Comparing the Enthalpy Changes of Combustion of Different Alcohols
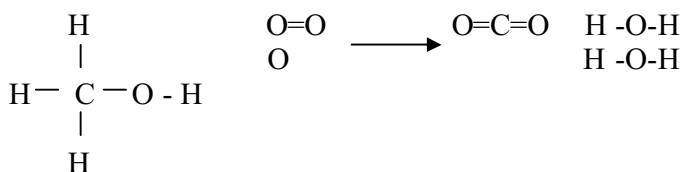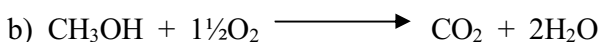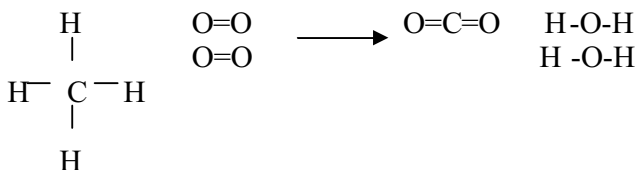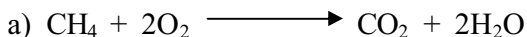
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Background Information

The enthalpy change of the combustion of a fuel depends on two things. First, there is the number of bonds to be broken and made – and that depends on the size of the molecule involved.

The ΔH°_c also depends on the type of bonds involved:

e.g. combustion of a) methane and b) methanol

a) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

```
    H          O=O              O=C=O    H-O-H
    |          O=O                       H -O-H
H⁻  C⁻H
    |
    H
```

b) $CH_3OH + 1\frac{1}{2}O_2 \longrightarrow CO_2 + 2H_2O$

```
     H            O=O            O=C=O   H -O-H
     |            O                      H -O-H
 H⁻  C⁻O - H
     |
     H
```

From the examples shown above, the products are the same, but the key difference is that methanol already has an O-H bond; one of the bonds to oxygen is already made, unlike with methane, where all the new bonds have been made. The energy released during combustion comes from the making of bonds to oxygen. If methanol already has one bond made, it will give out less energy when it burns.

The enthalpy change of a fuel is a measure of the energy transferred when one mole of the fuel burns completely. A value for the enthalpy change can be obtained by using the burning fuel to heat water and using the fact that 4.17J of energy are required to raise the temperature of 1g of water by 1°C.

So, the aim of this investigation is to find the enthalpy change of combustion of a number of alcohols so that you can investigate how and why the enthalpy change is affected by the molecular structure of the alcohol.

Preliminary Investigation

To give a clear indication of how to conduct the experiment precisely and properly, preliminary tests may be required. The results from these particular tests may give you an indication as to what type of range and temperature difference you may wish to use in your actual experiment.

Combustion of methanol: test 1
- Mass of water = 60ml
- Temperature difference = 68ºC
- Difference in weight of methanol = 2.2g
- Weight of calorimeter = 65.4g
- Specific heat capacity (SHC) of water = 4.17 $Jg^{-1}K^{-1}$
- SHC of copper = 0.38 $Jg^{-1}K^{-1}$

We have already established that the aim of this experiment is to investigate how and why the enthalpy change is affected by the molecular structure of the alcohol. To do so, you need to burn a certain alcohol under a calorimeter containing water and calculate the energy enthalpy change being discharged. During the experiment, you will notice that heat energy is not only lost as steam, from the water evaporating, but also from the copper calorimeter, which absorbs some of the heat energy.

Using the results above, to calculate the total energy enthalpy change, you add the energy gained by the copper with the energy given when heating the water…

Total enthalpy change = mass x specific heat capacity x difference in temperature

E	=	m	c	ΔT
(J)		(g)	$(Jg^{-1}K^{-1})$	(ΔK)

Enthalpy change for calorimeter: Enthalpy change for water:
= 65.4 x 0.38 x 68   = 60 x 4.17 x 68
= 1689.9 J   = 17013.6 J

So, 1689.9 + 17013.6 = 18703.5 J

Having calculated the total energy, you need to calculate the moles of the alcohol, in order to calculate the enthalpy change per mol.
e.g. methanol (using the results from above)

mol = mass ÷ relative molecular mass
     = 2.2 ÷ 32
     = 0.07 M

So, energy per mol = 18703.5 ÷ 0.07 = 267192.9 $Jmol^{-1}$

Combustion of methanol: test 2
Total energy = 18703.5 J
Mol of methanol = 0.03 M
Energy per mol = 544101.9 $Jmol^{-1}$

The results obtained from the preliminary experiments indicate that the enthalpy change is fairly high. So, to get a clearer view of the enthalpy changes of

combustion of the other alcohols, certain variables may need to be adjusted. For example, in this particular experiment, the temperature difference was 68ºC, there is no need for this to be quite high so a 20ºC temperature difference may be more sensible, thus allowing you to compare the results from the combustion of other alcohols with ease, producing a suitable graph of results.

        Another reason why the enthalpy change of the combustion of methanol in this experiment is fairly high may be because of what is known as 'temperature lag'. This occurred mainly because during the experiment, the burner was extinguished as soon as the temperature on the thermometer reached a 68ºC difference; by doing so, you are allowing the temperature to rise a little further, because the water is still being heated and so you do not gain 68ºC worth of the energy, instead you receive more, resulting in inaccuracy of results. To ensure that this does not happen in the real experiments, you need to extinguish the burner before the temperature reaches a difference of 20ºC, thus improving the accuracy of results.

Plan

We cannot measure the enthalpy of a substance. What we can do is measure the change in enthalpy when a reaction occurs. The enthalpy change in a chemical reaction gives the quantity of energy transferred to or from the surroundings, when the reaction is carried out in an open container. Like most physical and chemical quantities, enthalpy change varies according to the conditions. In particular, enthalpy change is affected by temperature, pressure and concentration of solutions.

In this particular experiment, temperature is a key factor and so the measurement of the temperature difference will be 20°C and this would need to be kept the same throughout each test; failure to do so will result in inaccuracy of results. With that said, the range to control would indeed apply to the five different alcohols, each with a molecular difference of one carbon atom in their atomic structure. The alcohols are: methanol, ethanol, propan-1-ol, butan-1-ol and pentan-1-ol. Obviously, repeats of each test per alcohol would need to be considered. Preferably 3 tests per alcohol, enabling you to average the results, therefore making a suitable comparison, thus improving the reliability of the results obtained.

All combustion reactions are exothermic, so the enthalpy change of combustion is always negative.

e.g. measuring bond enthalpies of the combustion of methanol (finding the expected value of enthalpy change)

$$CH_3OH + 1\tfrac{1}{2}O_2 \longrightarrow CO_2 + 2H_2O$$
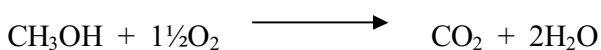
NOTE: when interpreting a combustion equation, you normally take in account of the combustion of 1 mol of the fuel.

Calculating the bond enthalpies before and after the reaction of the combustion of methanol…

Before
- 3 x C-H bonds (3 x 413)
- 1 x C-O bond (358)
- 1 x O-H bond (464)
- 1½ x O=O bond (1.5 x 498)

After
- 2 x C=O bonds (2 x 805)
- 4 x H-O bonds (4 x 464)

ΔH^o_c of methanol = -3466 + 2808 = -658 Kjmol^{-1}

There are certain aspects that could affect the conductivity of the experiments; these are known as the key variables. In this particular experiment, the temperature difference of the water and the volume of the water are the key variables that would need to be considered.

By measuring the bond enthalpies of molecules before and after a combustion reaction, you are able to see how much energy is released because making bonds release energy (as shown in the example above).

Having obtained some results from preliminary experiments, we now have a clear understanding of how to conduct the experiment properly, hopefully gaining accurate results during the process.

To conduct the experiment, follow this particular method:

1. Put 50ml of cold water in a copper calorimeter and record its temperature.
2. Support the calorimeter with a clamp, over a spirit burner containing the alcohol you are going to burn. Arrange a suitable draft exclusion system to reduce heat loss. To do so, place heatproof mats around the apparatus, shielding the calorimeter and the burner.
3. Weigh the burner and alcohol at the start.
4. Measure the temperature of the water before heating.
5. Stir the water in the calorimeter while heating, to ensure even distribution of energy being transferred.
6. When the water temperature has risen by 20ºC, extinguish the burner. To extinguish the flame, cover it with the lid provided with the burner. Calculate the change in temperature of the water by subtracting the final temperature of the water after heating by the start temperature.
7. Weigh the burner a final time, to find the mass of alcohol that had been burned. Calculate the change in mass of the burner by subtracting the start mass of the burner by the final mass.
8. Record all of your measurements in a suitable table.
9. Repeat the experiment 3 times per alcohol. Keep all other conditions the same, i.e. use fresh cold water each time per test, ensure that the calorimeter remains at the same height above the burner during each consecutive experiment, to improve fairness of conductivity. Use the same apparatus, the same mass of water, the same start temperature and go on heating until you have reached the same finishing temperature with a difference of 20˚C. The only thing that should be different is the mass of alcohol that is used up.

thermometer

copper calorimeter

clamp

water

Spirit burner

Liquid fuel
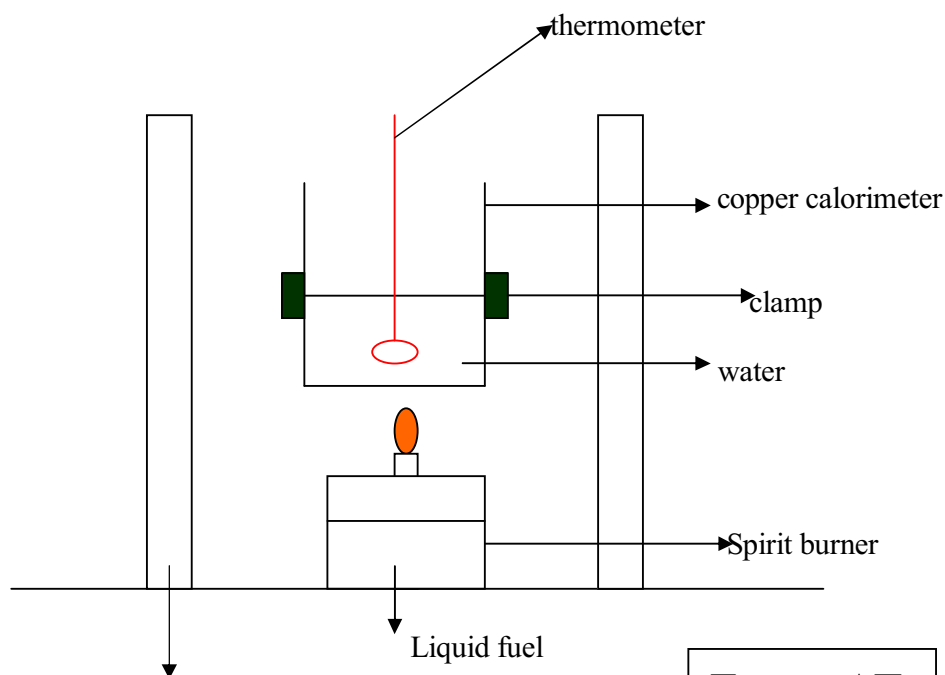
$$E = mc\Delta T$$

"draft" shield, heatproof mat

Note: the range you are testing refers to each of the 5 alcohols, methanol, ethanol etc. Ensure that you test each alcohol 3 times.

When conducting any lab experiment, safety is obviously a key issue. In this particular experiment, the safety precautions apply to the fact that you are

utilising flammable material, so it is advised for you to wear protective clothing of some sort. Since you are also dealing with heating substances such as water, it is also advised for you to wear safety goggles, to prevent injury to the eyes. Since alcohol is extremely flammable, it is important that when conducting the experiment, the alcohols, which are not being burned, would need to be away from the flame. So, spillages of any alcohol would need to be prevented.

Expanding on the strategic method of conducting the experiment, the reason why you place 50ml of cold water into the copper calorimeter is because this would produce adequate results. Also, it would be a lot quicker to heat a volume of 50ml than if it were doubled; this would enable you to work through your tests with quickness and with ease. Next, you support the calorimeter over the spirit burner so less heat energy would be lost to the surroundings or absorbed by the clamp. When supporting the calorimeter over the spirit burner, take note of the height and ensure that it is placed at this height throughout all experiments, to improve fairness of conductivity.

To prevent most of the heat energy being lost, you would have to devise an insulation system or a suitable draft exclusion system. In this case, the draft exclusion system consists of positioning heatproof mats around the apparatus, shielding the calorimeter and the burner; this would concentrate most the energy on heating the water. However, if some sort of draft exclusion system was not used, then more energy will be absorbed/lost to the surroundings, so less energy would be spent on heating the water; thus the enthalpy changes of the combustion of the fuel would be considerably less than the expected amount because most the energy was lost.

Beforehand, when measuring the amount of water to be heated by using a measuring cylinder, you need to make sure that the meniscus of the water lies exactly on the 50ml mark, to increase accuracy of measurement.

During the experiment, when the water temperature has risen by 20ºC due to the heat energy released when burning the fuel, you need to extinguish the burner. As stated before, extinguish the flame by covering it with the lid from the spirit burner. This would not only induce safety of conductivity but it would also prevent the temperature of the water to rise above the desired temperature. In this case, the temperature difference that would need to be obtained in each test is 20˚C.

To prevent 'temperature lag' from occurring (explained in preliminary work), it is advised that you extinguish the burner before the temperature reaches a difference of 20ºC from the starting temperature, because the temperature would only continue to slightly increase and so overall, you do not get 20ºC worth of the energy, instead you get more than expected and so this would give you inaccurate results.

It is extremely important that you weigh the burner before the experiment and after; enabling you to work out the difference in mass, which tells you how much of the fuel was burned and calculating the enthalpy change. The same applies to the temperature of the water. To weigh the burner, measuring scales would need to be used. A thermometer would obviously be needed to measure the temperature of the water.

It is advised that you conduct 3 tests per alcohol, as it would induce reliability of results, giving you a clear indication of the enthalpy change of the combustion of a specific fuel.

The type of results you would obtain is the enthalpy change – this is the energy required to break the bonds of the alcohol, forming new bonds. However, most importantly, is calculating both the expected and experimental value of enthalpy changes of combustion of the 5 alcohols.

To calculate the expected value, you need to be familiar with bond energy calculations. To do this, simply follow the diagram below:

$$\Delta H \text{ reaction}$$

Reactants $\longrightarrow$ Products

$$\Delta H_1$$

$$\Delta H_2$$

Gaseous atoms
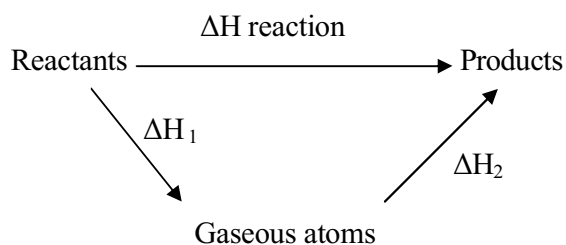
The diagram (above) refers to Hess' law; according to law, it states that the enthalpy change for any chemical reaction is independent of the intermediate stages, provided the initial and final conditions are the same for each route. An example of how to calculate the expected value of the enthalpy changes of combustions of an alcohol can be shown in the previous pages. To calculate your experimental value, simply get the average enthalpy change from your results and replace that figure with the 'actual' figure from the data book, of the intended alcohol. An example of how to calculate the experimental value can be shown in the 'analysis' section.

<u>Analysis</u>
Steps in calculating the experimental value (ΔH from bond enthalpy):
1. Write a balanced equation of reactants and products involved.

2. Split the reaction up into categories of "breaking bonds" and "making new bonds", so that the reactants go under the breaking bonds category and the products go under the making new bonds category.
3. Calculate the total energy of the reactants. To do so, add the average enthalpy change of that specific alcohol to the average bond enthalpy of the molecule the alcohol reacts with.
4. Calculate the total energy of the products. To do so, add the average bond enthalpies of the two products. E.g. when a hydrocarbon combusts, it usually produces carbon dioxide and water. The value you end up with when calculating the energy of the products, is always negative because making bonds release energy; it is an exothermic reaction.
5. To calculate the total enthalpy of combustion from bond enthalpies, add the value you calculated from breaking bonds with the value from making new bonds.

e.g. calculating the experimental value (ΔH from bond enthalpy) for methanol…

Breaking bonds   **Making new bonds**
CH_3OH + $1\frac{1}{2}O_2$ → CO_2 + $2H_2O$
(146 KJ)
↓
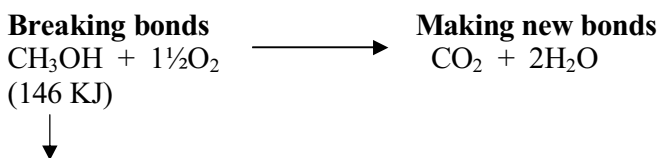
average enthalpy change (see table of results)

Bond	Average bond enthalpy/ $Kjmol^{-1}$
O=O	+498
C=O	+805
O - H	+464

- Total energy of breaking bonds = 146 + (1.5 x 498) = +893 KJ
- Total energy of making new bonds = (2 x 805) + (4 x 464) = -3466 KJ
- Experimental value of combustion of methanol = -3466 + 893
                = -2573 KJ

NOTE: all results of calculations for each alcohol are recorded in the table of results.

   Observing the table of results, you will notice an obvious trend; the enthalpy change increases as you go down the list of alcohols. The enthalpy change increases according to the number of bonds within a particular alcohol's molecular structure.
e.g.the molecular structure of the alcohols…

Methanol (CH_3OH)
```
                    H
                    |
          H—  C —O-H
                    |
                    H
```

Ethanol (C_2H_5OH)
```
              H     H
              |     |
        H —  C — C —O -H
              |     |
```

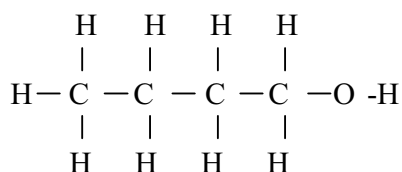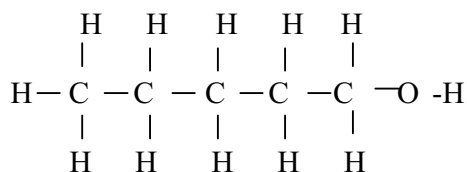Propan-1-ol (C₃H₇OH)

H   H

```
               H    H    H
               |    |    |
          H — C  — C  — C   O -H
               |    |    |
               H    H    H
```
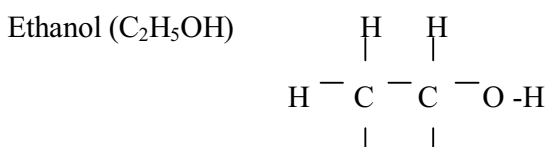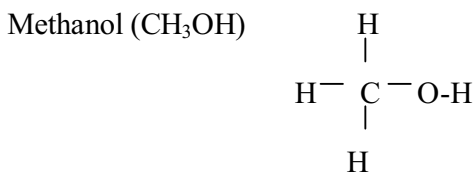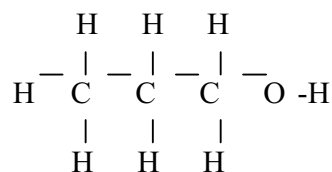
Butan-1-ol (C₄H₉OH)

```
          H    H    H    H
          |    |    |    |
     H— C — C — C — C —O -H
          |    |    |    |
          H    H    H    H
```

Pentan-1-ol (C₅H₁₁OH)

```
          H    H    H    H    H
          |    |    |    |    |
     H— C — C — C — C — C  ⌐O -H
          |    |    |    |    |
          H    H    H    H    H
```

As a general rule, the more carbons there are in the molecular structure of a specific alcohol, the more energy is released during combustion. This is because making bonds release energy; thus breaking more of the carbon-hydrogen bonds forms more of the new bonds and therefore more energy is released during the process.

All combustion reactions are exothermic, so ΔH_c is always negative. During an exothermic reaction the chemical reactants are losing energy. This energy is used to heat the surroundings – e.g. the air, the calorimeter and the water. The products end up with less energy than the reactants had, but the surroundings end up with more and so get warmer.

If the products end up with less energy than the reactants had, then what happened to the rest of the energy? Having established that the surroundings end up with more energy than the products, it is therefore safe to mention that much of the energy was wasted when the calorimeter was heated.

So, to calculate the total energy enthalpy change, you add the energy gained by the copper calorimeter with the energy given when heating the water…

Remember:

Total enthalpy change = mass x specific heat capacity x difference in temperature

$$E \qquad = \quad m \qquad\qquad c \qquad\qquad\qquad \Delta T$$
$$(J) \qquad\qquad (g) \qquad (Jg^{-1}K^{-1}) \qquad\qquad (\Delta K)$$

Energy change for calorimeter:
= 52 x 0.38 x 20
= 395.2J

Energy change for the water:
= 50 x 4.17 x 20
= 4170J

So, 395.2 + 4170 = 4565.2J

Having calculated the total energy, you need to calculate the moles of the alcohol, in order to therefore calculate the enthalpy change per mol.
e.g. for methanol:

mol = mass ÷ relative molecular mass
     = 1 ÷ 32
     = 0.031M

So, energy per mol = 4565.2 ÷ 0.031 = 147264.5 Jmol^{-1}

NOTE: all results are recorded on the table.

       The trend in which the graph of results sets, also apply to the fact that alcohols with the most carbon atoms in their molecular structure, generally release the most energy. So, referring to the line of best fit on the graph, it is fair to say that the number of carbon atoms within a particular alcohol, is proportional to the amount of energy released from the combustion of that specific alcohol. Another way of explaining the trend of the graph is that you will notice that there is a consistent jump in the combustion enthalpy change every time you go through the different alcohols. This is because you are adding a new CH_2 group each time, therefore adding the same amount of bonds each time and so you get an increase in the energy change of combustion. So ideally, the amount of energy that is released is doubled each time.
       The mole is the unit that measures amount of substance in such a way that equal amounts of elements consist of equal numbers of atoms, the mole is the unit that measures amount in the same way as the kilogram is the unit that measures mass.
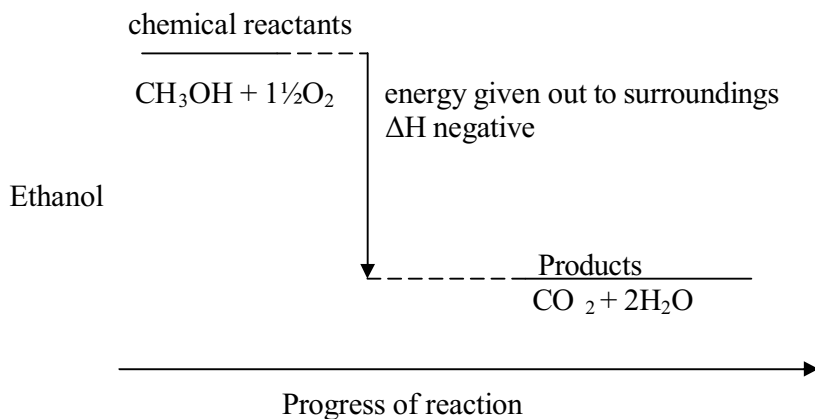To calculate moles…

= mass ÷ relative molecular mass

Observing the table of results, there is an obvious trend in the amount of moles in each of the alcohols; the amount of moles decreases as more bonds are added. So methanol, which has the least bonds, therefore has the higher concentration of moles and pentan-1-ol has the least amount of moles. Thus, moles are indirectly proportional to the number of bonds in the alcohol's structural formula.
       It also valid to state that the results obtained are fairly adequate, in the sense that accuracy is of a particular high standard, which means reliability of results is also of a high standard because it basically refers to the original theory: "…more energy is released from the alcohols with the most carbon atoms in their molecular structure, when they are burned; this is because breaking more bonds form more new bonds and therefore more energy is released in this exothermic reaction."
e.g enthalpy level diagram for an exothermic reaction, the burning of methanol…

chemical reactants

$CH_3OH + 1\tfrac{1}{2}O_2$ energy given out to surroundings
ΔH negative

Ethanol

Products
$CO_2 + 2H_2O$

Progress of reaction

Because you need to break bonds before product mole cules can begin to form, many reactions need heating to get them started. All reactions need energy to stretch, break bonds and start them off.

The burning of fuels is an example of reactions requiring heat to get them started. When you use a match to ignite methane for example, or a spark to ignite petrol vapour in a car engine, you are supplying the energy that is needed to stretch and break bonds so new bonds can begin to form.

It is not necessary for all bonds to b reak before the reaction gets going. If it were, you would have to heat things to very high temperatures to make them react. Once one or two bonds have broken, new bonds can start to form and this usually gives out enough energy to keep the reaction going, as in burning fuels; this can be described as an exothermic process.

Even though results were adequate enough to make a firm conclusion, there were a few that were anomalous, these are: methanol (test 3), propan-1-ol (test 3), butan-1-ol (test 3) and pentan-1-ol (test 3), all of which are highlighted in the table of results. To ensure that these particular results did not affect the experiment, they were to be repeated; thus the overall outcome is positive.

Note: explanations of how the anomalous results were acquired can be explained in the evaluation section.

Apart from the anomalous results, which may have affected the experiment, sources of error are another key issue. For example, the reading on the balance may only read to a certain degree of accuracy and so you may end up with a measurement, which has been rounded off from the actual value; so, if the measurement of the mass of the alcohol burned is not highly accurate, then the results obtained may not be as accurate. The same thing applies to measuring the volume of water, measuring the mass of the calorimeter and also with the measuring of the temperature of the water.
(Note: the percentage errors can be seen on the graph and the calculations of those errors are explained within the evaluation section).

Evaluation

       The experimental procedures, as in the method of conductivity, were fairly adequate, in the sense that successful results were produced. However, a number of features of the method can be improved, thus improving the results to an even greater degree of accuracy.

Improvements of the method of conductivity:
- You could improve the draft exclusion system by replacing the heatproof mats surrounding the apparatus, with appropriate insulation designed to insulate the calorimeter, thus allowing the bottom of the calorimeter being mostly heated instead of its sides and therefore heating more of the water.
- Instead of stirring the water with the thermometer, allowing even distribution of heat energy and ensuring that all parts of the water is at the same temperature, you could design a special rod that could possibly stir the water more efficiently than that of the thermometer.
- When measuring the volume of water, you could use a balance to weigh the mass. This is because the error of measuring the volume of water with a measuring cylinder is more than compared with the error produced when measuring the mass of water with a balance.

As previously stated, some anomalous results had occurred, however these are not included in the graph due to those results being re-investigated, thus producing even reliable figures. There are a number of reasons why those results appeared "anomalous":
- The thermometers that were used during the experiment may not have measured to a high degree of accuracy and so errors were produced. Also, it was possible that 'temperature lag' could have occurred, thus affecting the overall result.
- It is also quite possible that the water was not thoroughly stirred and so the distribution of heat energy may have been uneven.
- When heating the water, some energy was used in heating the surroundings and most of it was absorbed by the calorimeter.
- The measuring of the volume of the water may not have been as accurate as expected, possibly because the measuring cylinder's degree of accuracy may not be to a high standard.

However, it has been investigated that the main sources of error are produced from heat energy being lost to the surroundings when burning the fuel, i.e. heat loss to the air and heat loss to the apparatus, i.e. heat energy is also absorbed by the calorimeter. Another reason as to why errors were produced may be because of incomplete combustion of the alcohol, so not all the energy is being released; this may affect the results, thus reducing the accuracy. Although not very likely, the use of different burners may have also had a possible affect on the accuracy of results.

Errors in these cases will therefore have a negative affect on the results. Since much of the energy released is used to heat the surroundings, you do not obtain a precise value of the enthalpy of combustion of that particular alcohol. Instead you end up with a figure, which is far greater and less accurate than the expected value. (See graph: note the difference between the experimental value and the theoretical value; it shows that more energy is released from the experimental values).

S, to reduce the sources of error from occurring, certain modifications can be made to therefore improve both the reliability and accuracy of results:
- You could perhaps use more advanced and highly accurate equipment that was not previously accessible. E.g. a bomb calorimeter for making accurate measurements of energy changes; the fuel is ignited electronically and burns in the oxygen inside the pressurised vessel. Energy is transferred to the surrounding water, whose temperature is measured.
- You could replace the thermometer with an electronic thermometer.

- You could vary the amount of alcohols or types of alcohol, or even alter the number of repeats and investigate whether or not these could affect the experiment.

Justifying the attempts of modifying the method of conduction to improve both reliability and accuracy of results, the reason why the standard thermometer should be replaced with an electronic thermometer, is because it is highly accurate in its measurements and it enables you to set it to the desired temperature difference, so you need not worry about temperature lagging. By varying the variety (greater range) and type of alcohol, it would enable you to clarify and justify to a greater extent that alcohols release indeed more energy with the most bonds in their molecular structure. Also, by increasing the number of repeats on each test, it would allow you to obtain results of an even greater degree of accuracy simply because you would have a wider collection of results which can be averaged. By following such modifications, it may actually help to minimise the significant sources of error.

Calculating the percentage error:

Measurement	Value	Error	N°. of measurements taken	% error	Equipment used
Volume of water	50g	+/- 0.5	1	1	$100cm^3$ measuring cylinder
Temp. of water	20°C	+/- 0.1	2	1	Thermometer (-10 - 110°C)
Mass of calorimeter	52g	+/- 0.05	2	0.1	Balance
Mass of alcohols: methanol	1g	+/- 0.05	2	10	Balance
Ethanol	0.5g	+/- 0.05	2	20	Balance
Propan-1-ol	0.37g	+/- 0.05	2	27	Balance
Butan-1-ol	0.3g	+/- 0.05	2	33	Balance
Pentan-1-ol	0.26g	+/- 0.05	2	38.5	Balance

So, the total percentage error per test on each alcohol is:
- Methanol = 12.1%
- Ethanol = 22.1%
- Propan-1-ol = 29.1%
- Butan-1-ol = 35.1%
- Pentan-1-ol = 40.6%

Having calculated the percentage error of the tests on each of the alcohols, you are able to see how accurate the results actually are. Judging from the percentage errors, the results were fairly accurate and they are reliable in the sense that a firm conclusion is produced. Again, as previously stated, more energy is released by the alcohols with the most bonds in their molecular structure, because breaking those bonds by burning; it produces more bonds, which initially release more energy.

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