23.1 LATTICE ENERGIES AND BORN-HABER CYCLES

Understanding why ionic compounds are so stable — and how we measure it.

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🎯 Learning outcomes

Candidates should be able to:

1. Define and use the terms:
   (a) enthalpy change of atomisation, ΔH_{at}
   (b) lattice energy, ΔH_{latt} (the change from gas phase ions to solid lattice)
2. (a) Define and use the term first electron affinity, EA
   (b) Explain the factors affecting the electron affinities of elements
   (c) Describe and explain the trends in the electron affinities of the Group 16 and Group 17 elements
3. Construct and use Born–Haber cycles for ionic solids
   (limited to +1 and +2 cations, –1 and –2 anions)
4. Carry out calculations involving Born–Haber cycles
5. Explain, in qualitative terms, the effect of ionic charge and of ionic radius on the numerical magnitude of a lattice energy

Key Concept 5 – Energy changes

The energy changes that take place during chemical reactions can be used to predict the extent, feasibility, and rate of such reactions. An understanding is gained of why and how chemical reactions happen.

Initial assessment - Can you recall these?

1. Draw a fully labelled reaction pathway diagram (energy profile diagram) for an endothermic reaction. Explain how this diagram shows that the reaction is endothermic.
2. Explain these terms to one another: crystal lattice, bond energy, enthalpy change, activation energy, standard conditions, standard enthalpy change of formation.
3. Explain the Hess law.
4. Write an equation to represent:
   a. The enthalpy change of formation of calcium carbonate
   b. The enthalpy change of combustion of ethane
   c. The enthalpy change of neutralisation of sulfuric acid by sodium hydroxide

If any of these feel shaky, review Chapter 6 before continuing.

Lattice energy

When oppositely charged gaseous ions come together to form a crystal lattice, energy is released — and quite a lot of it. This released energy is what makes ionic compounds so remarkably stable. We call this energy the **lattice energy**.

- Lattice energy: **the energy change when 1 mole of an ionic compound is formed from its gaseous ions under standard conditions.** Strictly speaking, the values given usually refer to the lattice enthalpy rather than the lattice energy, but the difference is usually not significant.
- The enthalpy change for lattice energy ΔH_{latt}, is **always negative**.
- Cannot be measured directly (calculated via Born-Haber cycle).

e.g., $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$, the enthalpy change of this reaction is called the lattice energy of NaCl.

Enthalpy Change of Atomisation

- The **enthalpy change when 1 mole of gaseous atoms is formed from its element under standard conditions**.
  - Equations can be written to show the standard enthalpy change of atomisation ($\Delta H_{at}^{\ominus}$) for elements
  - For example, sodium in its elemental form is a **solid**
  - The standard enthalpy change of atomisation for sodium is the energy required to form 1 mole of **gaseous** sodium atoms:
    $Na\ (s) \rightarrow Na\ (g)\ \Delta H_{at}^{\ominus} = +107\ kJ\ mol^{-1}$

The standard enthalpy change of atomisation of lithium relates to the equation:

$Li(s) \rightarrow Li(g)$ $\Delta H^{\ominus}_{at} = +161$ kJ mol^{-1}

The standard enthalpy change of atomisation of chlorine relates to the equation:

$\frac{1}{2} Cl_2(g) \rightarrow Cl(g)$ $\Delta H^{\ominus}_{at} = +122$ kJ mol^{-1}

- Values of $\Delta H^{\ominus}_{at}$ are **always positive** (endothermic). This is because energy must be supplied to break the bonds holding the atoms in the element together.
- Standard conditions in this syllabus are a temperature of 298 K and a pressure of 101 kPa

First Electron Affinity (EA)

When a non-metal atom gains an electron, it becomes a negatively charged ion. The energy released (or rarely, absorbed) in this process is the **first electron affinity**.

First electron affinity, EA_1: **The enthalpy change when 1 mole of electrons is added to 1 mole of gaseous atoms to form 1 mole of gaseous ions with a single negative charge under standard conditions**.

There is less experimental data about electron affinities compared with ionisation energies. For some atoms, the variation in the experimental data is considerable.

Generally, electron affinities for non-metal atoms get more negative (more exothermic) across a period with a maximum at Group 17, but the pattern is not always clear.

There is no clear pattern in electron affinities down many groups, apart from Groups 16 and 17.

There is a trend to less negative (less exothermic) electron affinities as you go down the group, apart from the first member in the group.

Electron affinity / kJ mol^{-1}			
C = −122.3	N = 0 (±19)	O = −141.1	F = −328.0
		S = −200.4	Cl = −348.8
		Se = −195	Br = −324.6
		Te = −190	I = −295.4

Table: Selected electron affinities.

The value of the **first electron affinity depends on the attraction between the added electron and the positively charged nucleus**. The stronger the attraction, the greater the amount of energy released. These factors influencing the value of the electron affinity for Group 16 and 17 elements are the same as those relating to first ionisation energy:

- The greater the nuclear charge, the greater the attractive force between the nucleus and the outer electrons. So, chlorine, with a greater nuclear charge than sulfur, will tend to attract an electron more readily. This means that more energy is released when a chlorine atom gains an electron.
- The further away the outer shell electrons are from the positive nuclear charge, the less the attractive force between the nucleus and the outer shell electrons is. Since the number of electron shells (and the atomic radius) increases down Groups 16 and 17, the electron affinity decreases going from chlorine to bromine to iodine.
- The greater the number of electron shells, the greater the power of inner shell electrons to shield the outer shell electrons from the nuclear charge. This also helps to decrease the electron affinity as you go from chlorine to iodine.

The electron affinity of a fluorine atom is lower than that of a chlorine atom because the atomic radius of the fluorine atom is very small. The high electron causes a greater repulsion between the electrons within the atom. This greatly reduces the attractive effect between the incoming electron and the nucleus.

Born-Haber cycles

We have seen how we can apply Hess's law in energy cycles to work out enthalpy changes.

> **Hess's Law Reminder**
>
> The total enthalpy change for a reaction is the same regardless of the route taken, provided initial and final conditions are identical.

A *Born–Haber cycle* is a particular type of energy cycle used to calculate lattice energy. In simple terms, it can be represented by the following Figure.

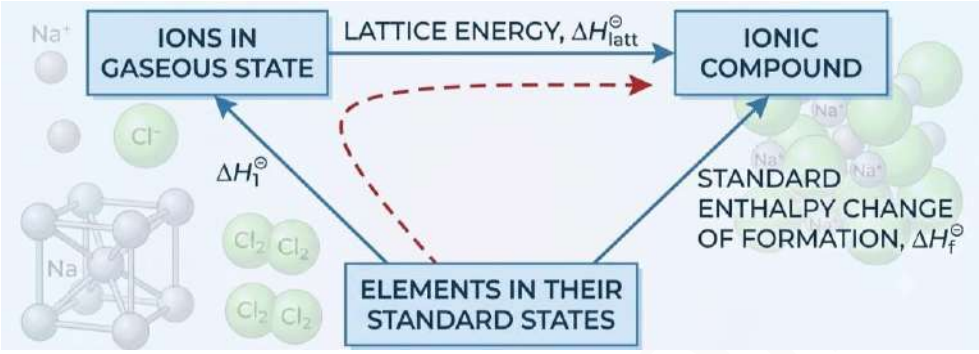

Figure: A simple energy cycle that can be used to calculate lattice energy. The dashed line shows the two-step route: using Hess's law, $\Delta H^{\ominus}_{1} + \Delta H^{\ominus}_{latt} = \Delta H^{\ominus}_{f}$

How to Draw Born-Haber Cycle of Ionic Compounds - Energetics

The EASIEST Method for Solving Born–Haber Cycles

The Five Steps for Building a Born–Haber Cycle

We break the overall formation of an ionic compound into five measurable steps:

Step	Process	Enthalpy term	Sign
1	Atomise the metal	ΔH°at (metal)	+
2	Ionise the metal (1st IE, 2nd IE if needed)	IE_1 (+ IE_2)	+
3	Atomise the non-metal	ΔH°at (non-metal)	+
4	Add electrons to non-metal atoms	EA_1 (+ EA_2)	− (usually)
5	Gaseous ions combine to form the lattice	ΔH°latt	−

To draw the cycle, you:

- Start by putting down the elements in their standard state on the left-hand side
- add the other enthalpy changes in the order of steps 1 to 4 shown in Figure
- complete the cycle by adding the enthalpy change of formation and lattice energy.

Note: the arrows going upwards represent an increase in energy ($\Delta H^{\ominus}$ is positive), and the arrows going downwards represent a decrease in energy ($\Delta H^{\ominus}$ is negative).

When constructing Born–Haber cycles, remember that the elements go near the bottom on the left-hand side and you atomise and ionise the metal first, then atomise and ionise the non-metal.

Some simple examples of Born-Haber cycles:

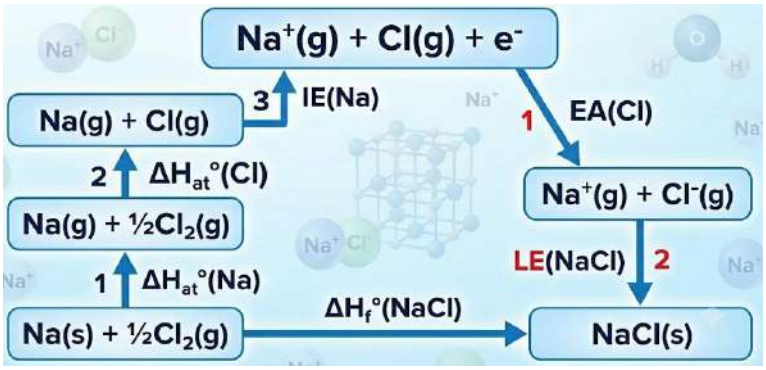

Figure: Born-Haber Cycle for NaCl

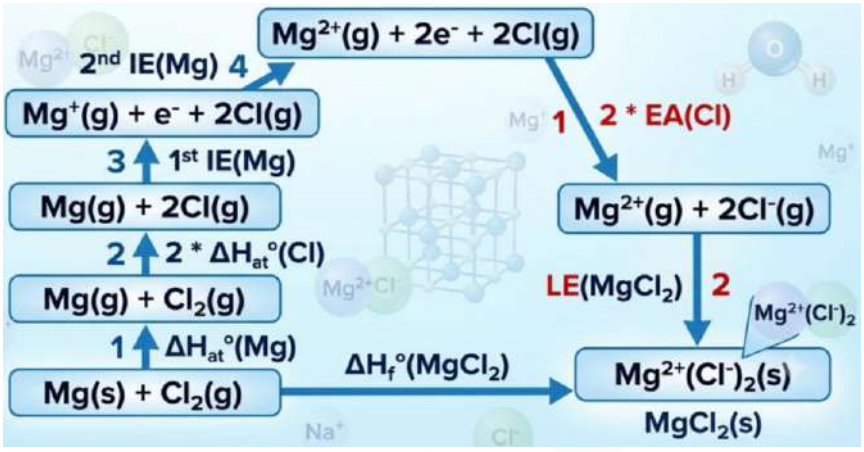

Figure: Born-Haber Cycle for $MgCl_2$

The EASIEST Method for Solving Born–Haber Cycles

Key Equation:

$\Delta H^{\ominus}_{latt} = \Delta H^{\ominus}_{f} - [\sum(\Delta H^{\ominus}_{at}) + IE + EA]$

⚠ Examiner Alert: Common Mistakes

- **Sign errors:** Always use brackets when substituting negative values.
- **State symbols:** They must be correct — (s), (g), (l), (aq). Getting these wrong loses marks.
- **Stoichiometry:** For $MgCl_2$, you need 2 × EA_1(Cl) and ΔH°at(Cl) must also be doubled.
- **Direction:** Arrows going UP = endothermic (+). Arrows going DOWN = exothermic (−).

Factors affecting the value of lattice energy

Lattice energies are determined by:

- the charges on the ions
- the inter-ionic distance (ion size)
- the type of lattice.

Factor 1: Ionic Charge	Factor 2: Ionic Radius
Greater ionic charge → stronger electrostatic attraction → **More exothermic lattice energy** e.g., Ca^{2+} has twice the charge of Na^+, so CaO has a far more negative lattice energy than NaCl.	Smaller ionic radius → ions pack closer together → stronger attraction → **More exothermic lattice energy** e.g., KF has a more exothermic lattice energy than CsF, because K^+ is smaller than Cs^+.

Comparison Example:

- **CsF vs KF:** Cs^+ is larger → CsF has **less exothermic** lattice energy.
- **CaO vs KCl:** Ca^{2+} & O^{2-} have higher charges + smaller size → CaO lattice energy is **much more exothermic**.

📌 Chapter Summary

- $\Delta H°_{latt}$ is always negative; it cannot be measured directly.
- $\Delta H°_{at}$ is always positive (endothermic); always refers to 1 mole of gaseous atoms.
- $\mathbf{EA_1}$ is usually negative (exothermic); F has a less negative EA than Cl due to electron repulsion in a small atom.
- Electron affinity becomes **less negative down Groups 16 and 17** due to increasing atomic radius and shielding.
- Born–Haber cycles apply **Hess's Law** to calculate lattice energy indirectly.
- Lattice energy is more negative with a **greater ionic charge** and **smaller ionic radius**.