RIVER VALLEY HIGH SCHOOL
YEAR 6 PRELIMINARY EXAMINATION

CANDIDATE NAME									
CLASS	6								
CENTRE NUMBER	S					INDEX NUMBER				

H2 CHEMISTRY 9647/03

Paper 3 Free Response

12 September 2011

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Graph Paper
Cover Page
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class, Centre number and index number on all the work you hand in.
Write in dark blue or black pen on both sides of paper.
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.
Begin each question on a fresh sheet of paper.
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.
At the end of the examination, fasten all your work securely together, with the cover page on top.

This document consists of **11** printed pages.

Answer any **four** questions.

1 Nitrogen is one of the most abundant elements on earth. It is present in many molecules that find applications in chemistry and biology, such as ammonia, haemoglobin and amino acids.

(a) During the combustion of ammonia, it reacts to form nitrogen gas and water vapour as seen in the equation below:

$$4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(g)$$

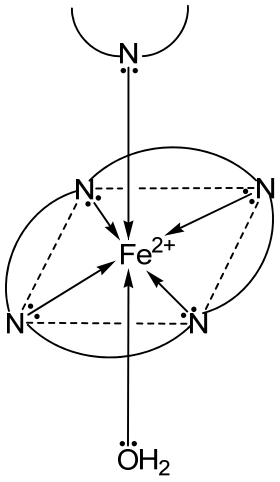
(i) Using relevant data from the *Data Booklet*, calculate the enthalpy change of the reaction.

(ii) Given that the theoretical value of enthalpy change of reaction is -1267 kJ mol^{-1}, explain why the calculated value is different.

(iii) State, with reason, the sign of the entropy change of the reaction. Hence, explain if the above reaction is spontaneous.

(iv) Rank the four gases of NH_3, O_2, N_2 and H_2O in order of increasing deviation from ideal behaviour. Explain your answer. [8]

(b) Haemoglobin is red pigment in blood responsible for carrying oxygen from the lungs to the cell of the body. The molecule consists of a Fe^{2+} ion, a porphyrin ring system and a complex protein known as globin. The structure of haemoglobin is given below.



(i) Describe the quaternary structure of haemoglobin.

(ii) It was found that one molecule of haemoglobin combines with four molecules of oxygen. If 2.00 g of haemoglobin combines with 3.06 cm^3 of oxygen at 37.0 °C and 98.7 kPa, what is the molar mass of haemoglobin? State any assumptions you made in your calculations.

(iii) The actual molar mass of haemoglobin is 6.90×10^4 g mol^{-1}. Based on your working in **(ii)**, suggest, with reasons, why there is a discrepancy in the two values. [6]

(c) Amino acids are critical to life, and they serve as the building blocks of proteins. Out of the vast variety of amino acids, eight are termed as essential because they cannot be created by the human body, and therefore must be supplied in the diet. They are shown as follows:

Amino acid	R group
Isoleucine (ile)	$-CH(CH_3)(CH_2CH_3)$
Leucine (leu)	$-CH_2CH(CH_3)_2$
Lysine (lys)	$-(CH_2)_4NH_2$
Methionine (met)	$-CH_2CH_2SCH_3$
Phenylalanine (phe)	$-CH_2(C_6H_5)$
Threonine (thr)	$-CH(OH)(CH_3)$
Tryptophan (trp)	$-CH_2(C_8H_6N)$
Valine (val)	$-CH(CH_3)_2$

(i) Valine is able to exhibit stereoisomerism.

State the type of stereoisomerism which occurs in valine and draw two structures which illustrate this isomerism.

(ii) State and draw **two** types of side chain interactions that can occur between these eight essential amino acids.

(iii) Draw the displayed formula of a tripeptide formed from **one** molecule of lysine, **one** molecule of threonine and **one** molecule of valine.

[6]

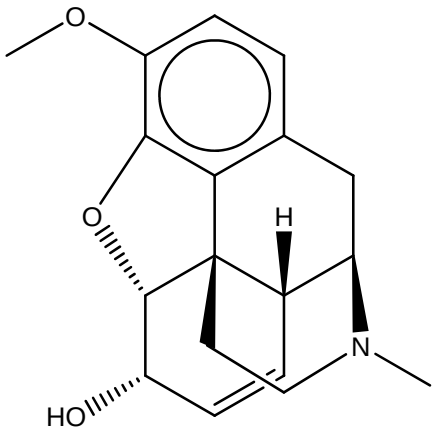
[Total: 20]

2 Compound **A**, $C_{16}H_{30}O_4$, is believed to be an anti-cancer drug found in one medicinal plant extract in the jungles of Southeast Asia. On testing, it was found that:

- Compound **A** is insoluble in both water and dilute aqueous HC*l*
- Upon heating with dilute HC*l*, compound **A** gives two compounds: compound **B**, $C_6H_{14}O$ and compound **C**, $C_4H_6O_4$.
- Compound **B** can rotate the plane of polarised light and reaction of compound **B** with hot acidified potassium permanganate (VII) produces compound **D**, $C_6H_{12}O$, which gives a yellow precipitate with iodine in aqueous sodium hydroxide.
- Heating compound **B** over Al_2O_3 produces compound **E**, C_6H_{12}, and vigorous oxidation of compound **E** produces butanoic acid as one of the products.
- Compound **C** can be synthesised by reacting 1,2-diiodoethane with hot ethanolic NaCN followed by warming with dilute sulfuric acid.

(a) Deduce the structures of compounds **A, B, C, D** and **E**. Explain the chemistry of the reactions described. [10]

(b) Codeine is a drug used to treat mild to moderate pain and to relieve cough. The structure of codeine is as shown below.



(i) Codeine has a tertiary amine functional group. Codeine can be sold in its ionic form of $(R_3NH)^+Cl^-$, which is known as codeine hydrochloride. Calculate the pH of a solution when 0.10 mol of codeine hydrochloride is dissolved in 500 cm^3 of water.

K_b of codeine = 1.62×10^{-6} mol dm^{-3}

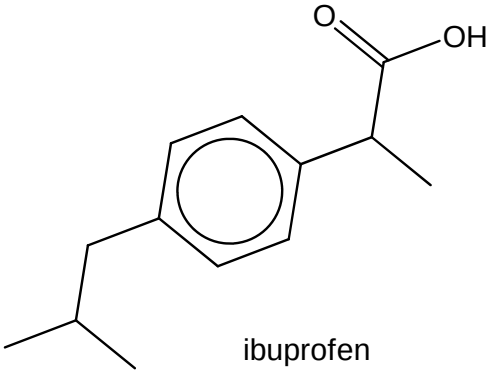
(ii) Calculate the pH of the resultant solution when 500 cm^3 of 0.20 mol dm^{-3} of NaOH is added to the codeine hydrochloride solution in **(i)**.

(iii) Using the answers in **(i)** and **(ii)**, sketch a titration curve when 0.20 mol dm^{-3} of NaOH is added to 500 cm^3 of codeine hydrochloride solution in **(i)**, showing clearly the pH at the point of maximum buffer capacity. [8]

(c) One of the properties of an ideal drug is that the drug can be synthesised quickly with high yield. Using a Boltzmann distribution curve, explain how the use of catalyst can speed up the rate of reaction of synthesising a drug molecule. [2]

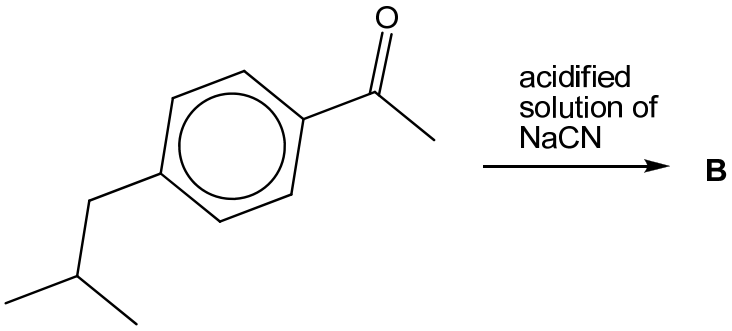
[Total: 20]

3 Ibuprofen belongs to a class of drugs called non-steroidal anti-inflammatory drugs (NSAIDs) used to reduce inflammation, pain and fever. Pain, fever, and inflammation are promoted by the release in the body of chemicals called prostaglandins. Ibuprofen blocks the enzyme that makes prostaglandins (cyclooxygenase), resulting in lower levels of prostaglandins.



ibuprofen

The following diagram shows the first step in the synthesis route to form ibuprofen from compound **A**.



1-(4-isobutylphenyl)ethanone

A

(a) A series of experiments were carried out to find the effect of initial concentration of hydrogen ions, cyanide ions and **A** on the initial rate of formation of **B**.

Experiment	Initial concentration / mol dm^{-3}			Initial rate of formation of **B** / mol dm^{-3} s^{-1}
	[**A**]	$[H^+]$	$[CN^-]$	
1	0.020	0.060	0.060	1.00
2	0.020	0.050	0.050	0.833
3	0.020	0.050	0.060	1.00
4	0.025	0.050	0.050	1.042

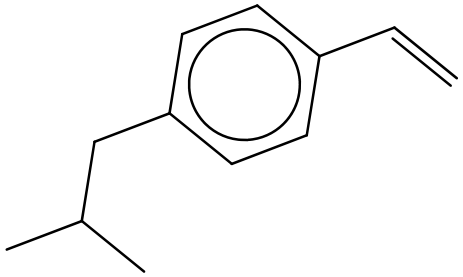
(i) Write a balanced equation for the reaction that produces compound **B**.

(ii) Use the data in the table to deduce the order of the reaction with respect to each of the three reactants, showing how you arrive at your answers.

(iii) Write a rate equation for this reaction.

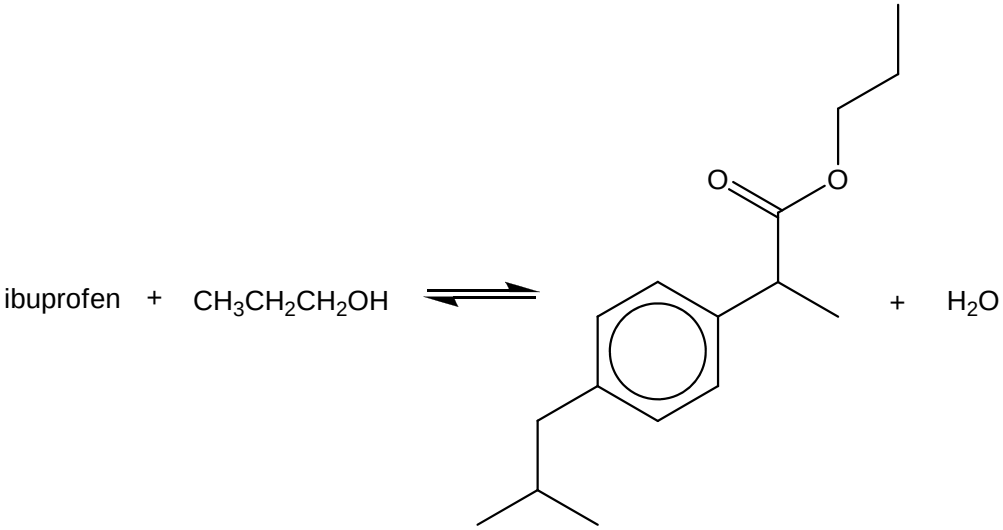
(iv) Describe a mechanism that is consistent the rate equation deduced in (b)(ii), and indicate which step in the mechanism is the rate determining step. Explain your reasoning. [8]

(b) Propose a 3-steps synthesis of ibuprofen starting from the compound 1-isobutyl-4-vinylbenzene. Indicate the reagents and conditions, and the structure of the intermediates.



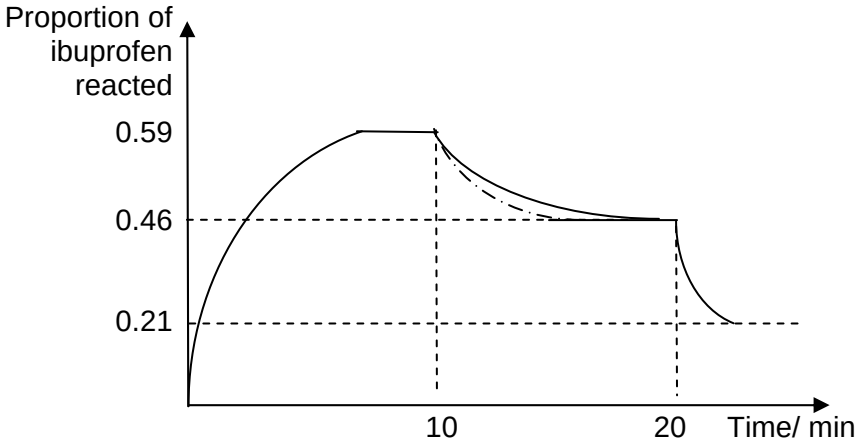
1-isobutyl-4-vinylbenzene [5]

(c) The reaction involving ibuprofen and propanol in equilibrium with the products can be represented as follows.



An experiment was set up to further investigate the effect of experimental conditions on the reaction between ibuprofen and propanol. In this experiment, 0.00500 mol of ibuprofen, 0.500 mol of propanol and 0.25 mol of concentrated sulfuric acid are mixed together in a flask at 20 °C.

The following graph shows the proportion of ibuprofen in the flask that had reacted over time.

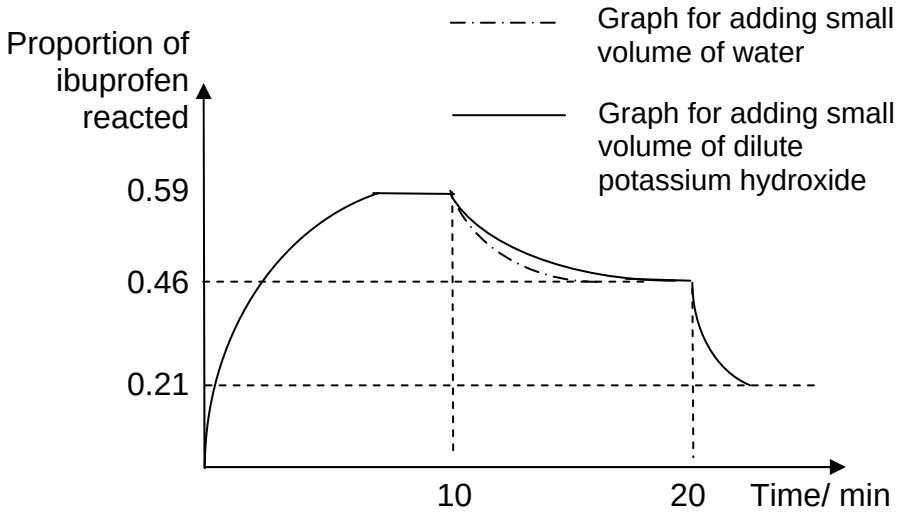


(i) Determine the K_c of the reaction at 19 min.

(ii) The temperature of the reaction mixture was increased to 45 °C at 20 min. Explain whether the forward reaction is endothermic or exothermic.

(iii) When the reaction is carried out at 45 °C under non-reflux condition, the drop in proportion of ibuprofen reacted was more drastic than expected for the change in temperature at 20 min. Suggest a reason for more than expected decrease.

(iv) In the original experiment, a small volume of water was added at 10 min. A student repeated the experiment and added the same volume of dilute potassium hydroxide solution instead of water at 10 min.



Account for the shape of the graph in both the original and the repeated experiment from 10 to 20 min. [7]

[Total: 20]

4 In 1810, British chemist Sir Humphry Davy determined experimentally that chlorine is a pure element and named it after the Greek word *"chloros"*, which means "green-yellow". Chlorine and its compounds are now widely used in the manufacture of many useful products.

(a) The active component in weed killers is sodium chlorate(V), $NaClO_3$, which can be synthesised by passing chlorine gas into a hot solution of sodium hydroxide.

(i) State the type of reaction and write an equation for the reaction.

(ii) Draw a dot-and-cross diagram for the ClO_3^- ion and hence suggest its shape. [4]

(b) Chlorine can also be used to synthesise a bromine-containing oxoanion that is mainly used in continuous or batch dyeing processes.

When chlorine is passed through an aqueous solution containing potassium hydroxide and potassium bromide, the bromide ions are oxidised to the bromine-containing oxoanion. Careful addition of aqueous lead nitrate to the resulting solution precipitates 4.17 g of $PbCl_2$. When this precipitate is filtered off and the resulting filtrate is evaporated, 0.835 g of a white crystalline solid is obtained. The white solid has the following composition by mass:

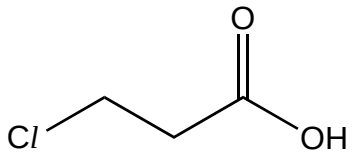
K, 23.4 %; Br, 47.8 %; O, 28.8 %

(i) Determine the formula of the white crystalline solid.

(ii) Calculate molar ratio of white crystalline solid to lead chloride formed.

(iii) Hence, construct a balanced equation for the reaction between chlorine, potassium bromide and potassium hydroxide. [5]

(c) 3-chloropropanoic acid is a drug used in scientific research due to its structural resemblance to 4-hydroxybutanoic acid, a naturally occurring substance found in the central nervous system.



3-chloropropanoic acid

(i) The pK_a of propanoic acid is 4.87. Predict, with reasons, how the pK_a of 3-chloropropanoic acid would differ from propanoic acid.

(ii) To determine the actual pK_a of 3-chloropropanoic acid, 0.020 mol of the solid acid was dissolved in 50 cm^3 of water and titrated with a 0.10 mol dm^{-3} solution of NaOH. After 20 cm^3 of NaOH was added, the pH of the solution was found to be 3.03.

Determine the pK_a of 3-chloropropanoic acid.

(iii) The resultant solution in **(ii)** is a *buffer solution*. Explain what is meant by a buffer solution.

(iv) Write an equation to illustrate how the resultant solution in **(ii)** acts as a buffer when acid is added.

(v) A positional isomer of 3-chloropropanoic acid is 2-chloropropanoic acid. Draw the **displayed** formula of the optically active isomer.

(vi) Compare the acid strength of 2-chloropropanoic acid with 3-chloropropanoic acid. Explain your answer. [11]

[Total: 20]

5 Cobalt, copper and zinc are elements in Period 4 of the Periodic Table. Cobalt and copper are considered to be transition elements but zinc is not.

(a) Explain why zinc is not considered to be a transition element. [1]

(b) One property of transition elements is the formation of complex ions.

(i) Explain why transition elements have a tendency to form complex ions.

(ii) Copper(II) sulfate reacts with excess aqueous ammonia to form a complex ion. Describe what you would observe when aqueous ammonia is added dropwise till in excess to a solution of copper (II) sulfate. Identify any coloured ions or compounds and write balanced equations for any reactions that occur. [6]

(c) By means of a fully labelled diagram, describe how the standard electrode potential of the Co^{2+}/Co system can be measured using a standard hydrogen electrode. [4]

(d) Cobalt(II) chloride forms a stable aqueous solution but a stable solution of cobalt(III) chloride is not known.

Explain why cobalt(III) chloride does not form a stable aqueous solution, using data from the *Data Booklet*. [2]

(e) Using data from the *Data Booklet*, predict what might happen when solutions of cobalt(II) chloride and acidified hydrogen peroxide are mixed. Write balanced equations for any reaction that might occur. [3]

(f) Transition elements and their compounds are often used as catalysts during the synthesis of organic compounds such as alkanes, alkenes and alcohols. These compounds are then used as feedstock to synthesise more complex structures.

Describe how you could distinguish the following pairs of organic compounds by means of a simple chemical test.

(i) $CH_3CH_2CH_2CH_2OH$ and $CH_3CH(OH)CH_2CH_3$

(ii) $CH_3CH_2CH_2CH_2CH{=}CH_2$ and $CH_3CH_2CH_2CH_2CH_2CHO$ [4]

[Total: 20]