Class Adm No

Candidate Name: _____

H

millennia institute

2011 Preliminary Examination II
Pre-university 3

CHEMISTRY **9647/02**

Paper 2 Structured Questions **16 September 2011**

Candidates answer on the Question Paper. **2 hours**

Additional Materials: 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.
You may use a soft pencil for any diagrams or graphs.
Do not use paper clips, highlighters, glue or correction fluid.

Answer **all** questions.
A Data Booklet is provided.

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

You are reminded of the need for good English and clear presentation in your answers.

For Examiners						
Q	**1**	**2**	**3**	**4**	**5**	**Total**
Score	/12	/4	/8	/41	/7	/72

This question paper consists of 18 printed pages.

[Turn over

1 Planning (P)

Biodiesel, which could be obtained from natural products such as soybean, is a renewable and generally cleaner-burning fuel than petroleum diesel. However, it was claimed that biodiesel is less efficient as the heat content of biodiesel is less than that of petroleum diesel.

The enthalpy change of combustion of straight chain alkanes can be estimated by finding the enthalpy change of combustion of a $–CH_2–$ unit. This data could be obtained from the standard enthalpy change of combustion of straight chain alkanes.

The enthalpy change of combustion of straight chain alkanes with 1 to 5 carbons are as shown:

No. of carbon atoms	Alkane	$\Delta H^{\ominus}_{combustion}$ / kJ mol^{-1}
1	CH_4	-890
2	C_2H_6	-1560
3	C_3H_8	-2219
4	C_4H_{10}	-2877
5	C_5H_{12}	-3509

In this question, it is assumed that petroleum diesel contained only hydrocarbon $C_{20}H_{42}$ (l), and that soybean oil used as a biodiesel.

a) i) Plan a series of experiments to find out the enthalpy change of combustion of successive alkanes shown in the table above. Illustrate by means of a well labelled diagram how the experiment will be set up.

ii) Show how you will use your data to estimate a value of the enthalpy change of combustion of $C_{20}H_{42}$ (l).
Use **c** to represent specific heat capacity of water and **C** to represent the heat capacity of the calorimeter.

[6]

b) A student calculated a value of enthalpy change of combustion of $C_{20}H_{42}$ (l) using the bond energy data from the Data Booklet. Explain if the value would be a reliable estimate of the actual value. [1]

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[Turn over

c) Soybean oil used as a biodiesel contained primarily the methyl ester of linoleic acid ($C_{19}H_{34}O_2$).

The enthalpy change of formation are given as follows:

Substance	$\Delta H^{\ominus}_{formation}$ / kJ mol^{-1}
CO_2 (g)	-394
H_2O (*l*)	-286
$C_{19}H_{34}O_2$ (g)	-605

The standard enthalpy change of vaporisation of $C_{19}H_{34}O_2$ (*l*) is +62.1 kJ mol^{-1}.

Using the information above, draw an energy cycle and use it to calculate the standard enthalpy change of combustion of $C_{19}H_{34}O_2$ (*l*). [3]

d) Using the data of enthalpy change of combustion of straight chain alkanes, estimate a value for the enthalpy change of combustion of $C_{20}H_{42}$ (*l*). Hence, justify the claim made about the efficiency of biodiesel. [2]

[Total: 12]

2 Deuterium, ^{2}D, is an isotope of hydrogen. D_2O can be used in the elucidation of molecular structures of substances.

a) Deduce the total number of neutrons present in D_2O. [1]

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b) Suggest how D_2O is different from H_2O. [1]

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c) Given the average relative atomic mass of hydrogen is 1.00015, assuming that ^{2}D is the only other isotope of ^{1}H, find the percentage abundance of deuterium. [1]

d) Write a balance equation to show the reaction between chlorine gas with NaOD dissolved in D_2O at $15^{o}C$. [1]

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[Total: 4]

3 'Hydrophobic' is a term derived from *hydro-* (water) and *phobos* (fear).

In water, hydrophobic molecules generally tend to aggregate to minimize their surface contact, and associated surface energy, with water molecules. Smaller hydrophobic molecules could, however, dissolve to a small extent in water as water molecules can arrange around them without breaking hydrogen bonds or losing much energy. Adding CH_2 groups to aliphatic alcohols increases the heat produced on solution ($\Delta H^{\ominus}$ per CH_2 unit = -5.4 kJ mol^{-1}) but causes a greater decrease in the entropy ($\Delta S^{\ominus}$ per CH_2 unit = -23.8 J mol^{-1})

a) Calculate $\Delta G^{\ominus}$ of the dissolution per unit of CH_2 group in aliphatic alcohols. [1]

b) Suggest why the entropy change per CH_2 unit is negative. [1]

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c) Predict the effect of temperature change on the spontaneity of dissolution of each CH_2 unit. [2]

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d) By studying a series of alkanes, the $\Delta G^{\ominus}$ of transfer of a hydrocarbon molecule from a dilute aqueous solution into a dilute solution of another hydrocarbon is measured. The $\Delta G^{\ominus}$ per CH_2 unit was found to be -3.8 kJ mol^{-1}.

$$-CH_2- (aq) \rightarrow -CH_2- (hexane) \qquad \Delta G^{\ominus} = -3.8 \text{ kJ mol}^{-1}$$

What could be deduced from the sign of $\Delta G^{\ominus}$ above? [1]

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e) A students wrote, "The $\Delta G^{\ominus}$ of transfer of $-SiH_2-$ (aq) to $-SiH_2-$ (hexane) is predicted to be about -3.0 kJ mol^{-1} as the *C-H bond is less polar than Si-H bond*."

Using your knowledge of periodicity, explain the phrase in italics. [1]

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f) Solubility of an organic compound can be altered by a chemical change.

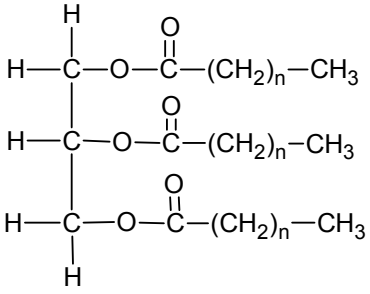
Octan-1-ol was refluxed in the presence of Na*Cl* and concentrated H_2SO_4. Draw the displayed formula of the product of the reaction. [1]

[Total: 8]

4 Saponification is a process where esters in triglycerides, commonly known as oil or fats, are hydrolyzed in the presence of a strong base to form soap – a mixture of glycerol and fatty acids.

A fatty acid contains both a hydrophobic group that allows it to dissolve oil-based substances, and a hydrophilic group that allows it to dissolve in water. This results in the cleaning action of soaps.

A saturated triglyceride molecule has a general structure:



where n is a whole number, usually between 16 to 20.

The Saponification (SAP) value is the mass of potassium hydroxide (in milligrams) required to hydrolyse 1 g of triglycerides under stated conditions. SAP value is inversely related to mean molecular mass:

$$\text{SAP} = \frac{168300}{\text{Average } M_r \text{ of triglyceride}}$$

The general procedures of saponification are as follow:

(1) To 5 g sample of triglyceride in a conical flask, add 50 cm^3 of 0.5 mol dm^{-3} potassium hydroxide dissolved in ethanol.
(2) Reflux the mixture in an oil bath.
(3) Titrate the excess potassium hydroxide with 0.5 mol dm^{-3} hydrochloric acid using phenolphthalein as indicator.

a) i) Assuming that the triglyceride used is saturated and has n = 16 on all 3 side chains, write a balanced equation of the reaction occurring in Step (1) above.

ii) Provide a reason why the hydrolysis reaction was found to be exothermic.

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iii) Acid hydrolysis of triglycerides is not a preferred method as the reaction is reversible. Using Le Chatelier's Principle, explain why alkaline hydrolysis of triglycerides is a complete reaction.

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iv) The SAP value of olive oil is about 196. Find the average molecular mass of olive oil, and find the volume of HC*l* required for complete neutralisation in Step (3).

[8]

b) i) State the structure and bonding in fats, and explain how the melting point of saturated fats vary with the value of n.

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ii) Explain the role of ethanol in **Step (1)** of the saponification process.

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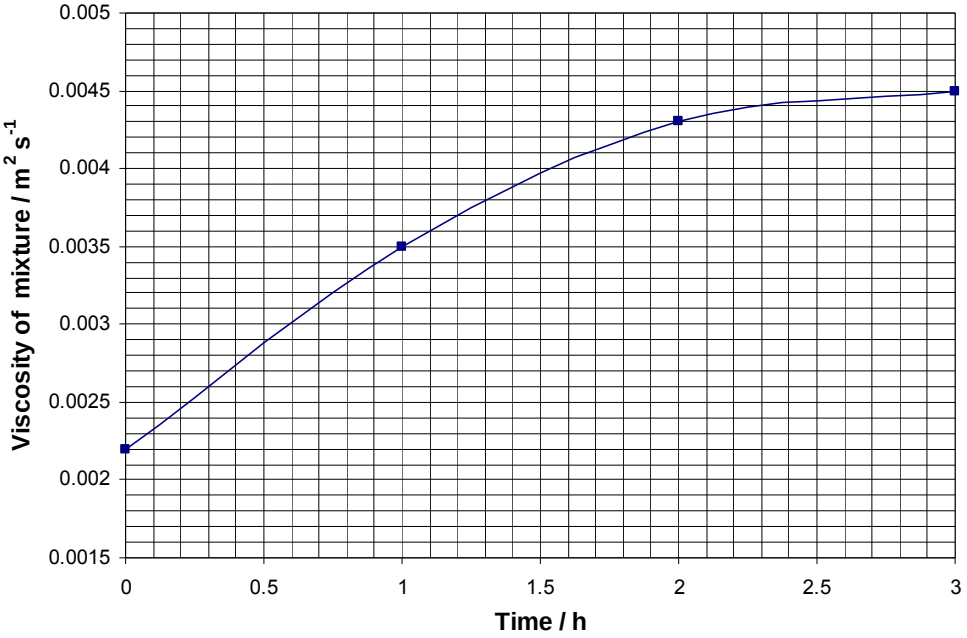
[3]

[Turn over

c) The kinetics of the hydrolysis of sunflower oil was investigated by a student.

To obtain the rate equation, the student performed a series of experiments. He dissolved 7 g of KOH in 10 cm^3 of water and added it to 50 g of sunflower oil maintained at 60^oC. The mixture was continuously stirred as the hydrolysis of sunflower oil proceeded. The viscosity of the mixture was measured at regular interval over 3 hours and is directly related to the amount of products formed.

He obtained a graph as shown below:



The amount of KOH and sunflower oil in the mixture at the respective times are determined:

Time / h	Amount of KOH / mol	Amount of sunflower oil / mol
0	0.125	0.0562
1	0.110	0.0519
2	0.082	0.0298

The student found that the order of reaction with respect to sunflower oil is 1.

i) Explain what is meant by *order of reaction*.

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ii) Determine the rate of reaction at time 1 h.

iii) Given that the rate of reaction at 0 h was 1.33 X 10^{-3} m^2 s^{-1} $h^{-1}$and rate at 2 h was 4.62 X 10^{-4} m^2 s^{-1} h^{-1}, deduce the order of reaction with respect to KOH.

iv) Hence, write a rate equation for the reaction.

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v) Discuss how using 10 g of KOH in the experiment above affects the rate of reaction.

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[7]

[Turn over

d) The number of double bonds in a fat can be determined by its iodine number. The iodine number is defined by the mass (in grams) of iodine that has reacted with 100 g of fats. As iodine is added to the fat, the colour of iodine will not appear until all C=C double bonds are saturated.

Linolenic acid is a carboxylic acid containing 18 carbon atoms with an iodine number of 261.

i) Write a balanced equation to show how $CH_3(CH_2)_{14}CHCHCOOH$ reacts with iodine.

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ii) Calculate the number of C=C double bonds in linolenic acid. Hence, deduce the molecular formula of linolenic acid.

iii) While the iodine number indicates the number of C=C bonds, it does not indicate the positions of the C=C bond. Suggest a method that could allow the position of the C=C to be determined in linolenic acid.

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iv) Predict and explain the relative acidity of linolenic acid and $CH_3(CH_2)_{15}CHICOOH$.

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v) $CH_3(CH_2)_{15}CHICOOH$ can react with NaOH under suitable conditions to form two different products. State the two conditions and draw the structural formula of the two products.

Condition 1:……..…

Structural formula of product:

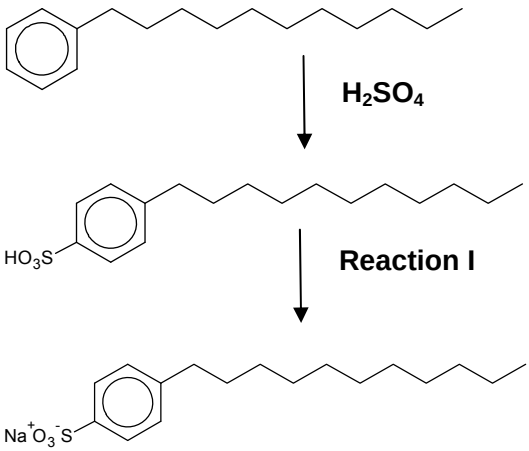
Condition 2:……..…

Structural formula of product:

[9]

e) Synthetic detergent consists of a hydrocarbon chain and polar group. As a surfactant, the synthetic detergent is more effective than conventional soap in hard water – water that contains dissolved minerals such as Ca^{2+} and Mg^{2+}.

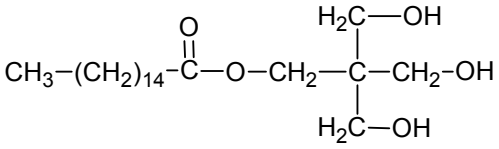
Anionic detergents contain groups with a negative charge such as $Na^+SO_3^-$. An example of synthesis of a detergent sodium-n-dodecylbenzenesulfonate is as follows:



[Turn over

Cationic detergents contain positively charged groups and can be found in hair conditioners. Keratin, a protein which contains negatively-charged groups which can be found on the surface of hair, binds strongly to the hydrophilic ends of cationic detergents. The hydrophobic ends of the surfactant molecules then act as the new hair surface. One example of such a detergent is trimethylhexadecylammonium chloride, $[CH_3(CH_2)_{15}N(CH_3)_3]^+ Cl^-$.

Non-ionic surfactants are commonly used in dish washing liquid. An example is pentaerythrityl palmitate:



i) State the type of reaction in **Reaction I**.

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ii) State possible reagents and conditions to synthesize $[CH_3(CH_2)_{15}N(CH_3)_3]^+$ from $CH_3(CH_2)_{15}NH_2$. Describe the mechanism of the synthesis.

Reagents:……..…

Conditions:……..…

iii) Suggest why non-ionic surfactants are commonly used in dish washing liquids.

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[5]

f) Apart from detergents or soap, cleaning products may also contain enzymes to degrade protein-based stains. Enzymes are proteins with a specific biological activity that are determined by their primary, secondary, tertiary and quaternary structures.

i) Illustrate the general arrangement of atoms in a protein by drawing a small section of a protein.

ii) Briefly describe with a well-labelled diagram, one example of a secondary structure of a protein.

iii) The effectiveness of enzymes depends on the pH of their environment. Explain the possible effects of varying pH on the primary, secondary and tertiary structures of enzymes.

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[Turn over

iv) State another possible factor which can influence the effectiveness of an enzyme.

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v) Explain the relationship between substrate concentration and the rate of an enzyme catalysed reaction.

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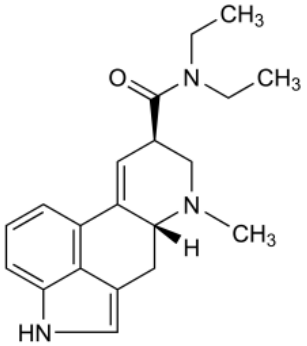
[9]

[Total: 41]

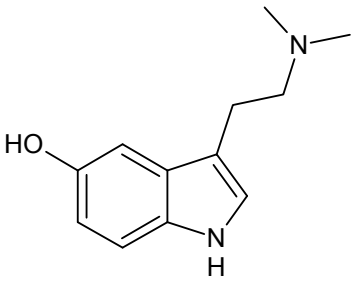
5 Urine is composed of water, electrolytes, and various waste products that are filtered out of the blood system. Thus, urine drug testing is widely used for testing for opioids and illicit drugs. Before a full analysis is made, the laboratory analyst needs to ensure that the urine is not tampered with by checking if the samples are consistent with human physiology.

Generally, urine pH is between 4.5 to 8.0, and urinary creatinine should be greater than 200 mg/L. A creatinine less than 50 mg/L is not consistent with human urine and the sample should be discarded.

Lysergic acid diethylamide (LSD) is an illicit drug which results in altered experience in senses and hallucinations in abusers. Bufotenine is another hallucinogenic agent, a plant extract from South America. Their structures are:



Lysergic acid diethylamide



Bufotenine

Rotation about the carbon –nitrogen bond in the  group above through 90^{o} require an energy of about 85 kJ mol^{-1}.

a) Suggest how a suspect could have tampered with his urine sample such that the creatinine concentration is less than 50 mg/L. [1]

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b) State one chemical test which could be used to distinguish LSD from bufotenine. State the observations expected for each substance. [1]

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[Turn over

c) i) State the bond angle about carbon in the  group in LSD.

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ii) Rotation through 90^{o} about a carbon – carbon bond in an alkane requires about 6 kJ mol^{-1}. Suggest a reason and explain the difference in energy required for rotation about a carbon – carbon bond compared to the carbon-nitrogen bond in  .

[3]

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d) Dinitrogen trioxide gas can be made from two oxides of nitrogen.

It has a similar shape to a  group.

i) Draw the dot-and-cross structure of dinitrogen trioxide.

ii) Suggest a balanced equation with state symbols to show how dinitrogen trioxide could be produced.

[2]

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[Total: 7]