

**ADVANCED GCE
CHEMISTRY (SALTERS)**

Chemistry by Design

THURSDAY 19 JUNE 2008

2854/01

Morning
Time: 2 hours

Additional materials: Scientific calculator
Data Sheet for Chemistry (Salters) (Inserted)



Candidate Forename

Candidate Surname

Centre Number

Candidate Number

INSTRUCTIONS TO CANDIDATES

- Write your name in capital letters, your Centre Number and Candidate Number in the boxes above.
- Use blue or black ink. Pencil may be used for graphs and diagrams only.
- Read each question carefully and make sure that you know what you have to do before starting your answer.
- Answer **all** the questions.
- Do **not** write in the bar codes.
- Write your answer to each question in the space provided.

INFORMATION FOR CANDIDATES

- The number of marks for each question is given in brackets [] at the end of each question or part question.
- The total number of marks for this paper is **120**.
- You will be awarded marks for the quality of written communication where this is indicated in the question.
- You may use a scientific calculator.
- You may use the *Data Sheet for Chemistry (Salters)*.
- You are advised to show all the steps in any calculations.

FOR EXAMINER'S USE

Qu.	Max.	Mark
1	33	
2	20	
3	25	
4	22	
5	20	
TOTAL	120	

This document consists of **20** printed pages and a *Data Sheet for Chemistry (Salters)*.

Answer **all** the questions.

- 1 There are several ways in which nitrogen gas in the air (dinitrogen) is 'fixed' (turned into nitrogen compounds) for use in the soil. These include natural processes such as lightning and the action of nitrogen-fixing bacteria that occur in the root nodules of certain plants.

(a) (i) Write a chemical equation for the overall reaction that occurs in a lightning flash to oxidise dinitrogen. Show state symbols.

[2]

(ii) Name the compound that is formed in the reaction.

..... [1]

(b) (i) Draw a dot-cross diagram for a dinitrogen molecule, showing the outer shell electrons only.

[2]

(ii) Explain the feature of the dinitrogen molecule that accounts for its lack of reactivity.

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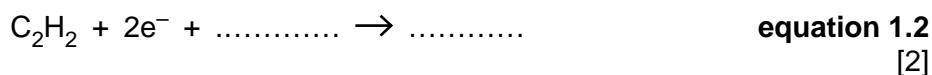
 [2]

(c) Chemists study the action of nitrogen-fixing bacteria. The enzymes in the bacteria catalyse the reaction shown below.



Chemists have discovered that the enzymes in these bacteria also catalyse the conversion of ethyne, C_2H_2 , to ethene.

(i) Complete the equation for the conversion of ethyne to ethene.



(ii) Suggest a full structural formula for ethyne and indicate the expected C–C–H bond angle in the molecule.

[2]

(d) The rate of reaction of a root nodule system with ethyne can be measured by leaving a portion of root nodule in ethyne. The gas mixture is sampled at intervals and analysed using a gas-liquid chromatograph. Ethene and ethyne show up on the detector trace.

(i) In this question, one mark is available for the quality of spelling, punctuation and grammar.

The sample is injected into the carrier gas stream and passes into the column of the gas-liquid chromatograph.

Describe:

- the contents of the column
- how the temperature of the column is maintained
- the measurement that distinguishes the gases.

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..... [4]

Quality of Written Communication [1]

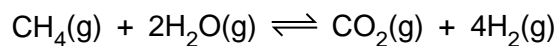
(ii) An experiment shows that a root nodule sample produces 1.3×10^{-5} g of ethene per second.

Use this result and the ratio of electrons in **equations 1.1** and **1.2** to calculate the equivalent rate of nitrogen fixation in **moles of dinitrogen per second**.

A_r : C, 12; H, 1.0

rate of nitrogen fixation = moles of dinitrogen per second [3]

- (f) The hydrogen required for the Haber process is produced by reacting natural gas and steam.



- (i) Write the equilibrium constant, K_p , for this reaction.

[2]

- (ii) The table below shows the composition of an equilibrium mixture at a particular temperature.

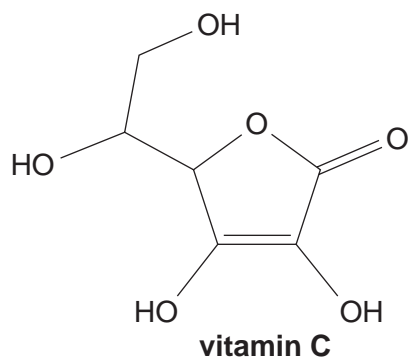
Use the data in the table to calculate a value of K_p for the reaction at that temperature and give its units.

substance	partial pressure/atm
CH ₄	0.0500
H ₂ O	0.0500
CO ₂	0.0020
H ₂	0.0040

$K_p = \dots\dots\dots$ units $\dots\dots\dots$ [3]

[Total: 33]

- 2 Vitamin C, 'ascorbic acid', is a powerful antioxidant in the body. It acts to remove the radicals that are thought to cause ageing. Its structure is shown below.

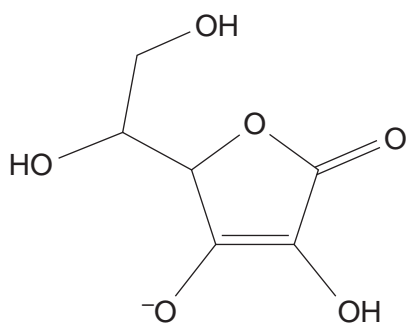


- (a) (i) Give the molecular formula of vitamin C.

..... [1]

- (ii) Circle a **primary alcohol** group on the structure above. [1]

- (b) In the bloodstream, vitamin C is present almost completely as the anion shown below.



- (i) In more alkaline conditions, vitamin C acts as a *diprotic acid*.

Suggest the hydrogen atom that is lost as a proton in more alkaline conditions. Circle this atom on the formula above. [1]

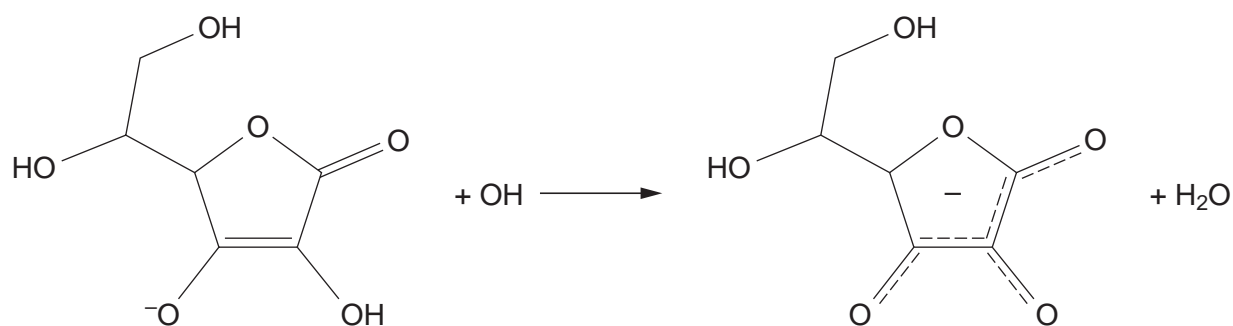
- (ii) The anion reacts with radicals to turn them into molecules.

For example, the anion reacts with OH radicals to form water.

Draw a dot-cross diagram for OH and explain why OH is described as a *radical*.

..... [2]

(iii) The reaction of vitamin C with an OH radical is shown below.



The dotted lines in the organic product indicate delocalised electrons.

Describe the meaning of the term *delocalised*.

.....
 [1]

(iv) Give the oxidation state of the oxygen in OH and H₂O, assuming that the oxidation state of hydrogen is the same in both.

OH H₂O [1]

(v) Ascorbic acid acts as an antioxidant in the reaction in (iii).

Use your answer to (iv) to suggest the meaning of the term *antioxidant*.

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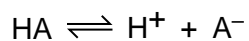
 [2]

(c) The rate constant for the reaction in b(iii) above is $1.0 \times 10^{10} \text{ mol dm}^{-3} \text{ s}^{-1}$.

What effect (if any) would raising the temperature have on the value of the rate constant?

..... [1]

(d) Vitamin C can be represented as an acid, HA.



equation 2.1

(i) Write the expression for the acidity constant, K_a , for **equation 2.1**.

[1]

(ii) Calculate the pH of a 0.10 mol dm^{-3} solution of vitamin C.

$$K_a = 7.9 \times 10^{-5} \text{ mol dm}^{-3}.$$

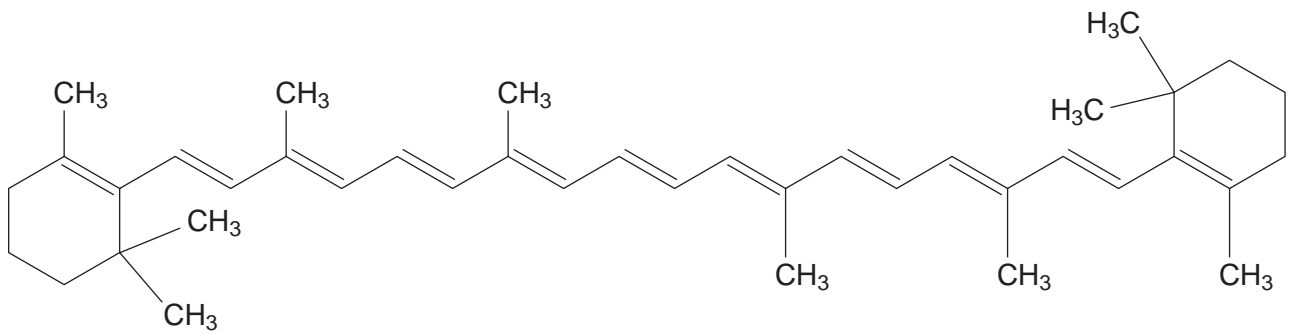
pH = [2]

(iii) Blood has a pH of 7.4

Use the expression $K_a = [\text{H}^+] \times [\text{salt}]/[\text{acid}]$ to calculate the ratio of $[\text{salt}]/[\text{acid}]$ in a solution of vitamin C at pH 7.4.

$[\text{salt}]/[\text{acid}] = \dots\dots\dots$ [2]

(e) Another antioxidant is beta-carotene, found in carrots.



beta-carotene

(i) Explain whether or not this compound is an *arene*.

.....
 [1]

(ii) Beta-carotene is bright red. Explain why a red substance looks red.

.....

 [2]

(iii) Explain, in terms of energy levels, why the beta-carotene molecule is coloured.

.....

 [2]

[Total: 20]

- 3 Sea water contains an appreciable concentration of sulphate ions. These ions cause problems in underwater oil drilling operations when they come into contact with water containing barium ions. The barium sulphate that precipitates can plug the mouths of the holes that have been drilled.

(a) Write the formula of the most common **anion** in sea water.

..... [1]

(b) The oceans contain 35 g dm^{-3} of salts. 7.7% of the total salts by mass is sulphate, SO_4^{2-} .

Show by calculation that the sulphate concentration in sea water is $2.8 \times 10^{-2} \text{ mol dm}^{-3}$.

A_r : S, 32; O, 16

[2]

(c) The solubility product of barium sulphate is $1.0 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$.

(i) Write the expression for the solubility product K_{sp} in terms of concentrations.

[2]

(ii) Calculate the maximum concentration of barium ions that can remain in solution without giving a precipitate of barium sulphate in sea water.

Give your answer to an **appropriate** number of significant figures.

concentration = mol dm^{-3} [3]

- (f) Many salts with a positive enthalpy change of solution are readily soluble in water.

Explain this in terms of ΔS_{tot} , ΔS_{sys} and ΔS_{surr} for the dissolving process.

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..... [4]

- (g) Oil wells are described as 'sour' when bacteria turn sulphate ions into hydrogen sulphide. This is because of the smell of the gas.

- (i) Give the oxidation states of sulphur in sulphate and hydrogen sulphide.

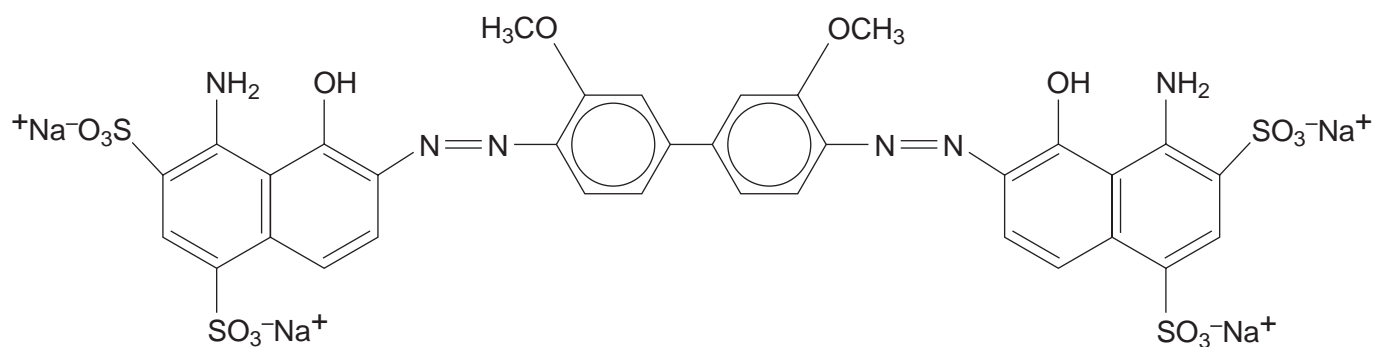
SO_4^{2-} H_2S [2]

- (ii) Complete the half-equation for the reduction of sulphate to hydrogen sulphide.

$\text{SO}_4^{2-} + \dots \text{H}^+ + \dots \rightarrow \text{H}_2\text{S} + \dots$ [3]

[Total: 25]

4 The dye *Direct Blue I* is an azo dye used to dye cotton.



Direct Blue I

(a) Name **three** functional groups in Direct Blue I, apart from azo groups and arene rings.

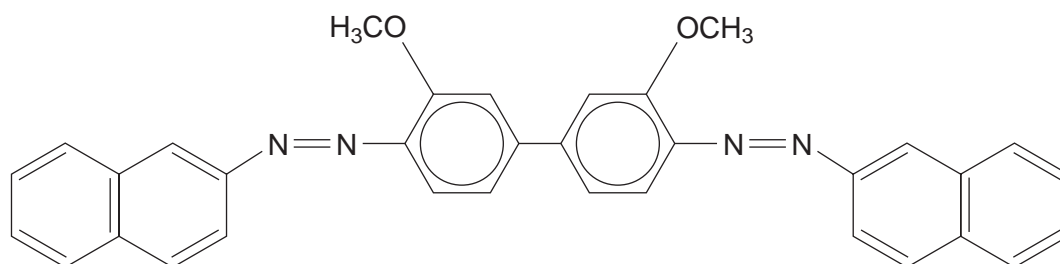
.....

.....

..... [3]

(b) (i) Direct Blue I is dissolved in sodium hydroxide solution.

Complete the structure below to show the ion that would form.



[3]

(ii) Suggest, with a reason, whether the action of sodium hydroxide on Direct Blue I would change its colour.

.....

..... [1]

(c) Direct Blue I is soluble in water.

Write the formula for the functional group that is most responsible for this.

Explain how this group aids the solubility.

The structure of Direct Blue I is shown on page 15 opposite.

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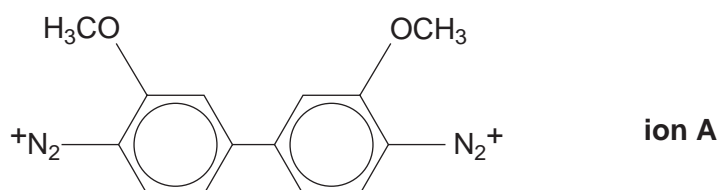
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..... [4]

(d) Direct Blue I can be made by reacting **ion A**, below, with another substance.



(i) Name the functional group that is present in **ion A** that is not present in Direct Blue I.

..... [1]

(ii) **Compound B** reacts with **ion A** to form Direct Blue I.

Draw the structure of **compound B**.

[1]

- (iii) Name the **type** of reaction in which an azo dye is made by reacting **ion A** with **compound B**.

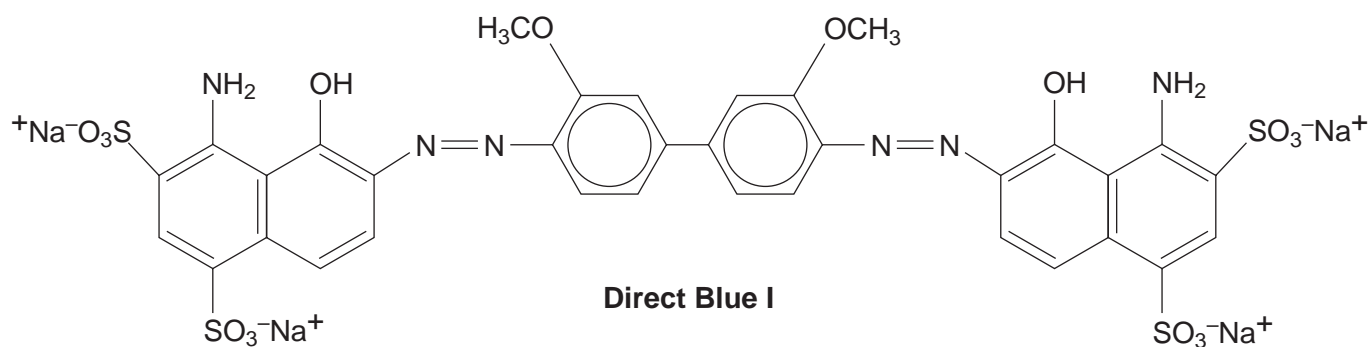
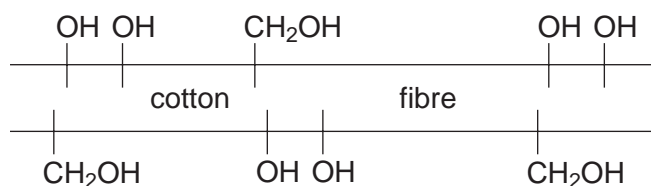
Also name the mechanism by which this reaction proceeds.

name of type of reaction [1]

name of mechanism

..... [2]

- (e) Direct dyes are used to dye cotton. The simplified structure of cotton and the structure of Direct Blue I are represented below.

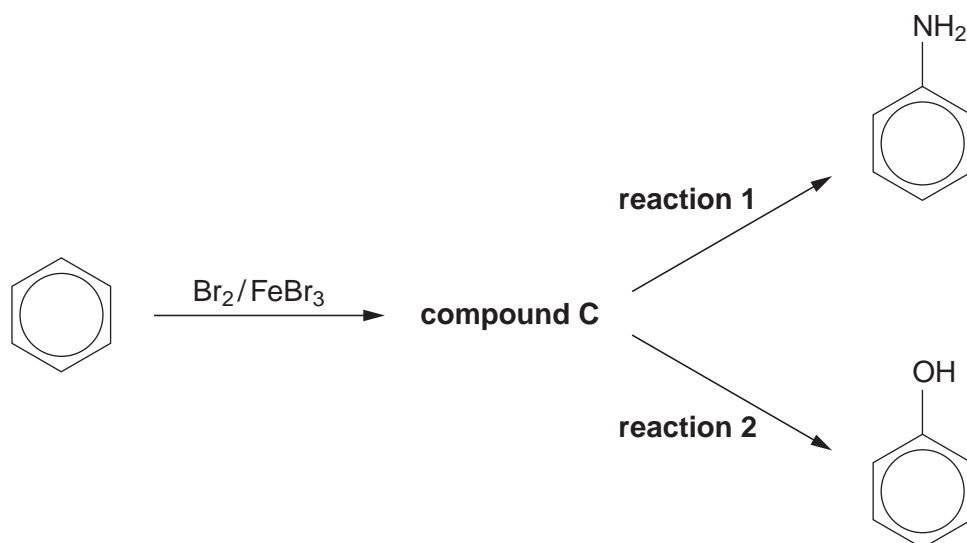


- (i) Suggest the strongest type of intermolecular force that holds Direct Blue I and cotton together.

..... [1]

- (ii) On the structures shown above, indicate **two** places where these intermolecular forces link Direct Blue I and cotton. [2]

- (f) It is not possible to substitute an -NH_2 group or an -OH group on to an arene ring directly. A student suggested using the reaction sequences below.



- (i) Give the **name** of **compound C**.

..... [1]

- (ii) Suggest possible **reagents** for **reactions 1** and **2**.

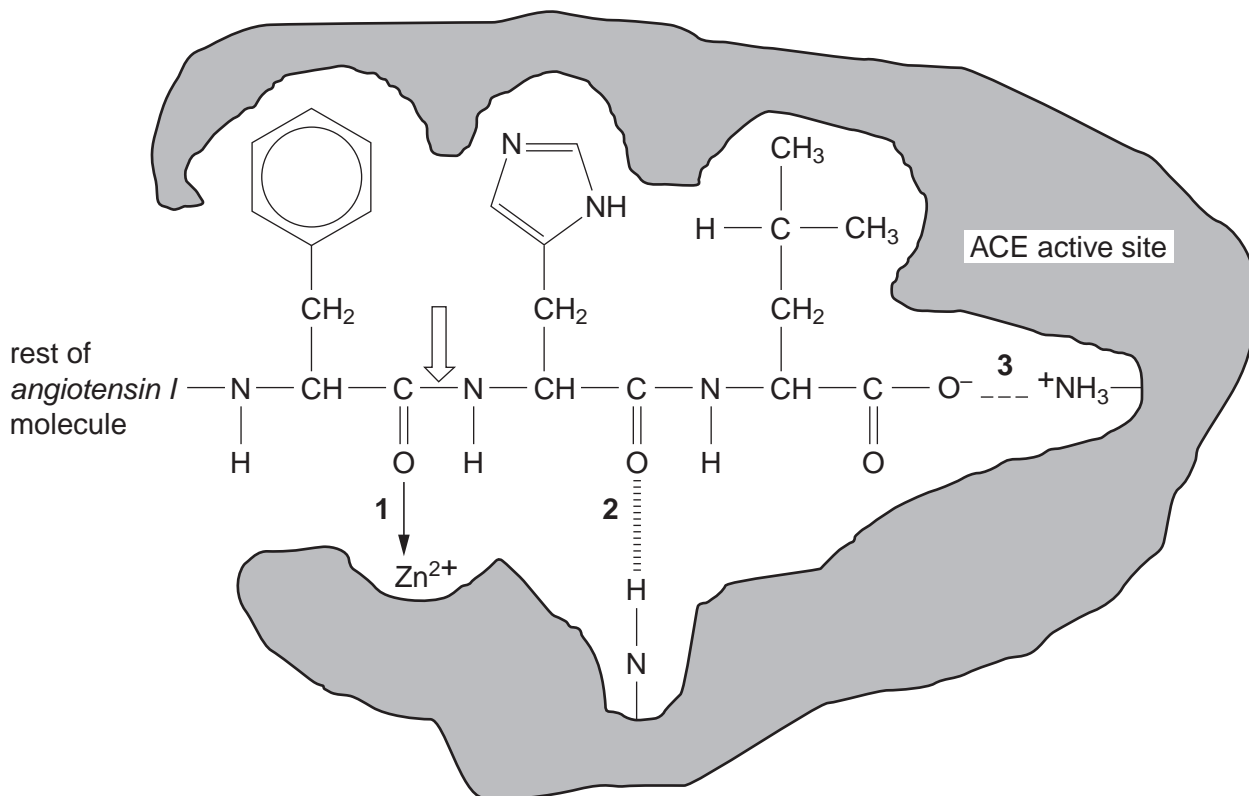
reaction 1

reaction 2 [2]

[Total: 22]

- 5 It has been discovered that high blood pressure is caused by an imbalance in the production of *angiotensin II*, a small peptide, in the body. *Angiotensin II* is made from *angiotensin I* by the action of an enzyme known as *ACE*.

The diagram shows one end of an *angiotensin I* molecule bound to the active site of *ACE*.



- (a) (i) The reaction that occurs when *angiotensin I* is turned into *angiotensin II* involves breaking the bond shown by an open arrow (\rightleftharpoons) on the structure.

Classify this bond-breaking reaction by circling **one** of the words in the list below.

condensation **elimination** **hydrolysis** **oxidation** **reduction** [1]

- (ii) Name the types of bond or intermolecular force that are represented at **1**, **2** and **3** on the diagram.

1

2

3 [3]

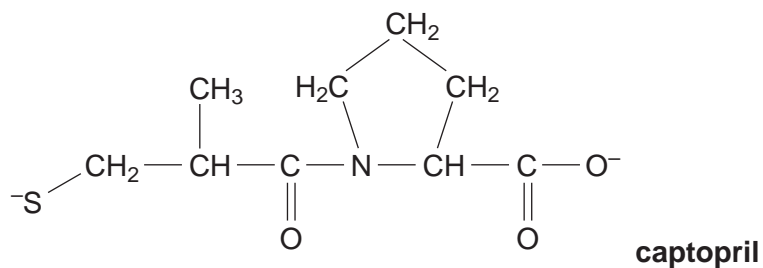
- (b) *ACE* inhibitors were found to be small peptides.

Suggest why peptides do not form effective medicines when swallowed.

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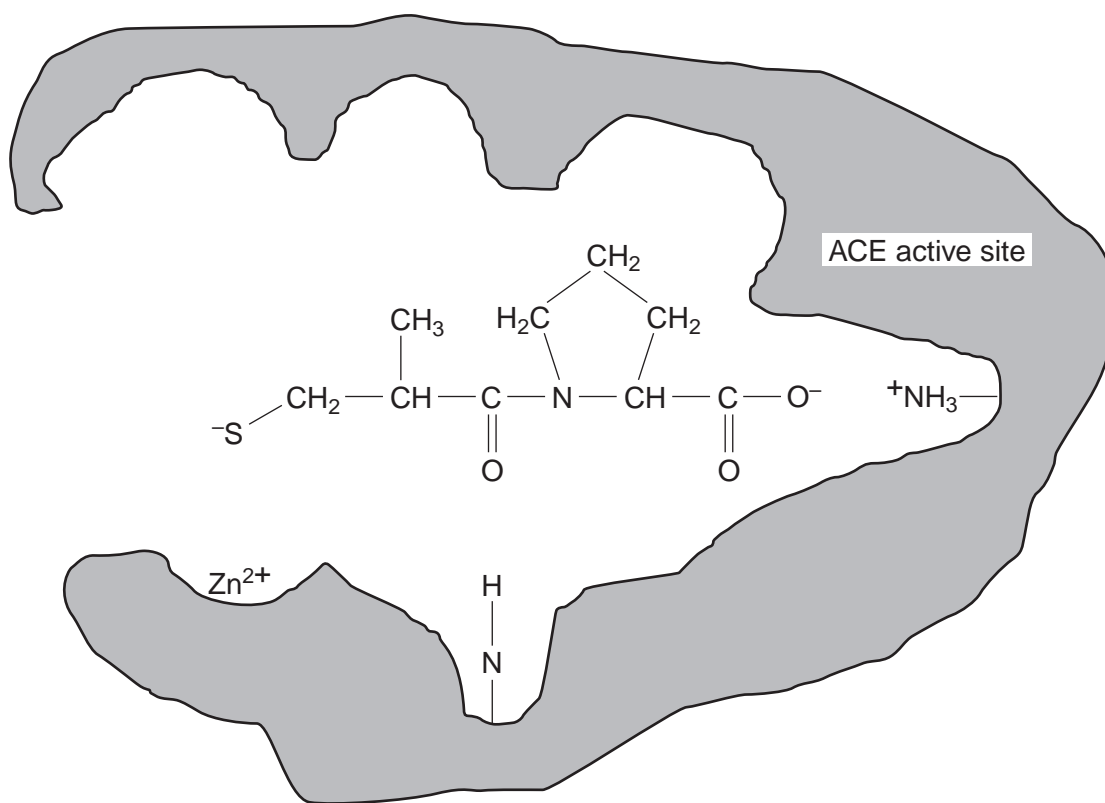
..... [1]

(c) A medicine called *captopril* reduces the blood pressure by inhibiting *ACE*.



- (i) Circle an *amide* group on the structure of captopril. [1]
- (ii) *Captopril* fits into the active site of *ACE* by forming bonds or intermolecular forces with the three groups shown on the active site.

Show these bonds or intermolecular forces by dashed lines (-----) in the diagram below.



[2]

- (iii) Suggest why the *captopril* molecule does not break down on the active site and thus why it **inhibits** the action of *ACE*.

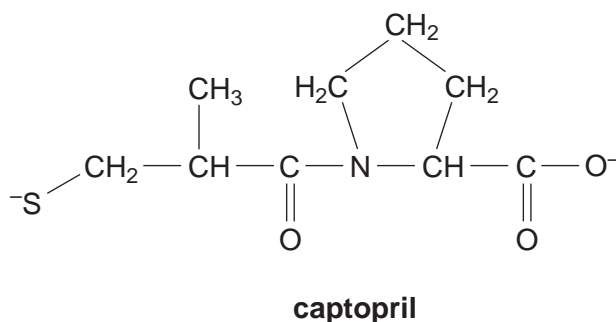
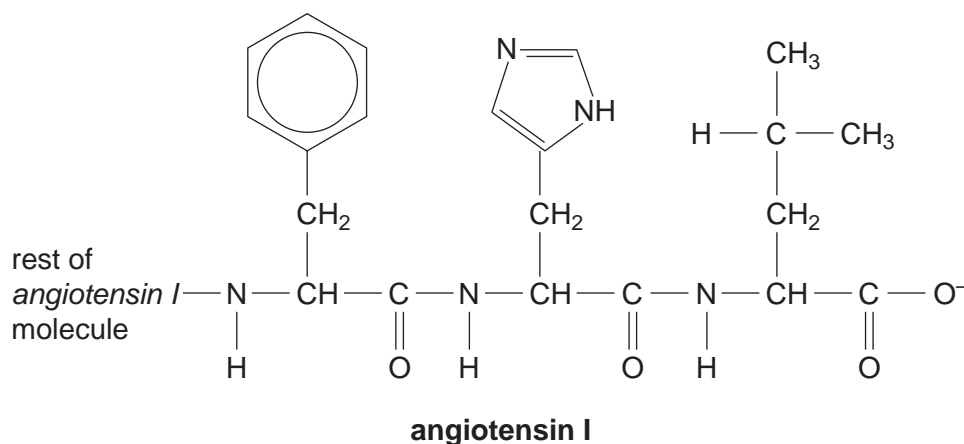
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..... [3]

19



- (iv) The infrared spectra of *angiotensin I* and *captopril* are compared. In the table below give details of **one** peak that would appear in **both** spectra and **one** peak that is in the **angiotensin I** spectrum only.

	bond causing peak	absorption/cm ⁻¹
peak in both spectra		
peak in <i>angiotensin I</i> spectrum only		

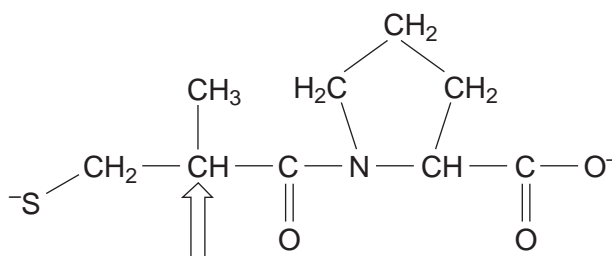
[2]

- (v) The n.m.r. spectrum of **captopril** was examined. Signals were found at chemical shifts (among others) of 1.2 and 1.4.

In the table below, give details of the protons causing these shifts and the ratio of their intensities.

shift	proton	ratio of intensities
1.2		
1.4		

[3]



captopril

- (vi) The carbon atom indicated by the arrow in the captopril structure gives rise to a certain type of isomerism.

Name this type of isomerism and explain how it arises.

name

how it arises

.....

.....

..... [3]

- (vii) Scientists developing captopril needed a technique that would enable them to study the shape and charge density of the active site.

Suggest the technique they used.

..... [1]

[Total: 20]

END OF QUESTION PAPER