

Energetics

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Special thanks to Ms Williams and Ms Matrella for their constant
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Please note that these guides are a collation of my personal notes, teachers' notes, chemistry books, and websites such as chemguide, chemsheets, chemwiki and wikipedia.

Definitions

Enthalpy

It is a measure of the heat content of a substance at constant pressure.

Hence enthalpy change is the change in that heat content. It is represented by ΔH where the H is enthalpy and the triangle is the delta sign or change in.

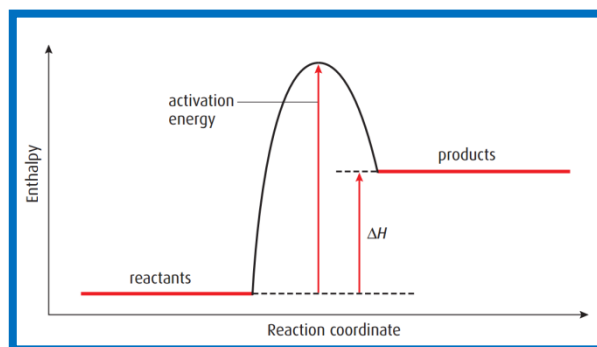
It is crucial to include a sign (even if a positive sign) when writing enthalpy change.

Endothermic reactions have a positive enthalpy change and exothermic reactions have a negative enthalpy change.

There are 2 types of enthalpy level diagrams you to be familiar with:

Endothermic Reactions:

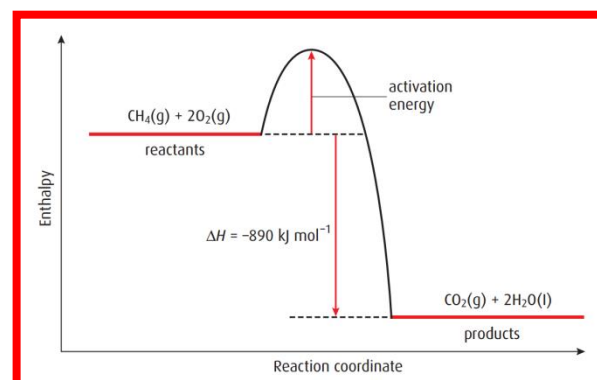
Here you can see that the reaction require quite a lot of Activation Energy (E_a) while the energy given out (the difference between the peak's energy and that of the products) is quite small compared to the E_a . The ΔH is positive as the products have more energy than the reactants.



Exothermic Reactions:

On the other hand, the E_a is small compared to the energy given out. Also note how the products have less energy than the reactants, hence ΔH is negative.

E_a is the minimum energy required to get the reaction going.



Through this guide standard conditions will be mentioned quite a lot, those are:

-1 atmospheric pressure (atm) $\sim$ 100 kPa

-25 °C = 298 K

Standard Enthalpy Changes of Reaction

It is the enthalpy change which occurs when the quantities of substances mentioned in a balanced equation react under standard conditions, and with everything in its standard state. This is represented by $\Delta H_r^\ominus$ where r is for reaction and finally theta as a superscript is used to represent standard conditions.

Standard Enthalpy Change of Formation

It is the enthalpy change when 1 mole of a compound is formed from its constituent elements, with all substances in their standard states and under standard conditions. This is represented by $\Delta H_f^\ominus$ where f is for formation.

Standard Enthalpy Change of Combustion

It is the enthalpy change which occurs when one mole of the compound is burned completely in oxygen under standard conditions, and with everything in its standard state. This is represented by $\Delta H_c^\ominus$ where c is for combustion.

Standard Enthalpy Change of Neutralisation

It is the enthalpy change when an acid neutralises an alkali under standard conditions to produce 1 mole of water. This is represented by $\Delta H_n^\ominus$ where n is for neutralisation.

Standard Enthalpy Change of Atomisation

The standard atomisation enthalpy is the enthalpy change when 1 mole of gaseous atoms is formed from the element in its standard state. Enthalpy change of atomisation is always positive. This is represented by $\Delta H_a^\ominus$ where a is for atomisation.

Calorimetry

The formulas

Calorimetry can be used to measure the enthalpy change in a reaction. To do so 2 formulas are used:

$$q_1 = m \cdot c \cdot \Delta T \quad \text{and} \quad \Delta H = q_2 / \text{moles reacting}$$

where:

q_1 = energy given out/absorbed (J)

q_2 = $q_1 / 1000$ (kJ)

m = mass of water heated (explained later) (g)

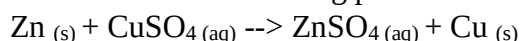
ΔT = temperature change ($^{\circ}\text{C}$)

c = specific heat capacity ($\text{J g}^{-1} \text{K}^{-1}$)

ΔH = enthalpy change (kJ/mol)

Reactions in Solution

Consider a reaction taking place in a solution such as



To measure the enthalpy change in such reaction we will use a **polystyrene (coffee) cup in a glass beaker** to minimise heat loss as much as possible. Add 50 cm^3 of copper (II) sulphate of concentration 0.2 mol dm^{-3} then measure the initial temperature. Then add 1.2g of powdered zinc, **put a lid** on the coffee cup and **stir the mixture**. Record the temperature every 30 seconds for 5 minutes.

Now we start using the formulas.

$$q_1 = m \cdot c \cdot \Delta T$$

m in this case is the mass of the solution. To calculate that we use the **density of the solution being 1 g/cm^3 (same as that of water)**. Hence, $m = \text{volume} \cdot \text{density}$

$$m = 50 \cdot 1$$

$$m = 50 \text{ g}$$

c in this case is **$4.18 \text{ J g}^{-1} \text{K}^{-1}$ (same as the specific heat capacity of water)**

ΔT can measure by finding the difference between max and initial temperature (let's assume we calculated 10.3°C and that **no heat was lost to the surroundings**)

$$\text{So } q_1 = 50 \cdot 4.18 \cdot 10.3$$

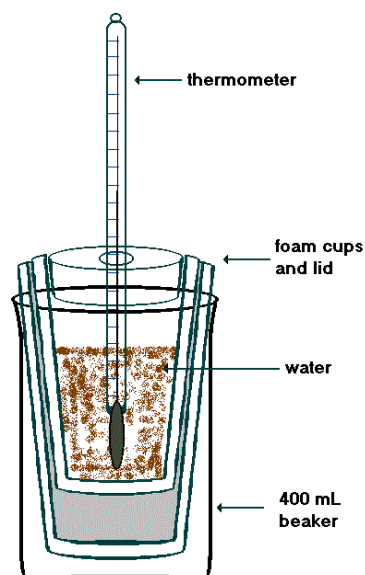
$$q_1 = 2150 \text{ J}$$

$$\text{Hence } q_2 = 2.15 \text{ kJ}$$

When calculating the moles reacting in this case we use the moles of the limiting reagent, and since it's a 1:1 ration, the copper sulphate is the limiting reagent.

Hence moles = concentration * volume

$$\text{moles} = 0.1 \text{ moles}$$



Finally $\Delta H = 2.15/0.1$

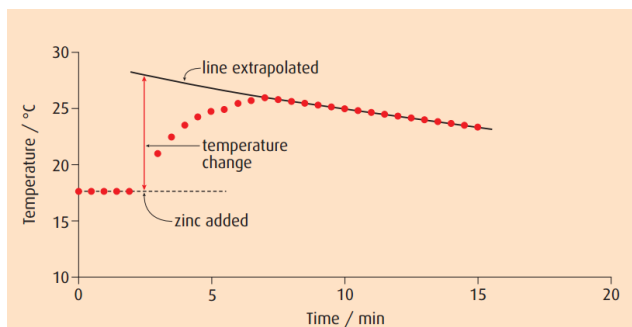
$\Delta H = -215 \text{ kJ mol}^{-1}$

Note how the **negative sign** is present because this is an **exothermic reaction** (temperature increased in the reaction). If this was an **endothermic reaction**, you **have** to include a **+** sign.

This set up can be used for other reactions that take place in solution such as neutralisation.

The **green text** above was dealing with precautions to be taken to minimise heat loss and ensure uniform distribution of heat...i.e. more accurate results. The **purple text** is used to highlight the assumptions you will make when carrying out such calculations.

In order to get more accurate figures for temperature change, the temperatures recorded are plotted and the max temp. is extrapolated. In this picture the kept measuring the temperature for 20 minutes. You can use the same method though. The red dots are the plotted points. The red line is the max temperature change. If this was an endothermic reaction, you will still plot the points, and extrapolate using a similar method.



Combustion Reactions

Consider the combustion (burning) of ethanol. Normally you would use this set up. The water will be in a **copper can** to maximize the heat gained by the water from the spirit burner. However that means the conducting nature of copper will make it lose heat to surroundings too.

The **distance between the spirit burner and the can must be kept as small as possible** for the same reason (maximize heat gain by water and minimize heat loss to surroundings).

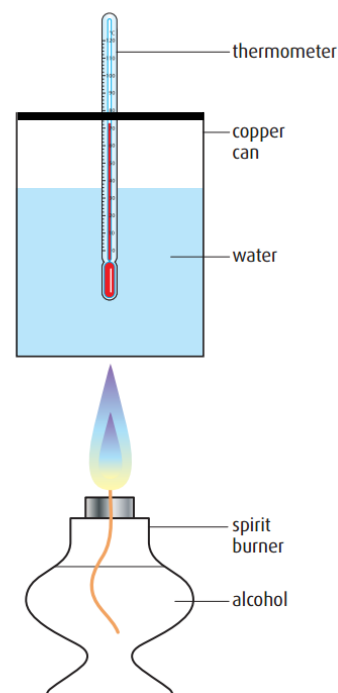
We have to weigh the burner before and after the combustion. The burner must **have the lid on** unless we are burning the fuel to reduce fuel evaporation.

We also **stir the water** to ensure uniform temperature in the water.

In this reaction all we care about is getting the maximum energy out of the fuel to the water. The precautions in this experiment are highlighted in **green**.

The calculations to be carried out are as follows:

$$q_1 = m \cdot c \cdot \Delta T$$



m = mass of water in the can

$c = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$

ΔT = max temperature of water - initial temp of water

Let's assume we calculated $q_1 = 16\,400 \text{ J}$

Then we do

$\Delta H = q_2 / \text{moles combusting}$

Mass of fuel burnt = Initial mass of spirit burner - its final mass

Then we divide that mass by the M_r of the fuel to calculate the number of moles combusting. Say we burnt 0.03 moles of ethanol. We then do the following:

$q_2 = 16\,400 / 1000 = 16.4 \text{ kJ}$

$\Delta H = q_2 / \text{moles combusting}$

$\Delta H = 16.4 / 0.03$

$\Delta H = -547 \text{ kJ mol}^{-1}$

Note the **negative sign** (due to temperature increase), it is crucial to get the full marks in the question.

Assumptions made in this experiment are:

- No heat has been lost to surroundings and all of it was transferred to the water.
- The difference in the mass of the spirit burner is fully due to the combustion of the fuel and there is no evaporation of the fuel. If some of the fuel evaporated, we haven't burnt that mass, hence that mass didn't give off energy.
- The fuel completely combusted and no incomplete combustion took place. If incomplete combustion took place, less energy will be given off per mole of the fuel.

The above points can be considered limitations too (heat will be lost, some fuel will evaporate and some of the combustion will be incomplete). Thus a smaller ΔH will be calculated than the actual value. This is because the increase in the temperature of water will be smaller than what it should've been.

Hess's Law

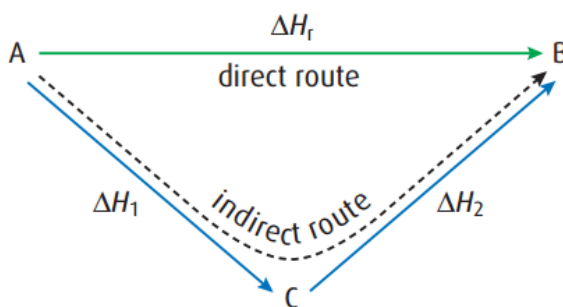
Hess's Law states that the change of enthalpy in a chemical reaction is independent of the pathway between the initial and final states.

This means that the enthalpy to go from A to B doesn't depend on the route taken. As a formula:

$$\Delta H_r = \Delta H_1 + \Delta H_2$$

Here is an example from a document called *Everything You Need To Know About Enthalpy* (I used that document quite a lot as you will see in the rest of the guide)

<http://www.school-portal.co.uk/GroupDownloadFile.asp?GroupId=1159782&ResourceID=4850246>

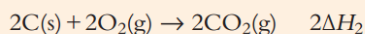


Method A (using a cycle)

The enthalpy changes given are used to construct a cycle. The enthalpy change that we have to find is put at the top of the cycle.

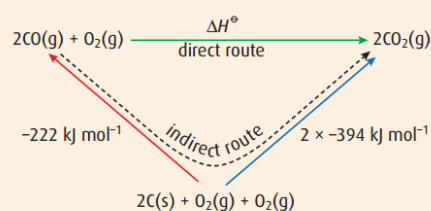
Only the first reaction has been added here. **Reaction 1** is highlighted in yellow and shows the reaction of 2C and 1 O₂ to form 2CO. The other O₂, highlighted in orange, remains unchanged, and there is no enthalpy change for this. This means that the total enthalpy change along the red arrow is ΔH_1 .

If **Reaction 2** is now added to complete the cycle, it must be multiplied by 2, as we need to form 2 mol CO₂. The enthalpy change must also be multiplied by 2, hence $2\Delta H_2$:



Reaction 2 is highlighted in green.

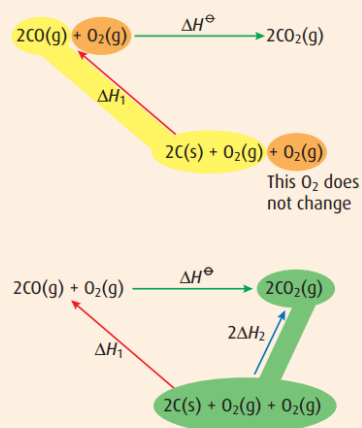
The values can now be put into the cycle:



The overall enthalpy change is given by

$$\Delta H^\ominus = -\Delta H_1 + 2\Delta H_2$$

$$\Delta H^\ominus = -(-222) + (2 \times -394) = -566 \text{ kJ mol}^{-1}$$



This is worked out from Hess's law: the enthalpy change for the direct route is the same as that for the indirect route. As the direction of the indirect route arrow is opposite to that of the red arrow, the sign of the quantity on the red arrow is reversed.

Method B (manipulating the equations)

In this method we rearrange the equations for the data given to give the equation for the reaction corresponding to the enthalpy change we have to find.

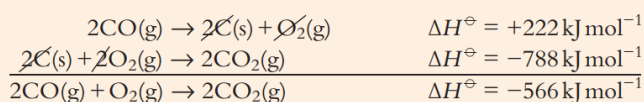
First, **Reaction 1** is reversed to give 2CO on the left-hand side, as in the overall equation:



Now **Reaction 2** is multiplied by 2 to give 2CO₂ on the right-hand side, as in the overall equation:



We now have 2CO on the left-hand side and 2CO₂ on the right-hand side, as in the overall equations. The two equations and their enthalpy changes are now added together and common terms cancelled to produce the overall equation and its enthalpy change:



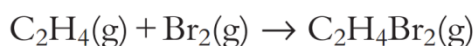
Bond Enthalpy

This is the enthalpy change to break **one mole** of covalent bonds in the **gas phase**.

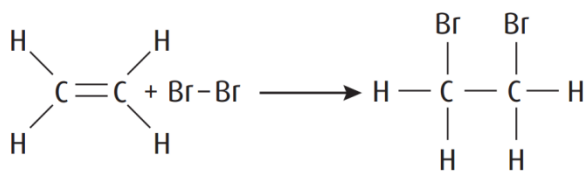
From there it follows that average bond enthalpy is the amount of energy required to break 1 mole of covalent bonds, in the gas phase. 'Average' refers to the fact that bond enthalpy is different in different molecules, hence a quoted value for a bond enthalpy is an average of the energy required to break a specific bond in a range of compounds.

Example:

Let's say we wanted to find the enthalpy change in:



First we need to draw the structural formula of all the substances present:



Now we will use the bond enthalpy values (which will be given, no need to memorize them) to calculate the enthalpy change in this reaction. We also need to take into consideration that **bond breaking** is **endothermic (positive enthalpy change)** while **bond making** is **exothermic (negative enthalpy change)**.

Bond broken	Bond energy / kJ mol^{-1}	Number of bonds	Total energy / kJ mol^{-1}
C-H	412	4	1648
C=C	612	1	612
Br-Br	193	1	193
Total energy to break all bonds			2453

The total enthalpy change when all the bonds are broken is $+2453 \text{ kJ mol}^{-1}$. This is positive, as breaking bonds is an endothermic process.

Bond made	Bond energy / kJ mol^{-1}	Number of bonds	Total energy / kJ mol^{-1}
C-H	412	4	1648
C-C	348	1	348
C-Br	276	2	552
Total energy released when bonds made			2548

The total enthalpy change when all the bonds are made is $-2548 \text{ kJ mol}^{-1}$. This is negative, as making bonds is an exothermic process.

If we add up these enthalpy changes, we get the overall enthalpy change for the reaction:

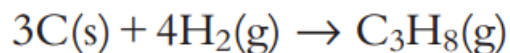
$$\Delta H^{\ominus} = 2453 - 2548 = -95 \text{ kJ mol}^{-1}$$

The overall process is sometimes summarised as:

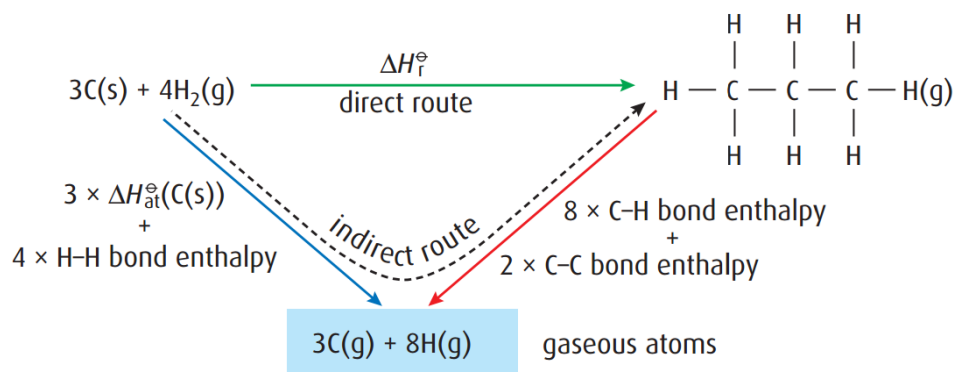
$$\Delta H_{\text{r}} = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds made})$$

Combining It All

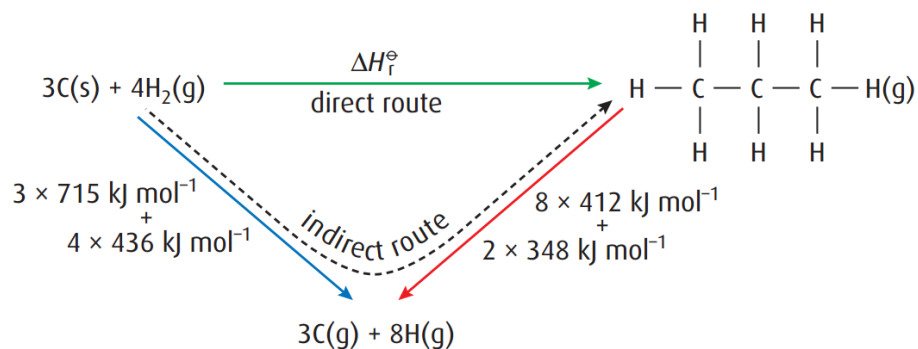
We can also use ΔH_a and Hess's Law with bond enthalpy in some reactions such as:



Now construct a cycle:



Putting in the values:



The value of the unknown enthalpy change is given by:

$$\Delta H^\ominus = ((3 \times 715) + (4 \times 436)) - ((8 \times 412) + (2 \times 348))$$

$$\Delta H^\ominus = -103 \text{ kJ mol}^{-1}$$