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CHEMISTRY

9701/42

Paper 4 Structured Questions

October/November 2015

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name 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.

DO **NOT** WRITE IN ANY BARCODES.

Section A

Answer **all** questions.

Section B

Answer **all** questions.

Electronic calculators may be used.

You may lose marks if you do not show your working or if you do not use appropriate units.

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.

For Examiner's Use	
1	
2	
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8	
9	
10	
Total	

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

Section A

Answer **all** the questions in the spaces provided.

- 1 (a) Calcium has atomic number 20.

Complete the electronic structures for a

calcium atom, $1s^2 2s^2 2p^6$

calcium ion in the +2 oxidation state. $1s^2 2s^2 2p^6$

[1]

- (b) Calcium nitrate, $\text{Ca}(\text{NO}_3)_2$, is used in fertilisers and can be prepared by an acid-base reaction.

Write an equation for the preparation of calcium nitrate by an acid-base reaction.

..... [1]

- (c) (i) When anhydrous calcium nitrate is heated strongly, it decomposes to leave a white solid.

Identify this white solid and suggest **another** observation for this reaction.

.....

..... [1]

- (ii) The ease of thermal decomposition of the Group II nitrates **decreases** down the group.

Explain this trend.

.....

.....

..... [2]

- (d) (i) What is meant by the term *standard enthalpy change of hydration*, $\Delta H_{\text{hyd}}^{\ominus}$?

.....

 [2]

- (ii) Use the following data to calculate the lattice energy, $\Delta H_{\text{latt}}^{\ominus}$, of calcium nitrate, $\text{Ca}(\text{NO}_3)_2(\text{s})$. You may find it helpful to construct an energy cycle.

enthalpy change	value
$\Delta H_{\text{hyd}}^{\ominus} (\text{Ca}^{2+}(\text{g}))$	$-1650 \text{ kJ mol}^{-1}$
$\Delta H_{\text{hyd}}^{\ominus} (\text{NO}_3^{-}(\text{g}))$	-314 kJ mol^{-1}
enthalpy change of solution for $\text{Ca}(\text{NO}_3)_2(\text{s})$	-19 kJ mol^{-1}

$$\Delta H_{\text{latt}}^{\ominus} \text{Ca}(\text{NO}_3)_2(\text{s}) = \dots\dots\dots \text{kJ mol}^{-1} \quad [3]$$

- (e) The standard enthalpy change of hydration for Ba^{2+} , $\Delta H_{\text{hyd}}^{\ominus} (\text{Ba}^{2+}(\text{g}))$, is $-1305 \text{ kJ mol}^{-1}$.

Suggest an explanation for why the $\Delta H_{\text{hyd}}^{\ominus}$ of the Ba^{2+} ion is **less** exothermic than the $\Delta H_{\text{hyd}}^{\ominus}$ of the Ca^{2+} ion.

.....

 [2]

[Total: 12]

- 2 (a) Complete the table to show the number of **unpaired** electrons in the outer shell of each of the gaseous atoms, Na to Ar.

	Na	Mg	Al	Si	P	S	Cl	Ar
number of unpaired electrons								

[3]

- (b) (i) Complete the table for the reactions of two Period 3 chlorides with water.

Period 3 chloride	observations	pH of solution formed
SiCl_4		
PCl_5		

[3]

- (ii) Write an equation for the reaction between SiCl_4 and H_2O .

..... [1]

[Total: 7]

3 The transition element iron is the most abundant element in the Earth's core.

(a) What is meant by the term *transition element*?

.....
 [1]

(b) In aqueous solution, iron can form complex ions which contain ligands.

(i) Name the *type of bonding* that occurs between a ligand and a transition element.

..... [1]

(ii) Which of the following species can act as a ligand?

Complete the table by placing a tick (✓) in the appropriate column to indicate whether the species can act as a ligand or not.

species	can act as a ligand	cannot act as a ligand
NO_3^-		
BF_3		
$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$		
NH_4^+		

[2]

(c) Manganese ions, $\text{Mn}^{2+}(\text{aq})$, show some similar chemical properties to those of copper(II) ions, $\text{Cu}^{2+}(\text{aq})$.

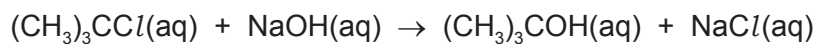
Use this information and the *Data Booklet* to suggest the formula of the manganese species formed in each of the following reactions. State the *type of reaction* taking place in each case.

	formula of manganese species formed	type of reaction
$\text{Mn}^{2+}(\text{aq}) + \text{NaOH}(\text{aq})$		
$\text{Mn}^{2+}(\text{aq}) + \text{concentrated HCl}$		
$\text{Mn}^{2+}(\text{aq}) + \text{H}_2\text{O}_2(\text{aq})$		

[5]

[Total: 9]

- 4 In aqueous solution, 2-chloro-2-methylpropane, $(\text{CH}_3)_3\text{CCl}$, reacts with sodium hydroxide, NaOH . This is a nucleophilic substitution reaction.

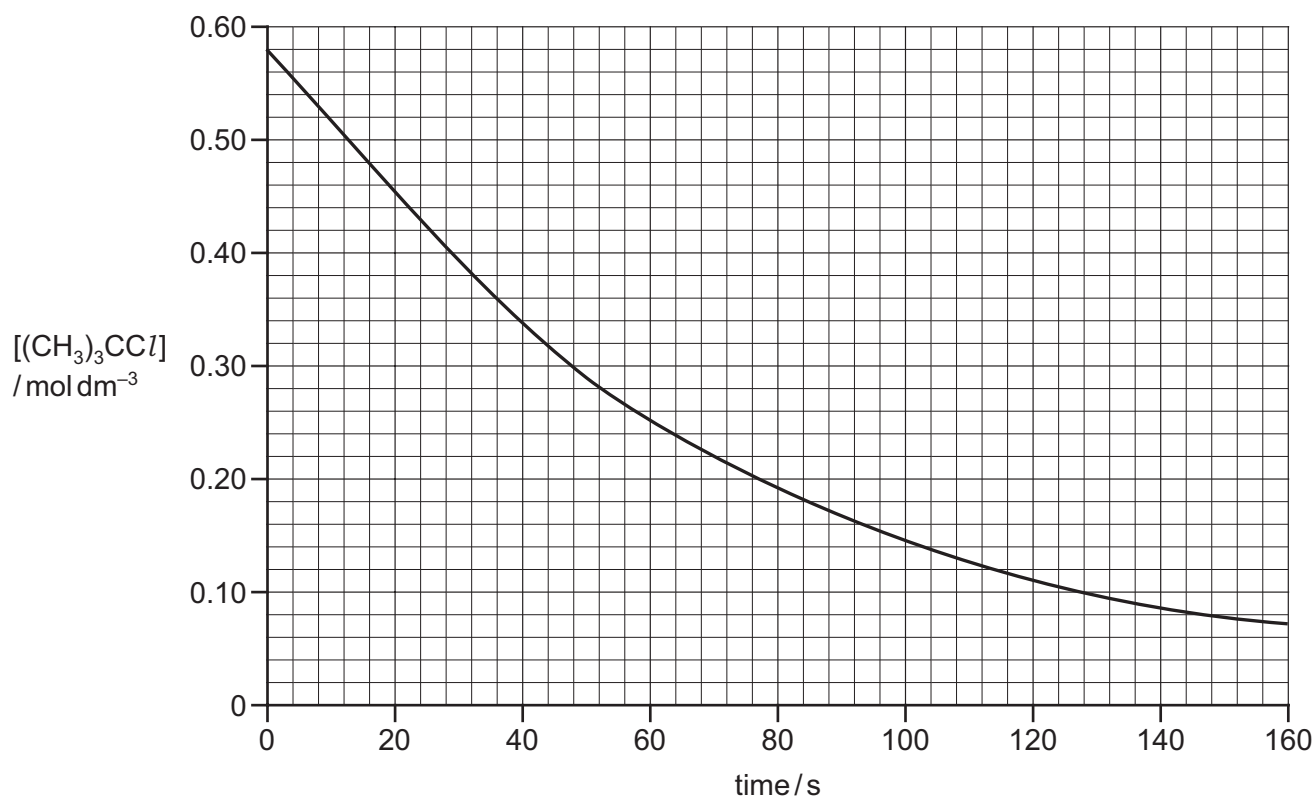


- (a) Show the mechanism for this reaction. Include all necessary curly arrows, lone pairs and relevant dipoles.

[3]

The rate of this reaction was investigated using a **large excess** of sodium hydroxide.

- (b) The graph below shows the results of the experiment.



The reaction is first order with respect to $[(\text{CH}_3)_3\text{CCl}]$. This can be confirmed from the graph using half-lives.

- (i) What is meant by the *half-life* of a reaction?

.....
 [1]

- (ii) Calculate the half-life for this reaction. Show all your working and show clearly any construction lines on the graph.

[1]

- (iii) What would be the effect on the half-life of this reaction if the initial concentration of $[(\text{CH}_3)_3\text{CCl}]$ was **doubled**?

..... [1]

- (c) (i) Use the graph in (b) to determine the rate of reaction at 80 s.
 Show all your working.

rate = units [2]

The rate equation for this reaction is shown.

$$\text{rate} = k[(\text{CH}_3)_3\text{CCl}]$$

- (ii) Calculate the value of the rate constant, k , for this reaction and give its units.

k = units [1]

[Total: 9]

5 X is a metallic element.

- (a) (i) Draw a fully labelled diagram to show how the standard electrode potential, $E^\ominus$, of $X^{2+}(aq)/X(s)$ could be measured.

[4]

- (ii) What are the conditions needed for the value measured to be a **standard** electrode potential?

..... [1]

- (iii) State the charge carriers that transfer current through

the solutions, the wire. [1]

(b) An electrochemical cell was set up consisting of an $\text{X}^{2+}(\text{aq})/\text{X}(\text{s})$ half-cell ($E^\ominus = -0.40\text{ V}$) and an $\text{Ag}^+(\text{aq})/\text{Ag}(\text{s})$ half-cell ($E^\ominus = +0.80\text{ V}$).

- (i) Write an equation for the reaction that would take place if the electrodes of this cell were connected by a wire.

..... [1]

When the current was allowed to pass for a period of time,

- the Ag electrode gained 1.30 g in mass,
- the electrode made of metal **X** lost 0.67 g in mass.

- (ii) Calculate the A_r of metal **X**; hence suggest an identity for **X**.
Show all your working. Use of the *Data Booklet* is relevant to this question.

$A_r =$

X is [4]

[Total: 11]

6 Boron forms many useful compounds.

- (a) The compound diborane, B_2H_6 , can be used as a rocket fuel.
It can be prepared by the reaction of boron trifluoride, BF_3 , with sodium borohydride, $NaBH_4$.

Balance this equation.



[1]

- (b) Primary and secondary alcohols can be formed by the reaction of carbonyl compounds with $NaBH_4$, which is a source of hydride ions, H^- .

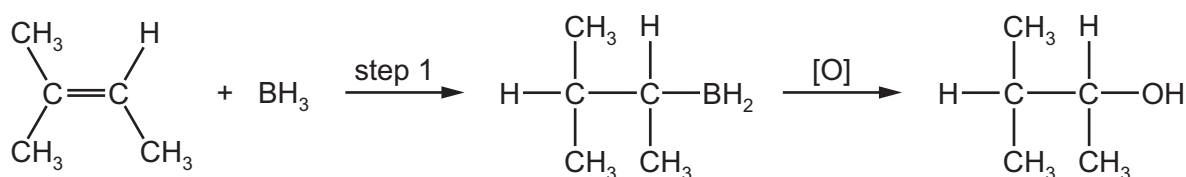
Complete the mechanism for the reaction of butanone with hydride ions, H^- , and draw the intermediate in the box. Include all necessary curly arrows and relevant dipoles.



[3]

- (c) Borane, BH_3 , is used to synthesise alcohols from alkenes.
The reaction occurs in two steps.

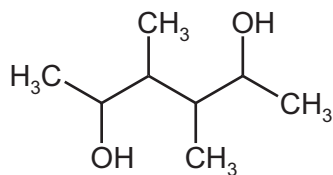
The BH_2 group from BH_3 bonds to the **least** substituted carbon atom of the double bond, and the remaining H from BH_3 bonds to the other carbon.



- (i) Suggest the *type of reaction* in step 1.

..... [1]

- (ii) The diol **Y** can be prepared by the same method.



Y

Draw the structure of the **diene** which could be used to prepare diol **Y**.

[1]

- (d) Benzene, C_6H_6 , and borazine, $B_3N_3H_6$, have planar, cyclic structures.

- (i) Describe the structure of and bonding in benzene, C_6H_6 .

.....

.....

.....

.....

.....

.....

..... [3]

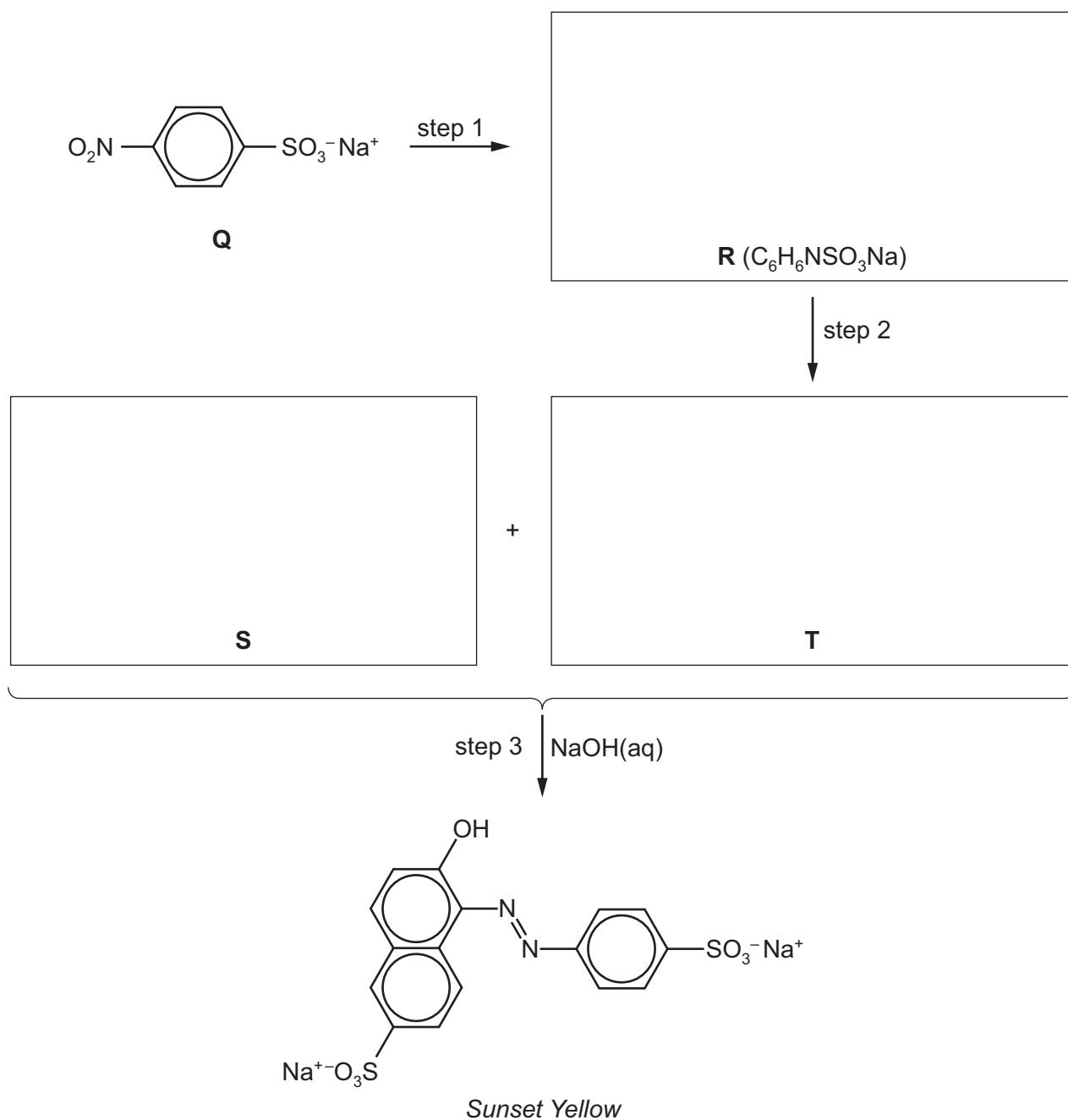
- (ii) In borazine, $B_3N_3H_6$, the boron and nitrogen atoms alternate around the ring. Each ring atom has a single hydrogen atom bonded to it.
All boron-nitrogen bonds in borazine are 0.144 nm in length, whereas in simple compounds B–N and B=N bond lengths are 0.154 nm and 0.136 nm respectively.

Suggest and draw the structure of borazine.

[1]

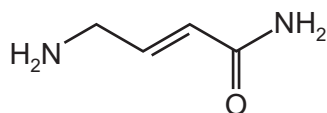
[Total: 10]

- 7 (a) *Sunset Yellow* is a yellow colouring agent used in food and drinks, which can be made by the following route.
 In step 3 of this synthesis, a phenol-like compound, **S**, reacts with intermediate **T** made from amine **R**.
 Assume that the $\text{SO}_3^- \text{Na}^+$ group does not react.



- (i) Suggest structures for compounds **R**, **S** and **T** and draw them in the boxes above. [3]
- (ii) Suggest reagents and conditions for
 step 1,
 step 2. [3]
- (iii) What type of organic salt is formed in step 2?
 [1]

(b) Compound **W** has the following structure.



(i) How many σ and π bonds are present in a molecule of **W**?

σ bonds π bonds [2]

(ii) The products of the reactions of **W** with cold HCl and with $\text{CH}_3\text{CH}_2\text{Br}$ are soluble in water but **not** in organic solvents.

Complete the table for these reactions of **W**.

reagent	structure of product (molecular formula given)	type of reaction
HCl	$(\text{C}_4\text{H}_9\text{N}_2\text{OCl})$	
$\text{CH}_3\text{CH}_2\text{Br}$	$(\text{C}_6\text{H}_{13}\text{N}_2\text{BrO})$	

[3]

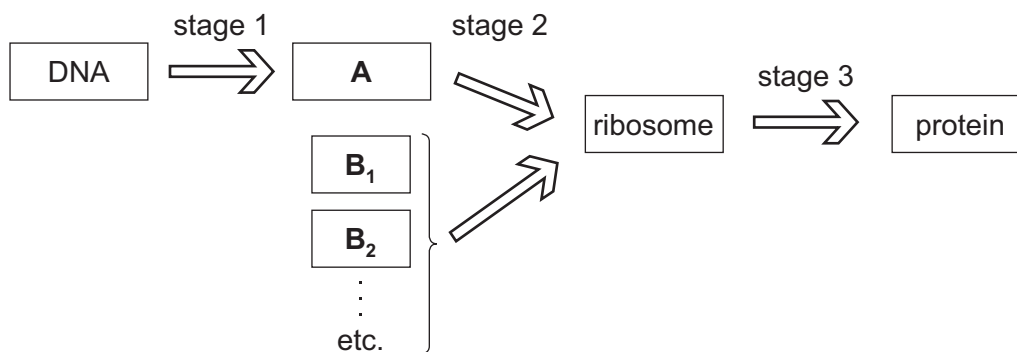
[Total: 12]

Section B

Answer **all** the questions in the spaces provided.

- 8 (a) The sequence of bases in DNA is a code for the order of amino acids in the primary structure of proteins.

The diagram represents the stages involved in the formation of a protein from DNA.



- (i) Identify the biochemical structures, **A** and **B₁**, **B₂** etc.

biochemical structure	identity
A	
B₁ , B₂ etc.	

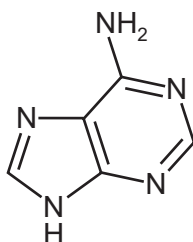
[2]

- (ii) Name the biochemical processes involved in stages 1 and 3.

process	name of biochemical process
stage 1	
stage 3	

[1]

(b) Adenine is an integral part of DNA.



adenine

(i) State the molecular formula of adenine.

..... [1]

(ii) Identify the three **other** nitrogenous bases in DNA.

..... [1]

(iii) DNA has a double helical structure that consists of two strands linked together.

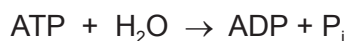
What type of bonding exists between the

phosphate and sugar groups within a DNA strand,

different bases on the two strands?

[2]

(c) The breakdown of adenosine triphosphate, ATP, provides the energy for many cellular reactions.



What *type of chemical reaction* is this?

..... [1]

(d) X-ray crystallography can be useful in obtaining information about the structures of large organic molecules, such as ATP. The technique involves X-rays interacting with the electrons within the molecule.

(i) Which element in the molecule of ATP will interact most strongly with the X-ray beam?

..... [1]

(ii) Explain why X-ray crystallography will **not** detect hydrogen atoms.

.....

..... [1]

[Total: 10]

- 9 (a) Some metals are essential to biochemical processes.

Complete the following table naming one metal in each case.

biochemical process	metal
haemoglobin in oxygen transport	
transmission of nerve impulses	
enzyme cofactor	

[2]

- (b) Enzymes are a special type of protein molecule that catalyse biochemical reactions.

Explain briefly the mechanism by which an enzyme breaks down a substrate molecule.

.....

.....

.....

.....

..... [3]

- (c) Disulfide bonds play an important role in the stability of some proteins such as the keratin in human hair.

The amino acid involved in the formation of a disulfide bond is cysteine, $\text{H}_2\text{NCH}(\text{CH}_2\text{SH})\text{CO}_2\text{H}$.

- (i) At which level of protein structure (primary, secondary, tertiary) are disulfide bonds formed?

..... [1]

- (ii) Use a functional group in cysteine to show how disulfide bonds are formed.

[1]

- (iii) What *type of chemical reaction* is this?

..... [1]

(d) The NMR spectrum of cysteine, $\text{H}_2\text{NCH}(\text{CH}_2\text{SH})\text{CO}_2\text{H}$, shows five absorptions.

After shaking a solution of cysteine with a few drops of D_2O , the NMR spectrum shows **only two** absorptions, **E** and **F**, shown below.



(i) Identify the **two** types of protons responsible for the absorptions **E** and **F**.

E

F

[1]

(ii) State and explain the splitting patterns of the absorptions **E** and **F**.

E

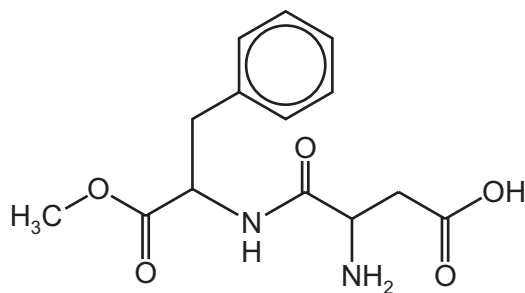
.....

F

..... [2]

[Total: 11]

10 (a) Aspartame is an artificial sweetener that has the structure shown below.

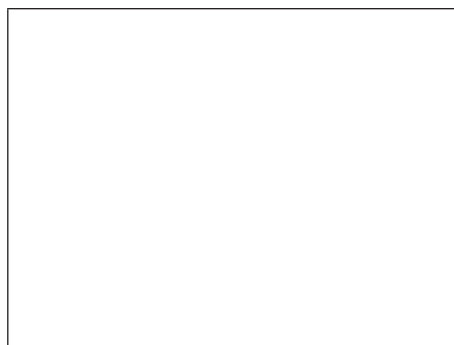
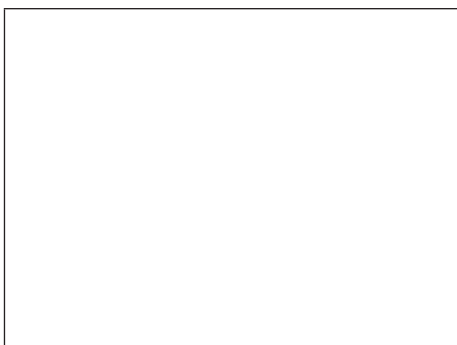


aspartame

- (i) Draw a circle around each chiral centre in aspartame. [1]

In the stomach, aspartame is hydrolysed by acid to form three organic products.

- (ii) On the diagram above, use arrows to indicate the **two** bonds that would be hydrolysed in the stomach. [2]
- (iii) Draw the structures of the **three** products formed after complete acid hydrolysis of aspartame.



[3]

- (b) Aspartame is soluble in water.

By referring to the structure of aspartame, explain why it is soluble in water.

.....

.....

..... [2]

- (c) Recently, nanotechnology has been involved in the development of a new natural sweetener, *Nano Sugar*, extracted from sugar cane.

What is the approximate width of a nanoparticle?

..... [1]

[Total: 9]

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