Experiment to Compare the Enthalpy Changes of Combustion of Different Alcohols

Introduction: This plan will try to outline how the experiment of comparing changes of combustion of different alcohols will be conducted and what results are expected.

Background

When chemical reactions take place they are often accompanied by energy changes.

Chemical reactions most frequently occur in open vessels. That is, they take place at constant pressure. **Enthalpy** refers to energy at constant pressure (volume may vary).

Enthalpy:

An example is best to illustrate to show enthalpy works. Methane - how much energy does its molecules contain? The first thing needed is the amount of methane present = 1 mole (16 g). What ever its value, the total amount of energy in a given amount of a substance (sometimes called the **Heat energy content**) is known as the **enthalpy**, denoted **H**.

Methane is a fuel to get energy from it, react it with oxygen.

$$CH_4(g) + 2O_2(g)$$
 \Box $CO_2(g) + 2H_2O(l)$

The above chemical equation shows that 2 moles (64 g) of oxygen molecules are required to burn 1 mole of methane. Again, it is impossible to know the total enthalpy (heat energy content) of the oxygen. Likewise, we can't know the total heat energy content of 1 mole of CO_2 and 2 moles of H_2O (the products).

Enthalpy Change

$$\Box H = (H_{CO2} + 2H_{H2O}) - (H_{CH4} + 2H_{O2})$$

In general,

$$\Box \mathbf{H} = \Box \mathbf{H}_{\text{products}} - \Box \mathbf{H}_{\text{reactants}}$$

But remember, this is theoretical; it is not possible to determine the absolute value of the enthalpy of a chemical element or compound. However, $\Box H$ values for chemical reactions can be obtained. They can be measured experimentally, or calculated using Hess's Law (see later), or worked out in other ways.

Exothermic and Endothermic Reactions

When chemical reactions take place they are often accompanied by *heat changes*. The **system** (the reactants which form products) may give out heat to the **surroundings**, causing them to

warm up. In this case the reactants have *more* stored energy (greater total enthalpy) than the products. Such chemical reactions are said to be **exothermic**. The system may take heat from the surroundings, causing them to cool down. In this case the reactants have *less* stored energy (less total enthalpy) than the products. Such chemical reactions are said to be **endothermic**.

Exothermic reactions give out energy to the surroundings. Endothermic reactions take energy from the surroundings.

Most reactions take place at constant pressure...

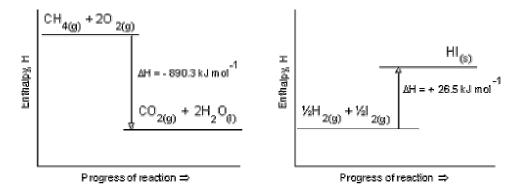
It is possible to measure changes in heat energy that accompany chemical reactions. Most reactions take place in vessels that are open to the atmosphere, that is, they take place at constant pressure (volume may vary). The special name given to a change in heat energy content measured at constant pressure is **enthalpy change**. This change in enthalpy is denoted by \Box **H**. The value of \Box H (often expressed in kJ, or kJ mol⁻¹ when appropriate) is given a **negative sign for exothermic reactions** and a **positive sign for endothermic reactions**, indicating whether the system loses or gains energy as a result of the reaction.

The value of \Box H is given a negative sign for an exothermic reaction. The value of \Box H is given a positive sign for an endothermic reaction.

Precise thermochemical measurements are made in a closed vessel of fixed volume, such as a calorimeter. For a reaction involving a change in volume of gases there is a small but real difference in the measured heat change. You can read more about this **here**.

Enthalpy Level Diagrams...

Enthalpy level diagrams can be used to illustrate overall exothermic and endothermic changes. They show the difference in total enthalpy of the reactants and products for a reaction:



For an exothermic reaction the total enthalpy of the products is less than that of reactants. For an endothermic reaction the total enthalpy of the reactants is less than that of the products. For each, the difference in these total enthalpies is equal to the overall enthalpy of the reaction, \Box H.

Temperature and pressure matter...

As well as the amounts of substances reacting (molar amounts are taken), the precise value of \Box H depends on both the temperature and pressure at which it is measured. For this reason \Box H

values are expressed at standard conditions (normally 298 K and 1 atm.). A standard enthalpy change is written as $\Box H^{\circ}_{298}$. You can read more about **temperature** and **pressure here**.

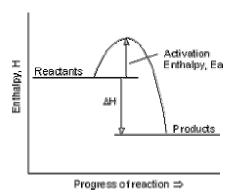
Thermochemical data for chemical reactions can be found in chemical data books.

Note the following changes:

$$\begin{array}{c} CO_{2(g)} + 2 \; H_2O_{(I)} \; \Box \; CH_{4(g)} + 2O_{2(g)} & \Box H^{\circ}_{298} = + \; 890.3 \; \, kJ \\ H_{2(g)} + I_{2(s)} \; \Box \; 2HI(g) & \Box H^{\circ}_{298} = + \; 53.0 \; kJ \end{array}$$

Activation Enthalpy

Methane and oxygen do not react spontaneously when mixed. An input of energy, such as a flame, is required to get the reaction started, after which its exothermic nature will sustain it. With regard to the *collision theory of reaction rates*, molecules react only if in a collision they possess between them energy equal to or greater than a certain critical value. This is called the **activation enthalpy**, **Ea**. An **enthalpy profile diagram** illustrates this:



Definitions:

Standard Molar Enthalpy of Combustion, \Box **H** $^{\circ}_{c,298}$. The heat evolved when 1 mole of an element or compound completely burns in oxygen, measured at 298 K and 1 atm. pressure.

Standard Molar Enthalpy of Formation, $\Box \mathbf{H}^{\circ}_{f,298}$. The heat change when 1 mole of a compound forms from its elements in their standard states, measured at 298 K and 1 atm. pressure. From the definition, the enthalpy of formation of an element at 298 K and 1 atm. is zero.

Here is a very useful equation that follows from the definition for enthalpy of formation. It can be used to calculate overall enthalpy changes when the <u>enthalpies of formation</u> of the reactants and products are given. It is

$$\Box \mathbf{H} = \Box \mathbf{H}_{f \text{ (products)}} - \Box \mathbf{H}_{f \text{ (reactants)}}$$

A **calorimeter** is used to measure heat changes directly (with adjustments made for standard conditions at constant pressure). However, this is not possible for some reactions. Their enthalpy changes can be calculated with the application of **Hess's Law**.

Hess's Law says that the overall enthalpy change accompanying a chemical reaction is independent of the route taken in going from reactants to products (provided that in each case the same initial and final states of temperature and pressure apply to the reactants and products).

Energy can neither be created nor destroyed.

Specific heat capacity is used in some thermochemical calculations. It is the amount of energy required to raise the mass of 1 gram of a substance by 1 °C.

 $q = \text{specific heat capacity x mass x } \square T.$

The specific heat capacity of water is $4.184 \text{ J g}^{-1} \text{ K}^{-1}$. This means that 4.184 J of energy are required to raise each gram of water by each °C.

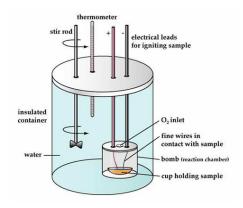
Heat capacity can also be used in calculations. It is the amount of energy required to raise the whole mass of a body by 1 °C.

 $q = \text{heat capacity } x \square T.$

Why do energy changes accompany chemical changes?

The answer involves the **chemical bonds** that hold atoms together in molecules. In chemical reactions the rearrangement of atoms involves breaking chemical bonds in reactant molecules and forming new bonds in product molecules. The atoms are themselves not created or destroyed, but are simply rearranged. Breaking chemical bonds requires energy; bond breaking is an endothermic process. Conversely, when chemical bonds form, energy is given out; bond formation is an exothermic process.

The energy needed to break a bond and the energy given out when a bond forms are definite and characteristic for each bond. The energy of the product molecules may therefore be greater or smaller than the energy of the reactant molecules. Thus a chemical reaction is accompanied by an overall enthalpy change. This is the **enthalpy of reaction**, $\Box \mathbf{H}$



The diagram above shows the correct way to measure enthalpy change of combustion of alcohols as it prevents anomalous results such as fluctuations in room temperature.

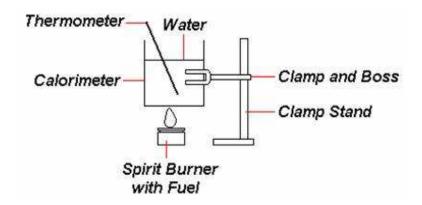
Sources:

- Salters Horners Chemical Ideas
- http://www.innovescent.com/gallery/design/illustrations.html

Apparatus needed for experiment:

- Spirit burner
- Alcohols e.g. methanol Hexanol
- Thermometers
- 100cm3 of coldwater.
- Digital scales
- Ruler
- Copper calorimeter able to hold 100cm3 of liquid.
- Splint
- Metal stand + clamp
- Safety goggles
- Tin foil
- Measuring cylinder
- Bunsen burner.

Aim: To determine the different enthalpy changes of combustion of different alcohols and to explain the trends and patterns.



Prediction:

As the amount of carbon atoms in the alcohol increases, the higher the enthalpy of combustion will be. I have made this prediction, using the values for the enthalpy change of combustion for each alcohol, calculated using bond enthalpies and Hess' law.

Methanol's molecular formula is CH3OH. This is the basic structure for all the alcohols, then to make the larger ones an extra carbon is added to the existing carbon each time and the oxygen-hydrogen molecule gets added to the atoms added to the new carbon atom

When methanol combusts in air, it reacts with oxygen molecules to from water and carbon dioxide. The balanced equation fort this is:

$$CH3OH(1) + 1.5O2(g)CO2(g) + 2H2O(1)$$

This means that the bonds broken are; 3 carbon- hydrogen, 1 carbon-oxygen, 1 oxygen-hydrogen and 1.5 oxygen- oxygen (double bond) and the bonds broken are; 2 carbon- oxygen (double bond) and 4 oxygen-hydrogen.

Constructing a Hess' law cycle will show how these are linked together:

If a calculation for the amount of energy needed to break the bonds is made and then the amount of energy given out from bond formation, the resultant energy difference (negative because the reaction is exothermic) is the enthalpy change of combustion.

Average bond enthalpies for elements in their gaseous states (kJmol-1):

Carbon - Carbon (C-C) = +347

Carbon - Hydrogen (C-H) = +413

Oxygen - Hydrogen (O-H) = +464

Carbon - Oxygen (C-O) = +358

Carbon - Oxygen double bond (C=O) = +805

Oxygen - Oxygen double bond (O=O) = +498

Energy absorbed when bonds are broken (positive): (E=Energy)

$$= E 3(C-H) + E (C-O) + E (O-H) + E 1.5(O=O)$$

$$= 3(413) + 358 + 464 + 1.5(498)$$

= 2808 k Jmol-1

Energy given out when bonds are made (negative): (E=Energy)

$$= E 2(C=O) + E 4(O-H)$$

$$= 2(805) + 4(464)$$

= -3466kJmol-1

Enthalpy change of combustion = Energy absorbed + energy given out

= 2808 + -3466

= -658kJmol-1

The combustion of methanol gives out -658kJ of energy for every mole of fuel burnt. This is only an approximate result and the actual value in my experiment may be different because, firstly the bond enthalpies are an average and they may vary in different molecules and secondly because the value are worked out assuming that the reactants and products are in a gaseous state, when in practise the water and alcohol are liquids. This means that my values for enthalpy change of combustion are likely to be different, but as long as the same method is used for each alcohol the pattern can be seen. I will now use the same bond enthalpy values to work out the estimation of enthalpy change of combustion for each alcohol.

Ethanol:

$$C2H5OH(1) + 3O2(g) 2CO2(g) + 3H2O(1)$$

Energy absorbed when bonds are broken (positive): (E=Energy)

$$= E 5(C-H) + E (C-C) + E (C-O) + E (O-H) + E 3(O=O)$$

$$= 5(413) + 347 + 358 + 464 + 3(498)$$

$$=4728kJmol-1$$

Energy given out when bonds are made (negative): (E=Energy)

$$= E 4(C=O) + E 6(O-H)$$

$$=4(805)+6(464)$$

$$=$$
 -6004kJmol-1

Enthalpy change of combustion = Energy absorbed + energy given out

$$=4728 + -6004$$

$$= -1276$$
kJmol-1

Propan1-ol:

$$C3H7OH(1) + 4.5O2(g) 3CO2(g) + 4H2O(l)$$

Energy absorbed when bonds are broken (positive): (E=Energy)

$$= E 7(C-H) + E 2(C-C) + E (C-O) + E (O-H) + E 4.5(O=O)$$

$$= 7(413) + 2(347) + 358 + 464 + 4.5(498)$$

= 6648kJmol-1

Energy given out when bonds are made (negative): (E=Energy)

$$= E 6(C=O) + E 8(O-H)$$

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$$=6(805) + 8(464)$$

$$= -8542$$
kJmol-1

Enthalpy change of combustion = Energy absorbed + energy given out

$$=6648 + -8542$$

= -1894kJmol-1

Butan1-ol:

$$C4H9OH(l) + 6O2(g) + CO2(g) + 5H2O(l)$$

Energy absorbed when bonds are broken (positive): (E=Energy)

$$= E 9(C-H) + E 3(C-C) + E (C-O) + E (O-H) + E 6(O=O)$$

$$= 9(413) + 3(347) + 358 + 464 + 6(498)$$

= 8568kJmol-1

Energy given out when bonds are made (negative): (E=Energy)

$$= E 8(C=O) + E 10(O-H)$$

$$= 8(805) + 10(464)$$

= -11080kJmol-1

Enthalpy change of combustion = Energy absorbed + energy given out

$$= 8568 + -11080$$

= -2512kJmol-1

Energy given out when bonds are made (negative): (E=Energy)

$$= E 6(C=O) + E 8(O-H)$$

$$=6(805)+8(464)$$

$$= -8542$$
kJmol-1

Enthalpy change of combustion = Energy absorbed + energy given out

$$=6648 + -8542$$

= -1894kJmol-1

Alcohol (carbon atoms) Enthalpy change of Combustion (kJmol-1)

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Methanol (1)	-658
Ethanol (2)	-1276
Propan1-ol (3)	-1894
Butan1-ol (4)	-2512

As you can see, as the number of carbon atoms (the larger the molecule) in the molecule increase, the enthalpy change of combustion (energy given out) increases. This is because there are more higher value bond enthalpies made, giving out more energy. The increase is a constant 618kJmol-1 per carbon atom or for every 2 hydrogen atoms, so the structure of the alcohol proportionally affects the enthalpy change of combustion. So the larger alcohols will give out more heat energy per mole and the temperature of the water will rise more while less of the fuel is burnt leading to a higher enthalpy change of combustion.

Safety-Hazard assessment:

These are the safety considerations I will take into account when doing my experiments-

- ? The alcohols are flammable, so they need to be handled carefully and never exposed to a naked flame
- ? The experiment produces heat, so I need to take care when handling hot equipment i.e. wait until they've cooled down
- ? Alcohol vapours can catch fire at very low temperatures, so whenever possible keep the lid on the spirit burners and re-fill them in a fume cupboard
- ? The fumes have a toxic effect if inhaled-make sure the room is well ventilated. Seek medical attention if they are inhaled
- ? They are irritating to skin so if split on skin or eyes, rinse with water and seek medical attention

- ? If they are any spillages, clear them up.
- ? Wear safety goggles at all times to protect my eyes and will cover my skin where possible
- ? Take care with other people's experiments as well, trying not to expose their alcohols to a naked flame

Method:

Check that all apparatus needed is available.

- 1. 100cm3 of water will be measured using a measuring cylinder and then poured into a clean copper calorimeter and then its temperature will be recorded using a thermometer.
- 2. A spirit burner filled with the first alcohol to be used methanol will be weighed, with its cap on to stop vapour escaping from the burner, using a set of digital scales. A clamp stand and clamp will be set up above the spirit burner.
- 3. To stop draughts affecting the alcohols flame when burning and therefore producing anomalous results, a foil wind block will be set up using tin foil wrapped into a cylinder and placed around the spirit burner.
- 4. The spirit burner will set up under the clamp stand and clamp, the copper calorimeter will be clamped 2cm above the tip of the wick of the burner, measured using a ruler.
- 5. The tin foil wind break will be placed around the spirit burner and the clamp stand placed over the burner again. A flame will be taken with a splint from a Bunsen burner, the cap from the spirit burner will be removed and the wick lit. A stop watch will be started and the temperature of the water observed using a thermometer in the water.
- 6. When the water has risen in temperature by 50oC, the flame will be extinguished by blowing it out.
- 7. Remove foil and weigh spirit burner. Record how much the spirit burner has decreased in mass using a table of results.
- 8. Repeat experiment using another spirit burner with the next alcohol to be tested, otherwise repeating all relevant steps. Record all results in a table.

Results

Methanol	Test 1	Test 2	Test 3	Average
Mass of the Spirit Burner, before the experiment (g to				
2d.p.)	208.98	206.95	204.99	206.97
Temperature before experiment (oC)	21.5	19.00	20.50	20.3
Temperature After experiment (oC)	71.5	69.00	70.50	70.3
Temperature change (oC)	50.00	50.00	50.00	50.00
Time (Mins, secs, milli secs)	5.28.56	5.13.4	5.32.35	
Mass of spirit Burner after experiment (g to 2d.p.)	206.95	204.99	203.11	205.02
Difference (g to 2d.p.)				1.95
Ethanol				
Mass of the Spirit Burner, before the experiment (g to				
2d.p.)	224.40	233.49	232.00	229.96
Temperature before experiment (oC)	20.50	24.00	23.50	22.6

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Temperature After experiment (oC) Temperature change (oC) Time (Mins, secs, milli secs) Mass of spirit Burner after experiment (g to 2d.p.)	70.50 50.00 4.10.39 223.03	74.00 50.00 5.03.00 232.00	73.50 50.00 4.53.25 230.50	72.6 50.00 228.51
Difference (g to 2d.p.)				1.45
Propan-1-ol				
Mass of the Spirit Burner, before the experiment (g to				
2d.p.)	252.84	251.40	250.05	251.43
Temperature before experiment (oC)	23.50	24.00	24.00	23.8
Temperature After experiment (oC)	73.50	74.00	74.00	73.8
Temperature change (oC)	50.00	50.00	50.00	50.00
Time (Mins, secs, milli secs)	3.49.54	3.29.37	3.25.68	
Mass of spirit Burner after experiment (g to 2d.p.)	251.40	250.05	248.77	250.07
Difference (g to 2d.p.)				1.36
Butan-1-ol				
Mass of the Spirit Burner, before the experiment (g to				
2d.p.)	144.13	142.80	141.71	142.88
Temperature before experiment (oC)	20.50	22.50	23.00	22.00
Temperature After experiment (oC)	70.50	72.50	73.00	72.00
Temperature change (oC)	50.00	50.00	50.00	50.00
Time (Mins, secs, milli secs)	3.60.79	2.54.39	2.54.63	
Mass of spirit Burner after experiment (g to 2d.p.)	142.80	141.71	140.67	141.73
Difference (g to 2d.p.)				1.15
Hexanol				
Mass of the Spirit Burner, before the experiment (g to				
2d.p.)	177.45	176.60	175.12	176.39
Temperature before experiment (oC)	20.50	23.50	21.00	21.6
Temperature After experiment (oC)	70.50	73.50	71.00	71.6
Temperature change (oC)	50.00	50.00	50.00	50.00
Time (Mins, secs, milli secs)	2.10.13	2.01.32	2.12.45	
Mass of spirit Burner after experiment (g to 2d.p.)	176.67	175.12	173.87	175.22
Difference (g to 2d.p.)				1.17