

Revision – Unit 3 and 4

- 1) A **pure**, mono-unsaturated hydrocarbon, labelled “A” in the diagram below, of mass 5.61 grams reacts with exactly 16.0 grams of Br₂.
a) Identify the formula of substance “A” and name all the possible compounds formed from this reaction.

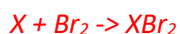
Unpacking the question we should identify some keywords

- mono-unsaturated means it has one double bond.

- one Br₂ molecule is added per double bond in an addition reaction.

Use this information to construct an equation.

Let X be the hydrocarbon.



Step 1 Find the mol of Br₂ that reacted.

=> 16.0 / 160 = 0.100 mol

Step 2 Find the mol of X

=> According to the stoichiometry it is a 1:1 ratio.

=> 0.100 mol of X

Step 3 Find the molar mass of X

=> molar mass = mass / mol = 5.61 / 0.100 = 56.1 g/mol

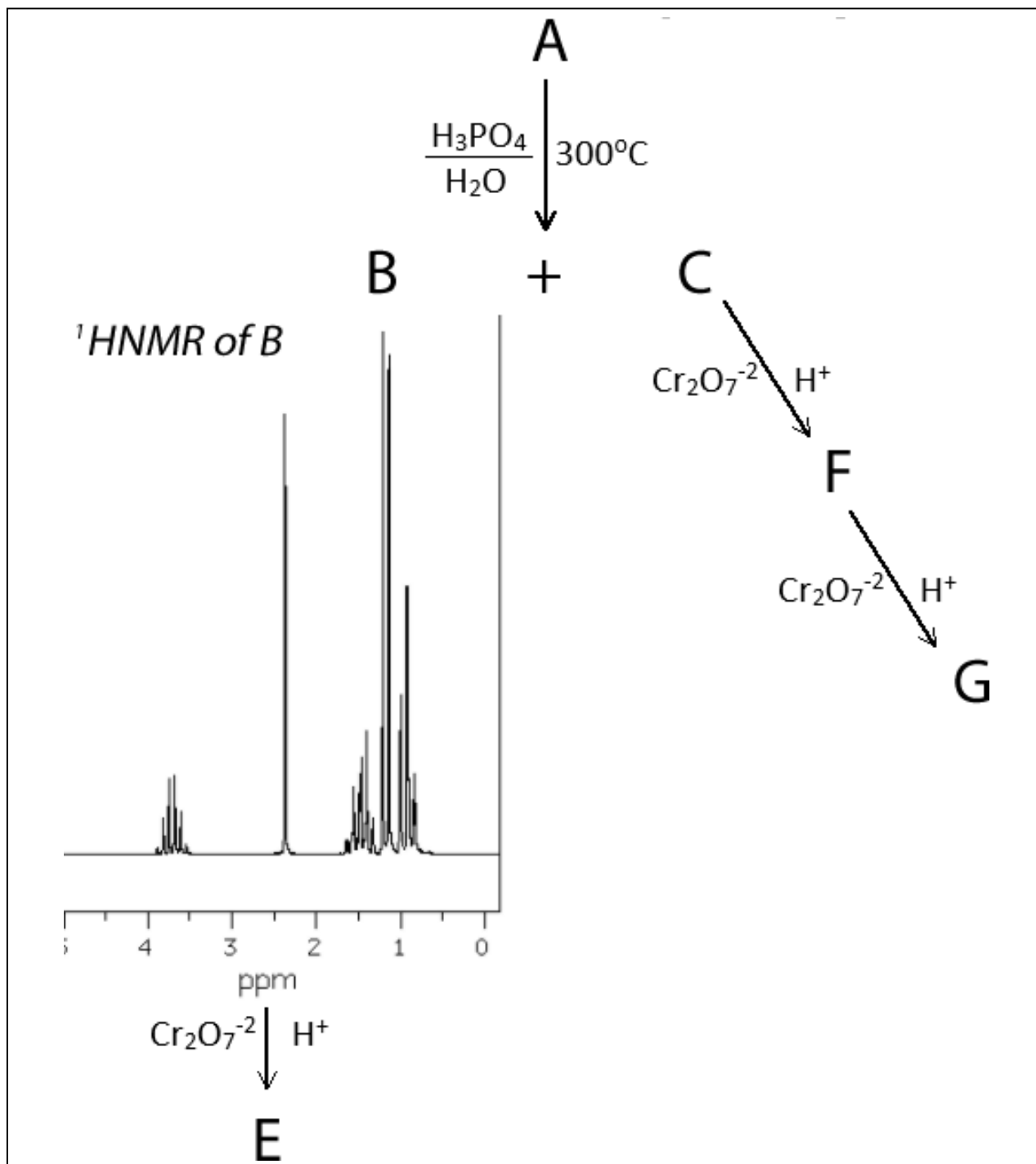
Step 4 Identify the hydrocarbons formula.

=> it is clearly an isomer of butane (C₄H₈)

The hydrocarbon can be either but-1-ene or but-2-ene

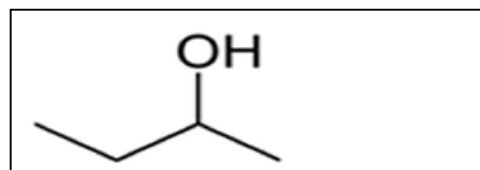
*Hence the possible products of an addition reaction with Br₂ are
1,2-dibromobutane or 2,3-dibromobutane*

Another sample of substance "A", this time weighing 10.00 grams, is taken through a set of processes shown in the diagram below. Consider the ^1H NMR of substance "B".

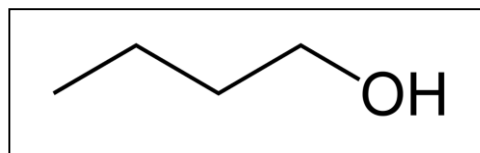


b) Name the following compounds and draw their skeletal structures in the box provided:

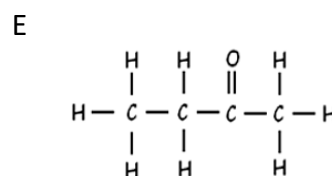
B *butan-2-ol*
This could be identified from the ^1H NMR



C *butan-1-ol*



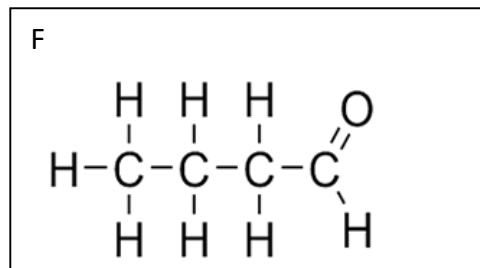
c) Draw the structural formula of substance "E" and "F" in the space provided



d) Identify one feature that is common to both IR spectra of both compounds "F" and "G".

An absorption of a C=O albeit at 1680-1850 for E and between 1660-1745 for F.

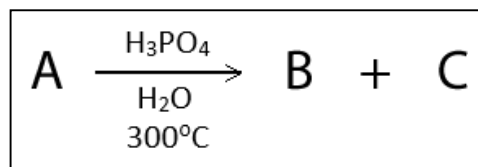
Of course absorption due to the C-H stretch around 3000



e) Consider the reaction on the right.

i. Name the type of reaction shown on the right.

Addition reaction



ii. Name an isomer of compound "A" that forms only one compound when undergoing the reaction in i. above

But-2-ene

iii. Name the type of reaction that forms compound "G"

Oxidation

iv. To what class of compounds does "B" belong to?

Secondary alcohol

v. Consider the possible ^1H NMR spectrum of compound "E". What type of signals appear and what is the simplest ratio of the area under each signal? Complete the table below. An example is shown on the right.

Type of signal	Simplest ratio of area
<i>singlet</i>	<i>3</i>
<i>quartet</i>	<i>2</i>
<i>triplet</i>	<i>3</i>

Type of signal	Simplest ratio
Triplet	2
Quintet	1
Sextet	3

f) Compound "G" was collected and dried. A 59.701 gram sample was obtained and placed in a 250 mL volumetric flask and made to the mark with distilled water. Five 20.00 mL aliquots of the solution were taken from the volumetric flask and placed in five separate 100 mL conical flasks. Each flask was then titrated against a 2.50 M NaOH and the 5 titres, listed below were obtained.

23.45 mL, 21.11 mL, 21.19 mL, 21.15 mL and 21.10 mL.

- i. Find the average titre.
Only use concordant titres (differ by no more than 0.100mL)
 $(21.11 + 21.19 + 21.15 + 21.10) / 4 = 21.14 \text{ mL}$
- ii. Give a balanced chemical equation of the reaction taking place in the conical flask. States not required.
From the reaction pathway compound G should be identified as butanoic acid and since it is a monoprotic acid it will react with NaOH in a 1:1 ratio.
Butanoic acid + NaOH \rightarrow sodium butanoate + H₂O
 $\Rightarrow \text{C}_4\text{H}_8\text{O}_2 + \text{NaOH} \rightarrow \text{NaO}_2\text{H}_7\text{C}_4 + \text{H}_2\text{O}$
- iii. Calculate the amount in mol of compound "G" present in the conical flask.
Step 1 - find the mol of NaOH delivered in the average titre.
 $\Rightarrow n = C \times V = 2.500 \times 0.02114 = 5.29 \times 10^{-2} \text{ mol}$
Step 2 - use the stoichiometric ratio to find the mol of G.
 $\Rightarrow 5.29 \times 10^{-2} \text{ mol.}$
- iv. Calculate the amount in grams of compound "G" in the volumetric flask
Step 1 Calculate the mol of "G" in the volumetric flask
 $\Rightarrow 5.29 \times 10^{-2} \times 250/20.00 = 0.6612 \text{ mol}$
Molar mass of butanoic acid is 88.1 g/mol
 $\Rightarrow \text{mass} = n \times \text{molar mass} = 0.6612 \times 88.1 = 58.3 \text{ grams}$
- v. Calculate percent purity of compound "G" in the 4.357 gram of the original sample, to the right number of significant figures.
 $\Rightarrow \text{percentage purity} = (\text{mass of compound} / \text{total mass of sample}) \times 100$
 $\Rightarrow (58.3 / 59.701) \times 100 = 97.7\%$
- vi. Each conical flask was washed with distilled water but was not given time to dry. What impact will this have on the percent purity of compound "G"? Explain.
No impact on the percent purity calculated. Water in the conical flask has no impact on the mol of butanoic acid delivered in the aliquot.
- vii. The volumetric flask was accidentally rinsed with the standardised sodium hydroxide solution but allowed to dry completely before use. What impact will this have on the percent purity of compound "G"? Explain.
This will cause the percent purity to be lower than the real value.
The NaOH in the conical flask, albeit dry, will react with the butanoic acid present in the sample. This will cause a lower titre to be delivered and hence give a lower value of the amount of butanoic acid present.

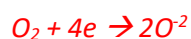
2) Propanol is used as a fuel in a fuel cell, pictured on the right, to generate electrical energy at 1.89V.

- i. Label the :
 - anode and give it's polarity.
 - cathode and give it's polarity.
 - label the direction of negative ion flow through the electrolyte.

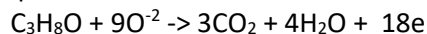
ii. Propanol is the fuel while oxygen gas from the atmosphere is the oxidant. Clearly label on the diagram the points of input of both propanol and oxygen gas.

iii. Clearly label the waste product/s

iv. Write the half equation for the reaction occurring at the cathode where oxygen molecules are converted to oxygen ions. States not required.



v. Calculate the electrical energy, in kilojoules, generated per mol of propanol consumed in the fuel cell. The half equation for the reaction of propanol at one of the electrodes can be simplified as shown below.



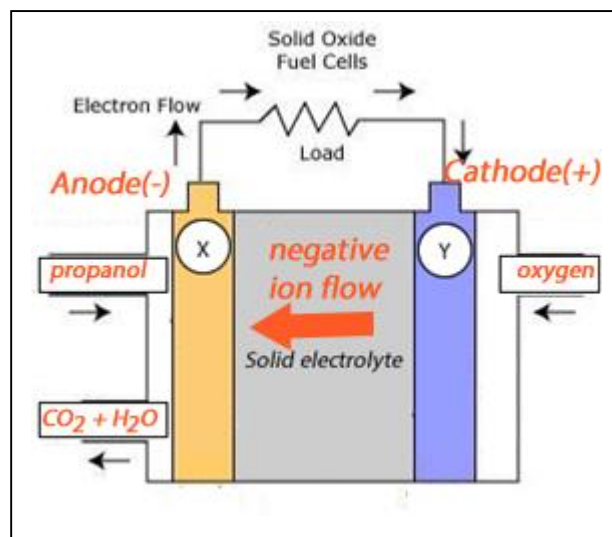
Unpacking the question.

The question asks us to find the electrical energy delivered by this reaction for every mol of propanol. No enthalpy is given for the reaction so we must now use formulae that we have come across during the course.

Energy = VIt (we have come across this formula when calibrating calorimeters using an electric current.)

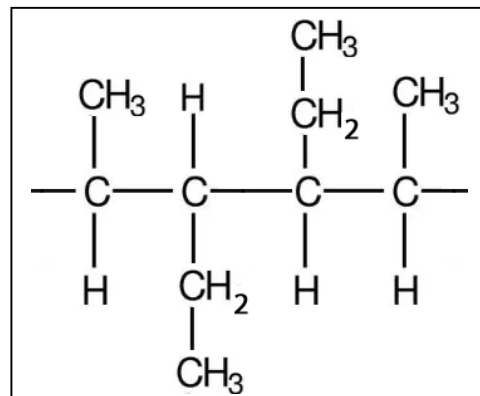
*Another formula we need to keep in mind is the formula for charge
 $Q = It = n \times 96500$ (where n is the mol of electrons)*

$$\Rightarrow \text{Energy} = VIt = V \times n \times 96500 = 1.89 \times 18 \times 96500 = 3.28 \times 10^3 \text{ kJ}$$

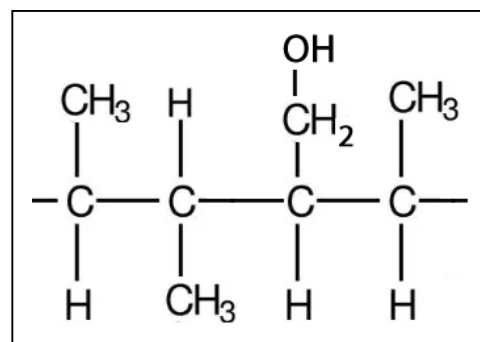


- 3) Three sections of polymer molecules are shown below.
i. Identify the monomer/s that formed each section by giving their systematic name/s in the space provided.

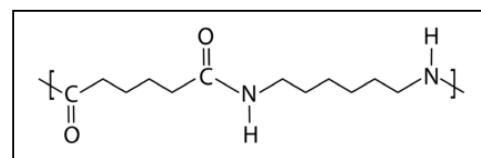
Monomer = *Pent-2-ene*



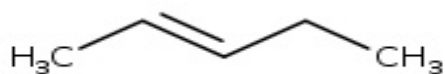
Monomer/s
but-2-ene and but-2-ene-1-ol



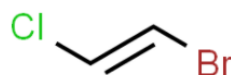
Monomer/s
hexandioic acid and hexan-1,6-diamine



- ii. Two molecules shown below, in skeletal form, are used as monomers for the formation of a long chain polymer. Name the monomers.

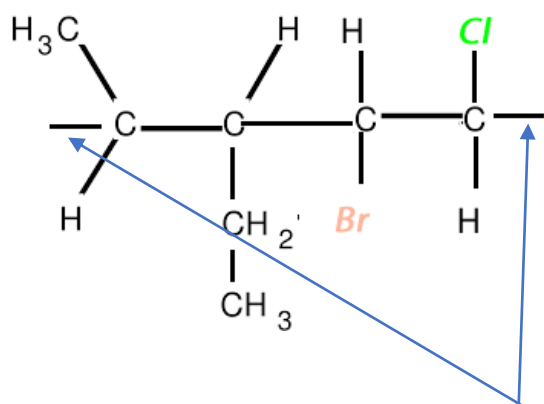
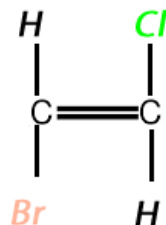
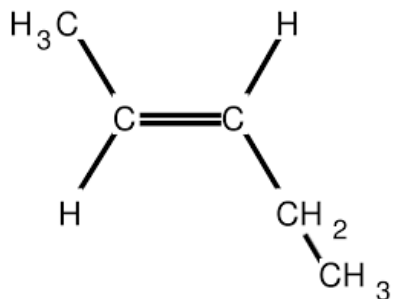


Name- *pent-2-ene*



Name *1-bromo-2-chloroethene*

iii. Draw the possible structural formula of the repeating unit of the polymer in the space below.



These dashes at the end of the section of polymer must be shown to indicate open bonds and a continuation of the molecule.

- 4) Biodiesel is a mixture of fatty acid methyl esters. A particular triglyceride used in the manufacture of biodiesel was hydrolysed with excess methanol and a potassium hydroxide catalyst. This reaction produced two liquid layers in the reaction vessel as shown on the right. The bottom layer is an aqueous solution.



- a) Other than water, name three other substances that could possibly be found in the aqueous layer. Justify your answer for each substance.

Substance 1 *Glycerol. Glycerol or propan-1,2,3-triol is liberated from the hydrolysis reaction and is a polar molecule and highly soluble in water due to hydrogen bonding.*

Substance 2 *KOH. Since it is a catalyst it will not be used in the reaction. It is also a very soluble ionic compound that readily dissolves in water.*

Substance 3 *Methanol. Methanol is a small polar molecule that readily dissolves in water due to hydrogen bonding and is in excess.*

- b) A 1.15 mL sample of the mixture in the top layer was analysed by reverse phase HPLC.

- i. How many compounds, possibly methyl esters, are present? *5.*

Five peaks indicate five distinct substances in the mixture.

- ii. Which methyl ester has the highest molar mass? *E* Justify your decision.

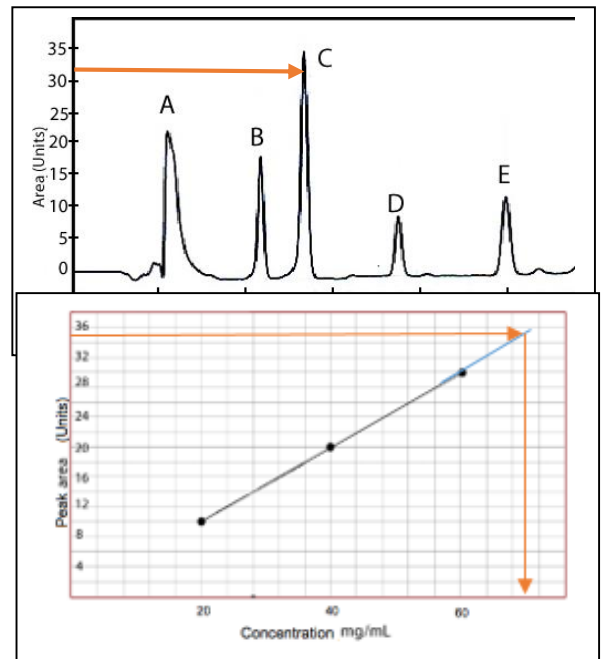
Reverse phase chromatography uses a hydrophobic stationary phase. Large methyl esters have long hydrophobic chains that readily interact with the stationary phase as opposed to the relatively more polar mobile phase. This causes the molecules to travel slowly through the column as they interact more with the stationary phase than the mobile phase and thus have a higher retention time.

- iii. Three standard solutions of a methyl ester ("X") suspected of being present in the top layer were made up and put through the column under the exact conditions as the 1.15 mL sample above. A calibration curve was constructed and shown on the right. Methyl ester "X" was eluted from the column in 6.5 seconds.

Is methyl ester "X" present in the original sample? Justify your answer. *Yes. Retention time is an identifying characteristic if both samples are run through the exact column under identical conditions. A retention time of 6.5 seconds correlates to methyl ester C.*

- iv. Calculate the concentration, in ppb, of methyl ester "X" in the top layer of the reaction vessel. *The original sample shows a peak area of methyl ester "C" of 35 units. When referenced to the calibration, albeit with a little extrapolation shown in blue, we find that this corresponds to a concentration of 70mg/mL. Answer can be within a range. This is then translated into the right units of ppm. => 70 mg/mL = 70mg/ mL X 1000 = 7.0 X 10⁴ ppm now translate to ppb 7.0 X 10⁴ X 1000 = 7.0 X 10⁷ppb.*

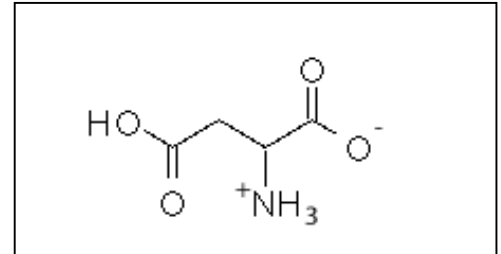
- v. Discuss why the accuracy of this measurement of the concentration of methyl ester "X" is not high and offer one suggestion of how it can be improved. *The most accurate region of a calibration curve is within its measured values. Values sourced outside of this range have a degree of error. We can improve the accuracy by selecting standard solutions of higher concentrations that increase the range of the calibration curve without the need to extrapolate.*



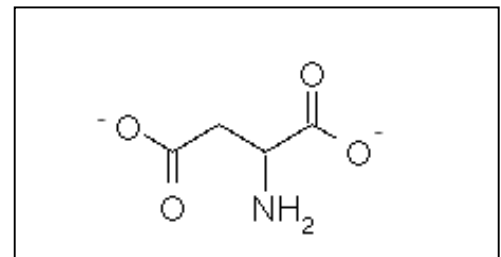
5) The isoelectric point of an amino acid is the pH at which the amino acid exists a neutral charged molecule (Zwitterion). Aspartic acid has an isoelectric point of 2.77.

a) In the space provided, draw the skeletal formula of aspartic acid:

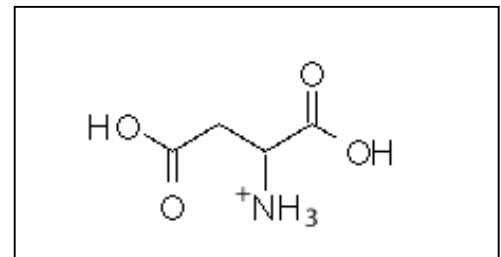
i. at a pH of 2.77



ii. when floating in a solution of pH 10.3



iii. in an acid bath of pH of 1.1



6) Consider the molecule shown on the right.

a) To what class of food molecules does this belong to?

Proteins

b) Circle and name three different functional groups that are visible in this structure.

The amine, any of the two carboxyl groups and any of the two amide groups would have sufficed.

c) Name the products of digestion of this molecule.

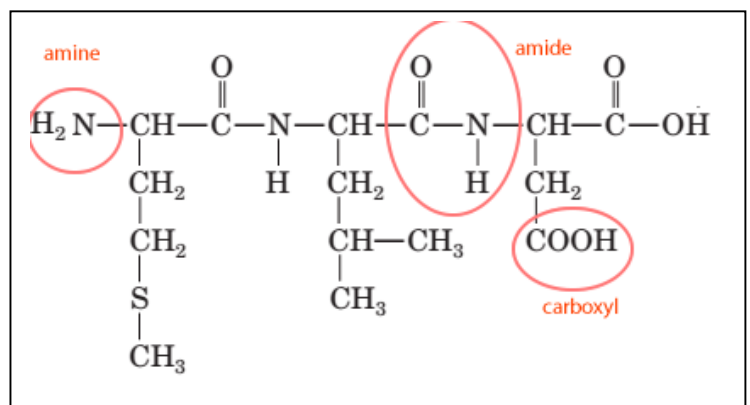
The amino acids, methionine, leucine, aspartic acid

d) What type of chemical reaction does this molecule undergo during digestion?

Hydrolysis

e) What is the mass difference, in grams, between one mol of the original molecule and the sum of its products after digestion?

Since water is added to break each amide bond and there are two amide bonds a gain of 36 grams is the difference in mass (2 X 18 = 36) .



7) Consider a small section of a protein molecule found in Human blood.

a) Two structures "A" and "B" of the molecule are shown with an arrow pointing to them. When this molecule is placed in ethanol it becomes denatured.

i. Which structure/s is/are most likely to be impacted by the ethanol and or a pH change? Explain your answer. *Ethanol will disrupt the hydrogen bonds that form between neighbouring amide bonds and are key to holding structure "A" together. Changes in pH also disrupt, hydrogen bonding and ionic bonding that occurs in the tertiary structure.*

Changes in pH cause chemical changes in the chemistry of amino acid molecules in the primary structure. For example, at low pH when an H⁺ attaches to a lone pair of electrons on a nitrogen of the amide link, it will cause disruption to the hydrogen bonding that this nitrogen can form with neighbours. Also at low pH levels the COO⁻ can be protonated to become COOH and hence unable to form ionic bonding in the tertiary structure. Also at high pH the NH₃⁺ side groups can lose a H⁺ to become NH₂ and again disrupt ionic bonding that forms part of the critical bonding that holds the tertiary structure together. It was enough for a student to suggest that ethanol and pH disrupt hydrogen bonding and identify structure "A" as the one impacted. The information given above is for revision purposes for students and can be used in question v. below.

ii. When the molecule is heated to 50 °C which structure/s remain unchanged? Explain your answer. *Structure "B" forms part of the primary structure of the protein molecule which is held together by strong covalent bonding. Covalent bonding cannot break down at a temperature as low as 50°C. The alpha helix, however, forms part of the secondary structure and is held together by much weaker hydrogen bonds and they can be disrupted at 50°C.*

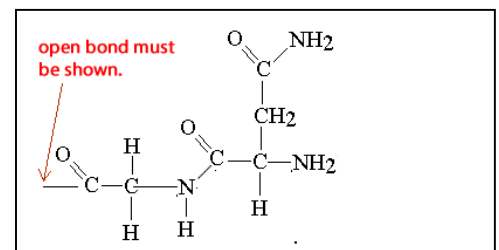
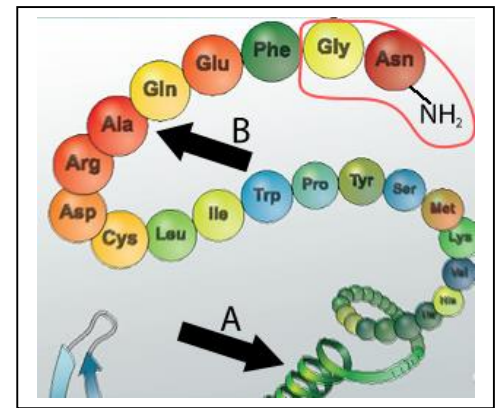
iii. Explain the bonding that holds structure "B" in shape. *The alpha helix is held in place by hydrogen bonding between the N-H and the C=O groups of neighbouring amide bonds.*

vi. In the space provided on the left draw the section with the last two amino acids enclosed by a red line.

When drawing polymers you must show open bonds at the ends where the molecule continues. It was also crucial to show the amide bond and the right orientation of the asparagine molecule.

v. Answer true or False to the following statements and justify your answer.

- during denaturing of a protein molecule both the primary and secondary structures are impacted. *False- Primary structure is held together by covalent bonds that cannot be easily broken by factors that would otherwise break weaker bonds and denature a protein. Factors such as pH change, dissolving in ethanol or heating disrupt weaker bonds such as hydrogen bonding, ionic bonding and dispersion forces.*
- At 60 °C most proteins are denatured when all forms of bonding in the tertiary structure are broken. *False. Tertiary structure contains all forms of bonding. These include covalent bonds (-S-S-) that cannot be disrupted by heat of 60°C.*
- Changes in pH disrupt only the hydrogen bonding between neighbouring amide groups in the protein chain. *False. Changes in pH also disrupt the ionic bonding and hydrogen bonding of the tertiary structure as well as the hydrogen bonding between neighbouring amide bonds forming the secondary structure.*



8) A student was set the task of finding the change in enthalpy of the reaction shown below.
 $2\text{NaHCO}_3(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g}) \Delta H = ?$

The student was provided with 1.100M HCl and 40 grams of NaHCO₃. When asked for assistance on how to tackle this problem the student was told to find the ΔH of each of the two reactions shown below whether by experimental means or by looking up the literature. Then apply their chemical knowledge of thermochemistry to solve the problem.

- i. $\text{HCl}(\text{aq}) + \text{NaHCO}_3(\text{s}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$
 ii. $2\text{HCl}(\text{aq}) + \text{Na}_2\text{CO}_3(\text{s}) \rightarrow 2\text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$

The student's experimental procedure to find the ΔH of equation i. is listed below.

Step 1 – weigh accurately about 10 grams of NaHCO₃ using an electronic balance and record the mass.

Step 2 – Using the calorimeter, shown on the right, place the NaHCO₃ from step 1 into the calorimeter with 100 mL of HCl solution measured with a 100mL measuring cylinder.

Step 3 – Quickly seal the calorimeter by tightly fitting the cup with the thermometer inserted and record the temperature reading of the contents.

Step 4- When the fizzing has stopped record the final temperature of the contents.



The student's results are shown on the right.

Mass of container	3.867 g
Mass of container + NaHCO ₃	13.547g
Mass of NaHCO ₃	9.68 g
Initial temperature of solution	23.2 °C
Final temperature of solution	19.8 °C
Change in temperature	3.4 °C

For reaction ii. above, the student researched the literature and came up with the following equation. $2\text{HCl}(\text{aq}) + \text{Na}_2\text{CO}_3(\text{s}) \rightarrow 2\text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g}) \Delta H = -27 \text{ kJ mol}^{-1}$

- i. Calculate the ΔH of reaction i. above from the student's results. Assume density of water is 1.00g/mL

Step 1 find which substance is in excess.

=> mol of NaHCO₃ = 9.68 / 84.0 = 0.1152 , mol of HCl = 1.100 X 0.100 = 0.110.

=> clearly NaHCO₃ is in excess but the acid measured with a measuring cylinder is not an accurate calculation of how much acid is present.

Step 2 Calculate the amount of energy absorbed.

=> E = 4.18 X 100 X 3.4 = 1.421 kJ

Step 3 Calculate the energy per mol of HCl acid absorbed.

=> 1.421 / 0.110 = 12.92kJ/mol

Step 4 Calculate the ΔH

=> HCl(aq) + NaHCO₃(s) → NaCl(aq) + H₂O(l) + CO₂(g) $\Delta H = +12.92 \text{ kJ/mol}$

Since the equation shows one mol of acid used then the ΔH is as calculated for the acid (positive sign indicates energy absorbed).

- ii. Using the information presented derive the ΔH for the reaction
 $2\text{NaHCO}_3(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$
Step 1 Write equation i. and ii. with the ΔH
 1----- $\text{HCl}(\text{aq}) + \text{NaHCO}_3(\text{s}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g}) \Delta H = +12.92 \text{ kJ mol}^{-1}$
 2----- $2\text{HCl}(\text{aq}) + \text{Na}_2\text{CO}_3(\text{s}) \rightarrow 2\text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g}) \Delta H = -36.0 \text{ kJ mol}^{-1}$
Step 2 Multiply equation 1 by 2
 3----- $2\text{HCl}(\text{aq}) + 2\text{NaHCO}_3(\text{s}) \rightarrow 2\text{NaCl}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{CO}_2(\text{g}) \Delta H = +25.84 \text{ kJ mol}^{-1}$
Step 3 Flip equation 2.
 4----- $2\text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g}) \rightarrow 2\text{HCl}(\text{aq}) + \text{Na}_2\text{CO}_3(\text{s}) \Delta H = +36.0 \text{ kJ mol}^{-1}$
Step 4 Add equations 3 and 4
 $2\text{NaHCO}_3(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g}) \Delta H = +61.84 \text{ kJ mol}^{-1}$ or 62 kJ mol^{-1} (2 sig figs)
- iii. Suggest two improvements to the experimental procedure and outline why this is an improvement in obtaining valid and reliable data.
Any plausible suggestion with a logical explanation of how it will improve the quality of data and ability to derive an accurate measurement of energy gain or loss.
Possible answers
- Conduct more than one trial. This should reduce the impact of random errors on the data obtained.
 - Use a digital thermometer. Accurate data is obtained quickly and without parallax error as may be the case with the analogue thermometer used.
 - Add the HCl solution to the calorimeter first and record its temperature before adding the carbonate. This should avoid any time in reading the thermometer while the reaction is in progress and give a more accurate reading of the initial temperature.
 - Calibrate the calorimeter. This will give a relationship between temperature change and energy change in the calorimeter, otherwise we assume that all the energy has come from the water and no heat has come from the surroundings.
 - A better way of determining the end of the reaction is needed as fizzing is not an accurate signal of the completion of the reaction. May be include a pH meter in the solution and record the progress in the pH change of the HCl solution.
- iv. It was suggested that the investigation be repeated several times as the design of the calorimeter was fairly poor which allowed heat to escape. Will this help to determine the energy loss more accurately?
No. Multiple trials can reduce the impact of random errors. A poorly insulated calorimeter is a systematic error which can only be addressed by improving the design of the calorimeter.
- v. It was suggested that the investigation be repeated several times in order to make up for the poor insulation of the calorimeter and improve the validity of the data collection. Is this true? Explain your answer.
No. Are we measuring what we are trying to measure. If not, the measurements are not valid. Although validity in data collection can be improved by changes to the procedure in this case improvement in equipment is also needed. For example, a better insulated calorimeter that has been calibrated.
- vi. Repeating the investigation several times will **increase** the reliability and therefore accuracy by removing systematic errors. Is this statement true? Explain your answer.
No. Reliability is a measure of how close results are from one trial to another. It has no bearing on accuracy. Systematic errors cannot be removed by repetition and so results can be reliable but not accurate. Repetition will identify if the results are reliable but will not increase reliability.

- vii. The calorimeter is held by the student in their right hand the same way during three separate trials. The student records the following results in the drop in temperature.
2.3°C, 2.4°C and 2.3°C

They note that their hand always feels cold. Discuss if the results are valid and reliable.

Since the student held the calorimeter the same way every trial the results can be considered reliable, but not accurate, as the amount of energy absorbed from the skin of the student is constant during every trial. This is an example of a systematic error. The results also show a high degree of reliability. Validity of the results is somewhat different. If we are measuring the temperature change due to energy absorbed by the reaction than the results are not valid as energy is absorbed from the skin and not only from the solution. For the results to be valid we must be sure that the temperature change is due to the energy absorbed from the solution by the reaction. Validity can only be improved by a change in the experimental design. In this case a calorimeter which is well insulated to make the results valid.