Ongoing revision of unit 3 and 4

1) Write the balanced thermochemical equation, with states, for the *complete* combustion of the following two substances :

   a. A fatty acid found in oil with the formula $C_{12}H_{21}COOH$

   According to the data sheet fats and oils have a heat of combustion of 37kJ/g.

   step 1 write a balanced chemical equation for the complete combustion of this fatty acid.

   $2C_{12}H_{21}COOH(l) + 33O_2\ (g) \rightarrow 24CO_2\ (g) + 22H_2O(l)$

   step 2 Find the molar mass of the fatty acid

   => 209 g/mol

   Step 3 calculate the amount of energy produced by 4 mol of the fatty acid, as per the equation.

   => (2 X 209g) X 37 kJ /g = 15466kJ

   Step 4 write the balanced thermochemical equation.

   => $2C_{12}H_{21}COOH(l) + 33O_2\ (g) \rightarrow 24CO_2\ (g) + 22H_2O(l)\ \Delta H = -\ 15466 kJ/mol$

   b. Liquid lactose $C_{12}H_{22}O_{11}$ (342.3 g/mol)

   According to the data sheet carbohydrates have a heat of combustion of 16kJ/g.

   step 1 write a balanced chemical equation for the complete combustion of lactose.

   $C_{12}H_{22}O_{11}(l) + 12O_2\ (g) \rightarrow 12CO_2\ (g) + 11H_2O(l)$

   step 2 calculate the amount of energy produced by 1 mol of the lctose,

   => (1 X 342.3g) X 16 kJ /g = 5477 kJ

   Step 4 write the balanced thermochemical equation.

   $C_{12}H_{22}O_{11}(l) + 12O_2\ (g) \rightarrow 12CO_2\ (g) + 11H_2O(l)\ \ \Delta H = -\ 5477\ kJ/mol$

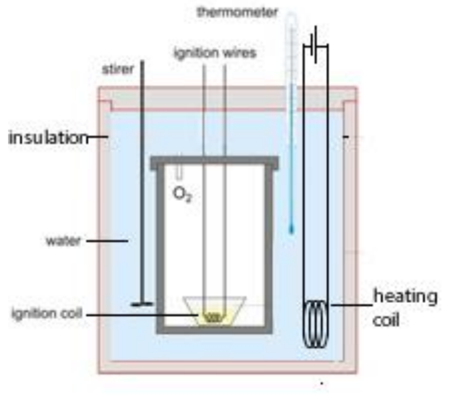
   c. Calculate the mass, in grams, of Br_2 that will react with one mol of the fatty acid with the formula $C_{12}H_{21}COOH$.

   The general formula of a saturated fatty acid is $C_nH_{2n+1}COOH$. For every double bond present the formula two less hydrogens. So a fatty acid with the formula $C_{12}H_{21}COOH$ has two double bonds.

   One Br_2 molecule attaches to each double bond in an addition reaction. So for every molecule of fatty acid we have two double bonds for 2 Br_2 molecules to attach to. So the mol ratio of fatty acid to Br_2 is 1 : 2

   Hence for one mol of fatty acid two mol of Br_2 will attach which is equivalent to (4 X 79.9) 319.6 grams of Br_2.

2. An unknown fatty acid "Y" was analysed using a bomb calorimeter to verify its molar heat of combustion.



A typical bomb calorimeter

The following steps were undertaken in order.
step 1 – the calorimeter was filled with 100 mL of water at 25.0 °C

Step 2 – 0.191 g of pure ethanol was placed in the bomb and ignited.
Step 3 – The temperature of the water was measured and recorded every 30 seconds, on a temperature vs time graph shown in diagram 1 on the right, while the ethanol underwent complete combustion.

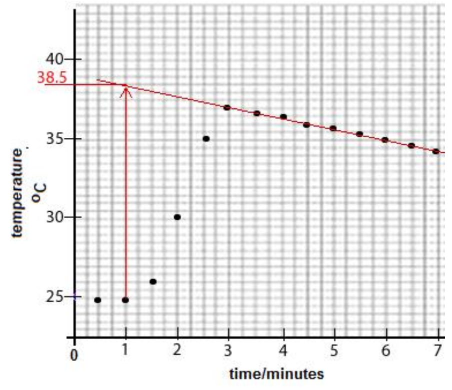


Diagram 1

Step 4 – The water in the calorimeter was allowed to cool back down to 25.0 °C before a 0.140 gram sample of the fatty acid "Y" was placed in the calorimeter and ignited.
step 5 – The temperature of the water was measured and recorded every 30 seconds as shown in diagram 2.

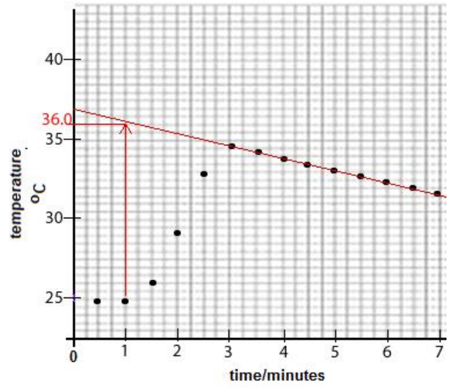


Diagram 2

a. Calculate the calibration factor of the bomb calorimeter. Express the answer to the right number of significant figures.
Step 1 – find the energy delivered by the 0.191 grams of ethanol. Refer to the data book.
=> 29.6 kJ/g X 0.191 = 5.654 kJ
Step 2 – find the temperature change by extrapolating, as shown in diagram 1.
ΔT = 38.5 – 25.0 = 13.5 °C
Step 3 – calculate the calibration factor
=> 5.654 / 13.5 = 0.419 kJ/°C

b. Calculate the amount of energy, in kJ, given out by the 0.140 grams of the fatty acid while undergoing complete combustion.
Step 1 – use the temperature time graph shown in diagram 2 to find ΔT
=> ΔT = 36.0 – 25.0 = 11.0 °C
Step 2 – find the amount of energy in kJ
=> 11.0 X 0.419 kJ/°C = 4.609 kJ

c. Calculate the heat of combustion (kJ/g).
find the heat of combustion => 4.609 kJ / 0.140 g = 33.2 kJ/g

d. Compare the value obtained in question c. above with the value of the energy content of lipids and fats given in the data book. Give an explanation for any discrepancy.
The energy content of lipids and fats given in the data book is 37 kJ/g. This value is higher than the value obtained through experimental means of 33.2 kJ/g. This may be explained by poor insulation of the calorimeter which is consistent with the shape of the temperature vs time graphs. A well-insulated calorimeter should have little or no negative gradient after the reaction has ceased. In this case it is clear that there is a significant negative gradient indicating a significant loss of heat.

e. The bomb calorimeter shown above has a heating coil.

i. What is the purpose of the heating coil?
To deliver a known amount of energy (VIt). This will enable the calculation of a calibration factor C_f . By delivering an accurate amount of energy (VIt) and recording the change in temperature we can calculate the C_f
=> $C_f = VIt / \Delta T$

ii. Is the heating coil essential? Explain.
No. As long as we know the amount of energy delivered and the temperature change the C_f can be calculated.
An amount of energy can be calculated in two ways.
By passing a known amount of current at a given voltage for an amount of time energy can be calculate via the formula VIt, where V = volt, I = amps, t = seconds.
The second method can be via an exothermic reaction that can deliver a known amount of energy that can be accurately calculated. This can be accomplished by measuring the mass of fuel whose molar heat of combustion is accurately known.

iii. Name one difference and two similarities in the use and operation between a solution calorimeter and a bomb calorimeter?
difference – bomb calorimeter is used to measure heat energy produced by the combustion of fuels in oxygen while solution calorimeter is used to measure energy produced or absorbed during reaction taking place in solution.
similarities
– both heat a known volume of water and measure the change in temperature.
- *both need calibrating*
- *both need to be very well insulated.*
  Or any other factor that relates to the operation and use of each type.

3. Consider the organic molecule with the molecular formula $C_3H_6Br_2$.

a. Name all the possible structural isomers with this formula

1,1-dibromopropane
2,2-dibromopropane
1,3-dibromopropane
1,2-dibromopropane

b. Identify the structural isomer that has only one signal, with no splitting pattern, in its ^{1}HNMR spectrum and give the number of signals that appear in its ^{12}CNMR spectrum

2,2-dibromopropane
2 signals appear in its ^{12}CNMR spectrum

c. Which structural isomer in question a. above has more than one optical isomer?

1,2-dibromopropane

d. Suppose that $C_3H_6Br_2$ was formed from a hydrocarbon and an inorganic substance according to the chemical equation shown below.

$A + B \rightarrow C_3H_6Br_2$

i. Identify A and B

A = *C_3H_6*
B = *Br_2*

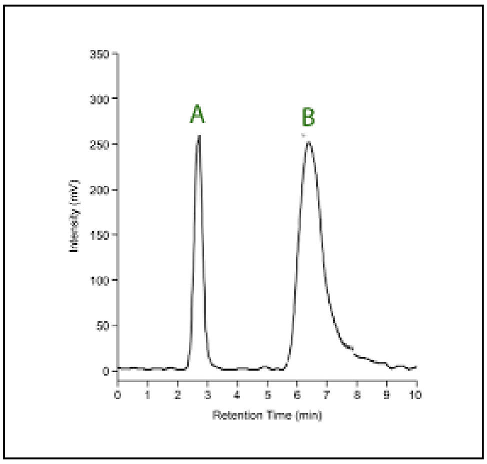
ii. What type of reaction is this?

addition

iii. What is the ***atom economy*** of this reaction?

100%

iv. A mixture of the organic reactant and $C_3H_6Br_2$ was separated into its components using normal-phase liquid chromatography. The chromatogram is shown on the right. Identify substance A and B and indicate which substance has the highest concentration in the mixture. Explain your reasoning.



Normal-phase liquid chromatography has a polar stationary phase and relatively polar non-polar stationary phase. $C_3H_6Br_2$ is more polar than the organic reactant C_3H_6 so it will come out in the eluent later as it will have a greater affinity with the stationary phase than the mobile phase so will adsorb strongly to it. So A = C_3H_6 while B = $C_3H_6Br_2$.
The area under B is greater than the area under A so $C_3H_6Br_2$ is in greater concentration.

e. Which isomer/s from the answer given to question a. above, could not have formed from the reaction $A + B \rightarrow C_3H_6Br_2$?

1,1-dibromopropane
2,2-dibromopropane
1,3-dibromopropane

4. Enzymes are proteins and act as biological catalysts. Being proteins, the tertiary structure of the enzyme is critical to its ability to perform its role in living organisms.

   i. Explain how enzymes act as catalysts with reference to the enzyme-substrate complex and make mention of the type of bonds that exist between the enzyme and the substrate.

      The enzyme reduces the activation energy required for a reaction to take place by offering an alternative pathway via the formation of an enzyme-substrate complex. This complex forms when a substrate is held in a particular part of the tertiary structure called the active site *by chemical bonds such as, dipole-dipole, h-bonding, ionic bonds*

   ii. Describe the chemical bonding that enables the tertiary structure to be maintained and offer some examples of the amino acids that take part in the strongest of these chemical bonds.

      The type of bonding that manifests to maintain the tertiary structure of the protein is wide ranging and is totally dependent on the side chains present on the amino acids in the primary structure.

      - covalent bonds in the form of disulfide bonds between cysteine – cysteine or cysteine – methionine.

      - hydrogen bonds.

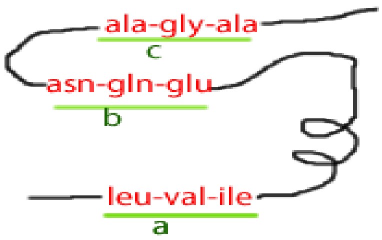
      - van der walls forces.

      - ionic bonds

   iii. Suggest how the tertiary structure facilitates the proteins function as an enzyme and its specificity to particular substrates.

      The active site is a specific region on the tertiary structure that has the ability to slightly change shape (induced fit model) to accommodate the substrates. Once bound to the active site the substrates are more likely to undergo a chemical change.

   iv. Consider the section of a protein shown on the right.



      i. What structure of the protein is represented by the segments a, b and c? *primary structure*

      ii. Which statement below is true?
      Offer an explanation for your choice.

      1 – Segments a and c will attract each other to influence the tertiary structure of the protein.

      2 – Segments a and b will attract each other to influence the secondary structure of the protein.

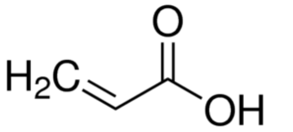
      3 – Segments c and b will attract each other to influence the tertiary structure of the protein.

      4– Segments c and b will attract each other to influence the secondary structure of the protein.

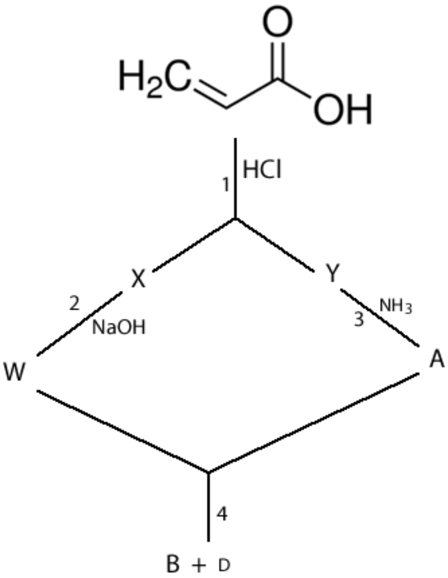
      Statement 1 is correct. Sections a and c are both made of amino acids with hydrophobic Z groups hence will be more likely to interact with each other than with section b which has amino acids with polar Z groups. Interaction amongst Z groups forms the secondary structure of the protein.

5. An organic compound is shown on the right.

a. Give the IUPAC name for the compound shown on the right. *Propenoic acid*



b. Consider the organic pathway shown on the right and the [1]HNMR spectrum for compound X.



i. Name the following compounds:

X _______________

3-chloropropanoic acid

Y _______________

2-chloropropanoic acid

W ______________

3-hydroxypropanoic acid

A ______________

2-aminopropanoic acid

ii. Identify the class of reaction that the following belong to.

Reaction 1 *Addition*

____

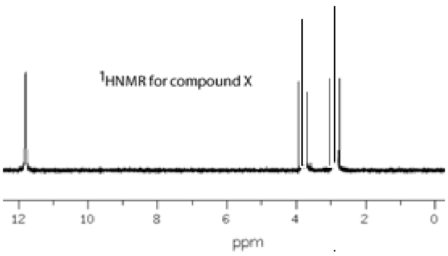
Reaction 2 *Substitution*

____

Reaction 3 *Substitution*

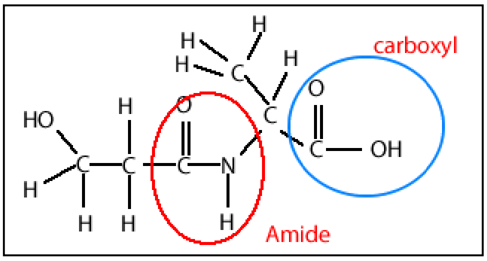
____

Reaction 4 *Condensation*



iii. Draw the structural formula of compound B, in the space provided on the right.

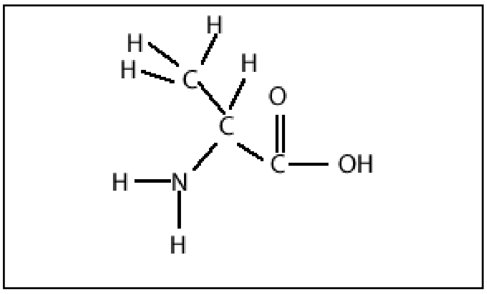
iv. Circle and label the functional group/s present in compound B



v. Identify substance D *H_2O*__

vi. A student classified compound A as a beta-amino acid.

Do you agree? Justify your response and draw the structural formula of compound A. *Alpha amino acids have the amino group on the second carbon. This is the case with compound A.*



vii. What wave numbers on the IR spectrum of compound B would you expect to show strong absorption that could identify important bonds within the molecule?

1630-1680 C=O of amides

3300-3500 N-H of amides although this might be swamped by the O-H absorption, 1680 – 1740 C=O of acids, 2500-3500 O-H of acid

6. Elaidic acid and oleic acid share the same molecular formula and semi-structural formula as shown on the right.

HO OC-$(CH_2-)_7$CH=CH-$(CH_2-)_7CH_3$

$C_{17}H_{33}COOH$

a. The table of the physical properties of both fatty acids is shown below.

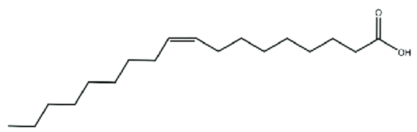
Acid	Elaidic	Oleic
Melting temperature (°C)	43	13.5
Boiling temperature (°C)	288	360
Flash point (°C)	110	189

i. Oleic acid can be classified as what type of omega fatty acid.

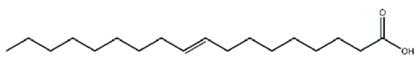
Omega 9. The double bond is on the 9th carbon in from the omega end, that is the opposite end of the carboxyl group, of the molecule.

ii. Using the information in the table above draw skeletal structures of the two geometric isomers in the space provided on the right.

Oleic acid



Elaidic acid

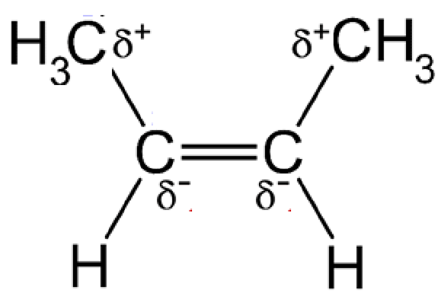


iii. Explain the difference between the melting points and boiling points of the two geometric isomers. You may draw a labelled diagram to assist in your explanation.

Cis isomers tend to have a double bond that causes a kink in the molecule. This also creates a polar region at the point of the double bond.

When molecules pack tightly together to form solids the trans molecules can pack more closely and hence the van der waals forces can exert a greater force of attraction. The cis configuration with kinked molecules, however, can cannot pack as close and hence the level of interaction between the molecules is not as great as in the trans configuration and is cause to weaken the force of attraction generated by van der waals forces. Weaker intermolecular forces lead to lower melting points.

Boiling points, however, are greater in cis than in trans configurations. This is due to the mobility of molecules and to the



polar nature of the cis double bond. The intermolecular force of attraction in the cis configuration is made up of van der waals forces as well as dipole dipole, while in trans configuration the intermolecular forces are solely due to the weaker van der waals forces.

iv. Explain the trend in the flash point between the two geometric isomers.

Since flash point is the lowest temperature at which the vapour above a liquid can be ignited it is reflective of the strength of the intermolecular bonds found amongst the particles of the liquid. The greater the intermolecular forces the harder it is for molecules to evaporate and form an ignitable mixture above the surface of the liquid. So the trend in flash point follows closely that of boiling point.

v. Using the data given in the table above suggest, with reasons, which of the two acids is the more viscous.

Since viscosity is a measure of how easy it is for molecules of fluid to flow past each other we can use viscosity as a measure of the strength of intermolecular bonds. Where there are strong intermolecular forces of attraction one would expect the viscosity of the liquid to be greater as molecules are attracted to each other and prevented from flowing freely past each other. Oleic acid with a boiling temperature of 360°C compared to 288°C for elaidic acid clearly has the strongest intermolecular bonds and hence the greater viscosity.

b. Biofuels are formed by a reaction with methanol in the presence of a catalyst (KOH) to form methyl esters.

i. Complete the equation for the formation of the methyl ester shown below (states not required)

$$C_{17}H_{33}COOH + CH_3OH \rightarrow C_{17}H_{33}COOCH_3 + H\text{-}O\text{-}H$$

ii. Identify this type of reaction

esterification (condensation)

iii. Oleic acid can be used to produce biodiesel for use in vehicles in cold environments. Discuss one advantage and one disadvantage of using oleic acid over elaidic acid based on the data given in the table above.

Advantages

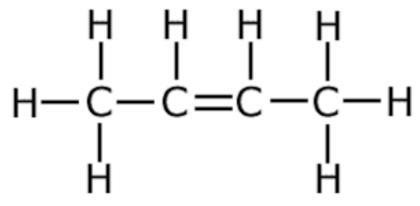
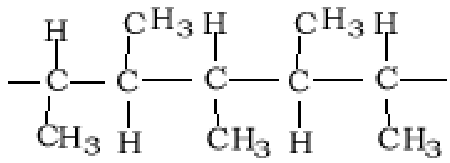
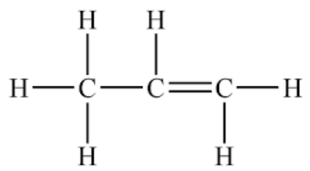
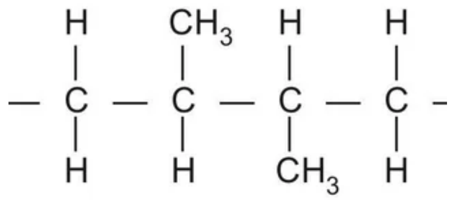
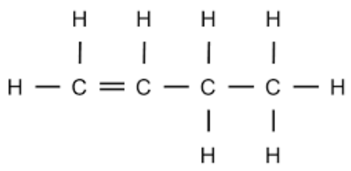
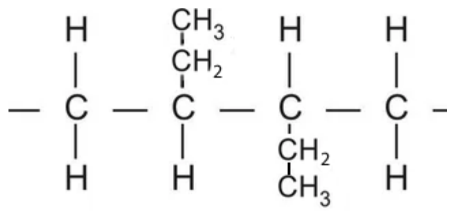
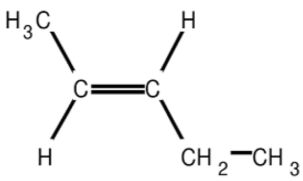
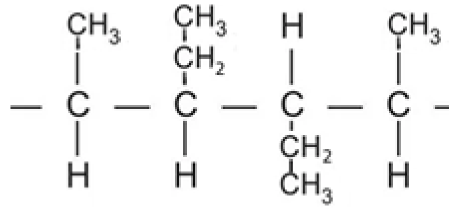
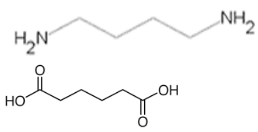
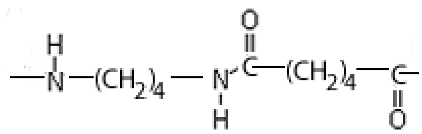
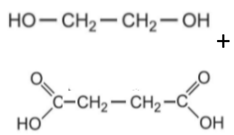
- Oleic acid has the lowest melting temperature and is unlikely that it will solidify and block fuel lines. Elaidic acid will most likely solidify and block the fuel lines.

- Oleic acid has a higher flash point and hence safer to store than elaidic acid which has a lower flash point.

Disadvantage.

- Elaidic acid on the other hand is less viscous and will have better flow rate properties through the fuel lines than oleic acid which has a higher viscosity.

7. Below are to columns. On the left are the monomers and on the right are the polymers formed by the monomers. Complete each square with the name and structural formula of each monomer and the structural formula of the repeating unit in the polymer.

a.	 But-2-ene	
b.	 propene	
c.	 But-1-ene	
d.	 Pent-2-ene	
e.	 Butan-1,4-diamine hexanedioic acid	
f.	 Ethan-1,2-diol Butanedioic acid