

3.11 Introduction to Energy and Enthalpy Changes

Why do we study energy changes during a reaction?

Because it helps us to answer many questions including

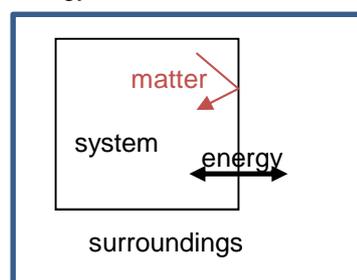
- why chemical reactions occur
- why a certain reaction is more likely to occur than another
- why the overall energy change accompanying a chemical change is independent of the route by which the change is achieved

Energy, Enthalpy and Heat

We can sometimes get bogged down in Chemistry with definitions, but they are important. We often use interchangeably the words 'heat' 'energy' and 'enthalpy' but they all mean different things. Most A-level students will have a reasonable understanding of energy and heat but enthalpy will be for many a new term and is more difficult to define.

In chemical reactions energy will be most often seen as Heat energy which will cause the temperature to change. Energy, however, can be transferred in other forms than just heat energy.

We often use the words **system** and **surroundings**. The word **system** means all the chemicals both reactants and products. The surroundings is everything else in the universe outside of the system. Energy can be transferred between the system and surroundings in both directions.



Definitions.

Energy is the ability of a system to do work.

Work is the energy transfer that is the result of a force moving an object through a distance

Heat is the energy transfer that is a result of a temperature difference between system and surroundings

In the above exploding hydrogen balloon reaction, the system is the hydrogen in the balloon and the oxygen in the air. These substances contain an internal energy. The internal energy of the system will be a combination of kinetic energy of the moving particles and the potential energy stored in the chemical bonds. During the reaction some of the internal energy will be converted into heat energy passed into the surroundings and also work. The expanding gases will have done some work pushing other molecules out of the way. The internal energy of the system will have decreased.

The above process can be represented by the following equation

$$\text{Change in internal energy} = \text{heat added to the system} + \text{work done to the system}$$

These would be negative values if heat energy was transferred away from the system or if work was done by the system

The problem with this equation is that it is difficult to measure internal energy and the work done to the system. It is relatively easy to measure the heat added to the system though. So how does Enthalpy fit into this?

Enthalpy change

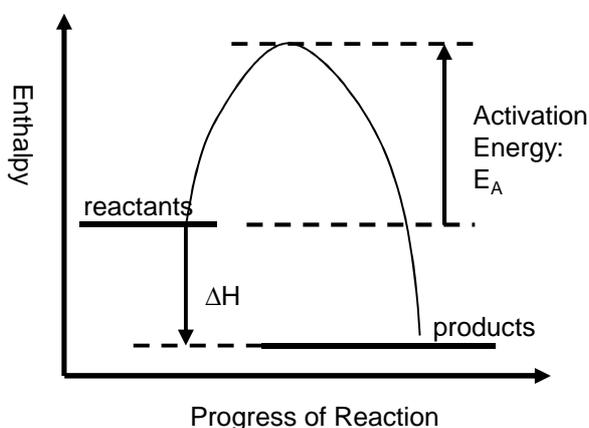
Definition: Enthalpy change (ΔH) is the amount of **heat energy** taken in or given out during any change in a system provided the **pressure is constant**.

Why is the condition **pressure is constant** important in this definition? To fully answer this we have to do some quite complicated maths- if you are interested look at page 4. However, when the maths is done if pressure is constant we can just look at the heat transferred (which is easy to measure) and ignore the work done. So in this case enthalpy is something similar to the internal energy of the system. When heat energy is transferred away from the system the enthalpy change (ΔH) (like internal energy change) will be negative.

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

Like internal energy, enthalpy is difficult to measure but it is easy to measure enthalpy change by measuring the amount of heat transferred during a reaction

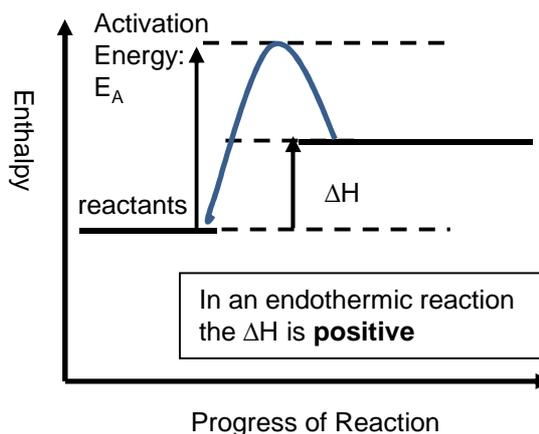
In an exothermic change heat energy is transferred from the system (chemicals) to the surroundings. The products have less enthalpy than the reactants



In an exothermic reaction the ΔH is **negative**

Common oxidation exothermic processes are the combustion of fuels and the oxidation of carbohydrates such as glucose in respiration

In an endothermic change, heat energy is transferred from the surroundings to the system (chemicals). They require an input of heat energy e.g. thermal decomposition of calcium carbonate. The products have more enthalpy than the reactants



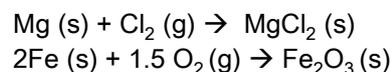
In an endothermic reaction the ΔH is **positive**

Standard Enthalpy change definitions

There are lots of enthalpy changes that we use in chemistry that can be further defined for specific reactions and processes. Listed below are some common enthalpy changes that are often met at A-level. They need exact definitions so scientists can know what the value quoted exactly refers to. Particular attention has to be paid to what substance the amount in moles refers to.

Standard enthalpy change of Formation

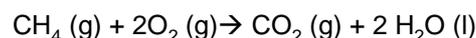
The standard enthalpy change of formation of a compound is the **enthalpy change** when **1 mole of the compound** is formed from **its elements** under **standard conditions (298K and 100kpa)**, all reactants and products being in their standard states
Symbol $\Delta_f H^\ominus$



The enthalpy of formation of an element = 0 kJ mol⁻¹

Standard enthalpy change of Combustion

The standard enthalpy of combustion of a substance is defined as the **enthalpy change** that occurs when **one mole of** a substance is **combusted completely in oxygen** under **standard conditions. (298K and 100kPa)**, all reactants and products being in their standard states
Symbol $\Delta_c H^\ominus$



Incomplete combustion will lead to soot (carbon), carbon monoxide and water. It will be **less exothermic** than complete combustion.

Definition: Enthalpy change of reaction is the enthalpy change when the number of moles of reactants as specified in the balanced equation react together

Enthalpy changes are normally quoted at **standard** conditions.

Standard conditions are :

- 100 kPa pressure
- 298 K (room temperature or 25°C)
- Solutions at 1 mol dm⁻³
- all substances should have their normal state at 298K

When an enthalpy change is measured at standard conditions the symbol \ominus is used
Eg ΔH^\ominus

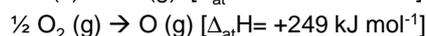
Enthalpy change of Neutralisation

The standard enthalpy change of neutralisation is the enthalpy change when solutions of an acid and an alkali react together under standard conditions to produce 1 mole of water.

Enthalpy changes of neutralisation are always exothermic. For reactions involving strong acids and alkalis, the values are similar, with values between -56 and -58 kJ mol⁻¹

Enthalpy of atomisation

The enthalpy of atomisation of an element is the enthalpy change when 1 mole of gaseous atoms is formed from the element in its standard state



Maths of Internal Energy and Enthalpy

This is extension material for those who want to delve deeper

Referring to the equation from page 1

Change in internal energy (U) = heat added to the system (q) + work done to the system (w)

$$\Delta U = q + w \quad (1)$$

Using some physics definitions work is defined as

$$\text{Work}(w) = \text{force} \times \text{distance moved} \quad (2)$$

Pressure is defined as

$$\text{Force} = \text{pressure} \times \text{area} \quad (3)$$

So combining equation (2) and (3) gives us

$$\text{Work} = \text{pressure} \times \text{area} \times \text{distance moved}$$

Which is the same as

$$\text{Work} = \text{pressure} \times \text{change in volume}$$

Using symbols

$$w = -p \Delta V \quad (4)$$

Given minus sign because work is being done by the system on the surroundings

Combining equations (1) and (4) give us

$$\Delta U = q - p \Delta V \quad (5)$$

Note if the **change in volume** is zero then no work would be done and the internal energy change ΔU would equal the heat transferred $\Delta U = q$

Now moving on to Enthalpy (H). This is **defined** by this different equation

$$H \equiv U + pV \quad (6)$$

For small changes in the enthalpy we can convert equation (6) into one that represents ΔH

$$\Delta H = \Delta U + p\Delta V + V\Delta p \quad (7)$$

Now we can substitute the equation (5) defining ΔU into equation (7)

$$\Delta H = q - p\Delta V + p\Delta V + V\Delta p$$

Simplify to

$$\Delta H = q + V\Delta p \quad (8)$$

If the **change in pressure is zero** then equation (8) simplifies to $\Delta H = q$ which takes us back to the exam board definition of enthalpy change which is *enthalpy change is the amount of heat energy taken in or given out during any change in a system provided the **pressure is constant***

So note that when the change in volume is zero we can say $\Delta U = q$ and when change in pressure is zero we can say $\Delta H = q$

Why do we prefer to measure ΔH rather than ΔU ?

- 1) It is more convenient to measure ΔH in the lab because we can open vessels and maintain constant pressure.
- 2) In reactions where there is no volume change (ones that are just solids and liquids). $\Delta H = \Delta U$
- 3) In reactions involving a volume change, the difference in ΔU is less than 5% if ΔH is greater than 40kJ.