RAFFLES INSTITUTION
2011 YEAR 6 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME			
CLASS		INDEX NUMBER	

CHEMISTRY 9647/02

Paper 2 Structured Questions **19 September 2011**
2 hours

Candidates answer on the Question Paper.

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. Do not write anything on it.
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	/ 20
3	/ 15
4	/ 12
5	/ 13
Total	/ 72

This document consists of **16** printed pages.

1 Planning (P)

You are to design an experiment to determine the identity of a soluble metal sulfate, MSO_4, by using a gravimetric method. A solid sample containing MSO_4, with some carbonate and sulfite impurities, is provided.

You may assume that the following are available:

- 1.0 g of the solid sample of MSO_4, of a known percentage purity
- 0.50 mol dm^{-3} aqueous barium chloride, $BaCl_2$
- concentrated hydrochloric acid, HCl
- 250 cm^3 and 500 cm^3 beakers
- weighing bottle
- measuring cylinders
- glass rod
- filter paper
- filter funnel
- deionised water
- infra-red lamp

You may also assume that standard laboratory apparatus are available.

(a) Write an ionic equation, including state symbols, for the reaction between the unknown metal sulfate and aqueous barium chloride.

…….. [1]

(b) Explain why concentrated hydrochloric acid should be added to the impure metal sulfate.

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…….. [2]

(c) Using your answers to **(a)** and **(b)**, outline a sequence of steps in which the experiment should be carried out to determine the identity of MSO_4. You should state clearly the measurements to take and any assumption(s) made.
[Treatment of results is not required.]

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..... [7]

(d) A 0.892 g impure solid sample of the unknown metal sulfate, MSO_4, reacted with excess acidified aqueous barium chloride to form 1.049 g of barium sulfate. Given that the sample contained 80.4% by mass of metal sulfate, determine the identity of the unknown metal sulfate.

The unknown metal sulfate is ..... [2]

[Total: 12]

2 The rate of reaction of bromine with bromopropanone was studied in acid solution at 25 °C. The table gives some results (repeated on page 6) obtained for the reaction

$$CH_3COCH_2Br + Br_2 \xrightarrow{H^+} CH_3COCHBr_2 + HBr$$

	initial concentration / mol dm^{-3}		$[Br_2]$ at specified times / mol dm^{-3}			
Expt	bromopropanone	hydrochloric acid	0 s	1500 s	3000 s	4500 s
1	0.050	0.50	0.050	0.036	0.025	0.019
2	0.050	0.50	0.100	0.086	0.076	0.068
3	0.020	0.50	0.050	0.044	0.038	0.034

The reaction may be followed by either chemical or physical methods of analysis.

Sampling & Titration

In each of the above experiments, the reagents were mixed and then three samples were successively withdrawn, at appropriate times, as the reaction proceeded. At 1500 s, ice-cold water was added to the first sample. To this, excess aqueous potassium iodide was added. The resultant solution was then titrated against standard sodium thiosulfate solution. This procedure was repeated with the second and third samples, with ice-cold water being added at 3000 s and 4500 s respectively.

(a) **(i)** Why was ice-cold water added?

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(ii) Suggest why aqueous sodium hydroxide should **not** be used in place of ice-cold water.

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(iii) Write an ionic equation to show the reaction involving potassium iodide.

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(iv) Suggest why an indicator was not needed for the titration.

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..... [4]

(b) Suggest how the above reaction could be followed by a physical method of analysis.

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..... [1]

The rate equation for the reaction is

$$\text{rate} = k\,[Br_2]^a\,[CH_3COCH_2Br]^b\,[H^+]$$

(c) (i) The orders of reaction with respect to Br_2 and CH_3COCH_2Br are to be determined. Use the data below (repeated from page 5) to plot suitable graphs on the grid given below.

	initial concentration / mol dm^{-3}		[Br_2] at specified times / mol dm^{-3}			
Expt	bromopropanone	hydrochloric acid	0 s	1500 s	3000 s	4500 s
1	0.050	0.50	0.050	0.036	0.025	0.019
2	0.050	0.50	0.100	0.086	0.076	0.068
3	0.020	0.50	0.050	0.044	0.038	0.034

[4]

(c) (ii) Determine the values of a and b, showing clearly how you arrived at your answers.

order of reaction with respect to **Br_2**, a = ...

order of reaction with respect to **CH_3COCH_2Br**, b = ...
[4]

(iii) What are the units of the rate constant for this reaction?

..... [1]

Successive bromination of propanone can also occur in basic solution as shown:

$$CH_3COCH_3 \longrightarrow CH_3COCH_2Br \longrightarrow CH_3COCHBr_2 \ \ldots$$

The steps involved in the mono-bromination of CH_3COCH_3 are given below.

Step 1 $\quad CH_3COCH_3 + OH^- \longrightarrow CH_3COCH_2^- + H_2O$

Step 2 $\quad CH_3COCH_2^- + Br_2 \longrightarrow CH_3COCH_2Br + Br^-$

Subsequent bromination occurs via similar steps shown above.

(d) (i) Give the equation to show the acid-base reaction that occurs when CH_3COCH_2Br is brominated to form $CH_3COCHBr_2$.

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(ii) In basic solution, successive bromination reactions take place more readily. Explain why this is so.

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..... [2]

The bromination of propanone in the absence of acid or base was studied over a temperature range of 516 K to 618 K. This system is an example of a homogeneous equilibrium.

$$CH_3COCH_3(g) + Br_2(g) \rightleftharpoons CH_3COCH_2Br(g) + HBr(g)$$

(e) (i) What do you understand by the term *homogeneous* equilibrium?

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(ii) State and explain the effect which an increase in the total pressure of the system will have on:

① the rate of bromination;

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② the position of equilibrium.

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..... [4]

[Total: 20]

3 Use the following data on Group II elements to answer the questions that follow.

	sum of 1st and 2nd ionisation energies / kJ mol^{-1}	metallic radius / nm	ionic radius / nm	enthalpy change of hydration, ΔH_{hyd} (M^{2+}) / kJ mol^{-1}
Mg	2190	0.160	0.065	–1920
Ca	1740	0.197	0.099	–1590
Sr	1610	0.215	0.113	–1450
Ba	1470	0.217	0.135	–1300

	lattice energy of $M(OH)_2$ / kJ mol^{-1}	$E^{\ominus}$ [M^{2+}(aq)/M(s)] / V	solubility of $M(OH)_2$ / mol dm^{-3}	ionic speed / mm s^{-1}
Mg	–2850	–2.38	1.5×10^{-4}	0.549
Ca	–2580	–2.87	1.5×10^{-2}	0.616
Sr	–2410	–2.89	3.4×10^{-2}	0.616
Ba	–2300	–2.90	1.5×10^{-1}	0.658

(a) When a salt such as a Group II hydroxide dissolves in water, its lattice energy must be overcome.

(i) Define *lattice energy*.

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(ii) Suggest a reason for the trend in the magnitude of the lattice energy of Group II hydroxides down the group.

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..... [2]

(b) **(i)** Write a balanced equation for the action of heat on strontium nitrate.

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(b) (ii) Using data provided in the table (page 9), describe and explain how the thermal stabilities of the nitrates of the Group II metals vary from magnesium to barium.

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..... [3]

(c) (i) Using data provided in the table (page 9), calculate the solubility product, K_{sp}, of $Mg(OH)_2$.

K_{sp} of $Mg(OH)_2$ .....

(ii) To a 1.0 dm^3 saturated solution of $Mg(OH)_2$, 10.0 cm^3 of 1.00 mol dm^{-3} aqueous NaOH is added. Find the mass of the precipitate formed.

mass of precipitate ..... [4]

(d) **(i)** Construct a labelled energy cycle for the process

$$M^{2+}(aq) + 2e^- \longrightarrow M(s)$$

(ii) Although the values of ionisation energies change substantially from calcium to barium, the values of $E^{\ominus}$ change only slightly. By considering the energy cycle in **(d)(i)** and the enthalpy changes involved, explain why these enthalpy changes tend to keep $E^{\ominus}$ nearly constant.

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..... [4]

(e) Ionic speeds show how fast aqueous ions move under standard conditions. Suggest why the ionic speeds of calcium and strontium are identical, even though their ionic radii are different.

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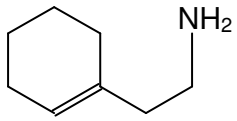
..... [2]

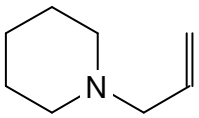
[Total: 15]

4 Compound **P**, known commonly as 2-(1-cyclohexenyl)ethylamine, is a clear, slightly yellow liquid which is used as an intermediate reagent in the pharmaceutical industry. It is a member of a large family of isomeric compounds with the formula, $C_8H_{15}N$.



compound **P**

Compound **Q**, *N*–allylpiperidine, is one such isomer.



compound **Q**

(a) At 298 K, the vapour pressure of **P** is 0.050 kPa while that for **Q** is 0.473 kPa. Explain why **P** has a lower vapour pressure.

……

……

……

…… [2]

(b) Give the structural formula of the major product formed when **P** is reacted with

(i) aqueous bromine;	**(ii)** a dilute solution of bromine in methanol.
	[2]

(c) Describe what you might observe when **Q** is heated with acidified potassium manganate(VII), and give the structural formula of the organic product.

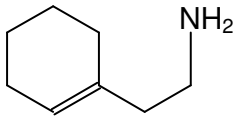
Observations: ……..

……

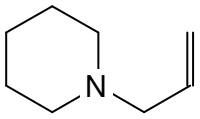
Organic product:

[3]

Some alkenes, such as hex-3-ene, occur in two isomeric forms but both compounds **P** and **Q** each occur in only one form.



compound **P**



compound **Q**

(d) Explain why **P** and **Q** do not exhibit the isomerism that hex-3-ene displays.

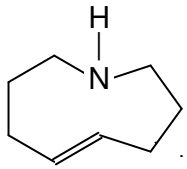
Compound **P** ……..……..

…..……..……

Compound **Q** ……..……..

…….. [2]

Compound **R** is another isomer of **P**.



compound **R**

R reacts with bromine to form two products: a mono-brominated organic compound **S**, and hydrogen bromide, HBr.

Bromine, Br_2, acts as an electrophile in this reaction. **S** is a tertiary amine.

(e) Give the structural formula of

(i) the reactive intermediate in this reaction;	**(ii)** compound **S**. [2]

(f) Compound **S** undergoes alkaline hydrolysis more readily compared to bromobenzene, C_6H_5Br. Explain why.

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…….. [1]

[Total: 12]

5 The table below shows the R groups of the various α-amino acids present in a polypeptide chain.

α-amino acid	aspartic acid	serine	cysteine	alanine	lysine
abbreviation	asp	ser	cys	ala	lys
R group	$-CH_2CO_2H$	$-CH_2OH$	$-CH_2SH$	$-CH_3$	$-(CH_2)_4NH_2$

Upon hydrolysis, a tripeptide **A**, which has the primary structure shown below, was obtained.

asp–ser–lys

(a) Draw the structural formula of tripeptide **A** at pH 12.

[2]

(b) Briefly describe **two** types of R group interactions that would occur between the residues of this polypeptide chain in an aqueous solution.

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..... [2]

(c) Describe a simple chemical test to distinguish between **aqueous solutions** of aspartic acid and serine.

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..... [2]

(d) Describe, with the aid of a diagram, how the polypeptide chain is held in the structure of an alpha helix.

[3]

(e) In a globular protein, how are the R groups of the amino acid residues arranged?

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..... [2]

(f) Give the structural formulae of the products obtained from the acidic hydrolysis of a dipeptide, ala–cys.

[1]

(g) A particular proteolytic enzyme **X** can hydrolyse the peptide bond between the carboxyl group of cysteine and the amino group of alanine of a pentapeptide to give the amino acid, cys, and two similar dipeptides, ala–cys.

Another proteolytic enzyme **Y** can hydrolyse the peptide bond between the carboxyl group of alanine and the amino group of cysteine of the same pentapeptide to give the amino acid, cys, and two similar dipeptides, cys–ala.

Give the primary structure of this pentapeptide.

…….. [1]

[Total: 13]

– END OF PAPER –