Candidate Name: _____

Class	Adm No

H

millennia institute

2014 Preliminary Examination II
Pre-university 3

H2 CHEMISTRY 9647/02

Paper 2 Structured Questions **Friday, 19 Sep 2014**

2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number in the spaces provided at the top of this page.
Write in dark blue or black pen in the spaces provided.
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 **all** 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 question.

For Examiner's Use	
1	/12
2	/18
3	/11
4	/ 9
5	/22
Total	/72

For Examiner's Use

1 Planning (P)

In metal displacement reactions, a more reactive metal will displace a less reactive metal from a solution. Copper, silver and gold appear as elements in the earth due to their poor reactivity with the environment. These metals are easy to extract.

You are required to plan an experiment to determine the enthalpy change of a metal displacement reaction between zinc and copper(II) sulfate solution. Zinc reacts with aqueous copper(II) sulfate as shown by the equation below.

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$

The reaction is **exothermic** and spontaneous, requiring only a few minutes to go to completion.

You are provided with the following chemicals

- Zinc powder,
- 0.8 mol dm^{-3} copper(II) sulfate, $CuSO_4$

as well as apparatus commonly found in the laboratory.

(a) State the observations when the reaction goes to completion.

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[1]

(b) Using the information above, write a plan to describe how you would determine the enthalpy change of the reaction between zinc and copper(II) sulfate.

Your plan must include

- a suitable mass of zinc to be used, and your justifications for choosing this mass,
- the volume of copper(II) sulfate solution to be used,
- detailed procedures of the experiment you would perform. Include details of the apparatus you would use, and
- the precautions you would take to minimise heat loss.

For Examiner's Use

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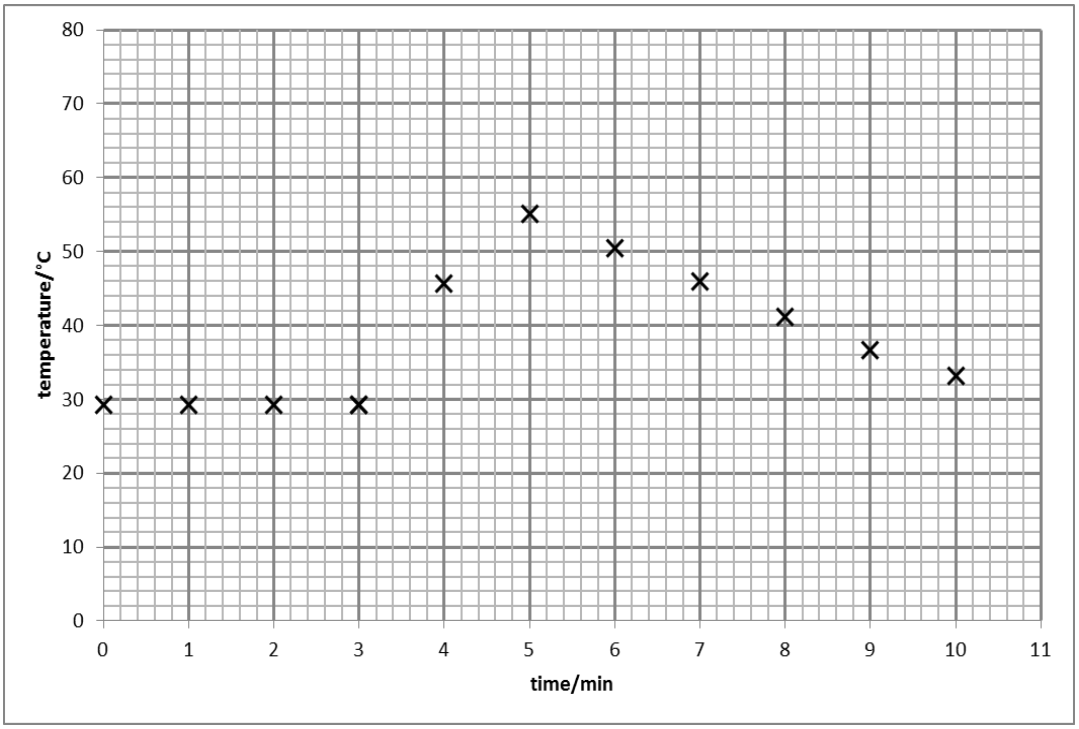
[4]

For Examiner's Use

(c) A student carried out the reaction between zinc powder and copper sulfate solution using a data logger with a temperature probe. The zinc powder was added in at the third minute. He obtained a set of temperature readings at different time intervals. The student then plotted a graph of temperature against time, shown below.



Using his graph, estimate a value for Δ**T** by extrapolating the curve to meet the vertical line representing the starting time of the experiment and hence determine the maximum temperature that could have been reached if heat loss to the surrounding were prevented.

[2]

For Examiner's Use

(d) Using your answers in **(b)** and **(c)**, determine the enthalpy change of the metal displacement reaction.

[4.2 J of heat energy raises the temperature of 1 cm^3 of any solution by 1 ^oC]

[1]

(e) Another student performed the same experiment but instead of using zinc powder, he used zinc metal strips. Identify one likely difference between this student's experiment and the one done in **(c)**. Explain your answer.

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[2]

(f) Reactive metals such as aluminium are more difficult to extract. They are always found as compounds in nature. Suggest one method by which these reactive metals can be extracted from its compounds.

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[1]

(g) Predict a probable enthalpy change value of the metal displacement reaction if the metal is now replaced with magnesium instead of zinc. Explain your answer.

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[1]

[Total:12]

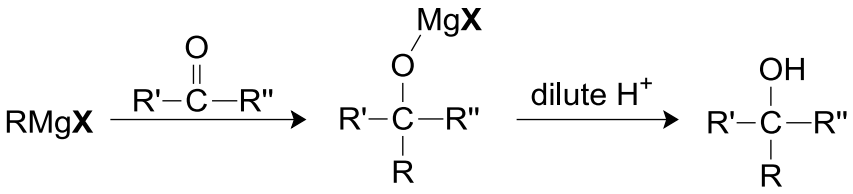
For Examiner's Use

2. This question concerns the conversion of a ketone to a tertiary alcohol using Grignard reagent.

Grignard reagent, RMg**X**, can be formed by reacting magnesium with a halogenoalkane, as shown in the equation below.

$$R\mathbf{X} + Mg \longrightarrow RMg\mathbf{X}$$

When Grignard reagent reacts with a ketone in the presence of dilute acid, the following reaction takes place.



The table below shows some physical properties of the reagents and the organic product of the reaction.

Substance	**Formula**	**Molar mass / g mol^{-1}**	**Density / g cm^{-3}**	**Solubility in water**	**Boiling point / °C**
1-Bromopropane	$CH_3CH_2CH_2Br$	122.9	1.35	Slightly soluble	71
Ethoxyethane	$C_2H_5OC_2H_5$	74.0	0.713	Slightly soluble	35
Magnesium	Mg	24.3	1.74	Insoluble	1110
Butanone	$CH_3COC_2H_5$	72.0	0.805	Soluble	80
Alcohol product			0.829	Slightly soluble	122

For Examiner's Use

(a) In **Stage One** of the conversion, 1.335 g of magnesium is added to a flask containing an equimolar quantity of 1-bromopropane dissolved in 20 cm^3 of ethoxyethane. The mixture is then refluxed

(i) Calculate the amount of magnesium used and hence the volume of 1-bromopropane used in **Stage One**.

Amount of Mg = …….

Volume of 1-bromopropane = ……....

(ii) Explain why ethoxyethane can be used to dissolve 1-bromopropane.

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(iii) Suggest why prolonged heating at high temperature is required for reactions such as this.

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For Examiner's Use

(iv) Give the structural formula of the Grignard reagent formed.

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[8]

(b) In **Stage Two** of the conversion, the mixture from **Stage One** is allowed to cool and 4.0 cm^3 of butanone is added dropwise. The mixture is then gently heated under reflux.

(i) Assuming that the reaction between magnesium and 1-bromopropane in **Stage One** had 100% yield, show with calculations that the Grignard reagent is in excess.

(ii) State the type of reaction undergone in **Stage Two**.

……

[3]

For Examiner's Use

(c) In **Stage Three** of the conversion, the mixture from **Stage Two** is cooled using an ice bath, and then 25 cm^3 of 4 mol dm^{-3} dilute hydrochloric acid is slowly added.

(i) Draw the structure of the tertiary alcohol produced from the reaction.

(ii) Suggest why the mixture is cooled before adding the dilute hydrochloric acid.

……

[2]

(d) After the formation of the tertiary alcohol, the mixture from **Stage Three** is added to a separating funnel. The lower aqueous layer is separated and shaken successively with two 10 cm^3 portions of ethoxyethane, retaining the ethoxyethane extracts and combining them with the original ethoxyethane layer.

(i) Using the data given in the table, explain why the ethoxyethane forms a layer above the aqueous layer.

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(ii) Suggest why the aqueous layer is shaken with ethoxyethane.

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[3]

For Examiner's Use

(e) The combined ethoxyethane layer is then washed successively with 20 cm^3 of each of the following:

- Saturated sodium carbonate solution
- Anhydrous calcium chloride

The solutions used to wash the ethoxyethane layer are each intended to remove a particular impurity.

Suggest the impurity removed in each step.

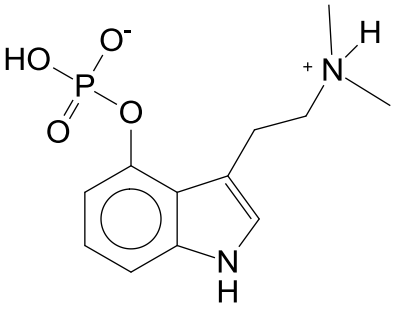
Solution	Impurity
Saturated sodium carbonate solution	
Anhydrous calcium chloride	

[2]

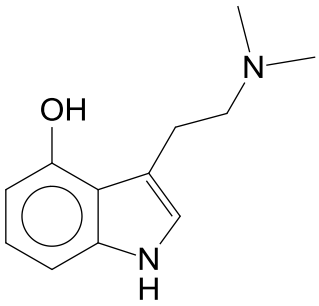
[Total:18]

3. Psilocybin is a naturally occurring psychedelic compound produced by more than 200 species of mushrooms, collectively known as psilocybin mushrooms. As a prodrug, psilocybin is quickly converted by the body to psilocin, which has mind-altering effects such as euphoria, hallucinations, and changes in perceptions. Recent studies done at Imperial College London and Johns Hopkins School of Medicine conclude, when used properly, psilocybin acts as an antidepressant.

The structures of psilocybin and psilocin are shown below.



psilocybin



psilocin

For Examiner's Use

(a) A prodrug is a precursor chemical compound to a drug to improve how the drug is absorbed, distributed, metabolised, and excreted.
Explain why psilocybin can be better absorbed by the body compared to psilocin.

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[2]

(b) Draw the structure of the major organic product formed when psilocin reacts with

(i) cold dilute $KMnO_4$ in aqueous NaOH

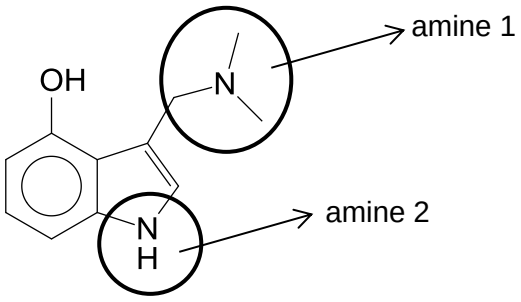
(ii) $Br_2(aq)$

(iii) CH_3COCl

[6]

For Examiner's Use

(c) Amines are weakly alkaline. There are two amine groups in psilocin with different basicity. State which amine group behaves as the weaker base. Explain your answer.



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[3]

[Total: 11]

4. **(a)** The major buffer system that is used to control the pH of blood is the carbonic acid – hydrogen carbonate buffer system.

$$H_2CO_3\,(aq) \rightleftharpoons HCO_3^-\,(aq) + H^+\,(aq)$$

(i) Give two equations to show how the buffer system in blood helps to control pH.

When small amount of acid is added:

……

When small amount of base is added:

……

For Examiner's Use

(ii) The pH of human blood plasma is usually maintained at about 7.4. The ratio of $[H_2CO_3]$: $[HCO_3^-]$ in blood plasma is 20 : 1.
Calculate the K_a of H_2CO_3.

K_a of H_2CO_3 = ……

[4]

(b) The temperature of a sample of gas **X** is measured at various pressures, keeping the volume of the system constant. The following results were obtained.

Pressure /kPa	Temperature /°C
6.0	27.0
8.0	127.0
10.0	227.0

(i) Deduce whether the sample of gas **X** is behaving ideally.

For Examiner's Use

(ii) Hence suggest a reason for the behaviour of gas **X** in this sample.

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[3]

(c) Electrosynthesis is the synthesis of chemical compounds using electrochemical cells. In one such reaction, a concentrated aqueous solution of sodium propanoate, $CH_3CH_2COO^-Na^+$, is electrolysed in an alkaline medium using platinum electrodes. At the anode, a mixture of carbon dioxide and butane is formed. At the cathode, hydrogen gas is evolved.

Write half equations for the reactions which occur at the anode and cathode respectively.

Anode: …….

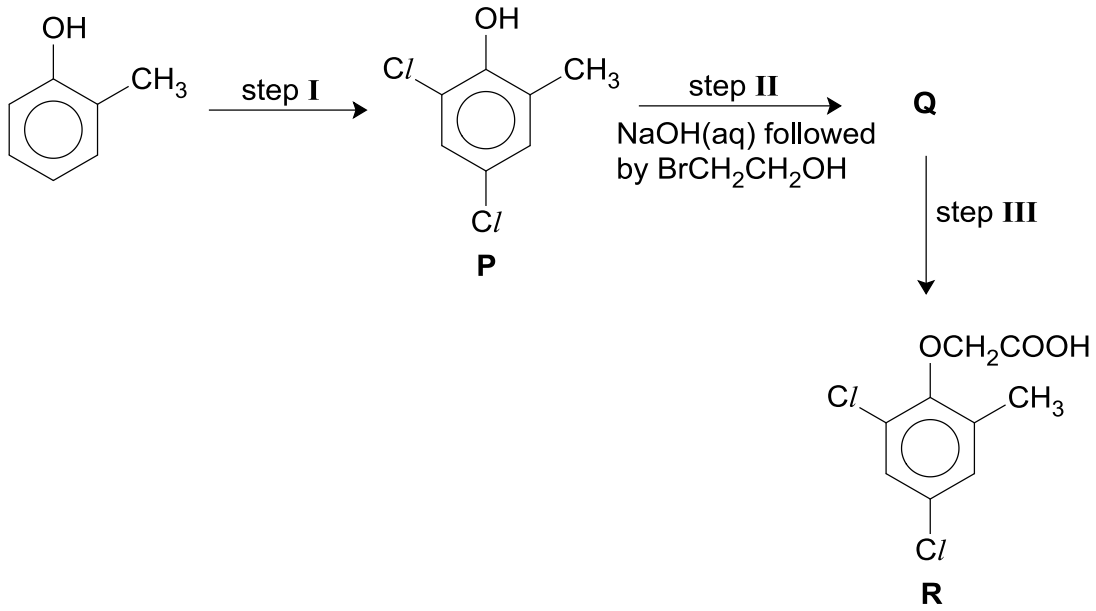
Cathode: ……..

[2]

[Total: 9]

For Examiner's Use

5. The reaction scheme below shows a three-step synthesis of compound **R** from 2-methylphenol.



(a) (i) State the reagents and conditions for steps **I** and **III**.

Step	Reagents and conditions
I	
III	

(ii) Draw the structure of **Q**.

(iii) Step **II** involves two types of reactions. State the two types of reactions and suggest the role of NaOH(aq) in this step.

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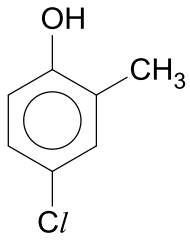
[6]

For Examiner's Use

(b) Compound **S** can also be formed from 2-methylphenol



S

(i) State the reagent and condition required for the conversion.

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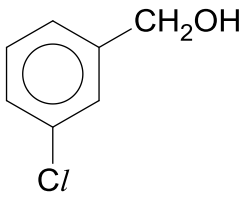
(ii) Give a simple chemical test that can be used to distinguish **S** from its isomer, **T**. State the reagent and condition used and the observation for both compounds.



T

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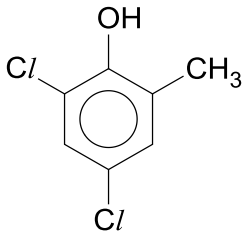
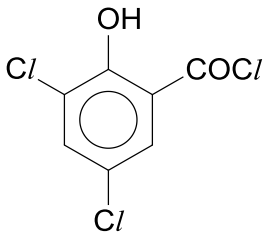
[3]

For Examiner's Use

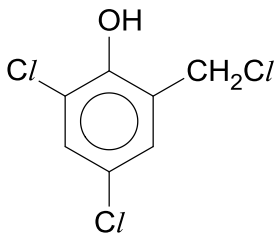
(c) Compound **P** and two other compounds, **X** and **Y**, are shown below



P



X



Y

(i) The three compounds are reacted with hot ethanolic silver nitrate. Compare and explain the relative rate of formation of white precipitate for the three compounds.

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(ii) **P** can be converted to **Y**.

Describe the mechanism for the conversion of **P** to **Y**.

For Examiner's Use

(iii) The white precipitate formed in **(c)(i)** is accidentally mixed with a sample of cream precipitate of AgBr(s). Explain how pure AgBr(s) can be recovered from the mixture, writing equation where appropriate.

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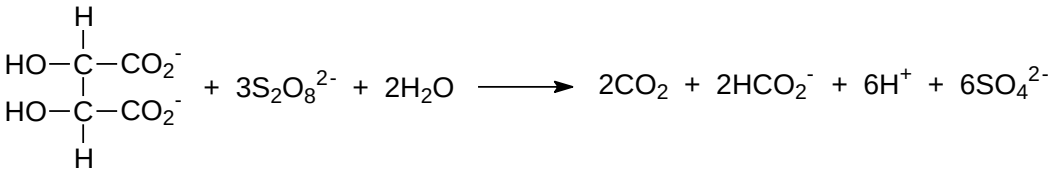
[10]

(d) Peroxodisulfate(VI) ion, $S_2O_8^{2-}$, is capable of oxidising the tartrate ion, $[CH(OH)(CO_2^-)]_2$, to carbon dioxide and methanoate ion.



The reaction is very slow, even at elevated temperature. The rate of reaction can be increased by adding in a suitable catalyst such as manganese(III) ions.

(i) State the property of transition metals which make them good homogeneous catalysts.

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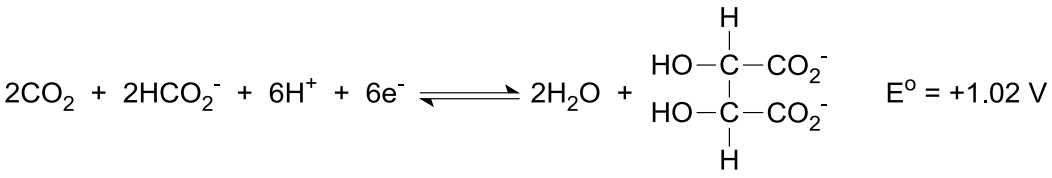
For Examiner's Use

(ii) Using data from the *Data Booklet* and the reduction potential given below, propose a mechanism to show how manganese(III) ion can work as a catalyst for this reaction.



[3]

[Total: 22]

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