HWA CHONG INSTITUTION
C2 Preliminary Examination
Higher 2

CANDIDATE NAME						**CT GROUP**	2	4	S
CENTRE NUMBER	S					**INDEX NUMBER**			

CHEMISTRY

9729/03

Paper 3 Free Response

18 September 2025

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your **name**, **CT group, centre number** and **index number** on all the work you hand in.

Write in dark blue or black pen.

You may use a HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

DO **NOT** WRITE ON ANY BARCODES.

Answer all questions in the spaces provided in 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.

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	**/ 22**
2	**/ 17**
3	**/ 21**
*** Circle your option below**	
*** 4 / 5**	**/ 20**
Deductions (s.f.)	
Deductions (units)	
Deductions (structures)	
Total	**/ 80**

Section A

Answer **all** questions in this section.

1 (a) Magnesium oxide, MgO, can be obtained from sea water which contains significant amounts of Mg^{2+} and Ca^{2+} ions.

The steps involved are shown in Fig. 1.1.

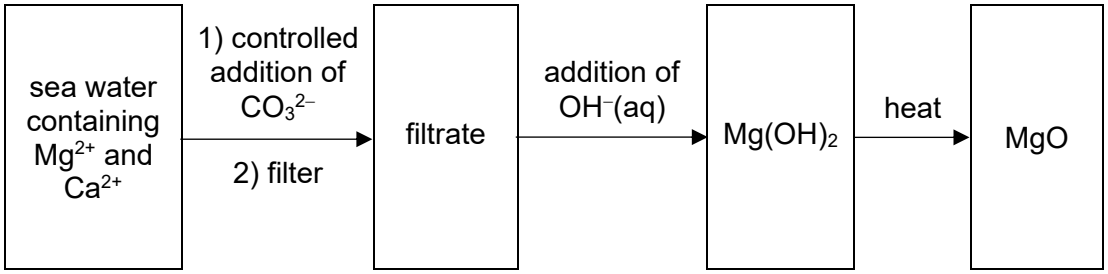

Fig. 1.1

The numerical values of the relevant solubility products, K_{sp}, are given in Table 1.1.

Table 1.1

compound	K_{sp}
$MgCO_3$	1.0×10^{-5}
$CaCO_3$	8.7×10^{-9}
$Mg(OH)_2$	1.1×10^{-11}
$Ca(OH)_2$	5.5×10^{-6}

(i) Calculate the solubilities of $MgCO_3$ and $Mg(OH)_2$ respectively, in mol dm^{-3}. [2]

(ii) If the concentration of Mg^{2+} ions in the filtrate is 3.0×10^{-5} mol dm^{-3}, calculate the concentration of OH^- ions present in the filtrate when the first trace of solid $Mg(OH)_2$ appears. [1]

(iii) Explain why CO_3^{2-} ions are added to the sea water before the addition of OH^- ions, and why this must be controlled. [2]

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(b) **(i)** Define the term *lattice energy*. [1]

(ii) Using the data in Table 1.2 and data from the *Data Booklet*, construct a Born-Haber cycle to calculate a value for the lattice energy of magnesium hydroxide, $Mg(OH)_2(s)$.

Table 1.2

	value / kJ mol^{-1}
standard enthalpy change of atomisation of Mg(s)	+148
standard enthalpy change of formation of $Mg(OH)_2(s)$	–925
standard enthalpy change of formation of OH(g), $\frac{1}{2}O_2(g) + \frac{1}{2}H_2(g) \rightarrow OH(g)$	+6
electron affinity of OH(g), $OH(g) + e^- \rightarrow OH^-(g)$	–173

[4]

(iii) Deduce the order of lattice energy, in decreasing magnitude, of MgO, $Mg(OH)_2$, and $Ca(OH)_2$. Explain your answer. [3]

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(c) Magnesium and aluminium are Period 3 elements with different physical and chemical properties.

(i) State the electronic configurations of Mg and A*l*, and explain why the first ionisation energy of aluminium is lower than that of magnesium. [2]

(ii) Both magnesium and aluminium react with chlorine to form their respective chlorides.

Describe and explain the reactions, if any, of each of these chlorides with an excess of water. Write equations for any reactions that occur and suggest the pH of the resulting mixtures. [4]

(d) Draw a labelled diagram of the electrolysis cell used to anodise aluminium. Include details of the cathode, anode and electrolyte. Write an equation for the reaction at **each** electrode. [3]

[Total: 22]

2 (a) Explain why phenols are more acidic than alcohols such as ethanol. [2]

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(b) Salbutamol is a bronchodilator drug used for the treatment of an asthma attack.

Fig. 2.1 shows a synthesis of salbutamol from methyl salicylate.

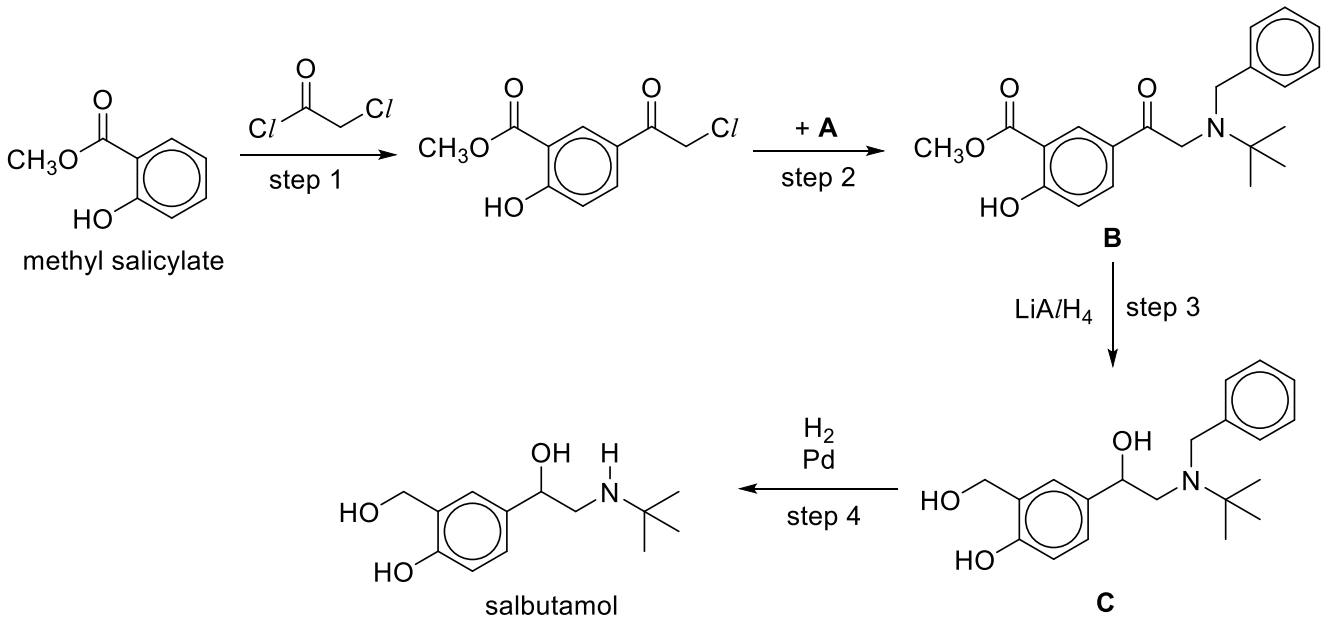

Fig. 2.1

(i) Name the mechanisms of the reactions in steps 1 and 2 respectively. [2]

(ii) Draw the structure of reagent **A** in step 2. [1]

(iii) Explain why the amine group in compound **C** would be a stronger base than the amine group in salbutamol in the gaseous phase. [2]

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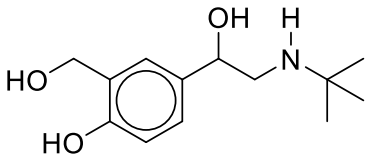
(c) The reaction of salbutamol (M_r = 239) with aqueous H_2SO_4 produces the ionic salt, salbutamol sulfate (M_r = 576.1), that is present in asthma inhalers.



salbutamol

(i) Draw the structure of salbutamol sulfate. [2]

(ii) Identify two types of forces of attraction that are responsible for the high solubility of salbutamol sulfate in water. [2]

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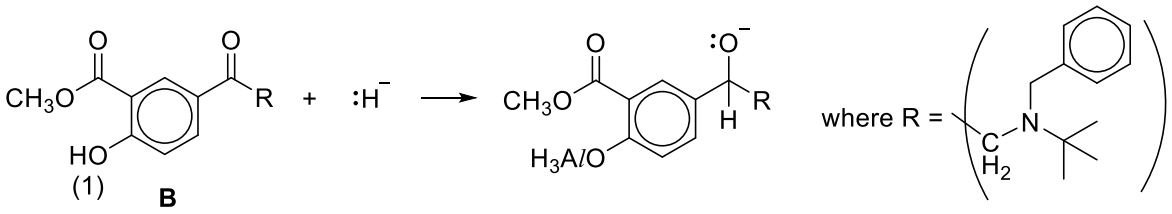
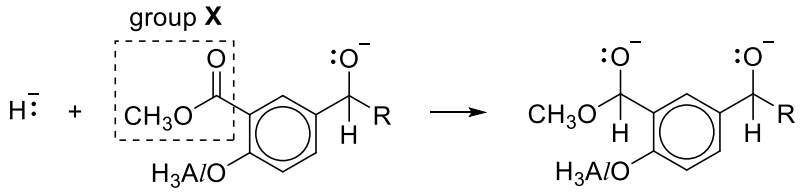
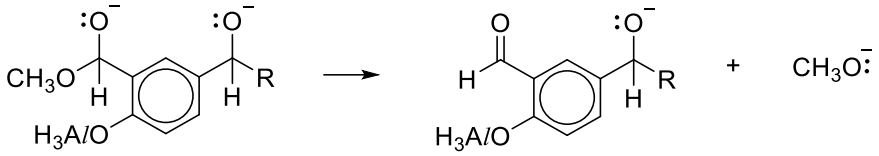
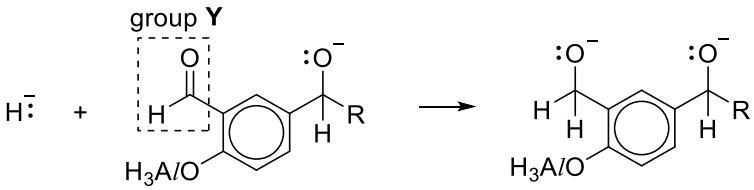
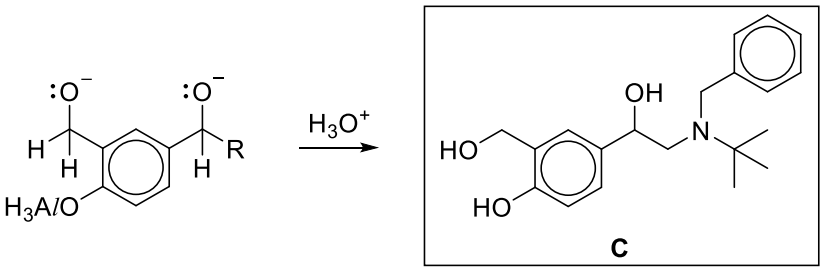
(d) Part of the mechanism for step 3 in Fig. 2.1 is illustrated by stages as shown in Table 2.1.

Table 2.1

stage	equation
1	 **B** As the −OH group (1) of compound **B** is acidic, it also reacts with LiA/H_4 to form $-OA/H_3$.
2	
3	
4	
5	 **C**

(i) The hydride ion, $:H^-$, is assumed to be the reacting species produced by LiA/H_4 and acts as a nucleophile in stages 1, 2 and 4.

Draw the curly arrows and all relevant dipoles in stages 2 and 3 of Table 2.1. [2]

(ii) In stage 4, group **Y** reacts with $:H^-$ in a similar manner to group **X** in stage 2.

Group **X** is expected to be less reactive towards $:H^-$ than group **Y**. Suggest two reasons to explain this. [2]

(iii) Label the chiral centre in compound **C** of stage 5 of Table 2.1 with an asterisk (*). [1]

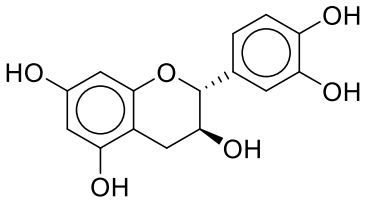
(iv) With reference to the mechanism in stage 1, explain why compound **C** produced in stage 5 is a racemic mixture. [1]

[Total: 17]

3 Cast iron kettles, or *tetsubin*, are traditionally used in Japan for boiling water. However, if the kettles are not dried thoroughly after use, rust (Fe_2O_3) forms readily on the inner surfaces.

To remove this rust, one method suggested on the Internet is to boil a mixture of water and green tea leaves in the *tetsubin* and leaving it overnight. When heated in water, rust forms $Fe(OH)_3$, which is sparingly soluble in water.

Green tea leaves contain catechins, which belong to a class of polyphenols.



(+)catechin

When the mixture of water and green tea leaves is boiled in a rusty *tetsubin*, $Fe^{3+}(aq)$ ions from $Fe(OH)_3$ can interact with catechins, giving a dark-coloured solution which is then discarded. Repeating these steps a few times apparently removes the rust.

(a) Explain why iron is classified as a *transition element*. [1]

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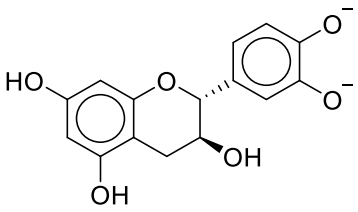
(b) Fe^{3+} ions can interact with the deprotonated form of catechin, Cat^{2-}.



Cat^{2-}

(i) Three Cat^{2-} ions bind to one Fe^{3+} ion to form an octahedral complex. Explain how each Cat^{2-} interacts with the Fe^{3+} ion to form the complex. [1]

(ii) Draw the 3-dimensional structure of the complex formed.

In your answer, you may simplify the structure of each Cat^{2-} ion to:  [2]

(iii) Name the type of reaction that occurs between $Fe^{3+}(aq)$ and Cat^{2-} ions to form the complex and write an equation to illustrate it. [2]

(c) Using the principles of solubility equilibria, suggest how the above method may be able to remove rust from the *tetsubin*. [2]

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(d) The five *d* orbitals in a transition metal ion are split into two levels when the ion is in an octahedral complex.

(i) Draw diagrams to illustrate the **two** different shapes of *d* orbitals in a transition metal ion. Explain why the *d* orbitals split into two levels in an octahedral complex, stating which of the *d* orbitals are in each level. [4]

(ii) Hence explain why transition element complexes are usually coloured. [2]

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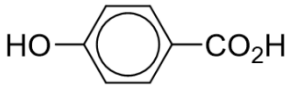
(e) The biosynthesis of catechin in green tea leaves involves the formation of compound **P**, $C_{15}H_{12}O_5$.

P is a *trans*-isomer which contains one six-membered aliphatic ring and one benzene ring.

P is also a tetraketone where each carbonyl carbon is separated from another by one carbon atom.

Heating **P** with acidified potassium manganate(VII) solution gives compound **Q** and 4-hydroxybenzoic acid as the only products.



4-hydroxybenzoic acid

P reacts with aqueous bromine to give compound **R**, $C_{15}H_{11}O_6Br_3$. Treatment of **P** with H_2 over Pd catalyst gives compound **S**.

Suggest the structures of **P**, **Q**, **R** and **S**.
For each reaction, state the type of reaction(s) described. [7]

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[Total: 21]

Section B

Answer **one** question in this section.

4 In the chemical industry, ethanoic acid, CH_3CO_2H, is produced via the Monsanto process, which uses a homogeneous rhodium catalyst to convert methanol and carbon monoxide into ethanoic acid under high pressure and temperature. The process involves the following stages:

stage 1: $CH_3OH + HI \rightarrow CH_3I + H_2O$

stage 2: $CH_3I + CO \rightleftharpoons CH_3COI$

stage 3: $CH_3COI + H_2O \rightarrow CH_3CO_2H + HI$

(a) Write the overall equation for the formation of ethanoic acid from methanol and carbon monoxide in this process. [1]

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(b) Stage 1 of the Monsanto process involves the reaction between methanol and hydrogen iodide to form methyl iodide and water.

(i) Suggest the type of reaction occurring in this stage. [1]

(ii) The mechanism involves the following steps:

- step 1: protonation of the −OH group by hydrogen iodide to form an intermediate
- step 2: attack of the intermediate by iodide ion to form the final products

Draw the mechanism described above. Include all relevant lone pairs, dipoles, curly arrows, charges and the structure of the intermediate. [2]

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(c) Stage 2 of the Monsanto process is a reversible, exothermic reaction.

stage 2: $CH_3I + CO \rightleftharpoons CH_3COI$

(i) State and explain the effect of:
- increasing the temperature
- presence of a catalyst

on the position of equilibrium of stage 2. [2]

(ii) An experiment was carried out at 400 K, where 0.400 mol of CH_3I and 0.300 mol of CO were mixed in 700 cm^3 of solvent. At equilibrium, the concentration of CH_3COI was found to be 0.150 mol dm^{-3}.

Write the expression for the equilibrium constant, K_c, for stage 2.
Calculate the value of K_c, stating its units. [4]

(d) In stage 2 of the Monsanto process, the active catalyst is a rhodium(I) complex, $[Rh(CO)_2I_2]^-$.

The mechanism involves several steps, with the first step shown in Fig. 4.1.

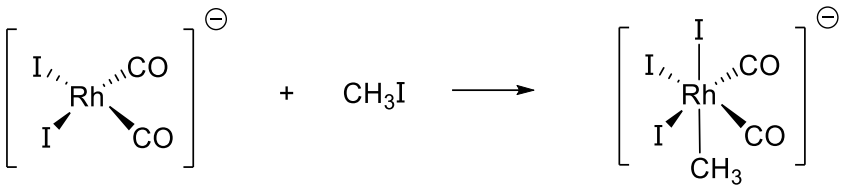

Fig. 4.1

In this first step, the catalyst undergoes an oxidative addition with CH_3I to produce a rhodium(III) complex, $[Rh(CH_3)(CO)_2I_3]^-$. The C−I bond breaks and new Rh−CH_3 and Rh−I bonds are formed.

(i) Explain the difference in the mode of action of a homogeneous catalyst as compared to a heterogeneous catalyst. [2]

(ii) With reference to its ligands and possible oxidation states, suggest two reasons how the $[Rh(CO)_2I_2]^-$ complex is able to function as a catalyst in stage 2 of the Monsanto process. [2]

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(e) To maintain the acidity within an optimal range for catalyst performance, a buffer is formed by adding a limited amount of sodium hydroxide to ethanoic acid.

A student adds 300 cm^3 of 0.500 mol dm^{-3} sodium hydroxide to 500 cm^3 of 0.800 mol dm^{-3} ethanoic acid to produce a buffer solution.

The K_a of ethanoic acid is 1.8×10^{-5} mol dm^{-3} at 298 K.

(i) Write the ionic equation for the reaction that occurs between ethanoic acid and sodium hydroxide. [1]

(ii) Calculate the concentrations of the acid and conjugate base present after the reaction. Hence, calculate the pH of the buffer. [3]

(iii) Explain, by reference to the equilibrium in the buffer, how this mixture resists pH changes on the addition of a small amount of acid. [2]

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5 The Maillard reaction is a series of chemical reactions that produces the characteristic browning of bread crusts in baking.

In one of the pathways of the Maillard reaction in the baking of bread, the reaction between ammonia and methanal produces a reactive imine intermediate, as shown in Reaction 1. This eventually leads to the production of compounds that gives bread crusts its brown colouration and flavour.

reaction 1 $NH_3(g) + HCHO(g) \rightleftharpoons \underset{\text{imine}}{CH_2{=}NH(g)} + H_2O(g)$ $\Delta H = -56 \text{ kJ mol}^{-1}$

(a) **(i)** State *Le Chatelier's Principle*. [1]

(ii) Explain the effect of increasing
- temperature
- pressure

on the position of equilibrium of reaction 1. [2]

(b) **(i)** An equilibrium mixture contains the four gases in reaction 1.

reaction 1 $NH_3(g) + HCHO(g) \rightleftharpoons CH_2{=}NH(g) + H_2O(g)$

At time t_1, a small amount of NH_3 is added while the temperature is kept constant. The mixture is then allowed to establish equilibrium again. At time t_2, a new equilibrium is established.

Complete the graph in Fig. 5.1 to show how the amount of each of the three gases would change from time t_1 until *after* time t_2. Show clearly the relative change in amount of each gas and the new amount of each gas at the new equilibrium.

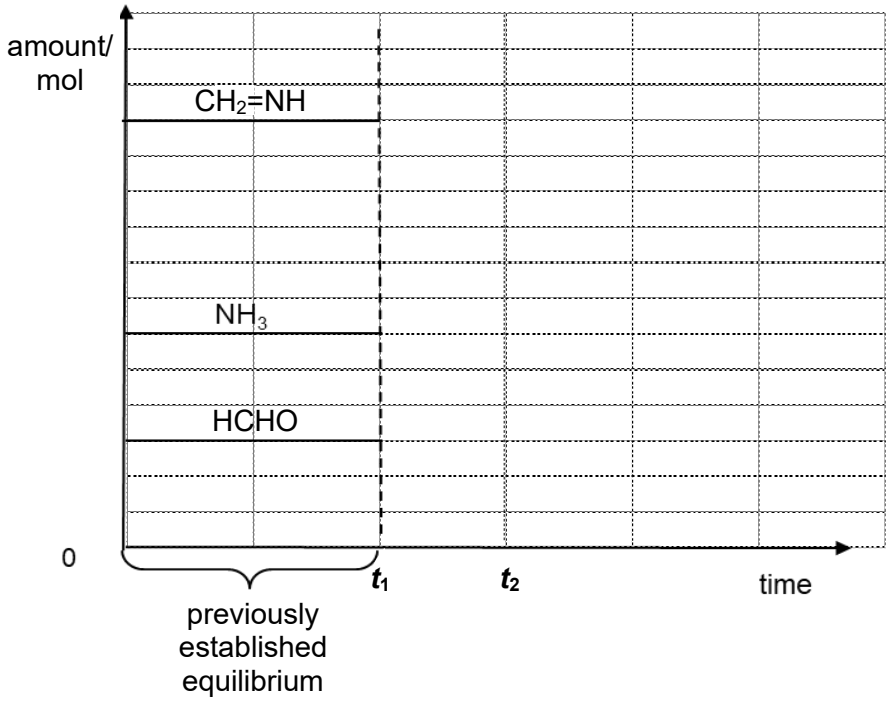

Fig. 5.1

[3]

(ii) Write the expression for the equilibrium constant, K_p, for reaction 1 and state its units. [1]

(iii) 5 moles of NH_3 and 5 moles of HCHO are introduced into a 1.2 dm^3 chamber at 180 °C. Reaction 1 occurs and when equilibrium is established, 9% of NH_3 remains unconverted.

Determine the value of K_p at 180 °C. [3]

(iv) Suggest the sign for the Gibbs free energy change of reaction 1 at 180 °C and comment on the position of equilibrium of the reaction. [1]

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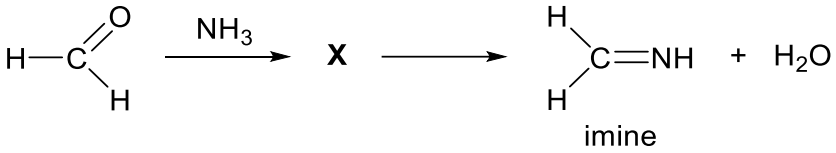
(c) **(i)** Suggest the type of reaction that has occurred in reaction 1. [1]

(ii) The imine in reaction 1 is formed in two steps via compound **X**, as shown below.



Suggest the structure of compound **X**. [1]

Reaction 1 is similar to the process that occurs when asparagine, an amino acid found in wheat flour, reacts with methanal in the bread crust at high temperatures during baking. This reaction leads to the formation of acrylamide, a potentially carcinogenic compound.

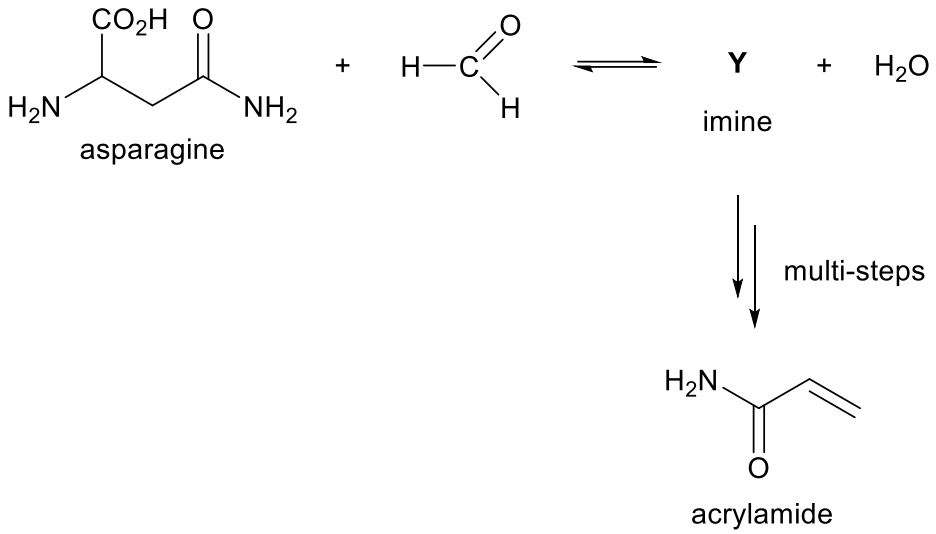


Fig 5.2

(iii) On Fig. 5.2, circle the functional group in asparagine that reacts with methanal to form the imine **Y**. [1]

(iv) Draw the structure of the imine **Y**. [1]

(v) Acrylamide formation is found to decrease in acidic medium. With reference to the role of asparagine to form **Y**, explain why this is so. [1]

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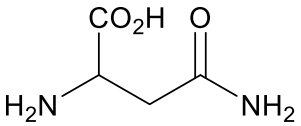
(d) A solution of asparagine is electrically neutral at pH 5.41. The pK_a values associated with asparagine are 2.02 and 8.80.



asparagine

(i) Draw the predominant form of asparagine present in the solution at pH 5.41. [1]

(ii) Write two equations to show how the asparagine in **(c)(i)** reacts with small amounts of acid and alkali when added separately. [2]

(iii) Calculate the ratio of the concentration of the two predominant forms of asparagine present in the solution at pH 8. [1]

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Additional answer space

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