NATIONAL JUNIOR COLLEGE
PRELIMINARY EXAMINATIONS
Higher 2

CANDIDATE NAME			
SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY
Paper 3 Free response

9647/03
Tues 13 Sep 2011

2 hours

READ THESE INSTRUCTIONS FIRST

Answer any ***four*** questions.

Start your answer to each question on a fresh piece of paper.

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.

At the end of the examination, fasten all your work securely behind the cover page.

This paper consists of **13** printed pages and **1** cover page.

Answer any **four** questions.

1 Barium carbonate, $BaCO_3$, also known as witherite, is often used as a rat poison.

(a) Draw the dot-and-cross diagram of barium carbonate.

[1]

(b) Given the following data, construct an energy level diagram to calculate the standard enthalpy change of solution of barium carbonate.

$\Delta H^{\theta}_{\text{lattice energy}}(BaCO_3)$ / kJmol^{-1}	−2554
$\Delta H^{\theta}_{\text{hydration}}(Ba^{2+})$ / kJmol^{-1}	−1305
$\Delta H^{\theta}_{\text{hydration}}(CO_3^{2-})$ / kJmol^{-1}	−1245

[3]

(c) **(i)** Given that the solubility of barium carbonate in water is 0.024 g dm^{-3}, calculate the value of the solubility product of barium carbonate, stating its units.

(ii) $\Delta G^{\theta}_{\text{solution}}$ can be calculated in J mol^{-1} using the formula

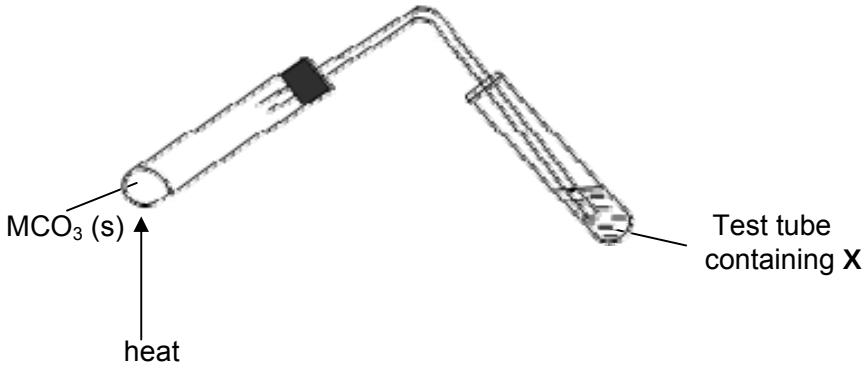
$$\Delta G^{\theta}_{\text{solution}} = -2.303\ RT\ \lg K_{sp}.$$

Calculate a value for $\Delta G^{\theta}_{\text{solution}}$ of $BaCO_3$ in kJ mol^{-1}.

[3]

1 (d) (i) Write an equation, with state symbols, for the thermal decomposition of barium carbonate.

(ii)



When the same amount of $MgCO_3$ and $BaCO_3$ was heated as shown in the above setup, the following data was obtained.

	Time taken for white precipitate to be observed in **X**
$MgCO_3$	3 minutes
$BaCO_3$	9 minutes

Explain the above observations. **[5]**

1 (e) When water is added to the white residue from **(di)**, an aqueous solution of barium hydroxide is formed. Barium hydroxide could be used in organic synthesis as a strong base under suitable conditions.

One example is the *aldol* reaction where barium hydroxide can act as a base to generate a nucleophile from ethanal.

$$CH_3CHO + OH^- \rightleftharpoons {}^-CH_2CHO + H_2O$$
(nucleophile)

(i) Explain why a nucleophile can be generated from an aldehyde molecule but not from an alkane molecule as shown below:

$$CH_3CH_3 + OH^- \rightleftharpoons {}^-CH_2CH_3 + H_2O$$

(ii) In the *aldol* reaction between 2 molecules of ethanal, the following product is obtained.

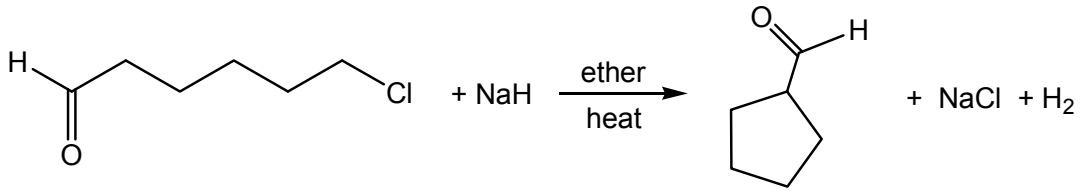
$$CH_3CHO + CH_3CHO \xrightarrow{OH^-} CH_3CH(OH)CH_2CHO$$
aldol

By considering the nucleophile generated from ethanal, state the type of reaction and describe the mechanism for the above *aldol* reaction.

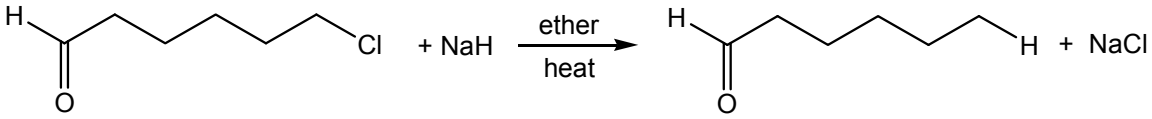
[5]

1 (f) Sodium hydride, NaH, is another inorganic compound which can take part in organic synthesis.

Reaction **I**



Reaction **II**



(i) State the type of reaction that has occurred in reaction **I**.

(ii) Suggest and explain why reaction **I** is more feasible than reaction **II** in terms of free energy and entropy changes.

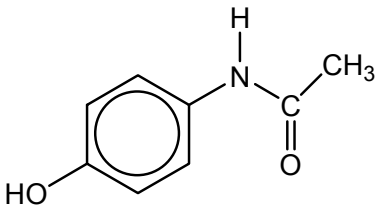
[3]

[Total: 20]

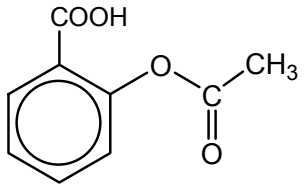
2 The use of medicine in the treatment of illnesses was revolutionised in the 19th and 20th century due to rapid advancements in chemistry, in terms of research work, laboratory techniques and equipments.

Aspirin and paracetamol are examples of drugs that have gained world-wide recognition for their medicinal properties. Aspirin and paracetamol are known as analgesics which is a group of drugs used to relieve pain.

(a) The structures of paracetamol and aspirin are given below:



Paracetamol



Aspirin

(i) Devise a three-step synthesis, starting with phenol, for the manufacture of paracetamol.

(ii) Suggest a method by which aspirin can be distinguished from paracetamol.

(iii) Predict, with a reason, whether aspirin or paracetamol has a lower pH.

(iv) Give the displayed formula of an isomer of aspirin which is not soluble in both hydrochloric acid and sodium hydroxide.

[10]

(b) The hydrolysis reaction of aspirin is catalysed by an acid. Four experiments were carried out to find the relationship between the rate of reaction and the initial concentrations of aspirin and the acid catalyst. The results are recorded in the table below.

Experiment	[aspirin] /mol dm^{-3}	$[H^+]$ /mol dm^{-3}	Initial rate / mol dm^{-3} h^{-1}
I	0.04	0.08	1.00
II	0.05	0.08	1.25
III	0.04	0.06	0.75
IV	0.05	0.06	0.94

(i) Write an equation to represent the hydrolysis of aspirin.

2 (b) **(ii)** Using the data in the table, deduce the order of reaction with respect to aspirin and the acid catalyst, showing how you arrive at your answers.

Hence determine the rate equation and calculate the rate constant for this reaction, giving its units.

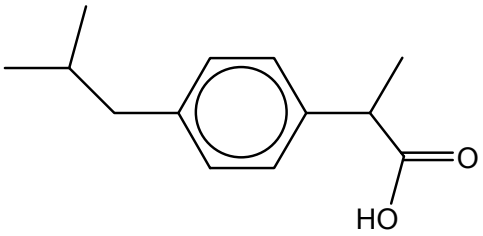
(ii) Given that the half-life of aspirin in experiment **I** was 3 hours, predict the half-life of aspirin in experiment **II** and in experiment **III**, giving your reasoning.

(iii) Sketch a graph showing how the concentration of one of the products of the hydrolysis reaction varies with time, by making use of the data given for experiment **I**.

[10]

[Total: 20]

3 Ibuprofen is an over-the-counter painkiller for mild to moderate pain which also reduces inflammation and fever.



Ibuprofen

In this question, ibuprofen is represented by RCOOH.

(a) Ibuprofen has a pK_a value of 4.4.

(i) Define the term pK_a.

(ii) 800 cm^3 of sodium hydroxide was added to 200 cm^3 of 0.5 mol dm^{-3} of ibuprofen to make a 1.00 dm^3 buffer solution of pH 5.00.

Prove that the ratio of the concentrations of the salt of ibuprofen to the concentration of unionised ibuprofen is 3.98.

Hence, calculate the concentration of the sodium hydroxide solution added to make the buffer solution.

[4]

(b) The values for ΔH^{θ} for the reactions of NaOH with HCl and ibuprofen are given below:

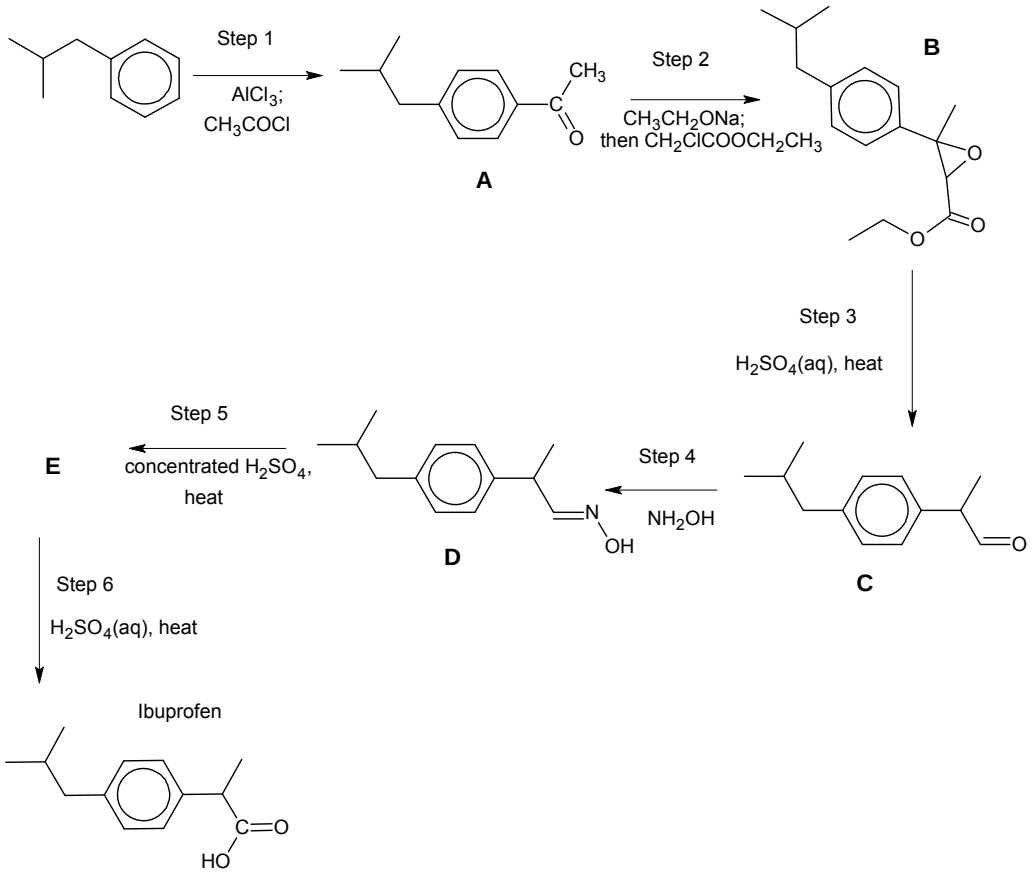
$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$ $\quad \Delta H_1^{\theta} = -57.3\ kJmol^{-1}$

$RCOOH(aq) + NaOH(aq) \rightarrow RCOONa(aq) + H_2O(l)$ $\quad \Delta H_2^{\theta} = -50.0\ kJmol^{-1}$

Comment on the values of ΔH_1^{θ} and ΔH_2^{θ} given and deduce the value of the enthalpy change of acid dissociation of ibuprofen by drawing a suitable energy cycle.

[4]

3 (c) Ibuprofen can be synthesized using the following steps. The starting material is 2-methylpropylbenzene.



(i) State the types of reactions taking place at step **1** and step **4**.

(ii) Suggest **two** tests (stating reagents and conditions) that will enable compounds **A** and **C** to be distinguished from each other.

(iii) Compound **B** is unstable.

Suggest the size of the bond angle in the three membered ring in **B.** Hence explain why **B** is unstable.

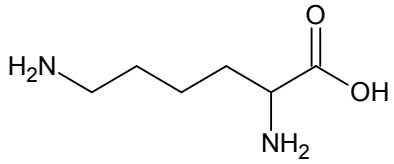
(iv) Suggest a structure for compound **E**.

[9]

3 (d) In order for ibuprofen to act quickly, it must be quickly absorbed into the bloodstream through the stomach lining. The more soluble it is in water, the faster the painkilling action.

(i) Explain why ibuprofen is not very soluble in water.

(ii) To make ibuprofen more soluble in water, manufacturers react it with lysine, an amino acid, first to form ibuprofen lysinate, a salt.



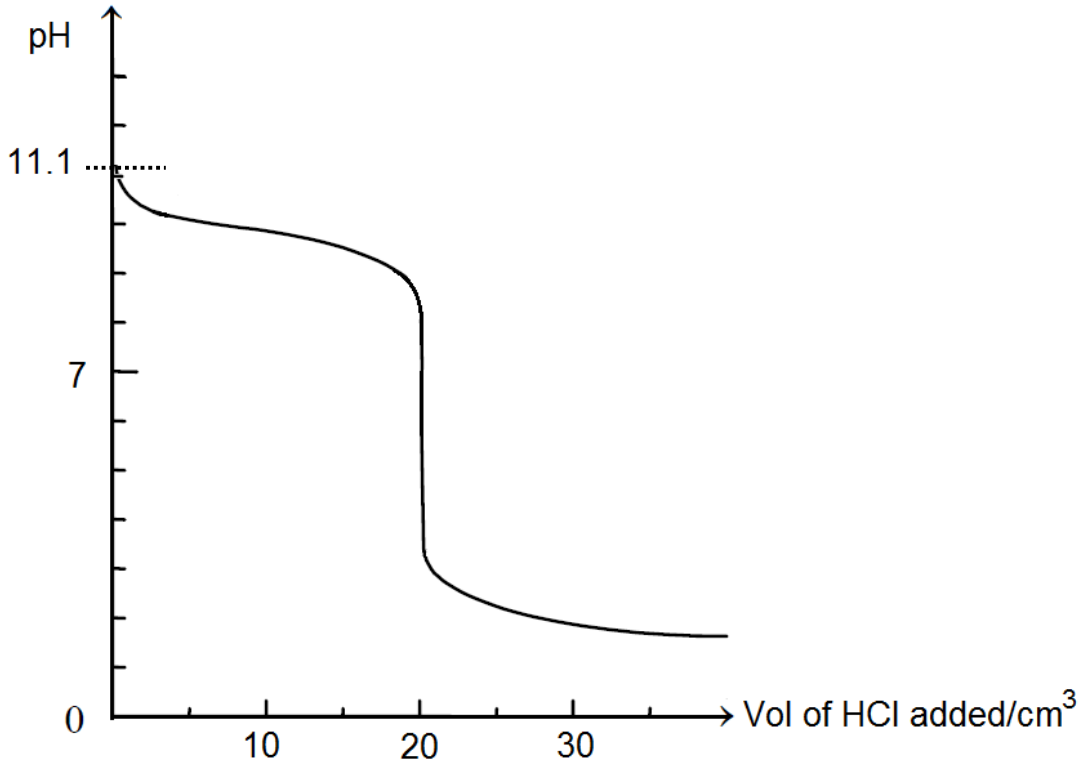
Lysine

Draw the structural formula of the salt formed when ibuprofen reacts with lysine and explain why this salt is more soluble than ibuprofen.

[3]

[Total: 20]

4 (a) 20.0 cm^3 of 0.10 mol dm^{-3} solution of propylamine, $CH_3CH_2CH_2NH_2$, was titrated against 0.10 mol dm^{-3} solution of hydrochloric acid. The following titration curve was obtained.



(i) Calculate the base dissociation constant, K_b, of propylamine with the use of initial pH on the titration curve.

(ii) Explain the pH value obtained at equivalence point with the aid of an appropriate equation.

(iii) A student used phenolphthalein to carry out the above titration. Comment on the suitability of this indicator.

(iv) An aqueous solution of propylamine, $CH_3CH_2CH_2NH_2$ and $CH_3CH_2CH_2NH_3Cl$ can act as a buffer solution.

(I) State the volume of hydrochloric acid at which the buffer operates at its maximum buffer capacity.

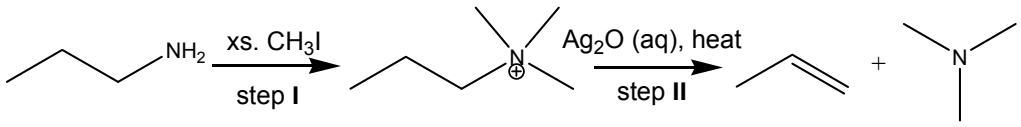
(II) Write suitable equations to illustrate the buffering action of an aqueous solution of $CH_3CH_2CH_2NH_2$ and $CH_3CH_2CH_2NH_3Cl$ when small amounts of NaOH or HCl is added to it.

[9]

4 (b) The following shows a 2-step reaction where

- an aliphatic amine is reacted with excess methyl iodide to create a quaternary ammonium salt, followed by
- treatment with heated aqueous silver oxide to give an alkene.

The 2-step reaction is performed on propylamine to yield propene.



(i) Name the type of reaction in step **II**.

(ii) When (1,N)-dimethylpropylamine, $CH_3CH_2CH(CH_3)NHCH_3$, undergoes the same 2-step reaction, three alkenes **F**, **G** and **H** are formed. Given that **F** and **G** are geometric isomers, draw the structures of **F**, **G** and **H**.

(iii) Draw the mechanism of the reaction between propene and HBr, considering only the major product. In your answer, show any relevant charges, dipoles or lone pairs of electrons you consider to be important in this mechanism.

[7]

(c) An alkene **J**, molecular formula C_6H_{12}, exhibits geometric isomerism. **J** is reacted with chlorine in the presence of ultraviolet light to form three isomers of $C_6H_{11}Cl$.

(i) Deduce the structural formula of **J**.

(ii) Suggest, with a reason, the approximate ratio in which the three monochlorinated alkenes are formed.

[4]

[Total: 20]

5 *Use of the Data Booklet is relevant to this question.*

(a) **(i)** Predict the products formed at the cathode, and at the anode, when the following are electrolysed.

(I) $K_2O(l)$ using graphite electrodes.

(II) $CuSO_4(aq)$ using copper electrodes.

In each case explain your reasoning.

(ii) The electrolysis of $K_2O(l)$ is carried out by passing a current of 5A for 30 minutes. Calculate the volume of gas collected at r.t.p.

[7]

(b) When concentrated hydrochloric acid is added to a blue solution of copper(II) sulfate, a yellowish green solution **X** is formed. When copper metal is added to this solution **X** and boiled, a colourless solution **Y** is obtained which forms a white precipitate **Z** when distilled water is added to it. When **Z** is filtered off and left exposed to air, it slowly turned green.

X and **Y** are complex ions of copper and chlorine while **Z** is a compound of copper and chlorine only. The oxidation number of copper in both **Y** and **Z** are the same.

(i) Identify **X**, **Y** and **Z**.

(ii) Explain why solution **X** is coloured while solution **Y** is colourless.

(iii) With the aid of relevant data, explain why **Z** slowly turned green when it is exposed to air.

[9]

5 (c) A Group I metallic salt has the formula MI_aCl_b. When 0.27 g of this compound was heated, it decomposed to form iodine vapour and a metallic chloride.

The iodine was then bubbled into excess potassium iodide and the resulting solution was titrated against aqueous sodium thiosulfate. It was found that 21.30 cm^3 of 0.0600 mol dm^{-3} of aqueous sodium thiosulfate was required.

When the residue was dissolved in water, the resulting solution required 6.40 cm^3 of a 0.100 mol dm^{-3} aqueous silver nitrate for complete reaction.

(i) Calculate the number of moles of iodine and chloride formed.

(ii) Determine the values of **a** and **b** and hence state the identity of the Group I metal.

[4]

[Total: 20]

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H2 CHEMISTRY **Tues 13 Sep 2011**
9647/03 **TIME: 2 hour**

Cover page for Paper 3

Staple this cover page in front of your writing paper.
Please **circle the question numbers** which you have attempted.

Question	For Examiner's Use
1	
2	
3	
4	
5	
Total	