Chem Factsheet

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How Science Works:
What do enthalpy of combustion of alcohols data tell us?

To succeed in this topic you need to:
- know the definition of standard enthalpy of combustion
- be able to write balanced equations for the combustion of alcohols
- understand the terms *endothermic* and *exothermic*
- know how to use bond enthalpies to calculate enthalpy changes of reactions

After working through this FactSheet you will:
- be able to describe how to measure and calculate enthalpy of combustion
- understand how enthalpy of combustion changes for a homologous series
- be able to explain how enthalpy of combustion data leads to a theory of mean bond enthalpies
- be able to compare enthalpies of combustion found by experiment and by mean bond enthalpies

What is enthalpy of combustion?

Standard enthalpy of combustion is defined as the energy given out when **one mole of a substance is combusted completely in excess oxygen** under standard conditions. Equation 1 shows the reaction for the enthalpy of combustion of ethanol.

Equation 1 $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

How can you measure enthalpy of combustion?

Enthalpies of combustion can be found by carrying out a simple calorimetry experiment (Fig 1). In this experiment, a known mass of alcohol (or other substance) is burned, the heat given out transferred to a known mass of water, and the increase in temperature of the water measured.

<u>Note</u> – there are other ways of measuring enthalpies of reaction. For more, see Factsheet 65, Calorimetry Experiments.

Fig 1. Measuring the enthalpy of combustion of an alcohol

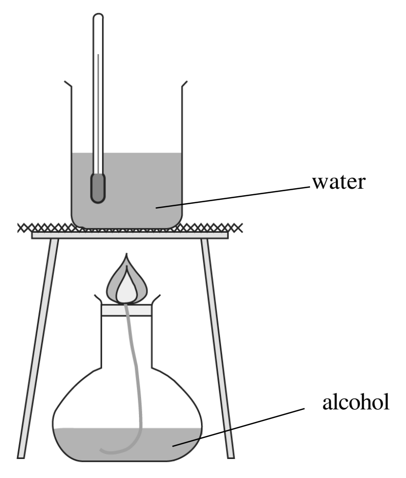


Table 1 shows a typical set of results for the first four alcohols.

Table 1: Typical results of a combustion of alcohols experiment

Alcohol	Mass alcohol burned (g)	Mass of water (g)	Starting temperature of water (°C)	Finishing temperature of water (°C)	Change in temperature (°C)
Methanol	1.00	100	20.0	74.3	54.3
Ethanol	0.90	100	20.0	84.0	64.0
Propan-1-ol	0.70	100	20.5	76.9	56.4
Butan-1-ol	0.50	100	20.0	63.3	43.3

To calculate the enthalpy of combustion, the following equation is used:

$Q = mc\Delta T$

where: Q = the heat energy exchanged in the reaction
m = mass of water in grams
c = specific heat capacity of water ($4.18\ JK^{-1}g^{-1}$)
ΔT = change in temperature of the water.

Having calculated Q, to find ΔH, divide Q by the amount of alcohol burned in moles.

For example, for methanol:
$Q = mc\Delta T = 100 \times 4.18 \times 54.3 = 22\,697\ J$

Moles of methanol burned = mass/molecular mass
= 1.0/32 = 0.03125 moles

$\Delta H = Q/\text{moles} = 22\,697/0.031 = 726\,300\ Jmol^{-1} = 726\ kJmol^{-1}$

All combustion reactions are exothermic,
so ΔH_c for methanol is $-726\ kJmol^{-1}$.

Table 2 shows the results for the first four alcohols.

Table 2. Calculating the enthalpy of combustion of the first four alcohols

Alcohol	Molar mass ($gmol^{-1}$)	Mass burned (g)	Moles burned burned (mol)	Change in temperature (°C)	$Q = mc\Delta T$ (J)	ΔH_c ($kJmol^{-1}$)
Methanol	32	1.00	0.03125	54.3	22 697	**-726**
Ethanol	46	0.90	0.01957	64.0	26 752	**-1367**
Propan-1-ol	60	0.70	0.01167	56.4	23 575	**-2021**
Butan-1-ol	74	0.50	0.00676	43.3	18 099	**-2676**

Note

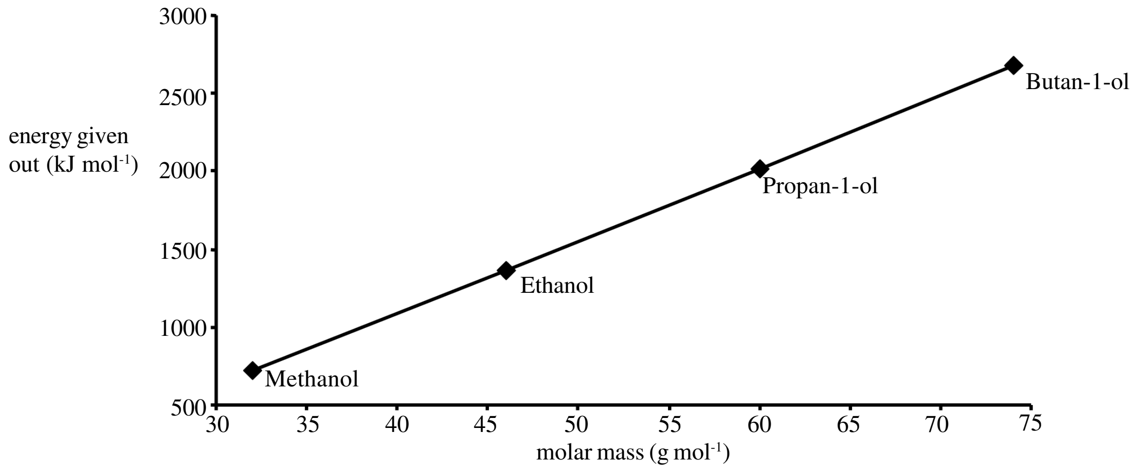
When you carry out this reaction in a school laboratory, the values for ΔH_c will be less exothermic than the values given here. There are two reasons for this:

1. Some of the heat given out by the burning alcohol will be lost to the atmosphere and not transferred to the water.
2. The alcohol is unlikely to combust completely and so not all the heat energy available in the molecules will be released.

What do the enthalpy of combustion values tell us?

The results can be plotted to show the enthalpies of combustion against the molecular mass of the alcohols (Fig 2). The enthalpies could also be plotted against the number of carbon atoms in the alcohol, but of course the pattern would be the same. For ease of comparison, enthalpies have been multiplied by –1 to give positive values.

Fig 2. Energy given out by combustion of the first four alcohols against M_r



The graph shows that the enthalpy of combustion steadily becomes more exothermic as the molecular mass increases. In fact, each successive CH_2 group added to the alcohol molecule leads to an increase in energy given out of around 650 $kJmol^{-1}$ (Table 3).

Table 3: Comparing enthalpy of combustion of the first four alcohols

Alcohol	ΔH_c ($kJmol^{-1}$)	Increase due to CH_2 ($kJmol^{-1}$)
CH_3OH	-726	n/a
CH_3CH_2OH	-1367	641
$CH_3CH_2CH_2OH$	-2021	654
$CH_3CH_2CH_2CH_2OH$	-2676	655

This leads to a theory: each bond broken or formed contributes a fixed amount to the energy given out overall.

Testing the theory by experiment

One way to test the theory would be to carry out the same experiment with isomers. Isomers should give out similar amounts of energy in combustion because the same number and type of bonds are being broken and formed (Table 4).

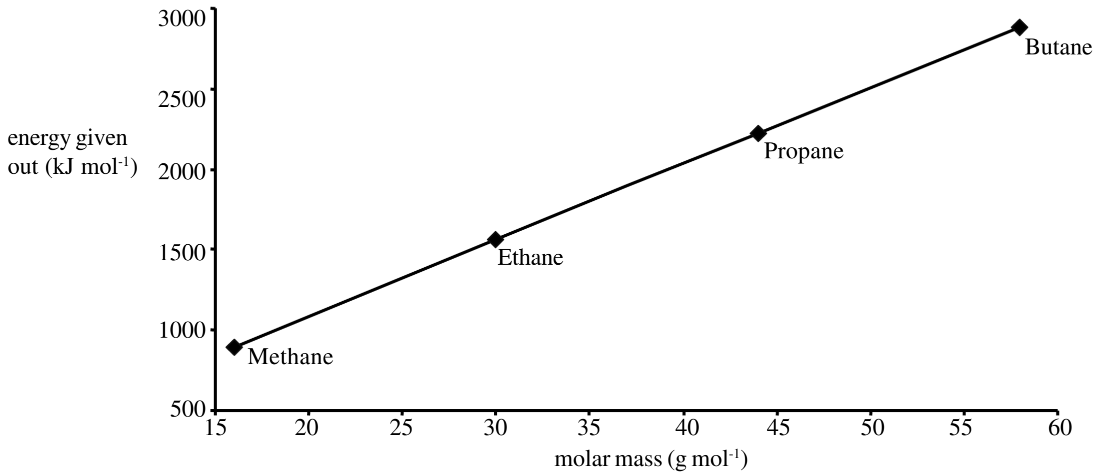
Table 4. Enthalpies of combustion of isomers of butan-1-ol

Alcohol	Molecular formula	Enthalpy of combustion (kJmol^{-1})
Butan-1-ol	$C_4H_{10}O$	-2676
Butan-2-ol	$C_4H_{10}O$	-2661
Methylpropan-1-ol	$C_4H_{10}O$	-2644

There are small differences in these enthalpies of combustion, which may be attributed to differences in structures, indicating that a bond in one molecule may have a slightly different energy from the same bond in a different molecule.

A further test would be to find the enthalpies of combustion of another homologous series. Fig 3 shows the enthalpies of combustion of the first four alkanes. Again, the steady increase in energy given out (about 660 kJ mole^{-1} CH_2) corresponds very well with the alcohols data. This can therefore be attributed to the successive addition of a CH_2 group and therefore to an increasing number of bonds being broken and formed.

Fig 3. Energy given out by combustion of the first four alkanes against M_r



The theory of mean bond enthalpies

Using the results of experiments like the ones described here, a set of mean bond enthalpy values can be derived (Table 5).

Table 5. Mean bond enthalpy values

Bond	Mean bond enthalpy (kJmol^{-1})
C-H	412
C-C	348
C-O	360
O=O	498
O-H	463
C=O	743

Each mean enthalpy value represents the average energy needed to break one mole of that bond in gaseous state under standard conditions

Two key points should be noted about mean bond enthalpies. First, they are quoted for *gaseous* substances. Second, they are the *average* values for each bond in similar environments, because bond enthalpy depends not only on the atoms in the bond, but also its environment.

Using mean bond enthalpies to calculate enthalpies of combustion

Mean bond enthalpy values can be used to calculate enthalpies of combustion.

Note – For an explanation of how to calculate enthalpy changes using mean bond enthalpies, see FactSheet 65, Calorimetry Experiments.

Calculating the enthalpies of combustion of the first four alcohols using mean bond enthalpies gives the results shown in Table 6.

Table 6. Calculating the enthalpy of combustion of the first four alcohols

Alcohol	ΔH_c by mean bond enthalpies ($kJmol^{-1}$)	ΔH_c by experiment ($kJmol^{-1}$)
Methanol	-532	-726
Ethanol	-1025	-1367
Propan-1-ol	-1518	-2021
Butan-1-ol	-2011	-2676

There is a significant difference between the two sets of values. This indicates deficiencies in the theory of mean bond enthalpies.

Firstly, bond enthalpies for any given bond vary depending on the bond's molecular environment. The energy needed to break a C-C bond, for example, will depend on whether the C-C bond is in an alcohol or an alkane, whether it is part of a long carbon chain or just in an ethane molecule.

The other deficiency is in the states used. Mean bond enthalpies are quoted for gaseous bonds, but of course not all substances are gases under standard conditions. In combustion, for example, the water product is a liquid. Since water will give out energy as it turns from vapour to liquid, this will give a more exothermic standard enthalpy of combustion than would be predicted from mean bond enthalpies. Also, the reactant (e.g. methanol) may be a liquid and therefore need vaporising. This causes the overall combustion to be less exothermic. Thus, using ΔH values for vaporisation, perhaps a better estimate can be made.

e.g. **For combustion of methanol:**

$CH_3OH(l) \rightarrow CH_3OH(g)$; +37 kJ mole^{-1}
$CH_3OH(g) + 1.5O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$; -532 kJ mol^{-1}
$H_2O(g) \rightarrow 2H_2O(l)$; -44 kJ mol^{-1}

Hence, $CH_3OH(l) + 1.5O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$; -583 kJ mol^{-1}

As you can see, mean bond enthalpies can still give only approximations of enthalpy changes, although often an approximation is all that is needed.

Summary

Enthalpies of combustion can be readily found by experiment, although experimental data are often inaccurate due to heat losses and incomplete combustion. Enthalpies of combustion increase as molecular size increases, due to increasing number of bonds broken and formed. This leads to a theory that particular bonds have an associated energy value. Using these mean bond enthalpies, enthalpies of combustion can be calculated. Discrepancies in the two values are caused by the use of mean bond enthalpies, and by differences in the standard states of the substances.

Practice Questions

1. Look again at the experiment in Fig 1
   (a) What are the main sources of error?
   (b) What effect will they have on the enthalpy of combustion measured in the reaction?
   (c) What improvements would you make to the experiment to try to minimise these sources of error?
2. An experiment was carried out to find the standard enthalpy of combustion of propane. It was found to be –2219 kJmol^{-1}. Using mean bond enthalpies to calculate the enthalpy of combustion of propane gives a value of –2054 kJmol^{-1}. Explain the difference.
3. The standard enthalpy of combustion of propan-1-ol is –2021 kJmol^{-1}, while the standard enthalpy of combustion of propan-2-ol is –2006 kJmol^{-1}. Explain the difference.

Answers

1. (a) Heat loss and incomplete combustion
   (b) Both will lead to less than the maximum possible energy being transferred into the water, so enthalpies of combustion measured will be less exothermic than expected.
   (c) To minimise heat loss, better insulation is needed, such as putting the burner and water in an insulated container. To give more complete combustion, a good supply of oxygen must be ensured.
2. Standard conditions means that water is produced in the liquid state. Bond enthalpies are measured for vapours, so values found using bond enthalpies are less exothermic than those found under standard conditions. Also, bond enthalpies vary from compound to compound, so mean bond enthalpy values may differ from those in the actual compound.
3. The enthalpies of combustion of these two isomers are very similar because they contain the same number and type of bonds. However, bond enthalpies depend on the environment of the bond as well as the atoms involved, and so will vary slightly from compound to compound.

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