

CIE Chemistry A Level

5 : Chemical Energetics

Notes



Enthalpy change, ΔH

Enthalpy is the **thermal energy** stored in a chemical system. It can't be measured directly.

Reactions and energy changes

Chemical reactions are accompanied by energy changes (typically heat energy changes). If energy is released into the surroundings, the reaction is **exothermic and ΔH is negative**. If energy is taken in from the surroundings, the reaction is **endothermic and ΔH is positive**. The temperature of the surroundings increases during an exothermic reaction and decreases during an endothermic reaction.

Enthalpy terms

- **Standard conditions** - temperature of 298 K (25°C), pressure of 100 kPa (1 bar), solution concentrations of 1 mol dm⁻³. All products and reactants are in their standard states.
- **Standard enthalpy change of reaction, ΔH_r^\ominus** - the enthalpy change that occurs when a reaction takes place in the molar quantities given in a chemical equation, all reactants and products in their standard states under standard conditions.
- **Standard enthalpy change of formation, ΔH_f^\ominus** - the enthalpy change that takes place when one mole of a given substance is formed from its elements under standard conditions.
- **Enthalpy change of combustion, ΔH_c** - the enthalpy change when one mole of a compound undergoes complete combustion.
- **Standard enthalpy change of hydration, ΔH_{hyd}^\ominus** - the enthalpy change that takes place when one mole of gaseous ions dissolves in water.
- **Standard enthalpy change of solution, ΔH_{sol}^\ominus** - the enthalpy change that occurs when one mole of an ionic solid dissolves in water.
- **Standard enthalpy change of neutralisation ΔH_{neut}^\ominus** - the enthalpy change when one mole of water is formed from a neutralisation reaction under standard conditions.
- **Standard enthalpy change of atomisation, ΔH_{at}^\ominus** - the enthalpy change when one mole of gaseous atoms are formed from the element in its standard state.

Bond energy is the energy required to break **one mole** of a given **gaseous bond** to form atoms. In the data book, bond enthalpies are quoted as a mean average because the actual enthalpy of a bond varies depending on which molecule it's in. Energy is required to break bonds so ΔH is positive (endothermic). Energy is released when bonds are made so ΔH is negative (exothermic).

Enthalpy calculations

The enthalpy change of a reaction can be calculated using the equation below:

$$\Delta H = -mc\Delta T$$

ΔH - enthalpy change (J)

m - mass of surroundings (g)

c - specific heat capacity (J g⁻¹ K⁻¹)

ΔT - temperature change (K or °C)



Lattice energy (A Level only)

Lattice formation enthalpy is the enthalpy change that takes place when **one mole** of a substance is formed from its **gaseous ions**. Lattice dissociation enthalpy is the enthalpy change that takes place when **one mole** of an ionic compound is broken down to form its **gaseous ions**. If gaseous ions are turned into a solid lattice, ΔH is negative.

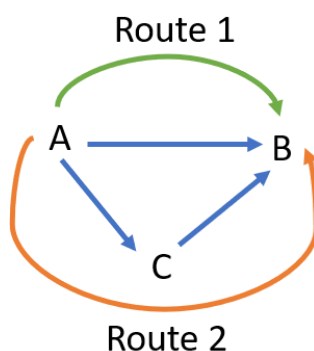
There are 2 factors that affect lattice enthalpy:

- **Ionic charge** - increasing the ionic charge increases the attraction between the positive and negative ions meaning a larger, more negative lattice formation enthalpy.
- **Ionic radius** - decreasing the ionic radius means the ions are closer together in the lattice so the attraction between the ions is stronger meaning a larger, more negative lattice formation enthalpy.

Hess' Law and Born-Haber Cycles

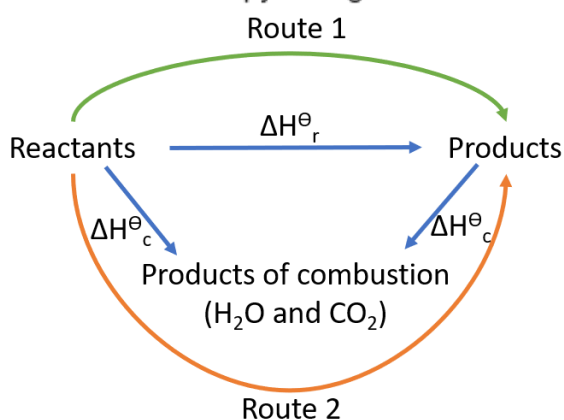
Hess' Law

Hess' Law states that the enthalpy change that accompanies a chemical change is **independent of the route** it takes. This is because the enthalpy of the reactants and products remain the same. Any energy released when forming intermediates will be used to break bonds to allow the product to form. In the diagram below, the enthalpy change of route 1 is the same as route 2:

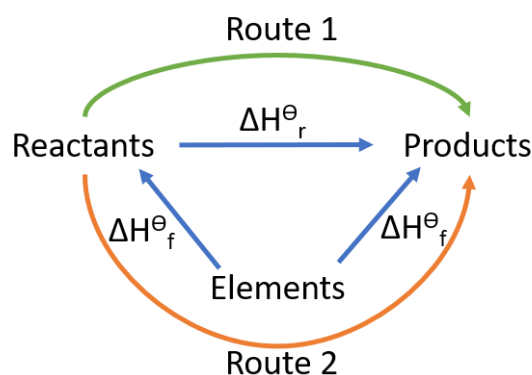


Enthalpy change of formation and combustion can be used with Hess' Law to determine the enthalpy change of a reaction. It is important to note the directions of the enthalpy change arrows in the cycles below:

Using enthalpy change of combustion to find enthalpy change of reaction:



Using enthalpy change of formation to find enthalpy change of reaction:



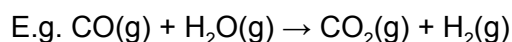
Average bond energies

Bond energies can be used to find the enthalpy change of a reaction when all reactants and products are **gaseous**.

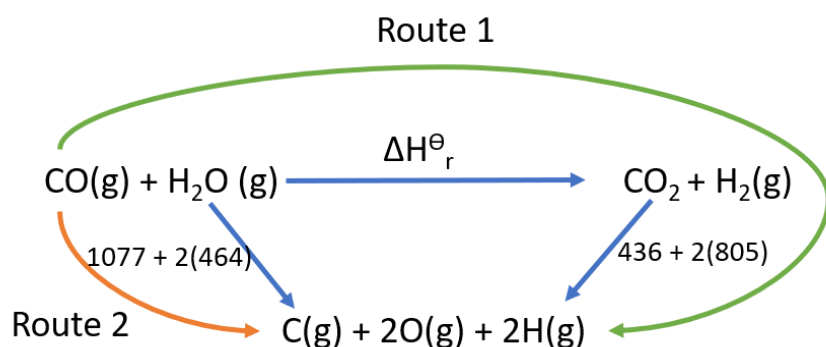
Method 1: $\Delta H = \text{total energy needed to break bonds} - \text{total energy made when making bonds}$

When totalling the energy released or made, the average bond enthalpies for each bond must be multiplied by the number of that bond present in the equation.

Method 2: use an enthalpy cycle



Bond	Bond enthalpy (kJ mol ⁻¹)
C-O (carbon monoxide)	+1077
C=O	+805
O-H	+464
H-H	+436



Using the cycle:

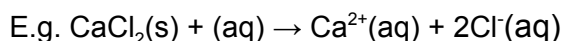
$$\Delta H + 436 + 2(805) = 1077 + 2(464)$$

$$\Delta H = 1077 + 2(464) - 436 - 2(805)$$

$$\Delta H = -41 \text{ kJ mol}^{-1}$$

Forming ionic solids from aqueous ions (A Level only)

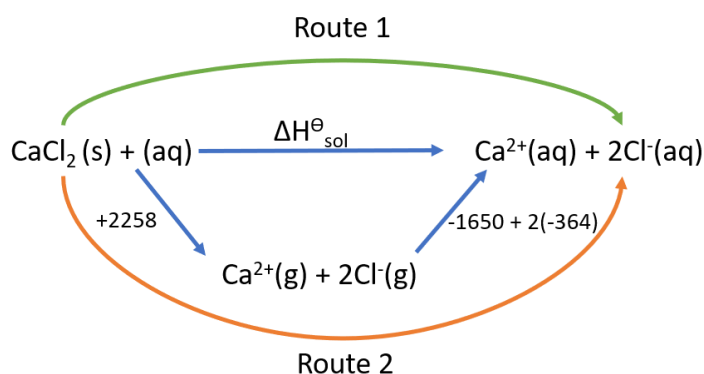
Hess' Law can also be used when calculating enthalpy change of solution:



	ΔH (kJ mol ⁻¹)
Hydration of $\text{Ca}^{2+}\text{(g)}$	-1650
Hydration of $\text{Cl}^-\text{(g)}$	-364
Lattice dissociation enthalpy	+2258

$$\Delta H_{\text{sol}} = +2258 - 1650 + 2(-364)$$

$$\Delta H_{\text{sol}} = -120 \text{ kJ mol}^{-1}$$

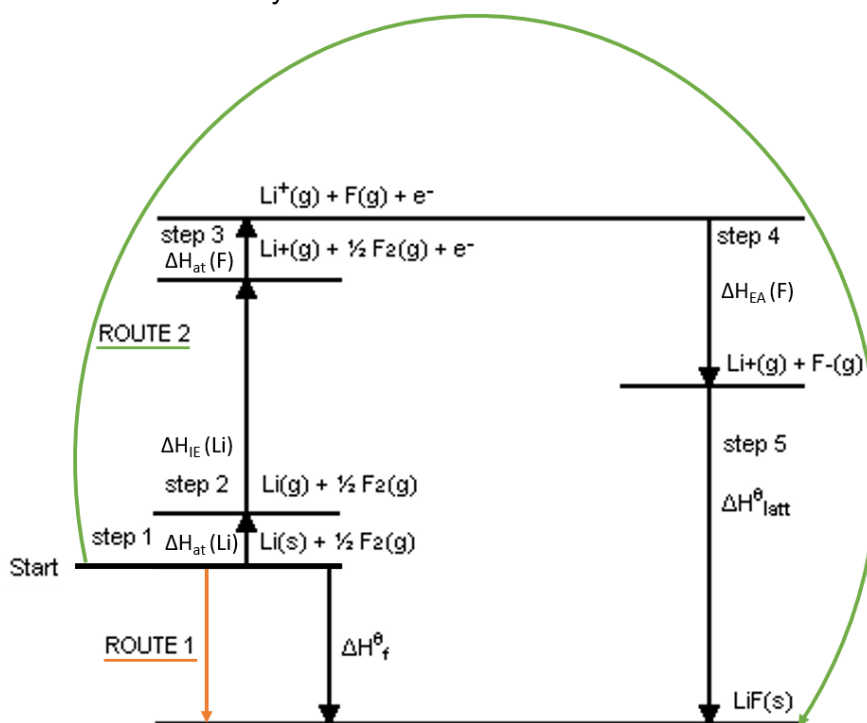


Born-Haber cycles (A Level only)

Lattice enthalpy is calculated using Born-Haber cycles. Born-Haber cycles use the following enthalpy changes:

- Lattice enthalpy of formation or lattice enthalpy of dissociation.
- Enthalpy change of atomisation.
- Enthalpy change of formation.
- First ionisation energy - the energy required to remove one electron from **one mole of gaseous atoms** to **form one mole of gaseous 1+ ions**. In Born-Haber cycles, this is only used for metals.
- First electron affinity - the energy released when each atom in **one mole of gaseous atoms** gains an electron **forming one mole of gaseous 1- ions**. In Born-Haber cycles, this only applies to non-metals.

Below is an example of a Born-Haber cycle for lithium fluoride and the calculation of the lattice enthalpy (ΔH_{LE}^{\ominus}):



	ΔH (kJ mol ⁻¹)
ΔH_f^{\ominus} of LiF(s)	-612
ΔH_{at}^{\ominus} of Li(s)	+161
ΔH_{IE}^{\ominus} of Li(g)	+79
ΔH_{at}^{\ominus} of $\frac{1}{2}F_2(g)$	+519
ΔH_{EA}^{\ominus} of F(g)	-348

$$-612 = 161 + 79 + 519 - 348 + \Delta H_{LE}^{\ominus}$$

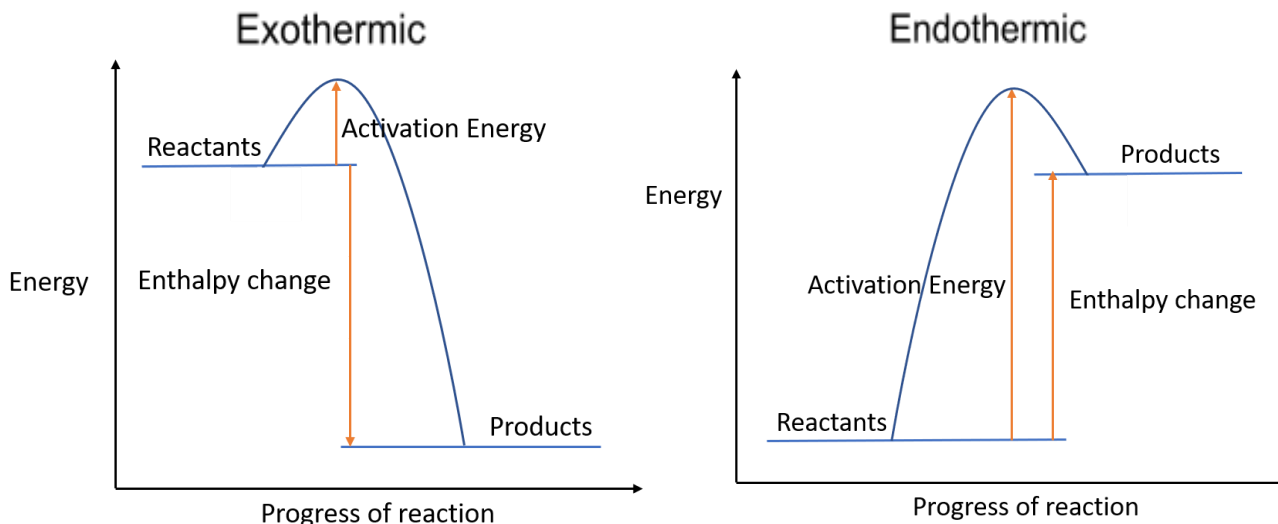
$$\Delta H_{LE}^{\ominus} = 348 - 161 - 79 - 519 - 612$$

$$\Delta H_{LE}^{\ominus} = -1023 \text{ kJ mol}^{-1}$$



Reaction pathway diagrams

Below are reaction pathway diagrams for exothermic and endothermic reactions:



Entropy change, ΔS (A level only)

Entropy is a measure of the **degree of disorder** in a system. A system becomes more stable when there is more disorder and the energy is more spread out.

Entropy **increases from solid to liquid to gas** and aqueous substances have a higher entropy than solids. This is because the particles become **more disordered** with these state changes and the energy spreads out.

If the number of gaseous moles increases during a reaction, the entropy change will be positive (entropy increases) because gases have a much higher entropy than liquids or solids due to their disordered movement.

Increasing the temperature may cause a state change which would increase the entropy. If temperature is increased without a change of state, entropy increases because the particles have **more kinetic energy** and faster moving particles are more disordered.

Entropy change of a reaction can be calculated using the following equation:

$$\Delta S = \Sigma S^{\ominus}(\text{products}) - \Sigma S^{\ominus}(\text{reactants})$$

Where Σ means 'the sum of' and the standard entropies of the reactants and products have been given. A negative result indicates that the entropy has decreased while a positive result shows the entropy has increased.



Gibbs free energy change, ΔG (A level only)

Gibbs free energy change can be calculated using this equation:

$$\Delta G = \Delta H - T\Delta S$$

ΔG - Gibbs free energy change (kJ mol^{-1})

ΔH - enthalpy change (kJ mol^{-1})

T - temperature (K)

ΔS - entropy change ($\text{kJ K}^{-1} \text{mol}^{-1}$)

A reaction or process is **spontaneous / feasible** when **ΔG is less than or equal to 0**. If ΔG is positive, the reaction is not spontaneous at the temperature used in the calculation. To find the minimum temperature at which a reaction is spontaneous when given ΔH and ΔS , rewrite the equation as: $\Delta H - T\Delta S < 0$ and rearrange to find temperature.

Predicting spontaneity

- When ΔH is negative and ΔS is positive: Using the equation, ΔH is negative and $T\Delta S$ is positive so $-T\Delta S$ is negative. Regardless of temperature, ΔG is always negative so the reaction is spontaneous at all temperatures.
- When ΔH is positive and ΔS is negative: Using the equation, ΔH is positive and $T\Delta S$ is negative so $-T\Delta S$ is positive. Both terms are positive regardless of temperature so ΔG is always positive and the reaction is never spontaneous.
- When ΔH and ΔS are positive: Using the equation, ΔH is positive and $T\Delta S$ is positive so $-T\Delta S$ is negative. Increasing the temperature causes $-T\Delta S$ to get more negative. At high temperatures, $-T\Delta S$ will outweigh ΔH and ΔG will be less than 0 so the reaction will be spontaneous. The reaction won't be spontaneous at low temperatures.
- When ΔH and ΔS are negative: Using the equation, ΔH is negative and $T\Delta S$ is negative so $-T\Delta S$ is positive. At high temperatures, $-T\Delta S$ becomes more positive so will outweigh ΔH meaning the reaction won't be spontaneous. The reaction will be spontaneous at low temperatures.

