

LATTICE ENTHALPY

DEFINITIONS

Lattice enthalpy is defined as the enthalpy change that happens when one mole of an ionic compound is either formed from gaseous ions or dissociates into gaseous ions under standard conditions. It is given the symbol $\Delta_{\text{LE}}H$ and can be represented in general as $nA^{m+}(g) + mB^{n-}(g) \rightarrow A_nB_m(s) \rightarrow nA^{m+}(g) + mB^{n-}(g)$ for formation (or the reverse for dissociation).

The standard enthalpy change of formation ($\Delta_f H$) is defined as the change in enthalpy when one mole of a compound is formed from its elements in their standard states under standard conditions.

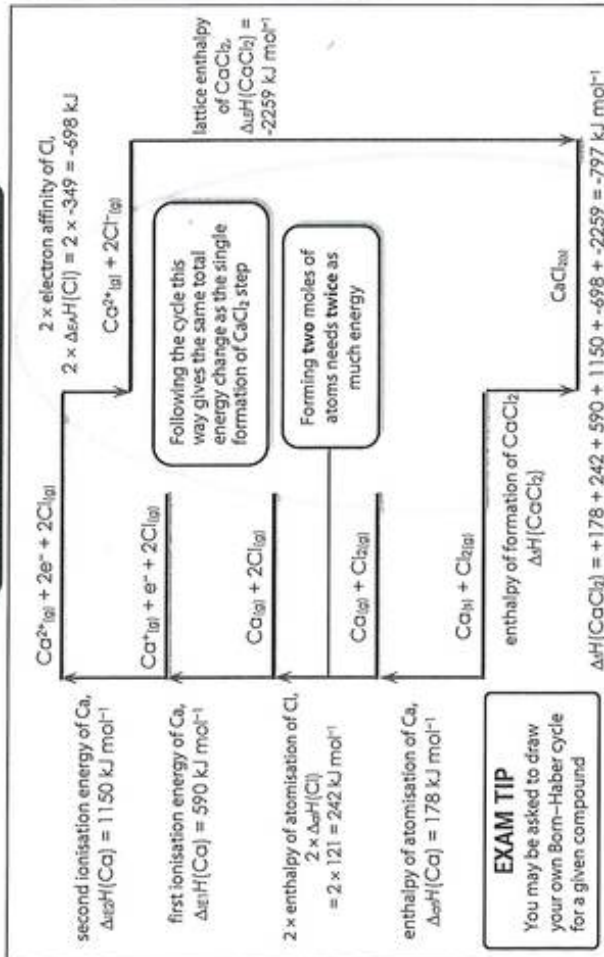
The standard enthalpy change of atomisation ($\Delta_{\text{at}} H$) is defined as the change in enthalpy when one mole of gaseous atoms is formed from an element in its standard states under standard conditions.

The first ionisation energy ($\Delta_{\text{IE}} H$) is the enthalpy change when one electron is removed from each atom in one mole of gaseous atoms, forming $1+$ ions.

The first electron affinity ($\Delta_{\text{EA}} H$) of an element is the enthalpy change when one electron is added to each atom in one mole of gaseous atoms, forming $1-$ ions.

The standard bond enthalpy is the enthalpy change when one mole of covalent bonds is broken under standard conditions.

BORN-HABER CYCLES



A sequence of steps involving the formation of an ionic compound is called a **Born-Haber cycle**. The one on the left is for calcium chloride and shows the value of enthalpy change for every step except the formation. Follow the arrows from the elements in the bottom left to CaCl_2 (bottom right) and add together all the enthalpy changes to calculate the enthalpy of formation.

EXAM TIP

You can calculate any enthalpy value if you know all the others. Follow the cycle the 'long way' around and add up all the enthalpy values. If you follow an arrow backwards, reverse the sign of the enthalpy change.

PERFECT IONIC MODELS

An ionic lattice (see Electrons, bonding and structure part 2) can be modelled by assuming that ions are perfect spheres with charges at points in their centres that are assumed to have no size. The ions occupy space, but the charges are at infinitely small points. This is called a **perfect ionic model**.

Calculations based on this model can work out the **theoretical lattice enthalpy**.

The lattice enthalpy that is worked out using experimental data in a Born-Haber cycle like the one shown here is called the **experimental lattice enthalpy**.

The theoretical and experimental values of lattice enthalpy would be very similar if perfect spheres with point charges was an accurate model of the ionic compound.

Sometimes the values are very close, suggesting some ionic compounds do behave like a perfect ionic model, but sometimes the experimental value is **higher** than the theoretical one – suggesting that there is something **more** than just ionic bonding holding the lattice together.

This is usually because the compound is not purely ionic – it is said to have some **covalent character**. This is often caused by small, high-charge ($2+$ or $3+$) ions polarising (distorting) large ions with a $2-$ or $3-$ charge.



Some ions behave according to the perfect ionic model. They have very similar theoretical and experimental lattice enthalpies.



Some ions cause other ions to polarise. This adds **covalent character** to the bonding. The experimental lattice enthalpy is **higher** than the theoretical one.

DISSOLVING IONIC COMPOUNDS IN WATER

Enthalpy of solution is the enthalpy change when one mole of a compound is dissolved in a solvent. The symbol is $\Delta_{\text{sol}} H$.

Enthalpy of hydration is the enthalpy change when one mole of gaseous ions dissolve in water. The symbol is $\Delta_{\text{hyd}} H$.

A sequence of enthalpy changes can form a cycle that allows the energy changes involved in dissolving an ionic solid in water to be calculated. An example of a cycle is shown for dissolving CaCl_2 . From this, it is possible to calculate the enthalpy change of solution of CaCl_2 :

$$\Delta_{\text{sol}} H(\text{CaCl}_2) = +2259 + (-1579) + (2 \times -378) = -76 \text{ kJ mol}^{-1}$$

This is energy required to separate the lattice into free gaseous ions – hence it is a positive value (moving up the page is always positive and down negative)

The hydration of two moles of ions releases twice as much energy

Dissolving CaCl_2 is **exothermic**. Some compounds dissolve **endothermally**.

Hydration enthalpy is affected by charge and radius:

- Higher charge = higher hydration enthalpy
- Smaller radius = higher hydration enthalpy

lattice enthalpy of CaCl_2 , $\Delta_{\text{LE}} H(\text{CaCl}_2) = -2259 \text{ kJ mol}^{-1}$

EXAM TIP

You may be asked to calculate any energy change – you will be given all except one

