Enthalpy changes, ΔH

Exothermic and endothermic reactions

> **An exothermic reaction is one which releases energy to the surroundings.**

An example of an exothermic reaction is combustion, where the reactants burn in oxygen, releasing heat(energy) to the surroundings.

The **system**(the reactants and products) **release energy**(heat) to the **surrounding**, **increasing the temperature**.

> An endothermic reaction is one which absorbs energy from the surrounding.

An example of an endothermic reaction is photosynthesis. Energy from the sun is absorbed by the leaves, so it is endothermic.

The **system**(the reactants and products) **absorb energy**(heat) from the **surrounding**, **decreasing the temperature**.

Enthalpy change

All substances store energy. This energy is the sum of

1. The **potential energy** stored by electrostatic forces within and between particles

2. The **kinetic energy** stored by the movement of particles(translational energy) and the vibrations and rotation of particles(vibrational energy and rotational energy)

In chemical reactions, energy transfer happens when bonds are broken and formed. Some reactants release energy to the surrounding(exothermic), and some absorb energy from the surrounding(endothermic).

> The energy stored in a compound is called the **enthalpy** and is given the symbol H.

Enthalpy cannot be measured on its own, but we can measure the amount of energy transfer that happens during a reaction. This is called the **enthalpy change**, and is given the symbol ΔH. The unit is $kJ\ mol^{-1}$.

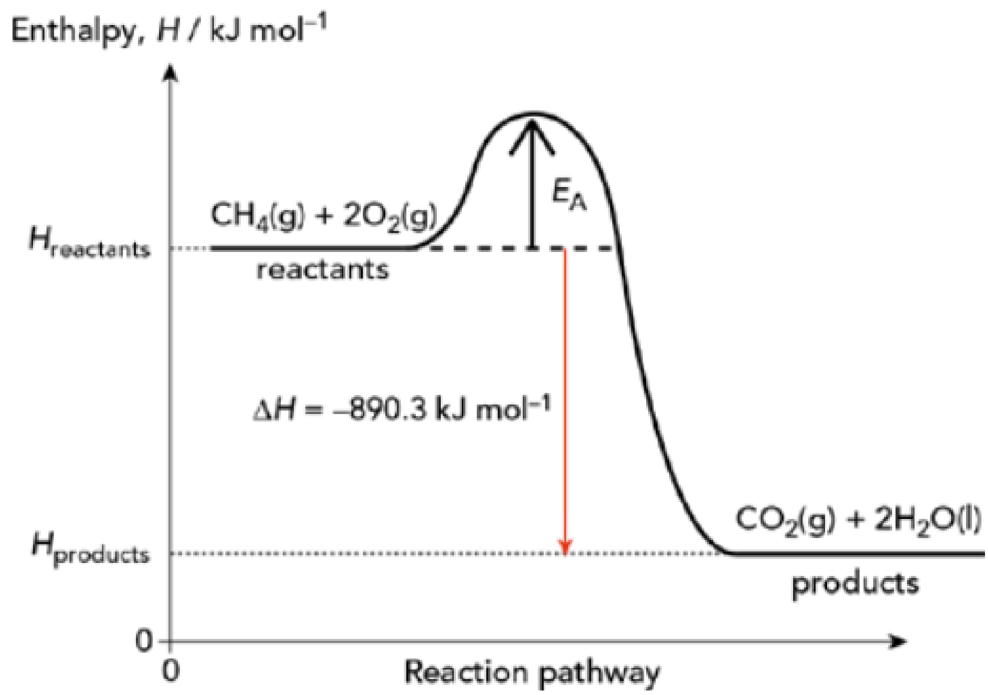
If energy is transferred to the surrounding, in other words exothermic, ΔH is negative.

If energy is transferred from the surrounding, or endothermic, ΔH is positive.

Reaction pathway diagrams

Enthalpy change can be shown with a reaction pathway diagram.

The bump in the diagram shows the **activation energy** E_A.



When methane burns, the enthalpy of methane and oxygen(the reactants) is higher than the carbon dioxide and water(the products), so the energy has been released to the surroundings. Therefore, it is an exothermic reaction.

Here, $\Delta H_{c}^{\ominus} = -890.3\ kJmol^{-1}$

'c' stands for combustion, since this is a combustion reaction(see more types of enthalpy change later), and $\ominus$ stands for the standard condition.

Types of standard enthalpy changes

Standard conditions

To make the comparisons of any enthalpy change fair, we must use standard conditions. Standard conditions include:

- A temperature of $25^{\circ}C$ or $298\ K$
- A pressure of $101\ kPa$ (approximately 1 atmosphere)
- Each substance involved in the reaction must be in its standard state, i.e., the state at $25^{\circ}C$ and $101\ kPa$ and be

the most common allotrope.

The symbol $\ominus$ is used to indicate that an enthalpy change happens at standard conditions.

Standard enthalpy of reactions, $\Delta H_r^{\ominus}$

> **Standard enthalpy of reactions, $\Delta H_r^{\ominus}$, is the enthalpy change that occurs when quantities in an equation for a chemical reaction react under standard conditions. Both reactants and products are in their standard state.**

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \quad \Delta H_r^{\ominus} = -572\ kJ\ mol^{-1}$$

Here, $\Delta H_r^{\ominus}$ is the enthalpy change when 2 moles of hydrogen react with 1 mole of oxygen to form 2 moles of water. The reaction is exothermic as we can see from the negative enthalpy change.

Standard enthalpy change of formation, $\Delta H_f^{\ominus}$

> **Standard enthalpy change of formation, $\Delta H_f^{\ominus}$, is the enthalpy change that occurs when 1 mole of a substance is formed under standard conditions from 2 or more elements in their standard state. The reactants and products must be in their standard states.**

$$H_2(g) + S(s) + 2O_2(g) \rightarrow H_2SO_4(l) \qquad \Delta H_f^{\circ} = -814\ kJ\ mol^{-1}$$

Sometimes, you will have to use fraction in the equation to get one mole of product. For example,

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O \qquad \Delta H_f^{\circ} = -285.8\ kJ\ mol^{-1}$$

Standard enthalpy change of combustion, ΔH_c°

> **Standard enthalpy change of combustion, ΔH_c°, is the enthalpy change that occurs when 1 mole of a substance reacts with excess oxygen and burns under standard conditions. The reactants and products must be in their standard states.**

Combustion reactions are always exothermic, so ΔH_c° will always be negative.

$$S(s) + O_2(g) \rightarrow SO_2(g) \qquad \Delta H_c^{\circ} = -296.8\ kJ\ mol_{-1}$$

Substances usually burn at temperatures higher than the standard temperature, so some adjustments have been made to experimental values to give data-values or web-page values. Here are enthalpy changes for some fuels.

Fuel	Main constituent	Formula and standard state	ΔH_c° of main consituent / $kJ\ mol^{-1}$
Hydrogen, compressed	Hydrogen	$H_2(g)$	-286

Fuel	Main constituent	Formula and standard state	ΔH_c° of main consitituent / $kJ\ mol^{-1}$
natural gas, liquid (CNG or compressed natural gas)	90% methane	$CH_4(g)$	-890
liquid petroleum gas (LPG)	95% propane	$C_3H_8(g)$	-2219
methanol	methanol	$CH_3OH(l)$	-726
ethanol	ethanol	$C_2H_5OH(l)$	-1367
petrol	octane	$C_8H_{18}(l)$	-5470

Standard enthalpy change of neutralisation, ΔH_{neut}°

> **Standard enthalpy change of neutralisation, ΔH_{neut}°, is the enthalpy change that occurs when 1 mole of water is produced from an acid and a base under standard conditions. The reactants and products must be in their standard states.**

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l) \qquad \Delta H_{neut}^{\circ} = -57.2\ kJ\ mol^{-1}$$

💡 Note that some reactions can apply to more than one enthalpy change. For e.g., $S(s) + O_2(g) \rightarrow SO_2(g)$ can be considered both a standard enthalpy change of combustion and formation, Since one mole of a reactant burning in air produces 1 mole of a substance.

Bond energies

When we measure enthalpy changes, we are measuring the amount of energy taken in or out of a reaction. Since chemical reactions break and form bonds, enthalpy change is really the difference between the energy released to break bonds and the energy absorbed to form bonds.

Breaking bonds require energy like we have said. Different bonds require different amounts of energy and stronger bonds need more energy than weaker bonds. However, the same amount of energy will be given out when the same bond is formed.

> **The energy required to break a particular bond in a gaseous molecule is called the bond energy.**

$$H_2(g) \rightarrow H(g) + H(g) \qquad \Delta H^{\ominus} = +436\ kJ\ mol^{-1}$$

Bond energy has the symbol E. It is written as $E(H-H) = +436\ kJ\ mol^{-1}$.

In this case, this means that $436\ kJ$ of energy is needed to break one mole of hydrogen. The same amount of energy is released when this bond is formed.

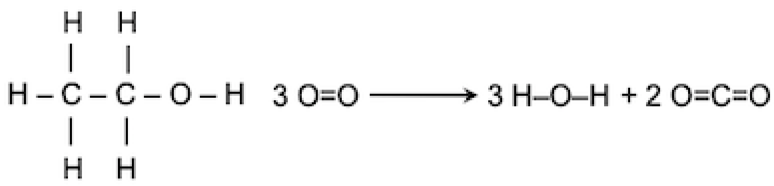
Calculating $\Delta H_r^{\ominus}$ from Bond energies

Bond energies can be used to calculate enthalpy changes. This is because bond breaking requires energy and is always endothermic while bond making releases energy so it is always exothermic.

Let’s see an example.

1. Calculate the enthalpy change for the combustion of one mole of ethanol.

- Step 1: Write the equation using displayed formula.



- Step 2: Look up the bond energies required to break the bonds. Since, bond breaking is endothermic, the values are positive ($kJ\ mol^{-1}$).

$5 \times (C-H) = 5 \times 410 = +2050$

$1 \times (C-C) = +350$

$1 \times (C-O) = +360$

$1 \times (O-H) = +460$

$3 \times (O-O) = 3 \times 496 = +1488$

So the total energy required to break all the bonds is $+4708\ kJ\ mol^{-1}$.

- Step 3: Look up the bond energies required to make the bonds. Since bond making is exothermic, the values are negative ($kJ\ mol^{-1}$).

$4 \times (C = O) = 4 \times 740 = -2960$

$6 \times (O - H) = 6 \times 460 = -2760$

So the total energy required to make bonds is $-5720\ kJ\ mol^{-1}$.

- Step 4: Calculate the enthalpy change

$\Delta H_r^{\circ} = +4708 - 5720 = -1012\ kJ\ mol^{-1}$

💡 Remember that bond energies refer to molecules in their gaseous state.

Exact and average bond energies

Bond energies are affected by other atoms in the molecule. For example, the $O - H$ bond in water has a slightly different bond energy than the $O - H$ bond in ethanol. In ethanol, the oxygen atom is connected to a carbon atom rather than another hydrogen atom, so the bond energy is slightly different. **This is called the exact bond energy.**

The $O - H$ bond is in **another environment**, and has a different bond energy. So, we use **average bond energy** which are taken from the same bond but in different environments. For this reason, the average bond energy is more useful in most situations.

Calculating ΔH in $kJ\ mol^{-1}$

Find the heat released with $q = mc\Delta T$

$$\Delta H = -\frac{q}{mol\ used}$$