Enthalpy Changes

Enthalpy changes of formation, combustion, reaction and neutralisation

Enthalpy change is the change in heat energy when a reaction takes place.

- **Exothermic** reactions release heat energy and the enthalpy change is **negative**.
- Endothermic reactions absorb heat energy and the enthalpy change is positive.
- The units are always kJ per mole (**kJ mol**⁻¹).

You might see a little circle with a line through it written next to the enthalpy sign. This refers to **standard conditions** and **standard states**. Standard conditions are a temperature of **298 K** (25 °C) and a pressure of **1 atm** (100 kPa).

There are different types of enthalpy change:

- Standard enthalpy change of reaction the enthalpy change that accompanies a reaction which occurs in the molar quantities as shown in the balanced symbol equation under standard conditions
- Standard enthalpy change of neutralisation the enthalpy change that accompanies the reaction of an acid and an alkali to form one mole of water under standard conditions
- Standard enthalpy change of combustion the enthalpy change that takes place when one mole of substance is completely burned in excess oxygen under standard conditions
- Standard enthalpy change of formation the enthalpy change that accompanies the formation of one mole of a compound from its constituent elements under standard conditions

Reaction profiles

Reaction profiles show the **amount of energy** that a substance has at the start and end of a reaction.

- During an **exothermic** reaction the reactants **lose energy** as they form products.
- The difference in energy between the reactants and products is the **enthalpy change** which is **negative** and the arrow points downwards.
- The initial increase in energy is the **activation energy**. Activation energy is the **minimum amount of energy needed to get a reaction going**.

The graph on the right shows an **endothermic** reaction.

- You can see from the diagram that the products have **more energy** than the reactants.
- This is because energy has been **absorbed** from the surroundings the enthalpy change is **positive** and the arrow points upwards.



EXCITERNIC ENTHALPY CHANGE (DH) IS NEGATIVE



ENTHALPY CHANGE (DH) IS POSITIVE

You may be expected to calculate the enthalpy of a reaction based on **experimental data**.



In these experiments, some sort of fuel (e.g. propane) will be burnt in a spirit burner beneath a beaker of water.

We can record the change in temperature of the water to

determine the enthalpy change of combustion of the fuel, using the equations:



Worked example: calorimetry

A student burns 2 g of ethanol which raises the temperature of water from 23°C to 60°C. The mass of water in the copper can is 100 g and the specific heat capacity of water is 4.18 JK⁻¹g⁻¹. Calculate the molar enthalpy change.

- Use the equation $\mathbf{Q} = \mathbf{mc} \Delta \mathbf{T}$ to calculate the heat energy released.
- Q = 100 x 4.18 x (60-23) = 15,466 J.
- Calculate the moles of ethanol burnt. Moles = mass / Mr.
- Moles of ethanol = 2 / 46 = 0.043 mol
- Calculate the enthalpy change by dividing Q by the number of moles. Remember to convert energy in J to kJ.
- Energy change = 15.466 kJ / 0.043 mol = 359.67 kJ/mol
- Since this is a combustion reaction, we need to remember that it is an exothermic reaction and add a negative sign. Our final answer = -359.67 kJ/mol

You can also use the $Q=mc\Delta T$ equation to calculate the enthalpy change of **neutralisation** experimentally. In this case, the **acid and the base will be mixed** in a **polystyrene cup** and the change in temperature of the solution is measured. This time our mass will be the **total mass of the solution**.

Variation in results

In a calorimetry experiment like the one described above, the data collected may **differ** from enthalpy values found in a **data book** for the following reasons:

- Non-standard conditions used
- Heat lost to the surroundings
- Heat absorbed by the apparatus
- Incomplete combustion
- Evaporation of fuel or water

To make calorimetry experimental data **more accurate**, you should try to minimise heat loss by using a **lid** or **insulated beaker**.

Bond enthalpies

- Breaking bonds is **endothermic** energy is required to break them.
- Making bonds is **exothermic** energy is released when new bonds form.

If a reaction is **exothermic** overall, we know that **more energy has been released** when the bonds in the products were **formed** than the **energy absorbed** to **break** the bonds in the reactants.

Likewise, if a reaction is **endothermic** overall, **more energy is required to break the bonds** in the reactants than was released when forming bonds in the products.

Bond enthalpies **aren't very accurate** since the actual amount of heat energy released when a bond is made depends on the **other atoms and bonds** in the molecule. We therefore use **average bond enthalpies** which are always measured when the atoms are in a **gaseous** state. The official definition for average bond enthalpy is '**the energy required to break one mole of bonds in the gas phase**'.

We can use average bond enthalpies to work out the overall enthalpy change for a reaction using the following equation:

ENTHALPY CHANGE (Δ H) = ENERGY TO BREAK BONDS - ENERGY RELEASED MAKING BONDS

This is the same as saying that **enthalpy change = sum of bond enthalpies in reactants – sum of bond enthalpies in the products**. Have a look at the worked example below to see how the total enthalpy change for the combustion of methane is calculated using average bond enthalpies.

Worked example: bond energies

Methane burns in oxygen in the following reaction:

 $(H_4 + 2O_2 \longrightarrow (O_2 + 2H_2O_2))$

The bond energies are: C-H: 413 kJ/mol O=O: 498 kJ/mol C=O: 745 kJ/mol O-H: 467 kJ/mol

Calculate the enthalpy change for the reaction.

Answer:

With these questions you may find it useful to draw out the molecules to make sure you don't miss out any bonds. Remember that when we have a big number in front of the molecule, we have to multiply the molecule by that number.

- Use the equation: **enthalpy change = bonds broken bonds formed**
- Energy to break bonds in the reactants: (4 x 413) + (2 x 498) = 2648 kJ/mol
- Energy needed to form bonds in the products: (2 x 745) + (4 x 467) = 3358 kJ/mol
- Enthalpy change = 2648 3358 = -710 kJ/mol
- Enthalpy change is **negative** which means this is an **exothermic** reaction.

Hess' law

Hess's law states that the **total enthalpy change of a reaction is the same, regardless of the route taken**.

It is useful for calculating enthalpy changes that **can't be determined experimentally**. You need to be able to draw and calculate the enthalpy change for a reaction when provided with either formation data or combustion data.

When you're given formation data

We can use standard enthalpy of formation data to calculate the enthalpy for the reaction between ammonia and hydrochloric acid to form ammonium chloride.

$$\text{NH}_{3}$$
 (g) + HCl (g) \longrightarrow NH_{4} Cl (s)

COMPOUND	∆H _f * (kJmol-')
NH3 (9)	-46.1
HCI rgs	- 92. 3
NH4CI (g)	-314.4

Step 1: When you're given enthalpy of formation data, you'll need to write the **elements** that make up the compounds along the bottom with **arrows pointing upwards**, because the elements are the reactants in the formation reactions.



Step 2: Alongside the arrows, **write the enthalpy of formation values** for the reactants and products. Remember to **multiply by the number of moles** of each reactant or product. This example is more straight-forward, because we only have one mole of each reactant/product so there is no need to multiply.

$NH_{3}(q) + HCI(q) \longrightarrow NH_{4}CI(s)$	COMPOUND	∆H _f [●] (kJmol ⁻ ')
	NH3 (9)	-46.1
-92·3 	HCI (g)	- 92. 3
$N_2 + H_2 + Cl_2$	NH4CI (g)	- 314: 4

Step 3: Work out the **two routes** to get from the elements to the product in the original reaction. There will be one direct route and one indirect route, made up of two arrows. Hess' law states that the **enthalpy change is independent of the route taken**, so the indirect route will be equal to the direct route. We can **rearrange** to find the enthalpy change of the original reaction.



COMPOUND	∆H _f (kJmol⁻')
NH3 (9)	-46.1
HCI (g)	- 92. 3
NH4Cl (g)	-314.4

$$-|38 \cdot 4 + x = -3|4 \cdot 4$$

x = -3|4 \cdot 4 - -|38 \cdot 4
x = -176 kJmol⁻¹

When you're given combustion data

It's the same idea for when we're given combustion data, except that this time we're going to write out the **products of combustion** (carbon dioxide and water) along the bottom of the cycle with our **arrows facing downwards**.

Let's look at how to calculate the enthalpy change for the formation of nonane, given the combustion data in the table below.

$9C_{(S)} + 10H_{2}_{(q)} \longrightarrow C_{9}H_{20}_{(1)}$	COMPOUND	∆Hc [®] (kJmol⁻')
5	(s)	- 394
	H2 (9)	- 286
	C9H20(1)	- 6125

Step 1: Write the **products of combustion** (carbon dioxide and water) along the bottom. It's not necessary to balance these. Your **arrows** will be **facing downwards** this time, from the things that you're burning to the products of combustion.



Step 2: Add values for the enthalpy change of combustion beside the arrows. Multiply by the number of moles of each reactant and product in the original equation.



Step 3: Work out the **two routes** you can take to go from the reactants to the combustion products. The sum of the enthalpies of the indirect route is equal to the enthalpy change of the direct route. **Rearrange** to find the enthalpy of the original reaction.

$PC_{(S)} + IOH_2_{(q)} \xrightarrow{\chi} C_9H_{20}_{(1)}$	COMP(
(9 × -394)	Ca
+ (10x - 286) = - 6406	H₂
$CO_2 + H_2O$	Cal

COMPOUND	∆Hc® (kJmol⁻')
C (s)	-394
H₂ (g)	- 286
C9H20(1)	- 6125

$$-6406 = x + -6125$$

x = -6406 - -6125
x = -281 kJmol⁻¹