CATHOLIC JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATIONS
Higher 2

CHEMISTRY

9647/03

Paper 3 Free Response

Friday 24 August 2012
2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper. **[PILOT FRIXION ERASABLE PENS ARE NOT ALLOWED]**
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.
A Data Booklet is provided
You are reminded of the need for good English and clear presentation in your answers.

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

Answer any **four** questions.

1 This question relates to the chemistry of Be, Mg, A*l* and their compounds.

(a) Beryllium compounds are toxic air pollutants. Inhalation of high levels of beryllium can cause inflammation of the lungs in humans and long-term exposure may cause chronic beryllium disease (*berylliosis*), in which granulomatous lesions develop in the lung.

(i) Given that charge density $\propto \frac{\text{ionic charge}}{\text{ionic radius}}$, calculate the relative charge densities of Be^{2+}, Mg^{2+} and Al^{3+}, using relevant data from the *Data* Booklet.

(ii) Hence, predict what is observed when aqueous sodium hydroxide is gradually added to aqueous beryllium sulfate until the sodium hydroxide is in an excess. Write equations for all reactions that have taken place.

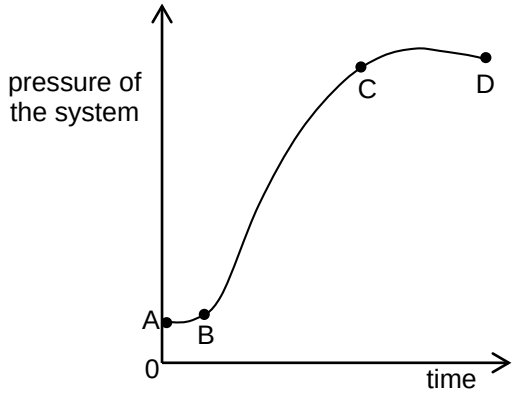
(iii) Suggest the pH of the solution formed when beryllium chloride is dissolved in water. Give your reasoning.

(iv) Magnesium ions are essential for the action of some enzymes (e.g. alkaline phosphatase found in the liver) by receiving electron pairs from oxygen and nitrogen atoms in the protein. It is thought that beryllium compounds are poisonous because they displace magnesium ions from these enzymes.
Suggest a reason why beryllium ions should behave in this way.

(v) Beryllium chloride may be used as a catalyst in the chlorination of benzene. Suggest a reason why this is possible. Outline the mechanism to show how beryllium chloride is involved in this reaction.

[10]

(b) A student carried out a kinetics experiment using a roll of magnesium ribbon that had been exposed to air for some time. He placed a piece of magnesium ribbon of mass 0.12 g into a flask containing 15.0 cm^3 of 1.0 mol dm^{-3} hydrochloric acid. The progress of the reaction was followed by measuring the pressure of the system at different times. The graph below shows the results of the experiment.



(i) Determine, by calculation, the limiting reagent for the experiment.

(ii) Account for the change in pressure of the system as shown in the graph at points **A**, **B**, and from **C** onwards.

[4]

(c) An alloy of aluminium and magnesium is used in boat-building.

A 1.75 g sample of the alloy was dissolved in the minimum volume of 4 mol dm^{-3} hydrochloric acid and the solution was then made alkaline by the addition of aqueous sodium hydroxide until no further reaction occurred. The resultant mixture was filtered and the residue, **X**, rinsed with distilled water, all washings being added to the filtrate, **Y**. After air drying, 0.18 g of **X** was obtained. Carbon dioxide was passed into **Y** and a white solid, **Z**, which contained aluminium, was collected. Heating **Z** to constant mass gave a residue of mass 3.16 g.

Suggest the identities of **X**, **Y** and **Z**, and determine the percentage composition by mass of the alloy.

[6]
[Total: 20]

2 2-chlorobutane undergoes hydrolysis with NaOH(aq) via two different reaction pathways, in the same reaction, to form a mixture of two enantiomeric products.

$$CH_3CHClCH_2CH_3 + NaOH \rightarrow CH_3CH(OH)CH_2CH_3 + NaCl$$

In one of the hydrolysis reaction pathways, only one product is formed and inversion of configuration occurs in the product. In the other reaction pathway, a racemic mixture is formed.

(a) In an experiment, one optical isomer of 2-chlorobutane undergoes hydrolysis and two enantiomeric products in a ratio of 95%:5% are formed.

(i) Draw the structures of the two enantiomeric products.

(ii) One enantiomer is formed in a much higher percentage compared to the other. Explain clearly how this disparity arises by examining the mechanisms of both reaction pathways. You should name both mechanisms involved but an outline of the mechanism is **not** required.

(iii) Write a rate equation for the reaction pathway that results in the inversion of the configuration and draw its energy profile diagram, given that the enthalpy change of the hydrolysis is exothermic.

(iv) Suggest the percentage of 2-chlorobutane that undergoes hydrolysis via the reaction pathway in **(a)(iii)**.

(v) Hence deduce how much faster the rate of this reaction pathway in **(b)(ii)** compares to that of the other reaction pathway.

[9]

(b) 2-chlorobutane is commonly produced from but-1-ene via reaction with hydrogen chloride.

$$CH_2{=}CHCH_2CH_3(g) + HCl(g) \text{ à } CH_3CHClCH_2CH_3(l)$$

(i) Name the other possible product in the above reaction.

(ii) Predict the sign of ΔS for this reaction, showing your reasoning.

(iii) Using relevant bond energy values from the *Data Booklet*, calculate the approximate value of ΔH for the reaction in **(b)**.

(iv) Bond energies quoted from the *Data Booklet* are average values. Other than this, explain why the method in **(b)(iii)** is not the most accurate for determining ΔH of the reaction.

(v) Deduce how the rate of reaction of but-1-ene with hydrogen halides will vary from H-F to H-I, and give your reasoning.

(vi) While HC*l* react readily with alkenes under room conditions, HCN does not. Based on concepts of chemical bonding, suggest possible reasons for this.

[10]

(c) HC*l* can be prepared by adding concentrated sulfuric acid to solid sodium chloride. However when concentrated sulfuric acid is added to sodium iodide, the yield of HI is very low. Explain. [1]

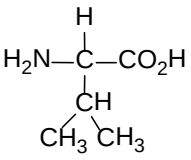
[Total: 20]

3 This question explores the chemistry of zinc in biochemistry, organic chemistry and electrochemistry.

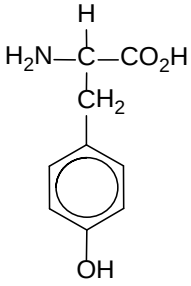
(a) Angiotensin I, a simple protein, undergoes hydrolysis with the aid of an enzyme, known as angiotensin-converting enzyme (ACE) to form angiotensin II. Angiotensin II is an important hormone that causes blood vessels to constrict, resulting in a rise in blood pressure.

(i) State how proteins can be hydrolysed to form a mixture of their constituent amino acids.

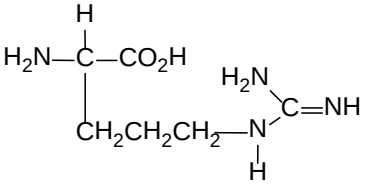
Some of the amino acids found in angiotensin II are shown below.



valine
(val)



tyrosine
(tyr)



arginine
(arg)

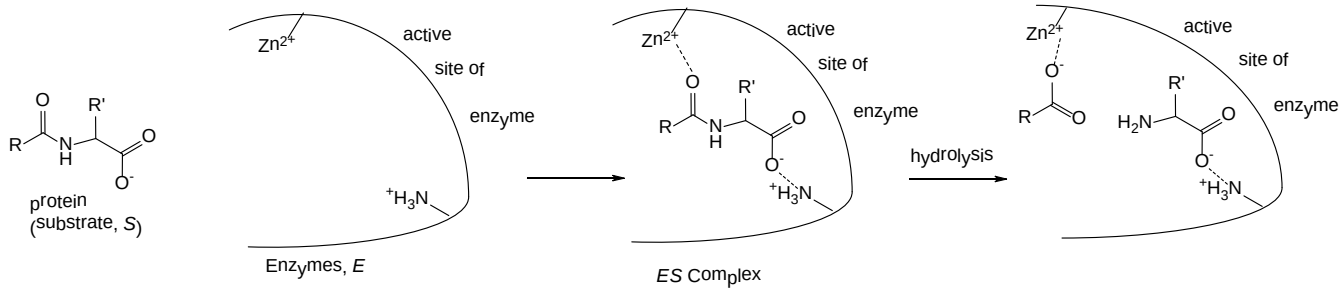
The side chains (R-groups) of angiotensin II could bind to targeted proteins through suitable R-group interactions. The R-group interactions are also used to maintain two specific protein structures.

(ii) Briefly describe **one** protein structure that involves R-group interactions.

(iii) Suggest **three** different types of R-group interactions in which the side chains of angiotensin II could bind to targeted proteins. Your answer should clearly indicate the side chains that might be involved.

(iv) Another enzyme that functions similarly as ACE is carboxypeptidase. The active site of carboxypeptidase contains $–NH_3^+$ group and a Zn^{2+} ion, which are both crucial in binding to suitable proteins.

Below shows the hydrolysis of a protein (represented by $RCONHCH(R')CO_2^-$) catalysed by this enzyme, where ------ represents interactions between the enzyme and the protein.



If there is a mutation such that carboxypeptidase does not contain Zn^{2+}, the enzyme will fail to function effectively as a catalyst. By using the above information, suggest why.

[6]

(b) Lucas reagent is used to distinguish primary, secondary and tertiary alcohols. It consists of a solution of anhydrous $ZnCl_2$ in concentrated HCl. Upon addition of Lucas reagent at 28 °C, tertiary alcohols give immediate cloudiness, secondary alcohols give cloudiness within 5 minutes and primary alcohols have no cloudiness. The overall reaction that has occurred can be represented as

$$ROH + HCl \rightarrow RCl + H_2O$$

(i) Draw **three** structural isomers with molecular formula $C_4H_{10}O$ that can be distinguished using Lucas reagent and state the observation for each isomer.

(ii) Hence from your observation in **(b)(i)**, suggest a possible product that is responsible for the cloudiness of the mixture.

(iii) Four structural isomers of molecular formula $C_3H_6O_2$ are as follows:

- **E**: $CH_3CH(OH)CHO$
- **F**: CH_3COCH_2OH
- **G**: $HOCH_2CH_2CHO$
- **H**: $HCO_2CH_2CH_3$

Show how isomers **E** to **H** can be adequately distinguished from one another by the use of simple chemical tests. You should also give brief descriptions of the chemical tests and expected observations for each isomer.

[7]

(c) About 12 million tonnes of zinc are produced every year, of which 70 % are obtained through mining. The ore is first roasted to produce zinc oxide, which is then further processed to obtain pure zinc through a series of steps.

(i) In the first step, ZnO is reacted with dilute sulfuric acid. Write a balanced equation for this reaction.

The next step involves electrolysis of the resulting solution obtained in **(c)(i).** A current of 10 000 A is passed through the solution in a series of electrolytic cells and zinc is deposited on the cathode of each cell. After 24 hours, each cell is shut down, the zinc coated cathodes are rinsed and pure zinc is mechanically stripped from the cathode.

(ii) Write the half-equations for each electrode reaction and hence, construct the overall balanced equation.

(iii) Assuming that only one cell is involved in the production in a 24-hour period

I Calculate the mass of zinc produced in 24 hours.

II Hence, calculate the thickness, in cm, of the zinc sheet produced.

Given: current density = 500 A m^{-2} of zinc deposited

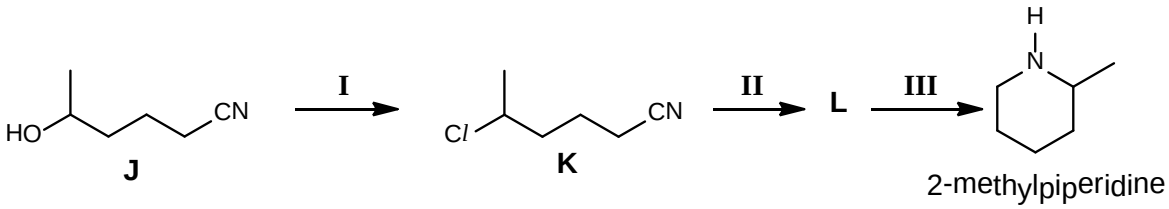
density of zinc = 7.14 g cm^{-3}.

[Current density is defined as the current flowing per unit area.]

[7]

[Total: 20]

4 Piperidines are widely-used building blocks in the synthesis of organic compounds in the pharmaceutical industry. A possible synthetic route to prepare of 2-methylpiperidine is shown below.



(a) **(i)** State the type of reaction that has occurred in stage **I** and identify a suitable reagent used.

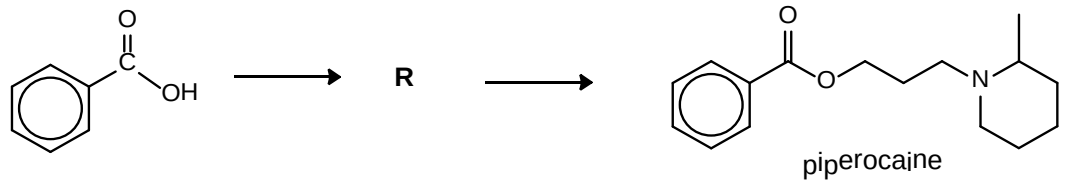
(ii) Explain why stage **I** has to be carried out in an anhydrous condition. Include in your answer any relevant equation.

(iii) Draw the "dot-and-cross" diagram of the reagent used in stage **I.**

(iv) Suggest the structure of compound **L** and state the reagent and conditions required in stage **II**.

[8]

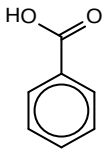
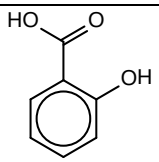
(b) Benzoic acid and 2-methylpiperidine can be used to synthesise piperocaine, a local anaesthesia used for infiltration and nerve block, via a two-step reaction. Benzoic acid is first converted into an intermediate, **R**, which is then converted to piperocaine.



Suggest the reagents and conditions required for each step and draw the structure of intermediate **R** produced.

[4]

(c) Benzoic acid is used as an antiseptic due to its ability to inhibit the growth of bacteria. Salicylic acid, a monohydroxybenzoic acid, has a similar function. The structure and solubility of both compounds in water are given in the table below.

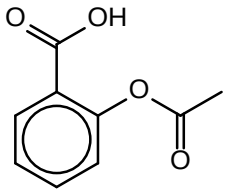
Name	Structure	Solubility / mol dm^{-3}
Benzoic acid		0.0238
Salicylic acid		0.0145

(i) By considering structure and bonding, explain the difference in solubility of benzoic acid and salicylic acid.

(ii) Suggest a simple chemical test that can be used to distinguish benzoic acid from salicylic acid. State the reagents and conditions used and describe clearly the observations for each of the compound. Write a balanced equation for any reaction that occurs.

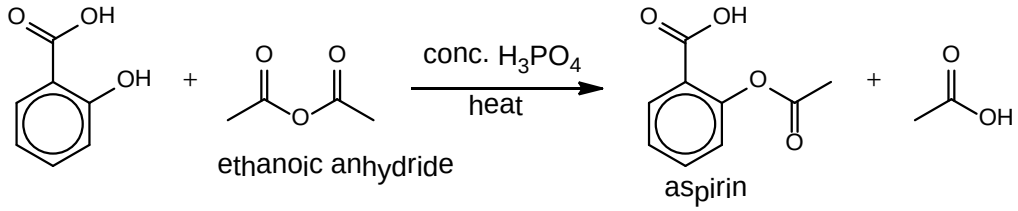
[5]

(d) Salicylic acid is also an important active metabolite of aspirin, a drug to relieve minor aches and pains, to reduce fever, and as an anti-inflammatory medication.



aspirin

The synthesis of aspirin involves treating salicylic acid with ethanoic anhydride, an acid derivative, in the presence of concentrated phosphoric acid. This esterification process (shown below) yields aspirin and ethanoic acid, which is considered a by-product of this reaction.



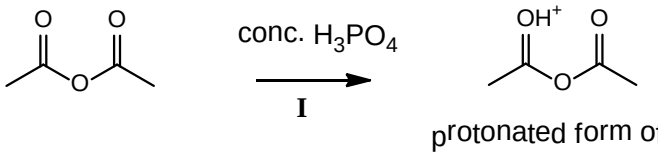
ethanoic anhydride

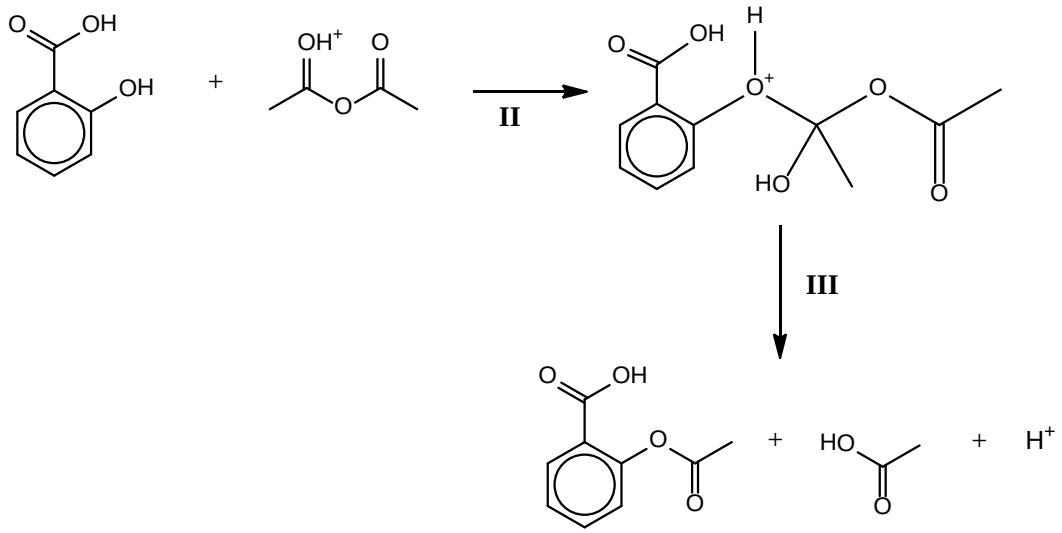
aspirin

(i) Suggest why salicylic acid will not react with itself to produce an ester given the conditions stated above.

(ii) Suggest another reagent that can be used in place of ethanoic anhydride in the synthesis of aspirin from salicylic acid.

(iii) The synthesis of aspirin from salicylic acid with ethanoic anhydride may occur as follows.





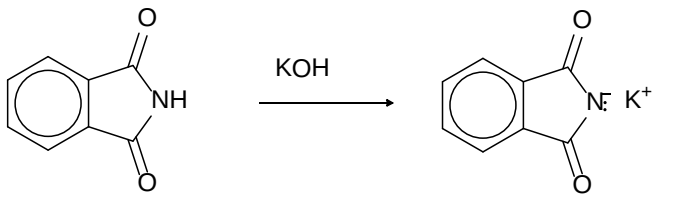
Suggest the types of reactions occurring in stages **I** and **II**.

[3]

[Total: 20]

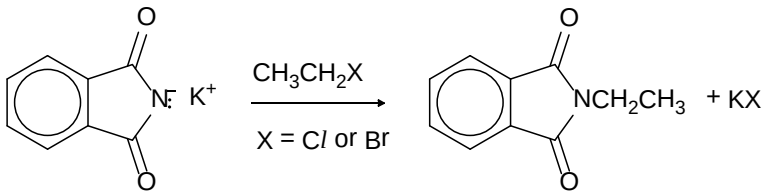
5 **(a)** The Gabriel synthesis is a chemical reaction that transforms primary alkyl halides into primary amines using potassium phthalimide. It gives a high yield of primary amines and an example of the Gabriel synthesis is shown below.

Step **I**

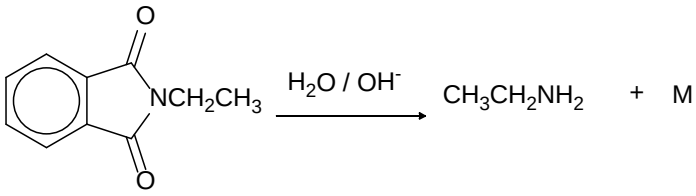


potassium phthalimide

Step **II**



Step **III**



(i) Step **I** is unusual as the amide hydrogen is quite acidic, hence it can react with KOH to produce potassium phthalimide. Suggest why the amide hydrogen is acidic in this case.

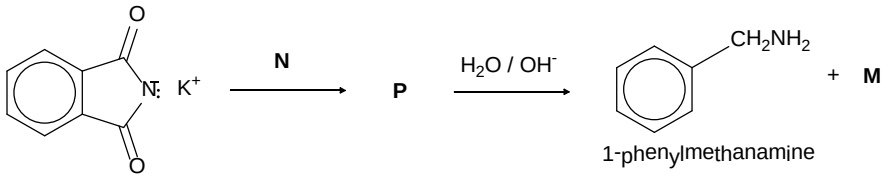
(ii) What *type* of reaction is step **III**?

(iii) Suggest a structure for **M**.

[3]

(b) 1-phenylmethanamine ($C_6H_5CH_2NH_2$) is a versatile organic compound which is used as a raw material for the production of Vitamin H. It is also an active ingredient in the production of nylon fibres.

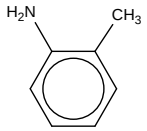
1-phenylmethanamine can be produced via a similar two-step Gabriel amine synthesis.



Suggest the structures of compounds **N** and **P**. [2]

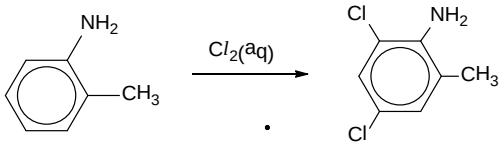
(c) Phenylamine, along with its chlorine-substituted derivatives, is widely used in biology, medicine, as well as the paint and varnish industry.

(i) Suggest a synthetic route to form 2-methylphenylamine from methylbenzene.



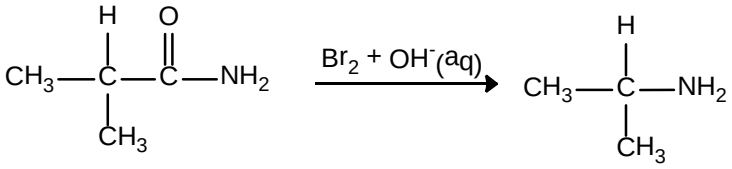
2-methylphenylamine

(ii) The reaction below can proceed in the absence of a catalyst. Explain why milder conditions are required for this reaction compared to chlorination of benzene.

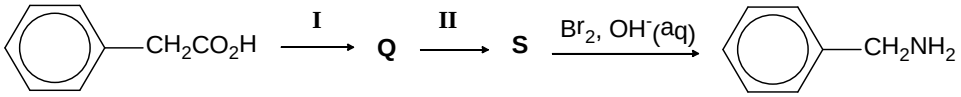


[3]

(d) The Hofmann rearrangement is another organic reaction used to synthesis primary amines. It involves the reaction of a primary amide with aqueous alkaline bromine to form a primary amine with one less carbon atom than the starting material.



1-phenylmethanamine ($C_6H_5CH_2NH_2$) can also be produced in a three-step sequence given below where the last step is a Hofmann reaction.

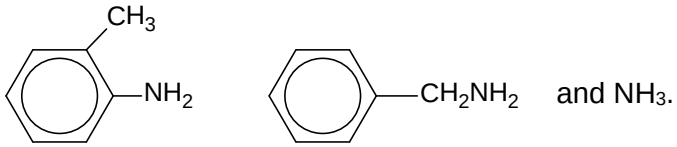


(i) Draw the structures of compounds **Q** and **S**.

(ii) Suggest reagents and conditions required for stages **I** and **II**.

[4]

(e) **(i)** Arrange the following compounds in order of decreasing basicity. Explain your answer.



and NH_3.

(ii) Calculate the pH of the resulting solution when 25 cm^3 of 0.0200 mol dm^{-3} HC*l* is added to 25 cm^3 of 0.0300 mol dm^{-3} 1-phenylmethanamine ($C_6H_5CH_2NH_2$).

(The K_b value of 1-phenylmethanamine is 2.19×10^{-5} mol dm^{-3}.)

(iii) A 0.0200 mol dm^{-3} solution of 1-phenylmethanamine was mixed with an equal volume of 0.00100 mol dm^{-3} of aqueous magnesium sulfate. Determine whether a precipitate would be formed in this experiment.

(The numerical K_{sp} value of magnesium hydroxide is 1.8×10^{-12}).

[8]

[Total: 20]

~ END OF PAPER ~