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9791/03

For Examination from 2016

2 hours 15 minutes

Additional Materials: Data Booklet

Write your Centre number, candidate number and name in the spaces at the top of this page.
Write in dark blue or black pen in the spaces provided.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.
DO NOT WRITE IN ANY BARCODES.

You may lose marks if you do not show your working, if you do not include appropriate units or if you do not give your answer to appropriate significant figures.
A Data Booklet is provided.

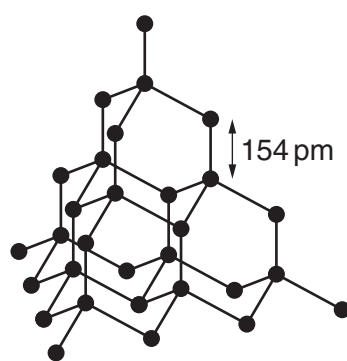
At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [] at the end of each question or part question.
Electronic calculators may be used.

The syllabus is approved for use in England, Wales and Northern Ireland as a Cambridge International Level 3 Pre-U Certificate.

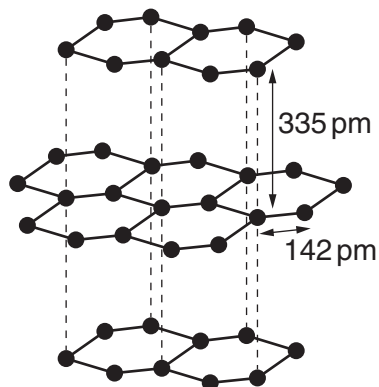
This document consists of **19** printed pages and **1** blank page.



1 The structures of two allotropes of carbon are shown.



diamond



graphite

(a) With reference to these structures

(i) explain the meaning of the term *allotropes*,

.....

[1]

(ii) state how and explain why the hardness and electrical conductivity of these allotropes differ.

.....

[4]

(b) In 2010 the Nobel Prize for Physics was awarded to two researchers from Manchester University for their work on preparing graphene from graphite.

(i) Describe the structure of graphene.

.....
[1]

- (ii) Graphene can be prepared from graphite by using sticky tape. Use your knowledge of the bonding in graphite to explain why it is possible to create graphene by this method.

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

- (c) Group 14 is considered to represent a spectrum of behaviour ranging from non-metal at the top of the Group, through metalloid, to true metal at the bottom.

With reference to

- the electrical conductivity of the element,
- the structure and bonding in the oxides,

justify this statement.

.....
.....
.....
.....
.....
.....
.....[3]

- (d) Here is some information about Group 14 oxides.

Tin(IV) oxide, SnO_2 , is easily prepared by oxidation of tin but lead(IV) oxide, PbO_2 , can only be prepared by the action of very powerful oxidising agents on lead(II) compounds.

PbO_2 decomposes on heating to lead(II) oxide, PbO .

PbO can also be prepared by heating lead in air but SnO is sensitive to oxidation.

Explain this information.

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

[Total: 12]

- 2 (a) When aqueous barium chloride is added to a solution containing sulfate ions a white precipitate of barium sulfate is formed. This white precipitate is very sparingly soluble in water.

(i) Write the **ionic** equation, including state symbols, for the formation of the white precipitate.

..... [1]

(ii) Write the expression for the solubility product, K_{sp} , of barium sulfate.

[1]

(iii) Given that the value of K_{sp} for barium sulfate is 1.08×10^{-10} at 298K, calculate the concentration of sulfate ions in a saturated solution of barium sulfate. Give your answer to **three** significant figures.

..... mol dm^{-3} [2]

(iv) Regulations state that the maximum permitted level of sulfate ions in drinking water is 250 mg dm^{-3} ($1 \text{ mg} = 1 \times 10^{-3} \text{ g}$).

200 cm^3 of aqueous barium chloride solution was added to 300 cm^3 of drinking water and a white precipitate formed. Assume that the sample of water contained the maximum permitted level of sulfate ions. Calculate the minimum concentration, in mol dm^{-3} , of barium chloride in the solution that was added to the sample of drinking water.

..... mol dm^{-3} [3]

- (b) The electrode potential of silver in contact with a solution of silver ions, $\text{Ag}^+(\text{aq})$, is impossible to measure directly but can be measured using a standard hydrogen electrode.

Using this method, the standard electrode potential of silver, E^\ominus , is found to be +0.80 V.

- (i) Complete the cell diagram for the cell used to measure the standard electrode potential of silver. State the concentration of $\text{H}^+(\text{aq})$ used.

..... | $\text{H}_2(\text{g})$ | $2\text{H}^+(\text{aq})$ ||

concentration of $\text{H}^+(\text{aq})$ = mol dm^{-3} [3]

- (ii) When an excess of sodium chloride solution is added to the right-hand half-cell the silver ions will be precipitated as solid silver chloride, AgCl . Use Le Chatelier's principle to explain qualitatively how the cell emf will change as a result.

.....

 [2]

- (iii) At 298 K, the expression below can be used to calculate the concentration of silver ions in solution under non-standard conditions, from a measurement of the electrode potential.

$$E = E^\ominus - 0.030 \log \frac{1}{[\text{Ag}^+(\text{aq})]^2}$$

E = electrode potential of silver under non-standard conditions

E^\ominus = standard electrode potential of silver = +0.80 V

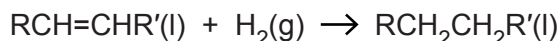
The addition of excess aqueous sodium chloride, $\text{NaCl}(\text{aq})$, to the right-hand half-cell results in a chloride ion concentration of 2.1 mol dm^{-3} .

Given that K_{sp} for silver chloride, AgCl , is 1.8×10^{-10} at 298 K, calculate the value of E , in the cell shown in (b)(i), after the addition of the excess aqueous sodium chloride to the right-hand half-cell.

E = V [3]

[Total: 15]

- 3 (a) The reaction shown represents the hydrogenation of a vegetable oil.



This reaction can be catalysed by several different transition metals and gives an example of heterogeneous catalysis.

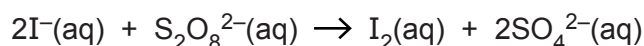
State the three stages involved in a typical reaction involving a heterogeneous catalyst.

1.

2.

3. [1]

- (b) An example of homogeneous catalysis is the use of iron(II) ions or iron(III) ions to catalyse the reaction between iodide ions and peroxodisulfate ions, $\text{S}_2\text{O}_8^{2-}$, as shown.



The relevant half-equations and standard electrode potentials are given in the table.

| half-equation | E^\ominus / V |
|--|------------------------|
| $\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{SO}_4^{2-}(\text{aq})$ | +2.01 |
| $\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$ | +0.77 |
| $\text{I}_2(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{I}^-(\text{aq})$ | +0.54 |

- (i) What is meant by the term *homogeneous catalysis*?

.....
 [1]

- (ii) Use the standard electrode potentials given to calculate the standard cell potential, E_{cell}^\ominus , for the reaction between iodide ions and peroxodisulfate ions.

..... V [1]

- (iii) Use your answer from (b)(ii) to calculate the standard Gibbs energy change, $\Delta_r G^\ominus$, of the reaction between iodide ions and peroxodisulfate ions. Give the sign and units in your answer.

..... [2]

- (iv) Explain how your answer to (b)(iii) confirms that the reaction between iodide ions and peroxodisulfate ions shown in (b) represents the feasible direction of reaction.

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

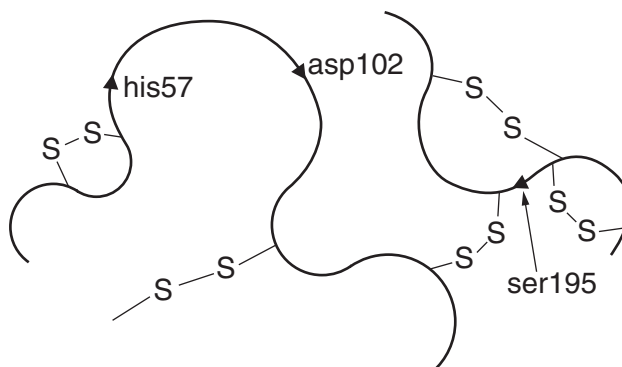
- (v) State and explain why, despite being feasible, the reaction between iodide ions and peroxodisulfate ions is not seen to occur in the absence of a catalyst.

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

- (vi) By constructing suitable equations from the data given, explain why the reaction between iodide and peroxodisulfate can be catalysed by either iron(II) or iron(III) ions.

.....
.....
.....
.....
.....
.....[3]

- (c) Part of the structure of chymotrypsin, an enzyme produced by the pancreas that is responsible for catalysing the hydrolysis of certain proteins in the small intestine during the digestive process, is shown.

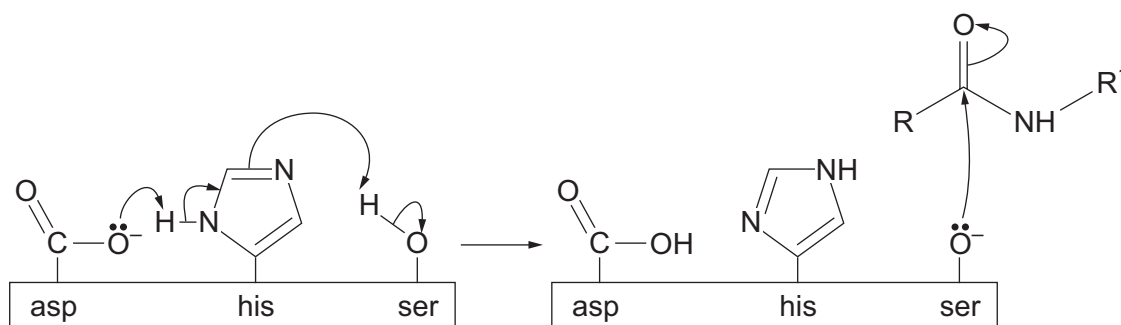


The three main amino acids involved in the catalytic activity of the enzyme are labelled as his57, asp102 and ser195.

- (i) What is the name of the region of the enzyme molecule that contains the three labelled amino acids and interacts with the protein being hydrolysed?

.....[1]

The first stage of the mechanism of action of chymotrypsin is illustrated.



- (ii) Explain what is represented by a curly arrow as used in the mechanism shown.

.....[1]

- (iii) Name the type of acid-base behaviour shown by the O^- in serine in its interaction with the protein chain.

..... [1]

- (iv) With reference to the illustration of the mechanism, explain why the action of chymotrypsin would be inhibited if the pH was too low.

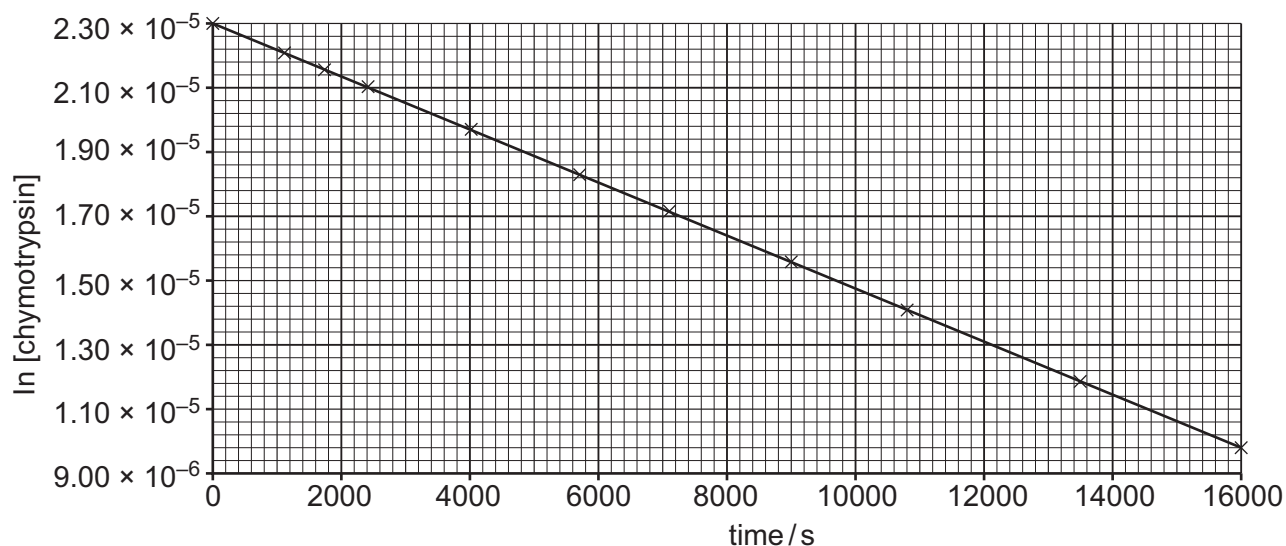
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.....

.....[2]

(v) Chymotrypsin is denatured by sodium hydroxide, with the mechanism dependent on the pH.

- At pH12 the reaction is first order with respect to both the chymotrypsin and the hydroxide.
- In the presence of excess alkali the denaturation of the enzyme was monitored.
- The plot of the time course of the reaction is shown.



The first order rate equation given in the *Data Booklet* can be rewritten.

$$\ln C_t = -kt + \ln C_0$$

Given that this equation is in the form $y = mx + c$, explain how the plot of the time course of the reaction confirms that the denaturation is first order with respect to chymotrypsin and how the conditions chosen give rise to first order kinetics overall.

.....

.....

.....

.....[2]

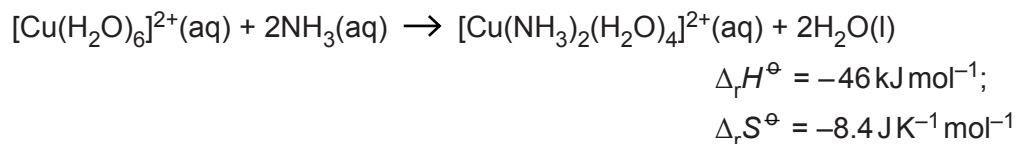
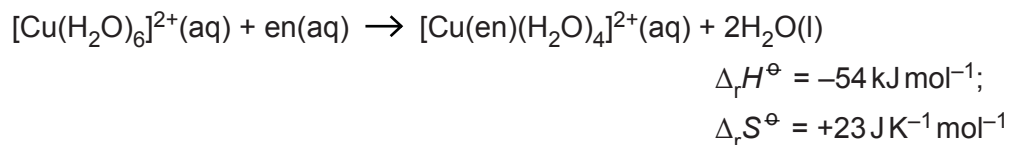
(vi) Use the plot of the time course of the reaction to calculate the value of the first order rate constant for this denaturation.

$k =$ [2]

[Total: 20]

- 4 The familiar light blue colour of copper(II) sulfate solution is due to the presence of the hexaaquacopper(II) ion, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$.

Equations for two different partial ligand substitution reactions of the hexaaquacopper(II) ion are shown. In the first of these equations 'en' represents diaminoethane, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$.



- (a) Explain why the enthalpy changes, $\Delta_r H^\ominus$, of the two partial ligand substitution reactions shown are so similar.

.....

.....

.....

.....[2]

- (b) Comment on the values of the entropy changes, $\Delta_r S^\ominus$, of the two partial ligand substitution reactions shown and explain why they are different.

.....

.....

.....

.....[2]

- (c) The cation produced in the reaction with ammonia, NH_3 , can exist as two different isomers.

- (i) State the type of isomerism exhibited by this cation.

.....[1]

- (ii) Draw and label the two different isomers of this cation.

[2]

(d) Further ligand substitution leads to the production of the complex ion $[\text{Cu}(\text{en})_3]^{2+}$, which also exhibits isomerism.

(i) State the type of isomerism exhibited by $[\text{Cu}(\text{en})_3]^{2+}$.

.....[1]

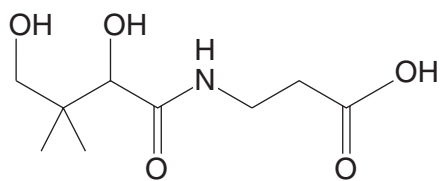
(ii) Draw 3-D representations of the two isomers of $[\text{Cu}(\text{en})_3]^{2+}$.

[2]

[Total: 10]

- 5 Pantothenic acid, vitamin B₅, is a water-soluble vitamin needed to form coenzyme-A (CoA), and it is critical in the metabolism and synthesis of carbohydrates, proteins and fats.

The skeletal formula of pantothenic acid is shown.



- (a) Name fully all the functional groups present in a molecule of pantothenic acid.

.....

 [4]

- (b) Give the structures of the organic products that would be formed if pantothenic acid was

- (i) hydrolysed by reaction with aqueous acid,

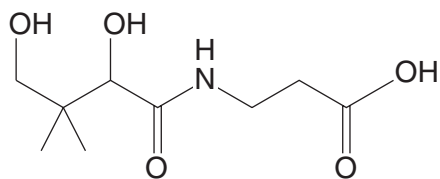
[2]

- (ii) reacted with sodium metal.

[2]

- (c) Pantothenic acid is a chiral molecule and the full name of the biologically active form includes the prefixes *R* and (+).

(i) Draw a circle around the chiral carbon in the molecule of pantothenic acid shown.



[1]

(ii) Explain the meaning of each of the prefixes in the name *R*-(+)-pantothenic acid.

(+)

.....

R

.....

.....

.....[3]

- (d) The value of the acid dissociation constant, K_a , for pantothenic acid is 3.98×10^{-5} , whilst that for propanoic acid is 1.32×10^{-5} .

(i) Calculate the pH of a 0.20 mol dm^{-3} solution of pantothenic acid.

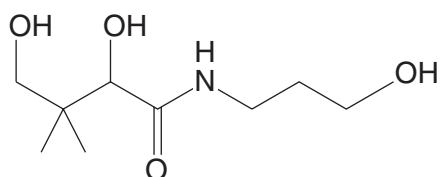
pH =[3]

- (ii) The inductive effect can be used to account for the difference in the acid dissociation constants of pantothenic acid and propanoic acid. Explain why.

.....

[3]

- (e) A derivative of pantothenic acid, pantothenol, is a more stable form of the vitamin. It is often used in multivitamin supplements as it is converted to pantothenic acid in the body. Its structure is shown.



The structural formula of pantothenol is $\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{CHOHCONH}(\text{CH}_2)_3\text{OH}$ and its molecular formula is $\text{C}_9\text{H}_{19}\text{NO}_4$.

- (i) With reference to the idea of functional group level, explain what type of reaction is involved in the conversion of pantothenol into pantothenic acid.

.....

[2]

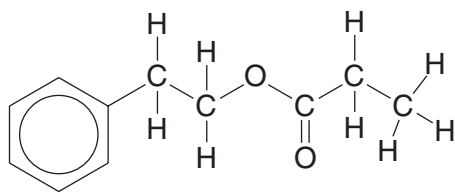
- (ii) Give the structural formula of the organic product of the reaction of pantothenol with ethanoyl chloride.

- (iii) Complete and balance the equation below for the reaction of pantothenol with ethanoyl chloride, using **molecular formulae** for the products.

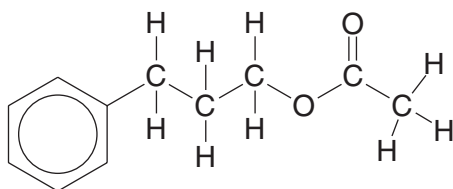


[Total: 23]

6 The structures of a pair of isomers are shown.



isomer 1



isomer 2

(a) Give the molecular formula of these isomers.

.....[1]

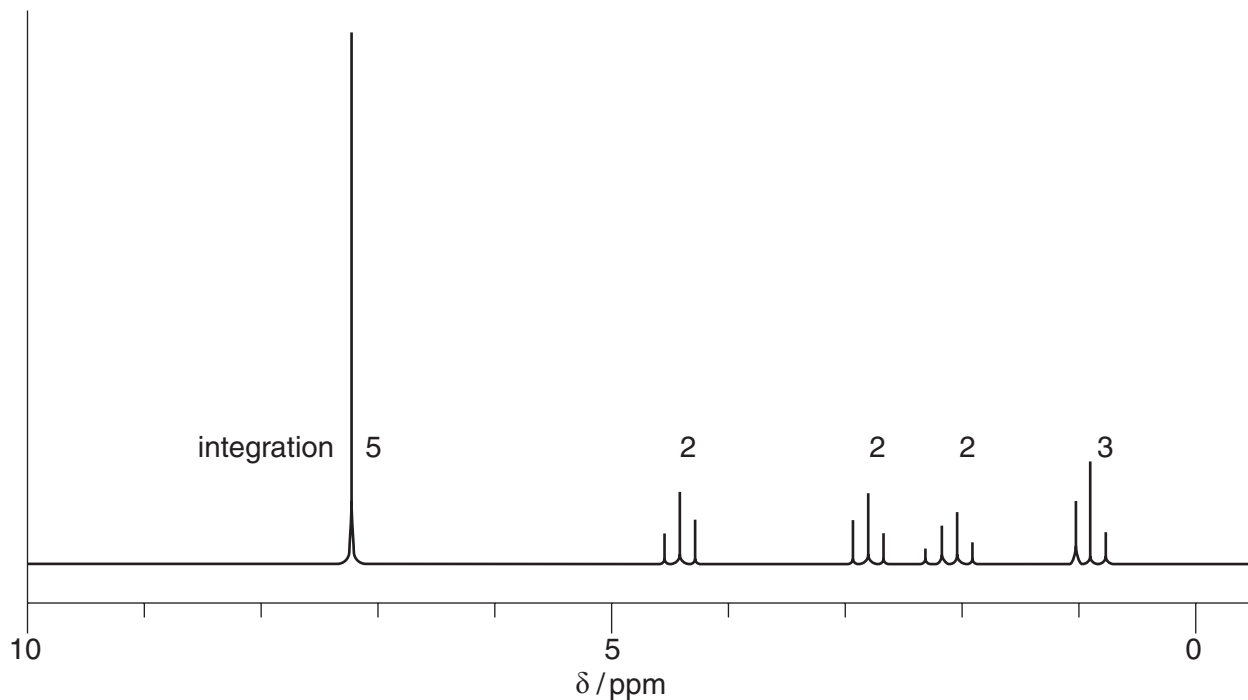
(b) What type of isomerism is shown by these two isomers?

.....[1]

(c) Isomer 1 is called 2-phenylethyl propanoate. Give the name of isomer 2.

.....[1]

(d) The ^1H NMR spectrum of one of the isomers is shown.

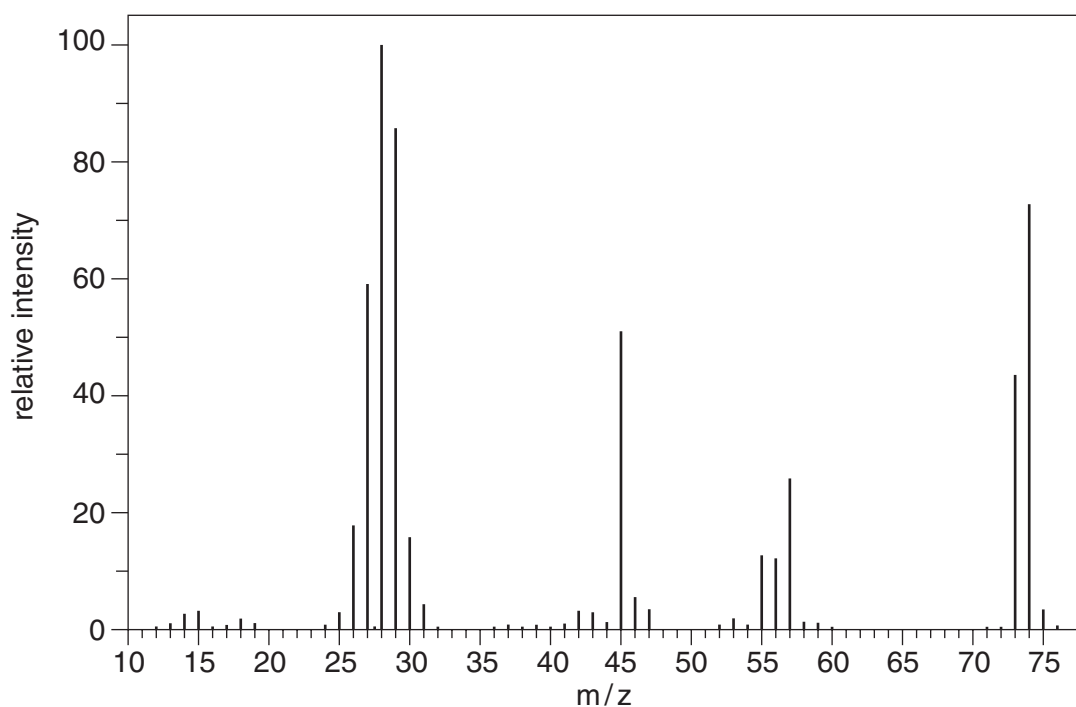


Explain which of isomers 1 or 2 corresponds to the ^1H NMR spectrum shown. You should refer to the splitting patterns and integration values of **all** the peaks in your answer. Note that the phenyl group protons appear as a single peak.

[6]

(e) **X** and **Y** are two compounds that can be made by hydrolysis of isomer 1.

X has the composition by mass C, 48.6%; H, 8.11%; O, 43.2%. The mass spectrum of **X** is shown.



(i) Calculate the empirical formula of **X**.

empirical formula of **X**[2]

(ii) Deduce the molecular formula of **X**.

molecular formula of **X**[1]

(iii) Identify the particle responsible for the peak at m/z 45.

.....[2]

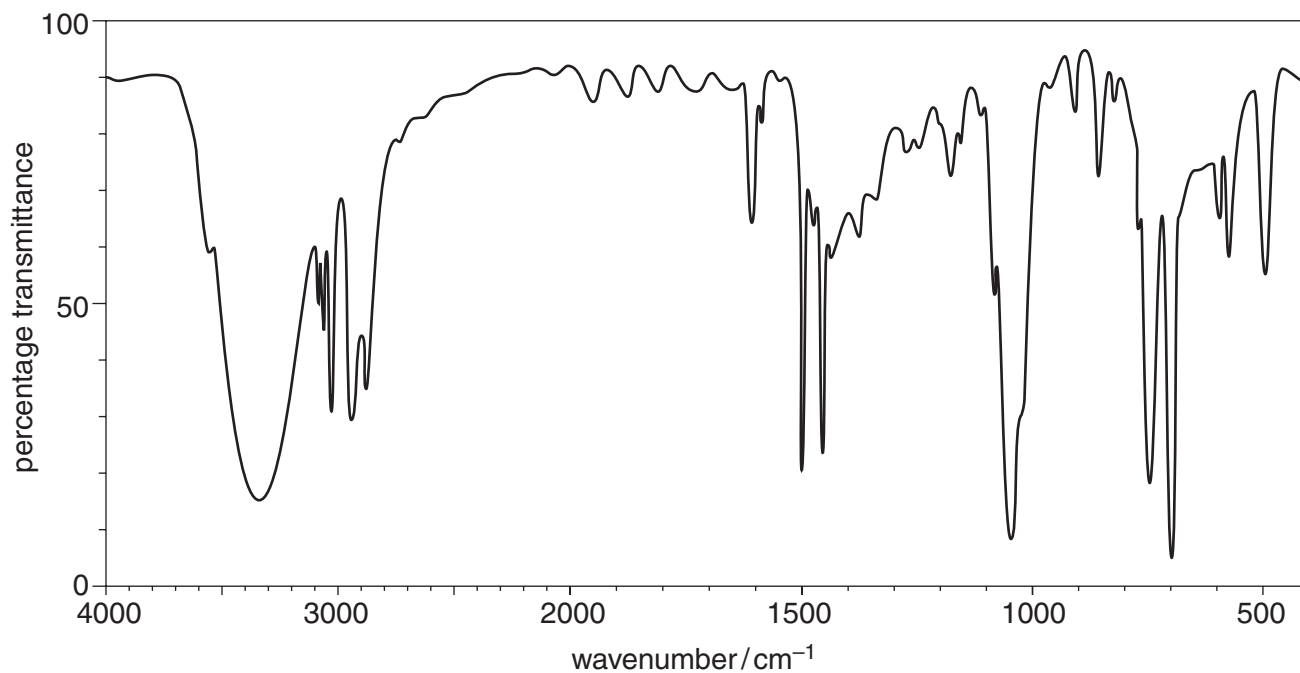
(iv) Explain the origin and relative intensity of the peak at m/z 75.

.....

.....

.....[2]

(f) The IR spectrum of **Y** is shown.



(i) Show the structure of **Y** and explain how the IR spectrum confirms the identity of the functional group present.

.....

 [2]

(ii) Show the structure of **X** and explain how its spectrum will compare to that of **Y**.

.....

 [2]

[Total: 20]

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