Cambridge International AS & A Level

Cambridge International Examinations
Cambridge International Advanced Subsidiary and Advanced Level

CANDIDATE NAME	

CENTRE NUMBER						CANDIDATE NUMBER					

1230660070

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **May/June 2016**

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.

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.

This document consists of **20** printed pages.

IB16 06_9701_42/5RP

CAMBRIDGE
International Examinations

[Turn over

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

1 **(a)** Magnesium nitrate, $Mg(NO_3)_2$, is very soluble in water. When a hot saturated solution of magnesium nitrate is cooled, crystals of the hydrate, $Mg(NO_3)_2.6H_2O$, are formed.
In the crystals, six water molecules bond to each Mg^{2+} ion, and some of these water molecules are **also** bonded to the nitrate ions.

(i) Suggest the type of bonding that occurs between

H_2O and Mg^{2+}, ...

H_2O and NO_3^-. .... [2]

(ii) Describe the arrangement of the water molecules around the Mg^{2+} ion.

.... [1]

(iii) Describe in detail what you would observe when crystals of $Mg(NO_3)_2.6H_2O$ are heated in a boiling tube, gently at first and then more strongly.
Write equations for any reactions that occur.

....

....

....

....

....

....

....

.... [4]

(iv) Calculate the percentage **loss** in mass when $Mg(NO_3)_2.6H_2O$ is heated strongly to constant mass.

percentage loss = ... % [2]

(b) Explain why the Group 2 nitrates become more stable to heat down the group.

....

....

....

....

.... [2]

(c) Magnesium nitrate and silver nitrate, $AgNO_3$, decompose on heating to produce the same gases. Silver nitrate also produces silver metal during decomposition.

Write an equation for the decomposition of $AgNO_3$.

.... [1]

[Total: 12]

2 Ethanoic acid is a weak acid.

(a) Explain what is meant by the term *weak* acid.

....

.... [1]

(b) The pK_a values of four acids are listed below.

acid	structural formula	pK_a
1	CH_3CO_2H	4.8
2	$CH_3CH_2CO_2H$	4.9
3	$CH_3CHC\mathit{l}CO_2H$	2.8
4	$CH_2C\mathit{l}CH_2CO_2H$	4.0

(i) State the mathematical relationship between pK_a and the acid dissociation constant K_a.

.... [1]

(ii) With reference to acidity, explain the difference in pK_a values between

- acid 1 and acid 2,

....

....

- acid 2 and acid 3,

....

....

- acid 3 and acid 4.

....

....

[3]

(c) **(i)** Draw a fully labelled diagram of the equipment needed to measure the voltage of an electrochemical cell consisting of the standard hydrogen electrode and the standard Cu / Cu^{2+} electrode.

[4]

(ii) For the cell drawn in **(i)**, calculate the $E^{\ominus}_{cell}$ and state which electrode is positive.

$E^{\ominus}_{cell}$ = ... identity of the positive electrode ....
[1]

(d) A monobasic acid, **D**, has $K_a = 1.23 \times 10^{-5}\,mol\,dm^{-3}$.

(i) Calculate the pH of a $0.100\,mol\,dm^{-3}$ solution of **D**.

pH = ... [2]

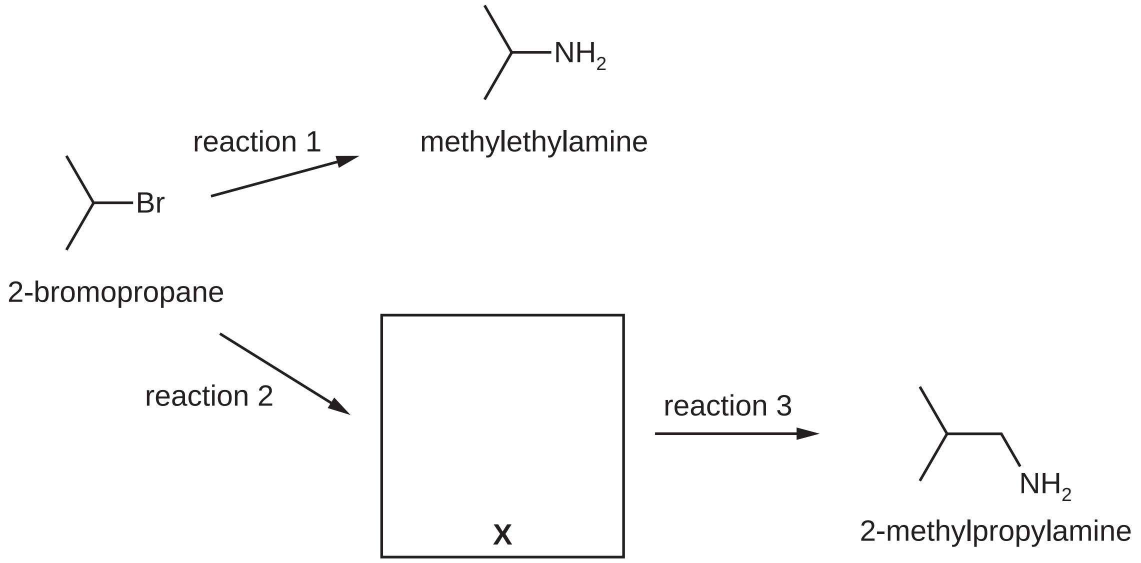
(ii) An electrochemical cell similar to the one you have drawn in **(c)(i)** was set up using a $0.100\,mol\,dm^{-3}$ solution of **D** in the hydrogen electrode instead of the standard solution.

Use the data and the Nernst equation, $E = E^{\ominus} + 0.059\log[H^+(aq)]$, to calculate the new E_{cell} in this experiment.

E_{cell} = ... V [2]

[Total: 14]

3 **(a)** 2-bromopropane can be used to synthesise methylethylamine and 2-methylpropylamine.



(i) Draw the structure of the intermediate **X** in the box above. [1]

(ii) Suggest reagents and conditions for

- reaction 1, ...
- reaction 2, ...
- reaction 3. ....

[3]

(b) **(i)** Write an equation showing why aqueous solutions of ethylamine are alkaline.

.... [1]

(ii) Compare the basicities of ethylamine and ammonia. Explain your answer.

....

....

....

.... [2]

(c) Solutions containing mixtures of amines and their salts are buffer solutions.

(i) Explain what is meant by the term *buffer solution*.

....

.... [1]

(ii) Write two equations to show how a solution containing a mixture of CH_3NH_2 and CH_3NH_3Cl acts as a buffer.

....

.... [2]

[Total: 10]

4 **(a)** There are two isomeric complexes with the formula $Pt(NH_3)_2Cl_2$, one of which is an anti-cancer drug.

(i) Draw diagrams to show the three-dimensional structures of the two isomers.

isomer 1

isomer 2

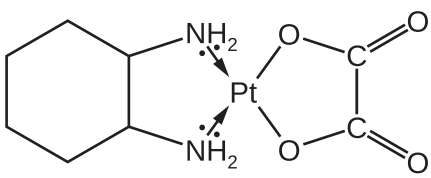
[2]

(ii) Comment on the polarity of the two isomers of $Pt(NH_3)_2Cl_2$. Explain your answer.

....

.... [1]

Oxaloplatin is another successful anti-cancer drug in which the stereochemistry around the platinum atom is the same as that in $Pt(NH_3)_2Cl_2$.



oxaloplatin

(iii) Explain why there are no isomers of oxaloplatin.

....

.... [1]

(b) Only one structure of the complex $[Ni(R_3P)_2Cl_2]$ is known. ($R = CH_3$, R_3P is a monodentate ligand)

(i) What does this indicate about the stereochemistry around the nickel atom?

.... [1]

(ii) Draw a three-dimensional diagram showing the structure of this complex.

[1]

[Total: 6]

5 Cadmium ions form complexes with primary amines and with 1,2-diaminoethane.

$Cd^{2+}(aq) + 4CH_3NH_2(aq) \rightleftharpoons [Cd(CH_3NH_2)_4]^{2+}(aq)$ $K_{stab} = 3.6 \times 10^6$ equilibrium **I**

$Cd^{2+}(aq) + 2H_2NCH_2CH_2NH_2(aq) \rightleftharpoons [Cd(H_2NCH_2CH_2NH_2)_2]^{2+}(aq)$ $K_{stab} = 4.2 \times 10^{10}$ equilibrium **II**

(a) **(i)** Write an expression for the stability constant, K_{stab}, for equilibrium **I**, and state its units.

K_{stab} =

units ....
[2]

Cadmium ions are poisonous and need to be removed from some water supplies. This is often done by adding a complexing agent.

(ii) In a sample of ground water the concentration of $Cd^{2+}(aq)$ is 1.00×10^{-4} mol dm^{-3}.

Calculate the concentration of $CH_3NH_2(aq)$ needed to reduce the concentration of $Cd^{2+}(aq)$ in this dilute solution by a factor of one thousand.

concentration of $CH_3NH_2(aq)$ = ... mol dm^{-3} [2]

(b) Values for $\Delta H^{\ominus}$ and $\Delta G^{\ominus}$ for equilibria **I** and **II**, and the value of $\Delta S^{\ominus}$ for equilibrium **I**, are given in the table below. All values are at a temperature of 298 K.

equilibrium	$\Delta H^{\ominus}$ / kJ mol^{-1}	$\Delta G^{\ominus}$ / kJ mol^{-1}	$\Delta S^{\ominus}$ / J K^{-1} mol^{-1}
I	–57.3	–37.4	–66.8
II	–56.5	–60.7	to be calculated

(i) Suggest a reason why the $\Delta H^{\ominus}$ values for the two equilibria are very similar.

....

.... [1]

(ii) Calculate $\Delta S^{\ominus}$ for equilibrium **II**.

$\Delta S^{\ominus}$ = ... J K^{-1} mol^{-1} [1]

(iii) Suggest a reason for the difference between the $\Delta S^{\ominus}$ you have calculated for equilibrium **II** and that for equilibrium **I** given in the table.

....

....

.... [1]

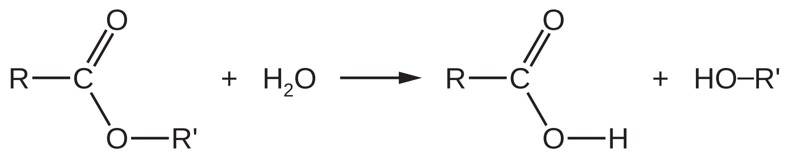
(iv) Which of the two complexes is the more stable? Give a reason for your answer.

....

.... [1]

[Total: 8]

6 Esterases are enzymes that hydrolyse esters.



Enzymes can be quite specific in the structures of the substrates they act upon. For example, an esterase isolated from the mould *Aspergillus niger* will hydrolyse phenyl ethanoate, $CH_3CO_2C_6H_5$, but not its isomer methyl benzoate, $C_6H_5CO_2CH_3$.

(a) Outline how enzymes catalyse reactions, and explain their specificity.
Use diagrams in your answer where appropriate.

....

....

.... [3]

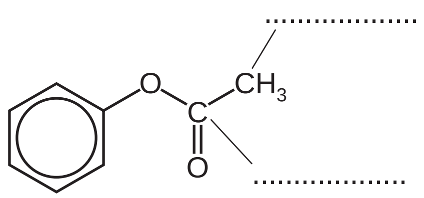
(b) Sample bottles of each of the isomers phenyl ethanoate and methyl benzoate have lost their labels and so have been named isomer **A** and isomer **B**.

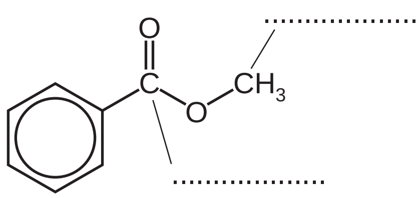
(i) The carbon-13 NMR spectra of isomers **A** and **B** contain the following peaks.

isomer **A**	isomer **B**
δ 52	δ 26
δ 128	δ 122
δ 129	δ 126
δ 130	δ 129
δ 133	δ 151
δ 167	δ 169

The identity of the compound responsible for each spectrum can be deduced by studying the chemical shifts (δ) of the peaks in the spectra.

Use the *Data Booklet* to assign the correct peaks to the labelled carbon atoms in the structures of the isomers below. Write each value next to the relevant carbon atom and hence deduce the identity of each isomer.





phenyl ethanoate is isomer ....

methyl benzoate is isomer ....

[2]

(ii) These two isomers are difficult to distinguish chemically.

Describe a method of converting them to suitable products in step 1 which can then be tested in step 2.
You should state the reagents and conditions for each step, and any observations you would make.

step 1 ....

....

....

step 2 ....

....

....

[3]

[Total: 8]

7 **(a)** Amino acids can be separated by electrophoresis.

(i) Draw a labelled diagram of the apparatus used to separate a mixture by electrophoresis.

[3]

(ii) Explain the principles of the separation of amino acids by electrophoresis.

....

....

.... [2]

(b) Electrophoresis is usually carried out in a buffer solution.

Given three buffers, with pH values of 2.0, 7.0 and 12.0, suggest, with a reason, which buffer would be the most suitable for the separation of the following amino acid mixtures.
Your reasons should refer to the structure of each molecule.
(The structures of these amino acids are given in the *Data Booklet*.)

(i) Asp and Val

buffer pH ....

reason ....

....

(ii) Lys and Ser

buffer pH ....

reason ....

....

(iii) Tyr and Phe

buffer pH ....

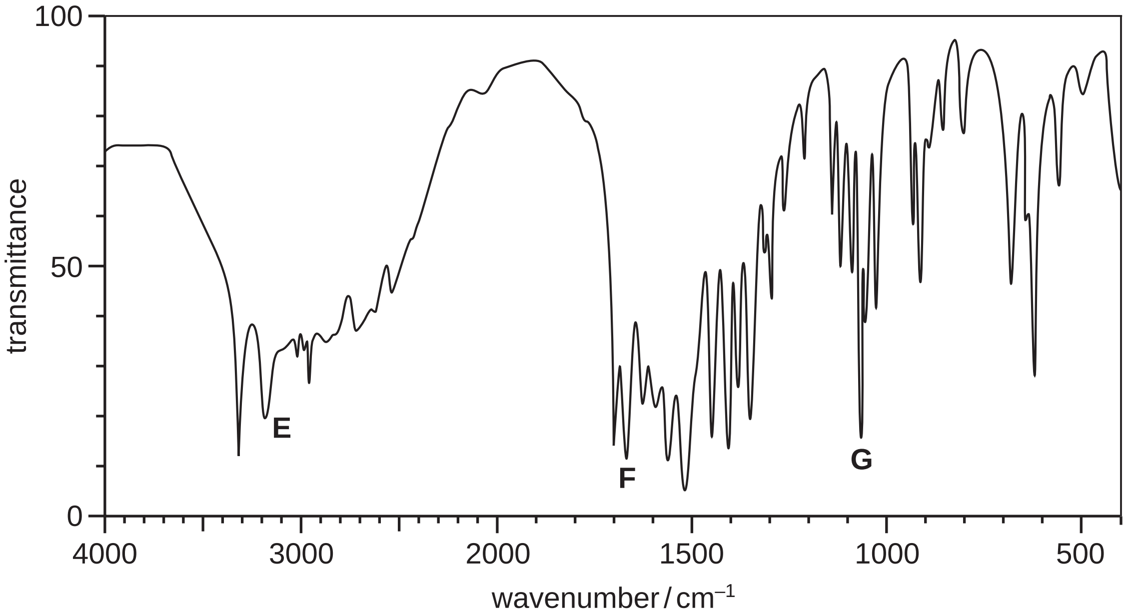
reason ....

....
[3]

(c) **(i)** Draw the structure of the dipeptide Gly-Ser, showing the peptide bond in full.

[2]

The infra-red spectrum of Gly-Ser is shown below.



(ii) Use the *Data Booklet* to identify the bond in the molecule of Gly-Ser that is responsible for each of the peaks indicated on the above infra-red spectrum.

E ....

F ....

G ....

[2]

[Total: 12]

8 **(a)** Describe and explain the trend in the solubility of the hydroxides down Group 2.

....

....

....

.... [3]

(b) Calcium reacts vigorously with $HCl(aq)$ producing $H_2(g)$.

$$Ca(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2(g)$$

(i) How would you expect the enthalpy change for this reaction to compare with the enthalpy change for the reaction where $HNO_3(aq)$ is used in place of HCl but all other conditions are the same?
Explain your answer.

....

.... [1]

(ii) The ionic equation for this reaction is shown.

$$Ca(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2(g) \qquad \Delta H^\ominus = \mathbf{x}\ kJ\,mol^{-1}$$

Construct a **fully labelled** Hess' Law cycle to connect each side of this equation to the relevant gas phase ions.

Use your cycle, the following data, **and** data from the *Data Booklet*, to calculate a value for **x**.

standard enthalpy of atomisation of Ca(s), $\Delta H^\ominus_{at}(Ca)$	+178 kJ mol^{-1}
standard enthalpy of hydration of Ca^{2+}(g), $\Delta H^\ominus_{hyd}(Ca^{2+})$	–1576 kJ mol^{-1}
standard enthalpy of hydration of H^+(g), $\Delta H^\ominus_{hyd}(H^+)$	–1090 kJ mol^{-1}

x = ... kJ mol^{-1} [4]

(c) The standard enthalpy change for the reaction between Ca(s) and CH_3CO_2H(aq) is **less negative** than **x** by 2 kJ mol^{-1}.

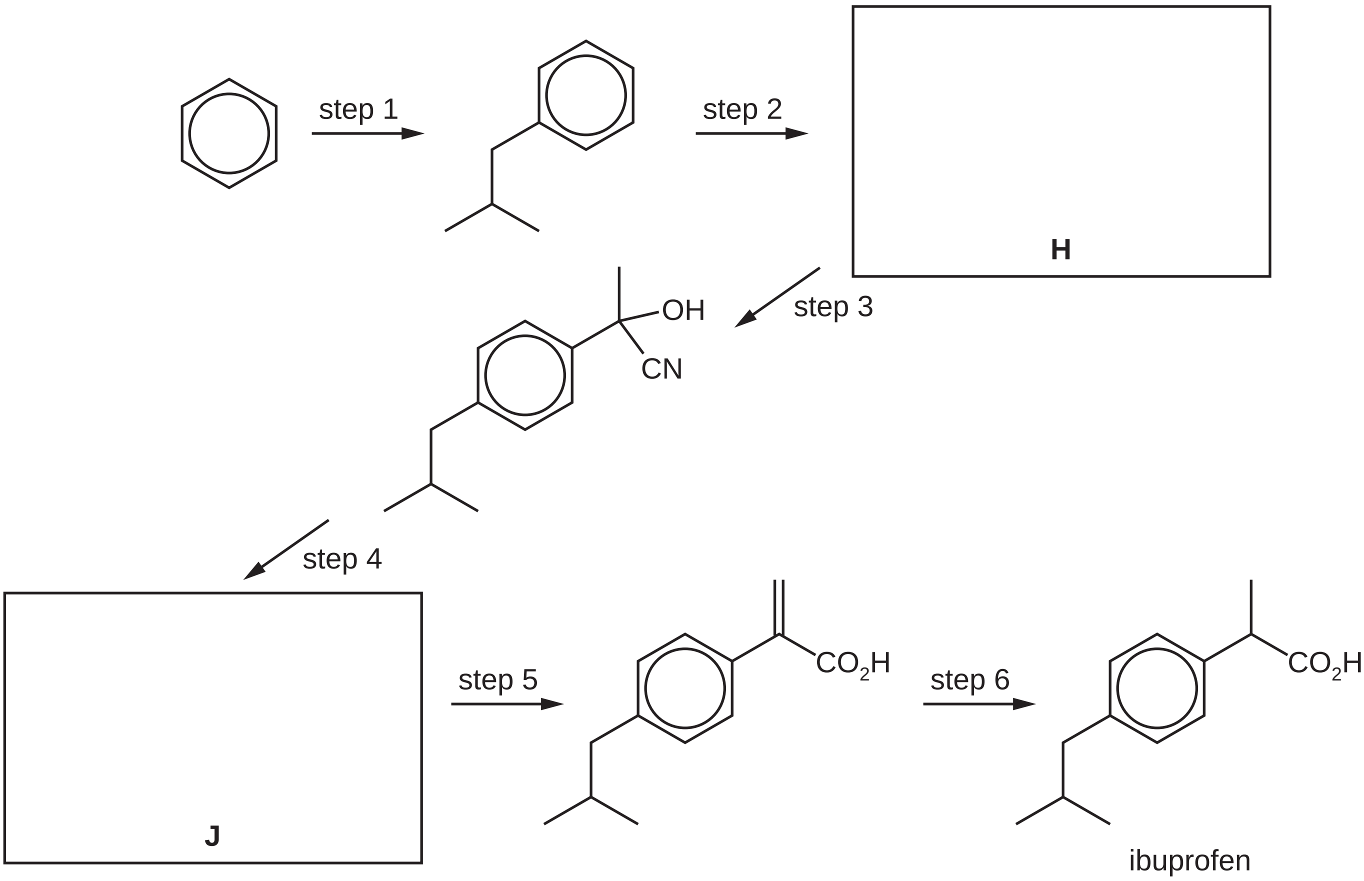
Suggest an explanation for this.

....

.... [2]

[Total: 10]

9 The anti-inflammatory drug ibuprofen can be synthesised from benzene via the following six steps.



(a) Draw circles around any chiral carbon atoms in the above five formulae. [1]

(b) Suggest the structures of compounds **H** and **J** and draw them in the boxes above. [2]

(c) Suggest reagents and conditions for steps 1-6.

step 1 ....

step 2 ....

step 3 ....

step 4 ....

step 5 ....

step 6 ....

[6]

(d) Name the mechanism of step 1 and state the *type of reaction* for step 6.

step 1 ....

step 6 ....

[2]

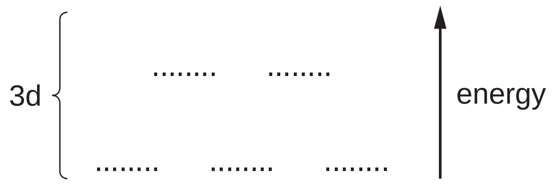
[Total: 11]

10 (a) (i) Complete the electronic configuration of the iron atom.

Fe $1s^2 2s^2 2p^6$.................................. [1]

(ii) In some of its complexes, the Fe^{3+} ion has **only one** unpaired electron in its d orbitals.

Using the symbols ↑ and ↓ to represent electrons of opposite spins, complete the following diagram to show the d orbital electronic configuration of **this** Fe^{3+} ion.



[1]

(b) A solution containing a mixture of Sn^{2+}(aq) and Sn^{4+}(aq) is added to a solution containing a mixture of Fe^{2+}(aq) and Fe^{3+}(aq).

Use $E^{\ominus}$ data from the *Data Booklet* to predict the reaction that might take place when the two solutions are mixed, and write an equation for the reaction.

....

....

.... [2]

(c) Hexaaquairon(III) ions are pale violet. They form a colourless complex with fluoride ions, F^-, equilibrium **1**, and a deep-red complex with thiocyanate ions, SCN^-, equilibrium **2**.

$[Fe(H_2O)_6]^{3+}$ + F^- $\rightleftharpoons$ $[Fe(H_2O)_5F]^{2+}$ + H_2O equilibrium **1** $K_{stab} = 2.0 \times 10^5\,mol^{-1}\,dm^3$
violet colourless

$[Fe(H_2O)_6]^{3+}$ + SCN^- $\rightleftharpoons$ $[Fe(H_2O)_5SCN]^{2+}$ + H_2O equilibrium **2** $K_{stab} = 1.0 \times 10^3\,mol^{-1}\,dm^3$
violet deep-red

(i) Predict and explain the **sequence** of colour changes you would observe in each of the following experiments.

- A few drops of KSCN(aq) are added to $5\,cm^3$ of Fe^{3+}(aq), followed by a few drops of KF(aq).

....

....

....

- A few drops of KF(aq) are added to $5\,cm^3$ of Fe^{3+}(aq), followed by a few drops of KSCN(aq).

....

....

....

[4]

(ii) What *type of reaction* is occurring during the experiments in **(i)**?

.... [1]

[Total: 9]