

RAFFLES INSTITUTION
2025 YEAR 6 PRELIMINARY EXAMINATION

Higher 2



CANDIDATE
NAME

CLASS

INDEX NUMBER

CHEMISTRY

9729/03

Paper 3 Free Response

23 September 2025

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not open this question booklet until you are told to do so.

Write your name, class and index 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 in the spaces provided on the Question Paper. If additional space is required, you should use the page 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. Do not write anything in it.

You are reminded of the need for good English and clear presentation in your answers.

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					
Section A		Section B		Total	
1	/ 20	(Circle the question you have answered)		/ 80	
2	/ 20	4	/ 20		
3	/ 20	5	/ 20		

This document consists of **30** printed pages and **2** blank pages

Section A

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

- 1** This question is about ammonia, its application in space missions and its versatility in chemical reactions.

(a) (i) State three basic assumptions of the kinetic theory as applied to an ideal gas. [2]

(ii) Sketch a graph of pV/T against pressure, p , for 1 mole of an ideal gas. [1]

(iii) On the same graph in **(a)(ii)**, sketch and label the graph for 1 mole of NH_3 gas. Explain the non-ideal behaviour of NH_3 gas at moderately high pressure. [2]

(iv) NH_3 gas is contained in a 5 dm^3 flask at a temperature of 27°C and a pressure of 4.00 atm . The gas is then compressed at constant temperature to half its volume and then heated to 227°C at constant volume.

Calculate the final pressure of NH_3 gas, in atm, in the container.

[Assume NH_3 gas behaves as an ideal gas under these conditions.] [2]

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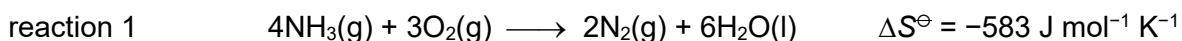
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- (b) Ammonia has been proposed as an alternative zero-carbon fuel for use in space missions. The combustion of ammonia proceeds as follows.



The following data is given.

Table 1.1

	$\Delta H^\ominus / \text{kJ mol}^{-1}$
standard enthalpy change of formation of $\text{NH}_3(\text{g})$	-46.1
standard enthalpy change of vaporisation of $\text{H}_2\text{O}(\text{l})$	+44.0

- (i) Define the term *standard enthalpy change of combustion* for ammonia gas. [1]
- (ii) Using the data in Table 1.1, together with data from the *Data Booklet*, construct an energy cycle to calculate a value for the standard enthalpy change of combustion, ΔH_c^\ominus , of ammonia gas. [5]
- (iii) Suggest a reason why ΔS^\ominus for reaction 1 is negative. [1]
- (iv) With reference to (b)(ii), calculate the standard Gibbs free energy change, ΔG^\ominus , for reaction 1. Comment on the effect of temperature on the spontaneity of the reaction. [2]
- (v) Under high temperature conditions, the N_2 gas produced in reaction 1 can undergo further reaction to produce oxides of nitrogen, NO_x . Suggest a reason why lower temperatures do not favour the formation of NO_x . [1]

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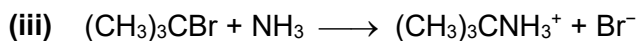
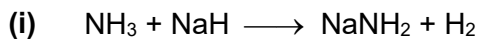
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- (c) The ammonia molecule can react in various ways: as an acid, as a base, as a nucleophile, as an oxidising agent and as a reducing agent.

State the role of ammonia in each of the following reactions. Explain your answers briefly.
[3]



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- 2 (a) Equation 1 shows the Haber process for manufacturing ammonia.



A mixture of H_2 and N_2 in the molar ratio of 3:1 is added to a sealed vessel and heated to $450\text{ }^\circ\text{C}$ with an iron catalyst. At equilibrium, the total pressure in the vessel is 200 atm and the partial pressure of NH_3 is 35 atm.

- (i) Write the expression for the equilibrium constant, K_p , for the reaction in equation 1. Use your expression to calculate the value of K_p for this reaction. Include its units. [3]
- (ii) The value of the equilibrium constant, K_p , for the Haber process measured at different temperatures is shown in Table 2.1.

Table 2.1

temperature / $^\circ\text{C}$	K_p
300	4.34×10^{-3}
400	1.64×10^{-4}
500	1.45×10^{-5}
600	2.25×10^{-6}

Deduce the sign for the enthalpy change of the forward reaction of equation 1. Explain your reasoning. [2]

- (iii) Predict the effect of adding a small amount of inert gas into the reaction vessel, under constant temperature and pressure, on the position of equilibrium for equation 1. Explain your answer. [2]
- (iv) Explain why iron can act as a heterogeneous catalyst. [1]
- (v) Explain the conditions used in the Haber process for manufacturing ammonia. [2]

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- (b) CoCl_3 reacts with the bidentate ligand, ethylenediamine (en), to form complex ions with the formula $[\text{Co}(\text{en})_2\text{Cl}_2]^+$.

The structure of ethylenediamine (*en*) is shown in Fig. 2.1.

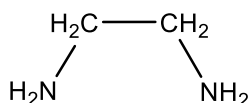
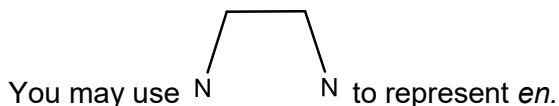


Fig. 2.1

- (i) Explain what is meant by the term *ligand*. [1]
- (ii) **A**, **B** and **C** are isomers of $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ with an octahedral configuration. Isomers **A** and **B** are non-superimposable mirror images of each other. Isomer **C** does not rotate plane-polarised light.

Draw and label the 3-dimensional structure of each isomer.



[2]

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- (c) Complex ions with a coordination number of 4, such as $[\text{Co}(\text{CN})_4]^{2-}$, can adopt either the tetrahedral or the square planar structure. Fig. 2.2 shows how the d-orbitals of the metal ion are split in such complexes.

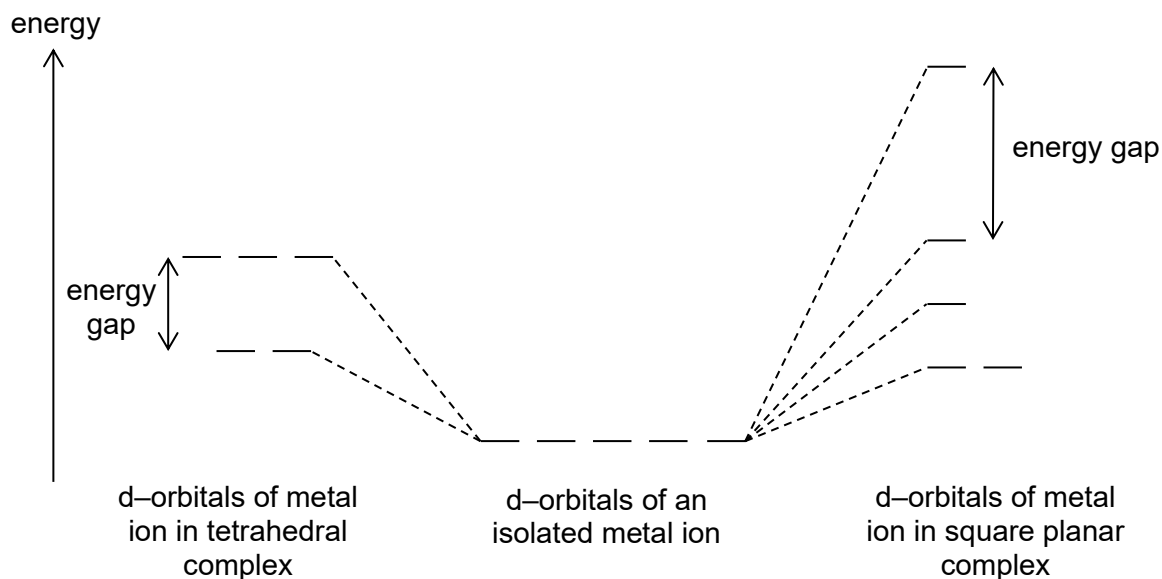


Fig. 2.2

The arrangement of electrons in the d-orbitals depends on the spin states of the complexes.

In a '*high spin*' state, the electrons occupy all the d-orbitals singly, before starting to pair up in the lower energy d-orbitals.

In a '*low spin*' state, the lower energy d-orbitals are filled first, by pairing up if necessary, before the higher energy d-orbitals are used.

- (i) State the electronic configuration of a cobalt(II) ion. [1]
- (ii) Explain why an aqueous solution of $[\text{Co}(\text{CN})_4]^{2-}$ is coloured. [3]
- (iii) Electrons usually occupy d-orbitals singly before pairing up.
Suggest why a complex might still adopt a *low spin* state. [1]

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- 3 (a) Compound **K** can be synthesised from an amide or a nitrile using the same reagents and conditions.

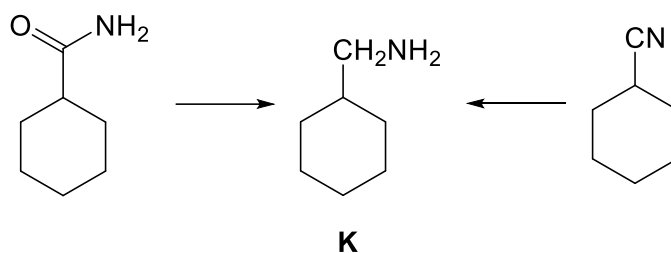


Fig. 3.1

- (i) State the reagents and conditions to synthesise compound **K** in Fig. 3.1. [1]
- (ii) Draw the displayed structure of **K**. [1]

[illegible]

$$\text{CH}_3\text{--C}\equiv\text{N} \xrightarrow{\text{step 1}} \text{CH}_3\text{--C}(\text{OH})\text{=N}^- \xrightarrow{\text{step 2}} \text{CH}_3\text{--C}(\text{OH})\text{=NH} \xrightarrow{\text{S}} \text{CH}_3\text{--C}(=\text{O})\text{NH}_2$$

Fig. 3.2

- (i) Name the mechanism for the overall reaction from CH_3CN to **S**. [1]
- (ii) State the type of stereoisomerism shown by **S**. [1]
- (iii) State the oxidation number of the carbon atom in the amide functional group. [1]

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(c) Primary amides can undergo elimination to form nitriles as shown in Fig. 3.3.

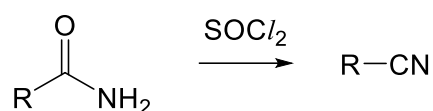


Fig. 3.3

The mechanism for this reaction, in the presence of a base, B^- , is shown in Fig. 3.4.

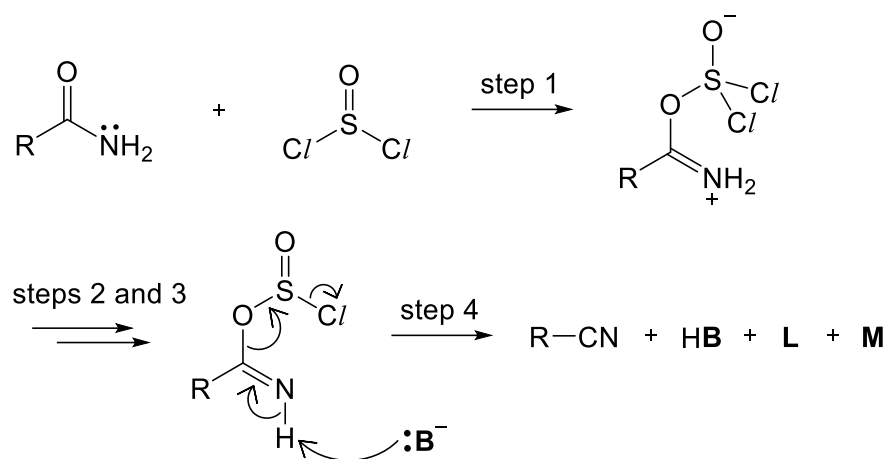


Fig. 3.4

- (i) Draw three curly arrows in **step 1** of Fig. 3.4 to complete the mechanism for **step 1**. [2]
- (ii) Identify **L** and **M**. [2]

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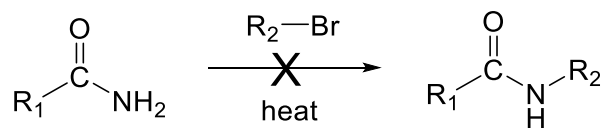
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- (d) A substituted amide cannot be synthesised from the corresponding primary amide using a nucleophilic substitution reaction.



- (i) Explain why an amide is not nucleophilic. [2]
- (ii) The Ritter reaction is a reaction between a nitrile and an alcohol, in the presence of concentrated H_2SO_4 , to form a substituted amide as shown in Fig. 3.5.

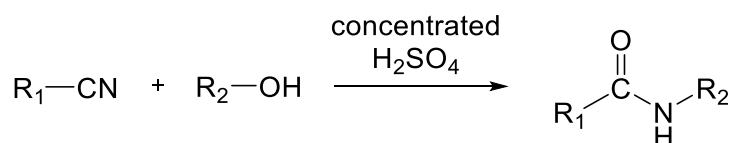


Fig. 3.5

Using the reaction in (c) and the Ritter reaction, a substituted amide **R** can be synthesised from a primary amide **P** and alcohol **Q** in two steps as shown in Fig. 3.6.



Fig. 3.6

Suggest the structures of primary amide **P** and alcohol **Q**. [2]

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- (e) **T**, C₈H₈, consists of two rings which share two adjacent carbon atoms and decolourises bromine water. When **T** is heated with acidified KMnO₄, **U**, C₄H₄O₅, was formed as the only carbon-containing product. **U** forms an orange precipitate with 2,4-dinitrophenylhydrazine and 1 mole of **U** reacts with excess Na₂CO₃(aq) to form 1 mole of CO₂ gas.

- (i) Suggest structures for **T** and **U** and explain the reactions described. [6]

- (ii) Write an equation for the reaction of **U** with LiAlH₄, using [H] to represent the reducing agent. [1]

[illegible]

[Total: 20]

Section B

Answer **one** question from this section.

4 (a) Elements in Group 17 are known as the halogens.

(i) Describe and explain how the volatilities of the halogens vary down Group 17. [2]

(ii) Predict the colour of the final solution that would be observed when the following pairs of solutions are mixed. Give equations for any reactions that occur. [2]

- $\text{Cl}_2(\text{aq})$ and $\text{NaBr}(\text{aq})$
- $\text{I}_2(\text{aq})$ and $\text{NaCl}(\text{aq})$
- $\text{Br}_2(\text{aq})$ and $\text{NaI}(\text{aq})$

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(b) Some hydrogen halides undergo thermal decomposition.

(i) Describe the thermal decomposition of the hydrogen halides HCl , HBr and HI and explain any variation in their thermal stabilities. [3]

(ii) Nitrogen triiodide, NI_3 , is a solid at room temperature. Unlike hydrogen iodide, HI , decomposes explosively to form nitrogen gas and iodine vapour even with a slight disturbance. Other than thermodynamic considerations, explain this difference in reactivity. [1]

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- (c) Silver nitrate can be used to detect the presence of halide ions in a solution. The sparingly soluble silver halides are obtained as precipitates.

- (i) Describe and explain how the solubility of silver bromide is affected by adding $\text{NH}_3(\text{aq})$. [2]

To determine the concentration of bromide ions in a sample solution, 25.0 cm³ of this solution is titrated against an aqueous solution of silver nitrate, AgNO₃(aq). 1.0 cm³ of 0.01 mol dm⁻³ potassium chromate(VI), K₂CrO₄, is added as indicator. As the titrant is slowly added, AgBr precipitate is formed. The end point of the titration is reached when 26.00 cm³ of AgNO₃(aq) has been added and a red-brown precipitate of Ag₂CrO₄ is just observed.

$$K_{\text{sp}}(\text{AgBr}) = 5.0 \times 10^{-13} \text{ mol}^2 \text{ dm}^{-6}$$

$$K_{\text{sp}}(\text{Ag}_2\text{CrO}_4) = 1.1 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$$

- (ii) Determine the concentration of silver ions at the end point of the titration. [1]

- (iii) Given that the concentration of bromide ions in the sample solution is 65 mg dm^{-3} , determine the percentage of bromide remaining in the solution at the end point of the titration. [2]

[illegible]

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- (d) In a separate experiment, an excess of solid silver phosphate, Ag_3PO_4 , is shaken with water. At equilibrium, the silver phosphate concentration in the solution formed is $4.26 \times 10^{-5} \text{ mol dm}^{-3}$.

Calculate the silver ion concentration when an excess of solid Ag_3PO_4 is shaken with a solution containing $0.020 \text{ mol dm}^{-3} \text{ Na}_3\text{PO}_4$. [2]

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- (e) Compound **P** is made from two Period 3 elements only. It reacts with hydrochloric acid, HCl(aq) , to give a solution **Q** and gas **R**.

Addition of aqueous sodium hydroxide, NaOH(aq) , to **Q** gives a white precipitate **S** that is insoluble in excess NaOH(aq) .

Gas **R** reacts explosively with oxygen to produce 2 moles of water and 1 mole of white solid **T** which is insoluble in HCl(aq) or NaOH(aq) .

State the identities of **P**, **Q**, **R**, **S** and **T**.

[5]

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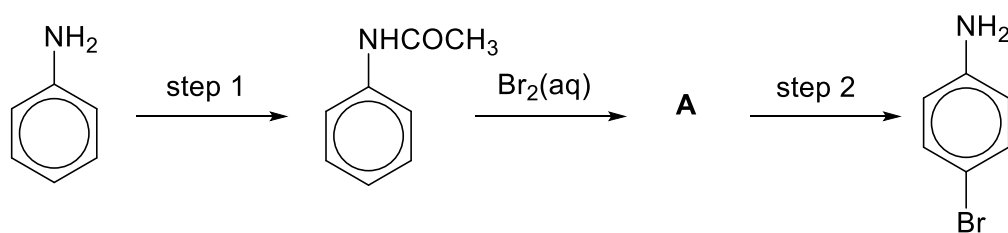
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- (i) Suggest the structure for organic compound **A**. [1]
- (ii) Suggest reagents and conditions for steps 1 and 2. [2]

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Blood maintains its pH within a narrow range through buffer systems like the carbonic acid-bicarbonate system in blood plasma. Without the buffer systems present, H^+ released from metabolic processes would significantly lower blood pH which can be detrimental.

(b) (i) With the aid of an equation, explain how the carbonic acid-bicarbonate ($\text{H}_2\text{CO}_3 / \text{HCO}_3^-$) buffer system in blood plasma helps to maintain the pH of blood when H^+ is released. [2]

(ii) At physiological pH of 7.4, the ratio of the concentration of $\text{HCO}_3^-(\text{aq})$ to $\text{H}_2\text{CO}_3(\text{aq})$ in blood plasma is 20 : 1.

Use this information to determine the pK_a of carbonic acid. [1]

(iii) At physiological pH of 7.4, the concentration of $\text{H}_2\text{CO}_3(\text{aq})$ in a person's blood plasma was initially $0.0020 \text{ mol dm}^{-3}$. When the body produced more H^+ , the concentration of $\text{H}_2\text{CO}_3(\text{aq})$ increased to $0.0024 \text{ mol dm}^{-3}$. Using your answer in **(b)(ii)**, calculate the change in pH in the blood plasma due to this change. [2]

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(c) Information about three amino acids found in proteins are provided in Table 5.1.

Table 5.1

name	structure	abbreviation	pK _a of α-COOH	pK _a of α-NH ₃ ⁺	pK _a of side chain
serine	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{OH} \end{array}$	ser	2.2	9.2	-
histidine	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{N} \quad \text{C} \\ \diagup \quad \diagdown \\ (1) \quad \text{NH} \\ \diagdown \quad \diagup \\ \text{C} \quad \text{N} \\ \diagup \quad \diagdown \\ (2) \end{array}$	his	1.8	9.2	6.1
aspartic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{C}=\text{O} \\ \\ \text{OH} \end{array}$	asp	1.9	9.6	3.7

Histidine plays a key role in buffering the pH in biological systems. Histidine is an amino acid with a five-membered imidazole side chain that contains two nitrogen atoms, one of which is protonated under acidic conditions.

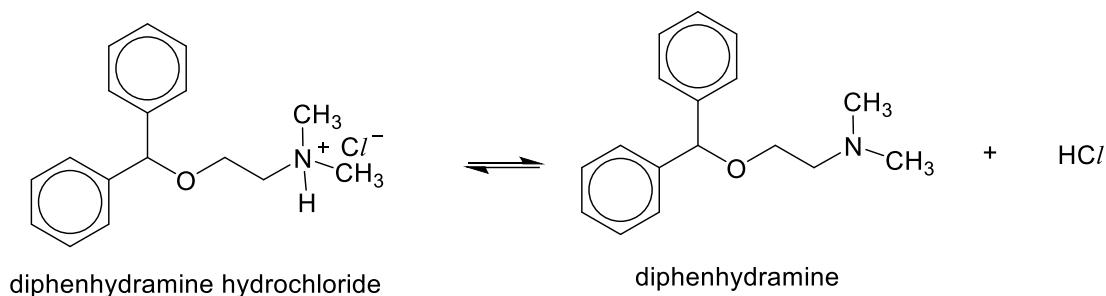
- (i) Define an Arrhenius acid. [1]
- (ii) Histidine contains two nitrogen atoms in its side chain. Explain why N(1) is more basic than N(2). [1]
- (iii) Ser–his–asp is a sequence of amino acid residues that is commonly found in the active sites of many enzymes. Draw the structure of the tripeptide ser–his–asp. [1]
- (iv) Explain whether the tripeptides ser–his–asp and asp–his–ser are the same compound. [1]
- (v) Draw the structure of the predominant species of aspartic acid at pH 7.4. [2]

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- (d) The blood-brain barrier only allows uncharged molecules to pass through it.

Diphenhydramine hydrochloride is an anti-histamine. An equilibrium is set up between the diphenhydramine hydrochloride and its uncharged form, diphenhydramine, as shown.



- (i) State the number of chiral centres in the structure of diphenhydramine hydrochloride. [1]
- (ii) A tablet contains 25 mg of diphenhydramine hydrochloride. The molar mass of diphenhydramine hydrochloride is 291.5 g mol^{-1} . Calculate the pH of the solution when this tablet is dissolved in 10 cm^3 of water. Assume that the other components of the tablet do not affect the pH of the solution.

Use $\text{NR}_3\text{H}^+\text{Cl}^-$ to represent diphenhydramine hydrochloride.

The $\text{p}K_a$ of diphenhydramine hydrochloride is 9.1. [2]

- (iii) When the drug enters the bloodstream at pH 7.4, the uncharged diphenhydramine molecules can pass through the blood-brain barrier and cause drowsiness as a side effect if there is at least 1 uncharged diphenhydramine molecule for every 100 charged diphenhydramine hydrochloride present in the bloodstream.

Calculate the ratio of uncharged diphenhydramine to charged diphenhydramine hydrochloride in the bloodstream under physiological pH of 7.4, and hence deduce if the drug can cause drowsiness. [3]

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Additional answer space

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