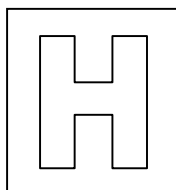


Candidate Name: _____

Class Adm No

--	--



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	7	41	5	72

This question paper consists of 21 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.

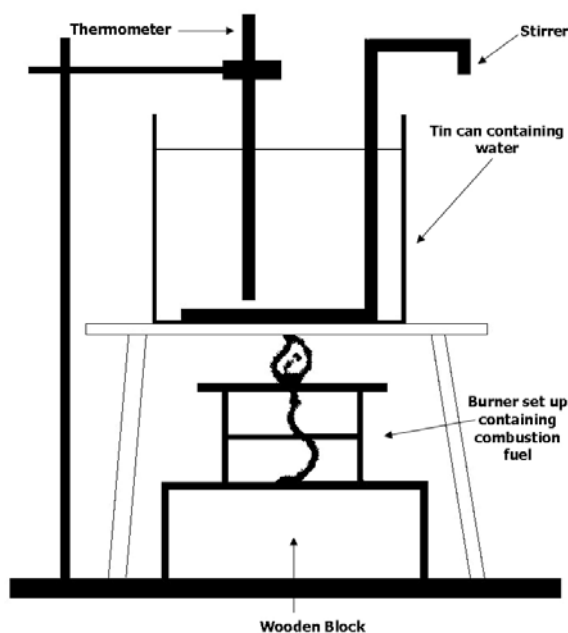
The enthalpy change of combustion of straight chain alkanes can be estimated by finding the enthalpy change of combustion of a $-\text{CH}_2-$ unit. This data could be obtained from the standard enthalpy change of combustion of straight chain alkanes.

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

No. of carbon atoms	Alkane	$\Delta H^\circ_{\text{combustion}} / \text{kJ mol}^{-1}$
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 $\text{C}_{20}\text{H}_{42}$ (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.



1 m for set-up

1. Weigh 30 g of CH₄ into a burner set up. Ensure that the wick is soaked in the fuel. Adjust the wick such that it is about 2 cm above the cap of the burner.
2. Using a measuring cylinder, add 200 cm³ of water into the empty tin can.
3. Using the stirrer, gently stir the water for 5 seconds. Measure the initial temperature of the water with the thermometer until the temperature becomes steady. Record the initial temperature, T_i.
4. Light the lamp, quickly place it in position and stir the water in the beaker gently with the thermometer.
5. As soon as a temperature rise of about 5°C has been obtained, blow out the flame. Record the final temperature, T_f.
6. Reweigh the burner and the unburnt fuel. Find the mass of alkane burnt.
7. Empty the water from the tin can and clean the soot off the bottom.
8. Repeat the experiment for the other 4 alkanes.

***1 mark for clear written procedures on how temperature rise is measured.
1 mark for clear written procedures on how mass of fuel burnt is measured.***

Bonus mark if calibration of combustion calorimeter with a substance with a known enthalpy change of combustion is stated.

- ii) Show how you will use your data to estimate a value of the enthalpy change of combustion of C₂₀H₄₂ (l).
Use **c** to represent specific heat capacity of water and **C** to represent the heat capacity of the calorimeter.

[6]

Heat evolved, Q

= mass of water in calorimeter x c x change in temperature of water + CΔT

Amount of C₂₀H₄₂ (l) = $\frac{\text{mass of alkane burnt}}{M_r \text{ of alkane}}$

$\Delta H = - \frac{Q}{\text{Amount of fuel burnt}}$ (allow e.c.f.)

Plot a graph of $\Delta H^\circ_{\text{combustion}}$ against no. of carbon atoms. Extrapolate to C₂₀ to find the $\Delta H^\circ_{\text{combustion}}$ of C₂₀H₄₂.

- 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]

It will not be a reliable estimate as it assumes that the reactants and products are gases which are not true in this case / oil is not in gaseous state.

(Do not accept: Bond energies are average values.)

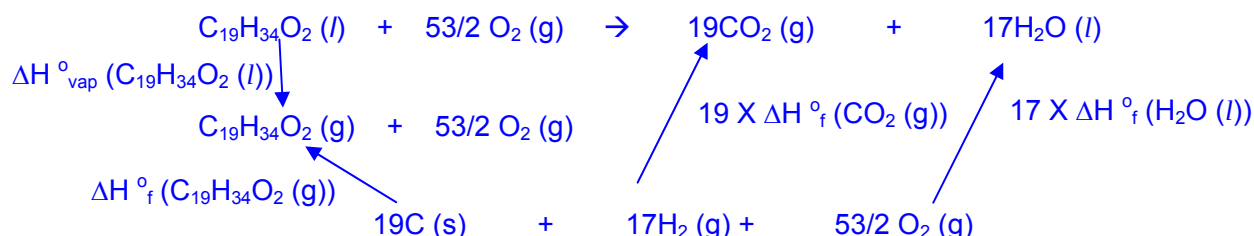
- c) Soybean oil used as a biodiesel contained primarily the methyl ester of linoleic acid ($C_{19}H_{34}O_2$). [3]

The enthalpy change of formation are given as follows:

Substance	$\Delta H^\circ_{\text{formation}} / \text{kJ mol}^{-1}$
$\text{CO}_2 (\text{g})$	-394
$\text{H}_2\text{O} (\text{l})$	-286
$\text{C}_{19}\text{H}_{34}\text{O}_2 (\text{g})$	-605

The standard enthalpy change of vaporisation of $\text{C}_{19}\text{H}_{34}\text{O}_2 (\text{l})$ is $+62.1 \text{ kJ mol}^{-1}$.

Using the information above, draw an energy cycle and use it to calculate the standard enthalpy change of combustion of $\text{C}_{19}\text{H}_{34}\text{O}_2 (\text{l})$.



$$\begin{aligned}
 &\Delta H^\circ_{\text{combustion}} \text{ of } \text{C}_{19}\text{H}_{34}\text{O}_2 (\text{l}) \\
 &= \Delta H^\circ_{\text{vap}} (\text{C}_{19}\text{H}_{34}\text{O}_2 (\text{l})) + 19 \times \Delta H^\circ_{\text{f}} (\text{CO}_2 (\text{g})) + 17 \times \Delta H^\circ_{\text{f}} (\text{H}_2\text{O} (\text{l})) - \Delta H^\circ_{\text{f}} (\text{C}_{19}\text{H}_{34}\text{O}_2 (\text{g})) \\
 &= 62.1 + 19(-394) + 17(-286) - (-605) \\
 &= -11680 \\
 &= -11700 \text{ kJ mol}^{-1} \text{ (3 s.f.)}
 \end{aligned}$$

- d) Using the data of enthalpy change of combustion of straight chain alkanes, estimate a value for the enthalpy change of combustion of $\text{C}_{20}\text{H}_{42}$ (l). Hence, justify the claim made about the efficiency of biodiesel. [2]
- Each CH_2 unit averages -655 kJ mol^{-1} .*

$$\begin{aligned}
 \Delta H^\circ_{\text{combustion}} \text{ of } \text{C}_{20}\text{H}_{42} &= -890 + 19(-655) \\
 &= -13335
 \end{aligned}$$

;

$$\approx -13300 \text{ kJ mol}^{-1}$$

As the combustion of $\text{C}_{20}\text{H}_{42}$ (l) is more exothermic than $\text{C}_{19}\text{H}_{34}\text{O}_2$ (l), the claim is ;
true that biodiesel is a less efficient fuel.

[Total: 12]

2 Deuterium, ^2D , 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]

Total number of neutrons = 1 + 1 + 8 = 10

;

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

D_2O has a slightly larger molecular mass than H_2O .

;

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

Let percentage abundance of the ^2D isotope be x .

$$1.00015 = \frac{x}{100} \times 2 + \frac{100-x}{100} \times 1$$

;

$$x = 0.015\%$$

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



;

[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 (ΔH° per CH_2 unit = -5.4 kJ mol^{-1}) but causes a greater decrease in the entropy (ΔS° per CH_2 unit = -23.8 J mol^{-1})

e) Calculate ΔG° of the dissolution per unit of CH_2 group in aliphatic alcohols. [1]

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -5.4 - 298(-23.8 \times 10^{-3}) \\ &= +1.69 \text{ kJ mol}^{-1} \end{aligned}$$

;

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

.....

 As the number of carbon increases, the hydrophobic effect / strength of ;
 temporary dipole-induced dipole interactions increases. More water molecules
 are arranged about the molecule, there is less degree of freedom / more order in
 the system.

- g) Predict the effect of temperature change on the spontaneity of dissolution of [2]
 each CH₂ unit.

.....

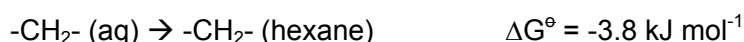
 ΔH° per CH₂ unit = -5.4 kJ mol⁻¹ < 0
 ΔS° per CH₂ unit = -23.8 J mol⁻¹ < 0

Exothermic reaction accompanied by decrease in entropy

Reaction is *spontaneous only at low temperature T* ;

as $|\Delta H| > |T\Delta S|$ to ensure that $\Delta G < 0$. ;

- h) By studying a series of alkanes, the ΔG° of transfer of a hydrocarbon molecule [1]
 from a dilute aqueous solution into a dilute solution of another hydrocarbon is
 measured. The ΔG° per CH₂ unit was found to be -3.8 kJ mol⁻¹.



What could be deduced from the sign of ΔG° above?

.....

*This shows that the CH₂ group would prefer to be in a non-polar environment ;
 than to be surrounded by water. / The dissolution of -CH₂- in hexane is a
 spontaneous process.*

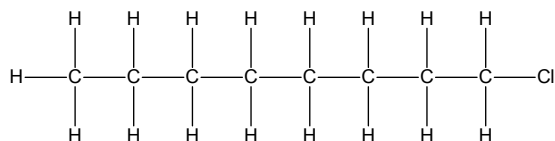
- i) A student wrote, "The ΔG° of transfer of -SiH₂- (aq) to -SiH₂- (hexane) is [1]
 predicted to be about -3.0 kJ mol⁻¹ as the *C-H bond is less polar than Si-H bond.*"

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

.....
.....
Si is less electronegative than C due to the lower effective nuclear charge down the Group. Hence, the difference in electronegativity between Si and H is greater, leading to a more polar bond.

- j) Solubility of an organic compound can be altered by a chemical change. [1]

Octan-1-ol was refluxed in the presence of NaCl and concentrated H₂SO₄. Draw the displayed formula of the product of the reaction.

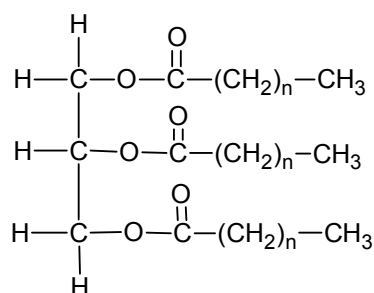


[Total: 7]

- 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:



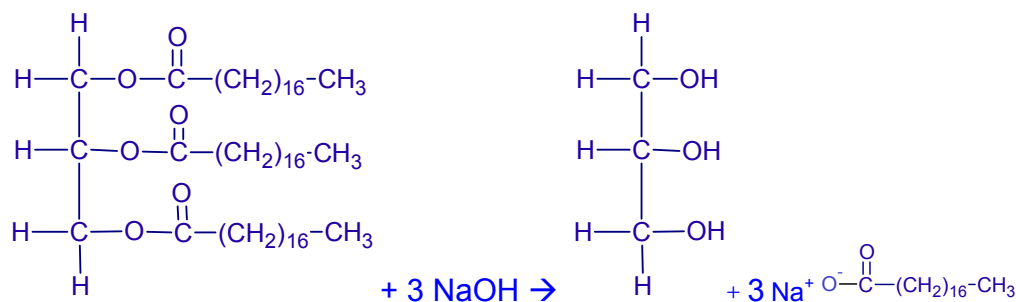
where n is a whole number, usually between 16 to 20.

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 cm³ 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.



1 m: balanced equation

1 m: correct products

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

.....

*The amount of energy required to break the chemical bonds in the reactants is ;
 less than the amount of energy produced in the formation of bonds.*

- 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.

.....

Ester (l) + H₂O (l) ⇌ carboxylic acid (l) + alcohol (l)

KOH reacts with the carboxylic acid to form a salt. As the concentration of carboxylic acid decreases, the system counteracts by favouring the production of carboxylic acid. ;

The position of equilibrium shifts to the right, and the forward reaction continues until all ester has been hydrolysed. ;

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

[8]

$$\text{Average molecular mass of olive oil} = \frac{168300}{196} = 858.7 \quad ;$$

$$\text{Amount of KOH added} = 0.5 \times 0.05 = 0.0250 \text{ mol}$$

$$\begin{aligned} \text{SAP} &= \frac{\text{mass of KOH} \times 10^{-3}}{\text{mass of fat}} \\ &= \frac{\text{mass of KOH}}{5} \end{aligned} \quad ;$$

$$\text{Mass of KOH} = 980 \text{ mg} = 0.98 \text{ g} \quad ;$$

$$\text{Amount of KOH reacted} = 0.98 / 56.1 = 0.017468 \text{ mol}$$

$$\text{Amount of excess KOH} = 0.0250 - 0.017468 = 7.531 \times 10^{-3} \text{ mol}$$

$$\text{Amount of HCl reacted} = 7.531 \times 10^{-3} \text{ mol}$$

$$\text{Volume of HCl required} = 7.531 \times 10^{-3} / 0.5 = 0.01506 \text{ dm}^3 = \underline{15.1 \text{ cm}^3} \quad ;$$

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

.....

Simple covalent structure with strong covalent bonds between the atoms and weak intermolecular forces (permanent dipole-permanent dipole) between the molecules. ;

As the value of n increases, the size of the electron cloud increases and the strength of the temporary dipole-induced dipole between the molecules increases. Thus, melting point increases as n increases. ;

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

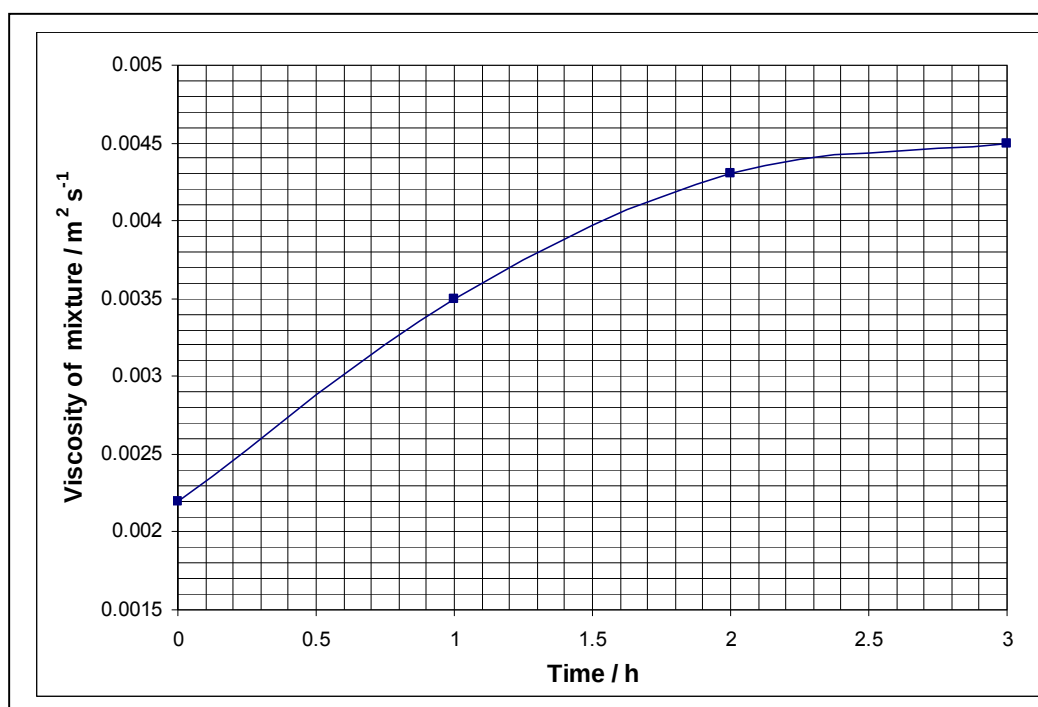
.....

Ethanol is used instead as a solvent as it is fats consist of large hydrophobic alkyl groups which are unable to form favourable H-bonds with water. ;

- 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 cm³ of water and added it to 50 g of sunflower oil maintained at 60°C. 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

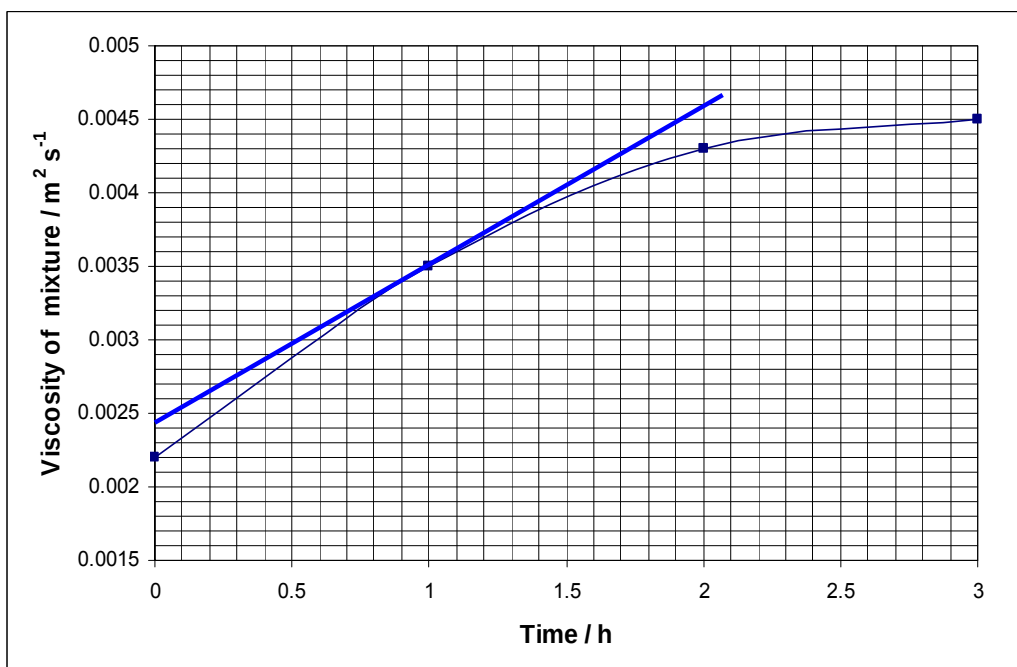
The student found that the order of reaction with respect to sunflower oil is 1.

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

Order of reaction with respect to a reactant is the power of the concentration of that reactant in the experimentally determined rate equation. ;

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

Rate of reaction at 1 h
 $= (0.0046 - 0.00245) / (2 - 0)$
 $= 1.08 \times 10^{-3} \text{ m}^2 \text{ s}^{-1} \text{ h}^{-1}$



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

Time / h	Amount of KOH / mol	Amount of sunflower oil / mol	Relative rate
0	0.125	0.0562	1.33×10^{-3}
1	0.110	0.0519	1.08×10^{-3}
2	0.082	0.0298	4.62×10^{-4}

Let rate = $k [\text{KOH}]^m [\text{sunflower oil}]^1$

$$\frac{1.33 \times 10^{-3}}{1.08 \times 10^{-3}} = \frac{k \times \left(\frac{0.125}{V_T} \right)^m \times \left(\frac{0.0562}{V_T} \right)}{k \times \left(\frac{0.110}{V_T} \right)^m \times \left(\frac{0.0519}{V_T} \right)} \quad \text{or} \quad \frac{1.33 \times 10^{-3}}{4.62 \times 10^{-4}} = \frac{k \times \left(\frac{0.125}{V_T} \right)^m \times \left(\frac{0.0562}{V_T} \right)}{k \times \left(\frac{0.082}{V_T} \right)^m \times \left(\frac{0.0298}{V_T} \right)}$$

$$1.231 = 1.136^m \times 1.082$$

$$1.137 = 1.136^m$$

$$m = 1$$

$$1.526 = 1.52^m$$

$$m = 1$$

Order with respect to KOH = 1

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

Rate = k [sunflower oil] [KOH]

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

As mass of KOH used increases, concentration of KOH increases.

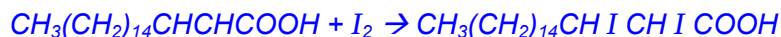
The frequency of effective collisions between the reactants increases, thus rate of reaction increases.

[7]

- 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 $\text{CH}_3(\text{CH}_2)_{14}\text{CHCHCOOH}$ reacts with iodine.



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

Assume molecular formula of linolenic acid be $\text{C}_{17}\text{H}_{36}\text{COOH}$,

$$\text{Amount of } \text{I}_2 = \frac{261}{127 \times 2} = 1.027$$

$$\text{Amount of linolenic acid} \approx \frac{100}{(17 \times 12) + 36 + 45} = 0.350$$

$$\text{No. of C=C} = \frac{1.0275}{0.350} \approx 2.92 = 3$$

3 double bonds

Molecular formula is $\text{C}_{18}\text{H}_{30}\text{O}_2$

- 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.

.....
.....
.....

Add hot, concentrated acidified KMnO_4 to linolenic acid. Analyse the oxidation products. The position of $\text{C}=\text{C}$ could be determined by determining the location of $\text{C}=\text{O}$. ;

- iv) Predict and explain the relative acidity of linolenic acid and $\text{CH}_3(\text{CH}_2)_{15}\text{CHICOOH}$.

.....
.....
.....
.....

$\text{CH}_3(\text{CH}_2)_{15}\text{CHICOOH}$ is more acidic than linolenic acid. ;

The presence of an electron withdrawing iodine group in $\text{CH}_3(\text{CH}_2)_{15}\text{CHICOOH}$ disperses the negative charges and stabilizes the resulting carboxylate anion formed. Thus, acidity is increased. ;

- v) $\text{CH}_3(\text{CH}_2)_{15}\text{CHICOOH}$ 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:

Conditions: aqueous NaOH , heat under reflux ;
Product: $\text{CH}_3(\text{CH}_2)_{15}\text{CHOHCOO}^-\text{Na}^+$;

Conditions: alcoholic NaOH, heat under reflux

Product: $\text{CH}_3(\text{CH}_2)_{14}\text{CHCHCOO}^-\text{Na}^+$

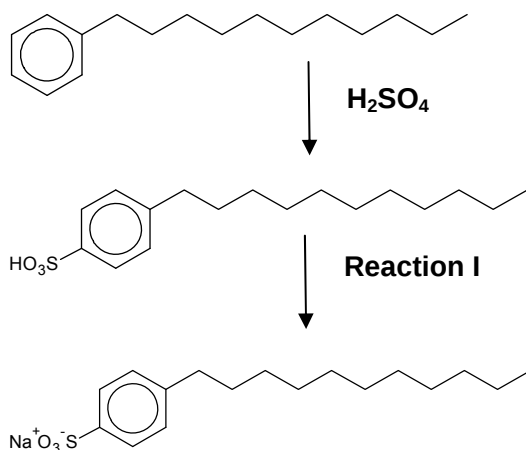
1 m: conditions

1 m each for products

[9]

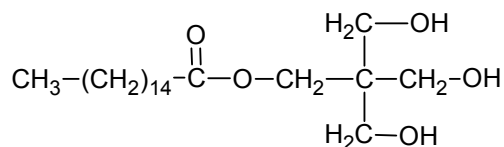
- e) Synthetic detergent consists of a hydrocarbon chain and polar group. As a surfactant, the synthetic detergent is more effective than conventional soap in hard water – water that contains dissolved minerals such as Ca^{2+} and Mg^{2+} .

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:



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, $[\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3]^+ \text{Cl}^-$.

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



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

.....
Acid-base neutralisation

- ii) State possible reagents and conditions to synthesize $[\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3]^+$ from $\text{CH}_3(\text{CH}_2)_{15}\text{NH}_2$. Describe the mechanism of the synthesis.

Reagents:.....

Conditions:.....

Reagents: Add excess CH_3Cl

Conditions: Heat

Mechanism: Nucleophilic substitution

Diagram: show movement of electrons through arrows

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

.....
.....
They do not posses charges and thus do not react with hard water.

[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.

Show presence of alpha C and peptide bonds

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

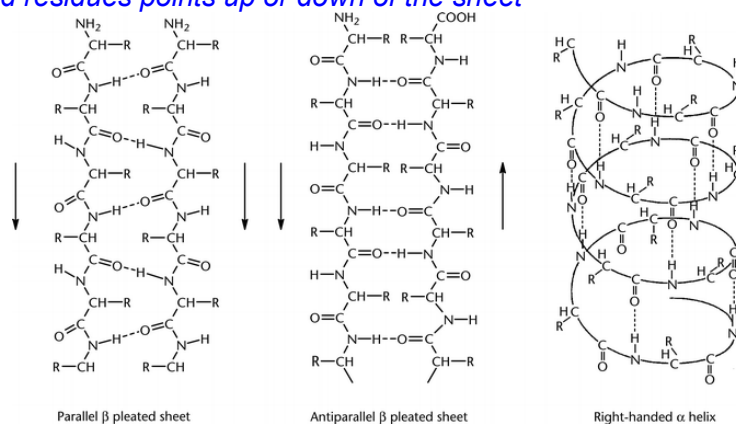
Either a diagram of β -sheet or α -helix with a brief description.

α -helix:

Helix is stabilized by hydrogen bonds which are arranged such that the O of the C=O group of the n^{th} residue points along the helix axis towards the N of the N-H group of the $(n + 4)^{\text{th}}$ residue

Parallel β -sheet:

Formed when segments of polypeptide chains lie adjacent to one another. Hydrogen bonds are formed between the C=O and N-H groups of adjacent chains, and are perpendicular to the direction of the sheet. R groups of adjacent amino acid residues points up or down of the sheet



- 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.

As pH is varied in the presence of heat, hydrolysis of the carbon-nitrogen bond in the peptide linkage could occur, disrupting the primary structure. ;

Secondary structure is unlikely to be affected greatly by pH changes. ;

The non-covalent interactions that maintain the protein's native conformation are disrupted in the tertiary structure as pH is varied. The ionization state of the amino acid side chains are affected, disrupting salt bridges that are held together by opposite charges. ;

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

Temperature, heavy metal ions (any 1) ;

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

At low concentration of substrate, the reaction rate is proportional to [substrate] / 1st order. ;

As the concentration of the substrate is increased, the rate reaches a maximum velocity V_{max} , which becomes independent of substrate concentration / 0 order. This is because the enzyme is fully saturated with substrate. ;

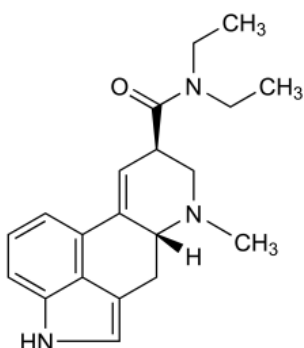
[9]

[Total: 41]

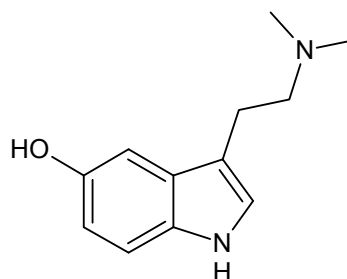
- 5 Urine is composed of water, electrolytes, and various waste products that are filtered out of the blood system. Thus, urine drug testing is widely used for testing for opioids and illicit drugs. Before a full analysis is made, the laboratory analyst needs to ensure that the urine is not tampered 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 $\begin{smallmatrix} \text{O} \\ \parallel \\ \text{C}-\text{N} \end{smallmatrix}$ group above through 90° 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]
Either through the addition of water in the sample or by drinking excessive amounts of water. / Any reference to dilution.
- b) State one chemical test which could be used to distinguish LSD from bufotenine. State the observations expected for each substance. [1]
Add a few drops of aq FeCl_3 to each compound. (Test for phenol.) ;
A purple complex is observed in bufotenine but not in LSD.
- c) i) State the bond angle about carbon in the $\begin{smallmatrix} \text{O} \\ \parallel \\ \text{C}-\text{N} \end{smallmatrix}$ group in LSD. ;
 120°
- ii) Rotation through 90° 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 $\begin{smallmatrix} \text{O} \\ \parallel \\ \text{C}-\text{N} \end{smallmatrix}$.

Restricted rotation about the C-N bond as the delocalisation of the lone pair of electrons on N into the carbonyl group results in a partial π bond character in C-N. ;

Rotation about C-N will result in the breaking of the π bond, hence, more energy is required to rotate about C-N. ;

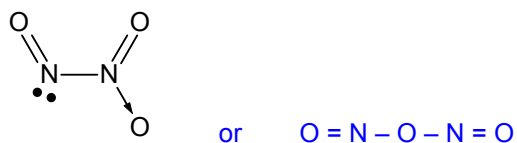
[3]

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

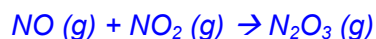
It has a similar shape to a $\text{C}=\text{O}-\text{N}$ group.

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

Show dot and cross of:



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



[2]

[Total: 7]