CAIE Chemistry A-level

23: Chemical Energetics
(A-level only)
Notes

Lattice Energy and Born Haber Cycles

Enthalpy Terms
- **Standard conditions** - temperature of 298 K, pressure of 100 kPa, solution concentrations of 1 mol dm^{-3}. All products and reactants are in their standard states.
- **Standard enthalpy change of atomisation, $\Delta H^{\ominus}_{at}$** - the enthalpy change when one mole of gaseous atoms are formed from the element in its standard state.
- **Standard enthalpy change of hydration, $\Delta H^{\ominus}_{hyd}$** - the enthalpy change that takes place when one mole of gaseous ions dissolves in water.
- **Standard enthalpy change of solution, $\Delta H^{\ominus}_{sol}$** - the enthalpy change that occurs when one mole of an ionic solid dissolves in water.

Lattice Energy
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 two 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.

Electron Affinity
First electron affinity is the energy released when **one mole of gaseous atoms** each **gains an electron** to form one mole of **1- ions**. It is measured in kJ mol^{-1} and always has a negative sign to show energy is released.

$$E.g. \ O(g) + e^- \rightarrow O^-(g)$$
$$Cl(g) + e^- \rightarrow Cl^-(g)$$
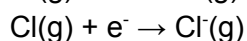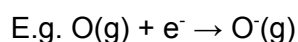
Electron affinity **decreases down the group** because although nuclear charge increases, **electron shielding and atomic radius increase** so there is less attraction between the nucleus and an incoming electron. This means less energy is released as you go down the group. Fluorine and oxygen are exceptions to this rule as they have lower electron affinities than expected. This is because they are relatively small so are already crowded with electrons which repel an incoming electron.

Second electron affinity is the energy required to add one electron to each ion in one mole of gaseous 1- ions to form one mole of gaseous 2- ions. This requires energy because the negative ion **repels** the incoming electron.

Born-Haber Cycles

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 ($\Delta H^\ominus_{LE}$):
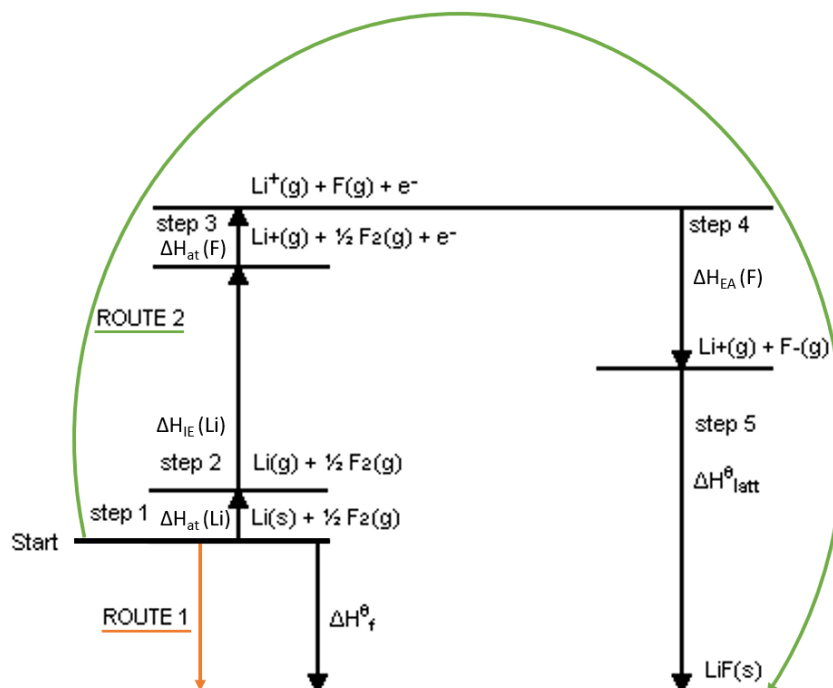
	ΔH (kJ mol^{-1})
$\Delta H^\ominus_f$ of LiF(s)	-612
$\Delta H^\ominus_{at}$ of Li(s)	+161
$\Delta H^\ominus_{IE}$ of Li(g)	+79
$\Delta H^\ominus_{at}$ of ½F$_2$(g)	+519
$\Delta H^\ominus_{EA}$ of F(g)	-348

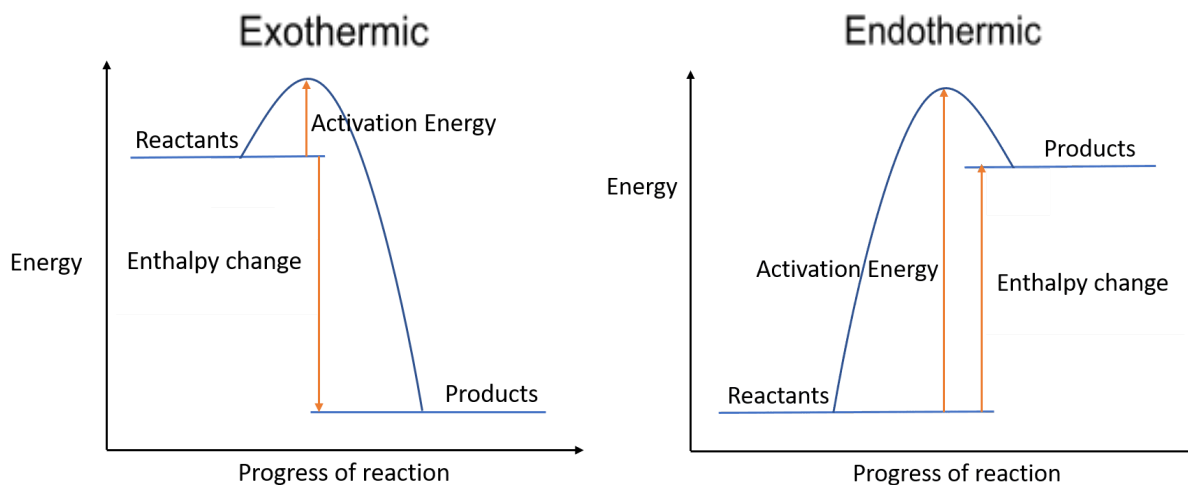$$-612 = 161 + 79 + 519 - 348 + \Delta H^\ominus_{LE}$$
$$\Delta H^\ominus_{LE} = 348 - 161 - 79 - 519 - 612$$
$$\Delta H^\ominus_{LE} = -1023 \text{ kJ mol}^{-1}$$
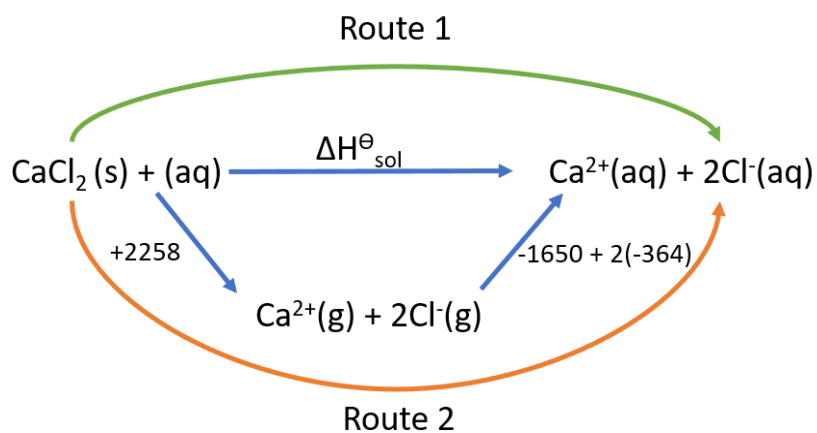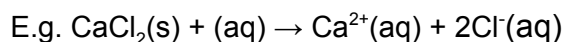
Reaction Pathway Diagrams

Below are reaction pathway diagrams for exothermic and endothermic reactions:

Enthalpies of Solution and Hydration

Forming Ionic Solids from Aqueous Ions

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

$$\text{E.g. } CaCl_2(s) + (aq) \rightarrow Ca^{2+}(aq) + 2Cl^-(aq)$$

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

$$\Delta H_{sol} = +2258 - 1650 + 2(-364) = -120 \text{ kJ mol}^{-1}$$

Entropy Change, ΔS

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. It is the number of possible arrangements of the particles and their energy in a given system.

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

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 (kJ K^{-1} 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: ΔH - TΔS < 0 and rearrange to find temperature.

Predicting Spontaneity

- **When ΔH is negative and ΔS is positive:** Using the equation, ΔH is negative and TΔS is positive so -TΔS 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 TΔS is negative so -TΔS 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 TΔS is positive so -TΔS is negative. Increasing the temperature causes -TΔS to get more negative. At high temperatures, -TΔS 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 TΔS is negative so -TΔS is positive. At high temperatures, -TΔS becomes more positive so will outweigh ΔH meaning the reaction won't be spontaneous. The reaction will be spontaneous at low temperatures.