

2.1 – Thermochemistry

Enthalpy changes, ΔH

Enthalpy change is the name given to the amount of heat given out or absorbed in a reaction carried out at constant pressure.

Exothermic reactions have negative ΔH values.

Endothermic reactions have positive ΔH values.

Standard conditions

For values to be compared, standard enthalpy change is measured when fixed conditions are used:

- all substances in their standard states
- temperature of 298 K (25°C)
- pressure of 1 atm (101 000 Pa)

The symbol for a standard enthalpy change is ΔH^θ .

Enthalpy change of formation, $\Delta_f H^\theta$

This is the enthalpy change when 1 mol of a compound forms from its constituent elements in their standard states under standard conditions.

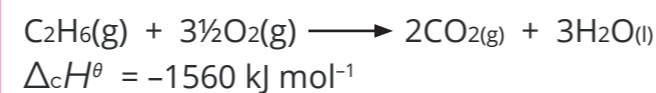


When writing an equation for enthalpy change of formation, you must end up with 1 mol of the compound. You may need to use fractions on the left-hand side of the equation.

The standard enthalpy change of formation of an element in its standard state is zero. If you are forming 1 mol of hydrogen gas from 1 mol of hydrogen gas, you aren't changing it in any way!

Enthalpy change of combustion, $\Delta_c H^\theta$

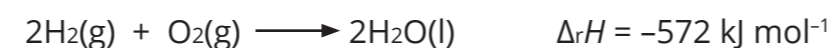
This is the enthalpy change when 1 mol of a substance is completely combusted in oxygen under standard conditions.



When writing an equation for enthalpy change of formation, you must start with 1 mol of whatever you are burning. You will often need to use fractions in the equation.

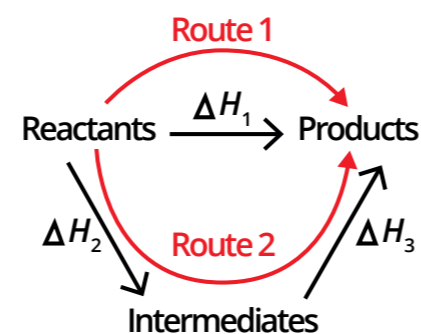
Enthalpy change of reaction, $\Delta_r H$

This is the enthalpy change when the reaction takes place between the reagents as indicated by the stoichiometric equation for the reaction under standard conditions.



Hess's Law

Hess's law states that the total enthalpy change for a reaction is independent of the route taken from the reactants to the products.



$$\text{Route 1} = \text{Route 2}$$

$$\text{i.e. } \Delta H_1 = \Delta H_2 + \Delta H_3$$

Using Hess's Law

Write down the enthalpy change you want to find as a horizontal equation and write ΔH over the top of the arrow.

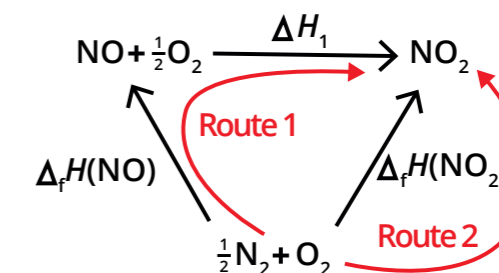
Make a cycle by putting the information you've been given into the same diagram, writing the known enthalpy changes over the arrows for each of the changes.

Find two routes around the diagram, always going with the flow of the various arrows.

If $\Delta_f H$ is given, the direction of the arrows is from the common elements to the reactants and products.

If $\Delta_c H$ is given, the direction of the arrows is from the reactants and products to the common combustion products.

Example: Calculate the enthalpy change of reaction for the formation of nitrogen dioxide from nitric oxide given the enthalpy changes of formation.



$$\Delta_f H(\text{NO}) + \Delta H_1 = \Delta_f H(\text{NO}_2)$$

$$\Delta H_1 = \Delta_f H(\text{NO}_2) - \Delta_f H(\text{NO})$$

$$\text{i.e. } \Delta H = \Delta_f H(\text{products}) - \Delta_f H(\text{reactants})$$

If you are given enthalpy changes of combustion, then

$$\Delta H = \Delta_c H(\text{reactants}) - \Delta_c H(\text{products})$$

2.1 – Thermochemistry

Bond enthalpies

Bond enthalpy is the enthalpy needed to break 1 mol of the bond to give separated atoms with everything being in the gaseous state.

Average bond enthalpy is the average value of the enthalpy required to break a given type of covalent bond in the molecules of a gaseous species.

Calculations of enthalpy changes of reaction based on average bond enthalpies will not be as accurate as results derived from experiments with specific molecules.

$$\Delta H = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds formed})$$

Measuring enthalpy changes practically

In a chemical reaction, the heat transferred to its surroundings can be measured by carrying out the reaction in an insulated container called a calorimeter. The simplest type of calorimeter is a coffee cup calorimeter.

The relationship between the temperature change, ΔT , and the amount of heat transferred, q , is given by the expression

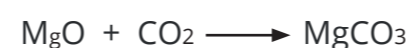
$$q = mc\Delta T$$

where m is the mass of the solution and c is the specific heat capacity of the solution ($4.18 \text{ J g}^{-1} \text{ K}^{-1}$).

To calculate the enthalpy change of reaction per mole, use the expression $\Delta H = -q/n$ where n is the number of moles that have reacted.

Use of coffee cup calorimeter

A range of enthalpy changes can be measured directly by reacting a solution and a solid (or two solutions). These can also be used with Hess's law, e.g. for the indirect determination of $\Delta_r H$ for reactions that don't occur spontaneously, such as



Measure an appropriate volume of acid using a burette or pipette (the mass of acid is used in the expression to calculate ΔH) and place it in a polystyrene cup. This must be in excess (to ensure that all the solid reacts).

Use an accurate thermometer to measure the initial temperature of the acid. When a steady value has been obtained, record the temperature (ΔT is used in the expression to calculate ΔH).

Accurately weigh the solid MgO (in powder form to ensure as rapid a reaction as possible) in a suitable container (the number of moles of the solid is used in the expression to calculate ΔH).

Add all the solid to the cup, stir the mixture well (to ensure that the reaction is as rapid as possible and that all the solid is used) and start a stopwatch.

Keep stirring with the thermometer and record the temperature regularly (about every 30 seconds). Stop recording the temperature when it has fallen for about 5 minutes.

Plot a graph of temperature against time to calculate the maximum temperature the mixture might have reached.

Repeat the procedure with MgCO_3 .

Calculate the amount of heat transferred in both reactions ($q = mc\Delta T$).

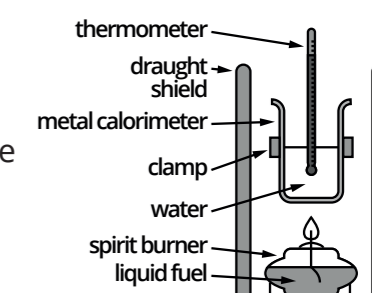
Calculate the enthalpy change for both reactions ($\Delta H = -q/n$).

Use Hess's law to calculate the required enthalpy change.

All actual values obtained this way are lower than book values due to heat loss from the simple type of calorimeter used.

Combustion of an alcohol

Allow a suitable gap between the base of the metal calorimeter (or insulated beaker) and the top of the spirit burner. Accurately measure the amount of water being added.



Use an accurate thermometer to measure the temperature of the water. When a steady value has been obtained, record the temperature. Weigh the spirit burner containing the alcohol and record the initial mass.

After lighting the wick, adjust the gap between the metal calorimeter and the spirit burner if necessary.

Allow the burning alcohol to heat the water to a suitable temperature – the smaller the increase, the greater the percentage error of the temperature change value.

Extinguish the flame and record the final maximum temperature.

Allow the spirit burner to cool before reweighing and recording the final mass.

The value is much lower than the book value because:

- some of the energy transferred from the burning alcohol is 'lost' in heating the apparatus and the surroundings
- combustion of the alcohol is not complete.