup>3+</sup> to Au is given below.



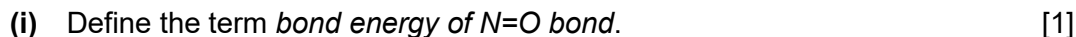
- (i) With the use of relevant data from the *Data Booklet*, explain why hydrochloric acid alone cannot dissolve gold. [1]
- (ii) Gold has the chemical properties of a typical transition element. Explain why gold can be considered a transition element. [1]

- (iii) Another method of extracting gold from low-grade ore involves converting the gold to a water-soluble dicyanoaurate(I) anionic complex,  $[\text{Au}(\text{CN})_2]^-$ .

Explain why the gold complex ion,  $\text{AuCl}_4^-$  in **(b)**, is coloured while the dicyanoaurate(I) complex ion,  $[\text{Au}(\text{CN})_2]^-$ , is colourless. [4]

[illegible]

Nitrosyl chloride can further decompose into nitrogen, chlorine and oxygen, as shown in the equation below.



(ii) Using data from the *Data Booklet*, calculate the bond energy of N=O bond in NOCl. [2]

(iii) The boiling points of  $\text{NOCl}$  and  $\text{NOF}$  are  $-5.6^\circ\text{C}$  and  $-72.4^\circ\text{C}$  respectively. Suggest a reason for the difference in their boiling points. [2]

(iv) Copper(II) oxide, CuO, is a common catalyst used for the decomposition of  $\text{NOCl}$ . Suggest the type of catalyst CuO acts as and describe its mode of action. [3]

[illegible]



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(d) Use of the Data Booklet is relevant to this question.

A student wanted to study the following reaction.



He first sets up an electrochemical cell which comprises of  $\text{Au}^{3+}/\text{Au}$  and  $\text{Ni}^{2+}/\text{Ni}$  half-cells prepared under standard conditions.

When the reaction begins,  $[\text{Au}^{3+}]$  starts to decrease while  $[\text{Ni}^{2+}]$  increases. In the study of electrochemical cells, the *Nernst equation*, given below, can be applied to determine the cell potential under non-standard conditions.

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{0.0592}{n} \log_{10} Q$$

where  $n$  is the number of moles of electrons transferred,  $Q$  is the reaction quotient

given by  $\frac{[\text{Ni}^{2+}]^3}{[\text{Au}^{3+}]^2}$  and  $E^{\ominus}_{\text{cell}}$  is the standard cell potential.

(i) Using the  $E^{\ominus}(\text{Au}^{3+}/\text{Au})$  given in (b), calculate the new  $E_{\text{cell}}$  using the Nernst equation, when  $[\text{Au}^{3+}]$  and  $[\text{Ni}^{2+}]$  are  $0.02 \text{ mol dm}^{-3}$  and  $2.47 \text{ mol dm}^{-3}$  respectively. [2]

(ii) Suggest and explain what happens to  $E_{\text{cell}}$  value of the electrochemical cell when the mass of nickel electrode is increased. [1]

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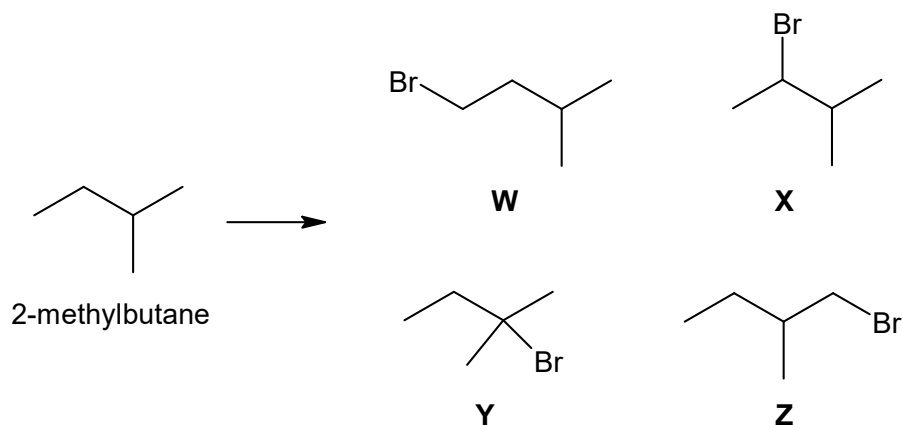
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## Section B

Answer **one** question from this section.

- 4 2-methylbutane reacts with bromine in the presence of UV light to give a mixture of products. There are four possible monobromoalkanes, **W** to **Z**, that can be formed.



- (a) (i) Draw both stereoisomers of **Z**. [1]
- (ii) Name and draw the mechanism for the formation of **W** from 2-methylbutane using curly arrows. [3]

Empirical evidence has shown that different types of carbons have a different relative probability of being substituted by bromine. These probabilities can be found in Table 4.1.

Table 4.1

type of carbon	relative probability of substitution
primary	1
secondary	62
tertiary	1640

- (iii) By considering the number of H atoms on each carbon, and information in Table 4.1, predict the relative proportions of **W**, **X**, **Y** and **Z** in the product mixture. [1]

The reaction of 2-methylbutane and bromine gas also forms a mixture of side-products with a molecular formula of  $C_{10}H_{22}$ .

- (iv) Use Table 4.1 to deduce the identity of the most stable alkyl radical present in the reaction mixture. Draw its structure using skeletal formula. [1]
- (v) Hence name the  $C_{10}H_{22}$  product that is formed in the highest proportion. [1]

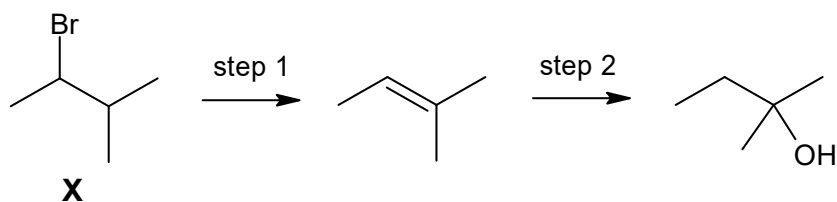
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**(b)** Fig. 4.1 shows a 2-step synthesis to obtain 2-methylbutan-2-ol from **X**.



**Fig. 4.1**

(i) State the reagents and conditions required for each step. [2]

Each step in the synthesis forms a mixture of products as there is more than one possible region for each reaction to occur. The term *regioselectivity* refers to the preference for a chemical reaction to occur at a specific region of a molecule to give the major product.

(ii) Explain if each step in Fig. 4.1 is regioselective for the intended product. Your answer should refer to the relative stability of relevant products or intermediates.

Hence conclude if the synthesis will give a good yield of 2-methylbutan-2-ol. [2]

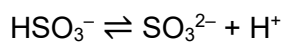
[illegible]



**(d)** Sodium bisulfite,  $\text{NaHSO}_3$ , is commonly used as a food preservative.

- (i) Given that the bisulfite ion contains a O–H covalent bond, draw a dot-and-cross diagram to show the bonding in a bisulfite ion,  $\text{HSO}_3^-$ . [1]
- (ii) Hence state the shape and bond angle around the sulfur atom within the bisulfite ion. Explain your answer using the Valence Shell Electron Pair Repulsion Theory. [2]

The bisulfite ion is a weak acid with a  $pK_a$  value of 6.97.



An aqueous mixture containing bisulfite ions,  $\text{HSO}_3^-(\text{aq})$ , and sulfite ions,  $\text{SO}_3^{2-}(\text{aq})$ , can act as a buffer.

- (iii) Write two equations to describe how a  $\text{HSO}_3^-/\text{SO}_3^{2-}$  mixture resists pH change when a small amount of acid or base is added. [1]

A buffer with pH 7.5 was prepared by mixing 30.0 cm<sup>3</sup> of 0.500 mol dm<sup>-3</sup> sodium bisulfite with 20.0 cm<sup>3</sup> of aqueous sodium hydroxide.

- (iv) Calculate the  $[\text{SO}_3^{2-}]:[\text{HSO}_3^-]$  ratio of the buffer. [1]
- (v) Hence calculate the concentration of sodium hydroxide used in the preparation of the buffer. [2]

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**[Turn over**

- 5 (a) (i)** Explain the difference in pH in Table 5.1. [2]

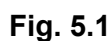
### Table 5.1

compound	pH of a 1.0 mol dm <sup>-3</sup> solution in water
NaCl	7.0
AlCl <sub>3</sub>	3.0

- (ii) With the aid of relevant equation(s), describe what happens when  $\text{Na}_2\text{O}$ ,  $\text{SiO}_2$  and  $\text{P}_4\text{O}_{10}$  are separately added to water. [3]

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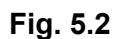


Strontium ions are reduced at the cathode to form molten strontium metal, which is then removed from the set up.

- (i) Write the half-equations, including state symbols, for the reactions at the anode and cathode. [2]
- (ii) A current of 5.0 A was passed through molten strontium chloride for 45 min.

Calculate the mass of strontium metal formed at the cathode. [2]

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- (i) Name and draw the mechanism for step 1. Include all relevant lone pairs, curly arrows and charges. Include the structure of the organic intermediate. [3]

In step 3, phenylamine is converted to cyclohexylamine using hydrogen gas dissolved in supercritical carbon dioxide in the presence of rhodium catalyst supported on alumina. This was carried out at high temperature and pressure.

- (ii) By considering the structure of phenylamine, suggest why its conversion to cyclohexylamine requires the use of a catalyst. [1]

[illegible]

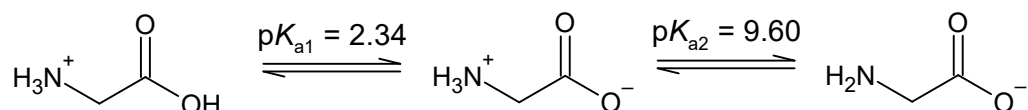
$$\text{CH}_3\text{Br} \xrightarrow{\text{step 1}} \text{CH}_3\text{CN} \xrightarrow{\text{step 2}} \text{C}/\text{CH}_2\text{CN} \xrightarrow{\text{step 3}} \text{intermediate } \mathbf{A} \xrightarrow{\text{step 4}} \text{H}_2\text{NCH}_2\text{CO}_2\text{H}$$

(i) State the reagents and conditions required for step 1. [1]

- (ii) Draw the **displayed** structural formula of intermediate **A** and state the reagents and conditions required for step 3. [2]

[illegible]

**(e)** Protonated glycine acts as a dibasic weak acid.



A student adds small portions of  $0.125 \text{ mol dm}^{-3} \text{ NaOH(aq)}$  to  $25.0 \text{ cm}^3$  of  $0.100 \text{ mol dm}^{-3}$  protonated glycine. The student uses a pH meter to measure the pH of the mixture.

- (i) Calculate the pH of  $0.100 \text{ mol dm}^{-3}$  protonated glycine. You may ignore the effect of  $\text{p}K_{\text{a}2}$  on the pH. [1]
- (ii) Calculate the volume of NaOH required to reach the first equivalence point. [1]
- (iii) Sketch the pH-volume added curve you would expect to obtain when a total of  $50 \text{ cm}^3$  of  $0.125 \text{ mol dm}^{-3}$  NaOH(aq) is added.

Label the following points on the curve.

- initial pH
- volume required for each equivalence point
- pH and volume at each point of maximum buffering capacity

You may assume that the pH of the solution is 12.2 upon addition of 50 cm<sup>3</sup> of NaOH. [2]

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**Additional answer space**

If you use the following page to complete the answer to any question, the question number must be clearly shown.

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