

Lattice Enthalpy and Born–Haber Cycles

How strong is an ionic lattice, and how is lattice enthalpy found?

●●○ Intermediate

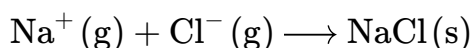
Thermochemistry & Thermodynamics

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Before you start: it helps to understand [Hess's Law and Enthalpies of Formation](#), [Ionic and Covalent Bonds](#) and [Periodic Trends](#).

What is it?

The **lattice enthalpy** of an ionic compound is the enthalpy change when **1 mol** of the solid forms from its **gaseous ions**, under standard conditions:



$$\Delta H_{\text{latt}}^\circ = -787.2 \text{ kJ/mol}$$

It is always **exothermic** (negative): oppositely charged ions attract, so energy is released as they come together. The **more negative** the lattice enthalpy, the **stronger** the ionic bonding.

Lattice enthalpy can't be measured directly: you can't collect a mole of separate gaseous ions and let them crash together. Instead it is calculated with a **Born–Haber cycle**, an application of Hess's law that builds the solid from its elements by two routes.

KEY IDEA

Lattice enthalpy measures the strength of an ionic lattice. It is found indirectly: the enthalpy of formation equals the sum of all the steps that turn the elements into gaseous ions and then into the solid, so the one unknown step can be calculated.

Why does it matter?

- **Properties of ionic solids.** A more negative lattice enthalpy goes with a higher melting point and greater hardness: MgO melts at about 2800 °C, NaCl at 801 °C.
- **Testing the ionic model.** Comparing a Born–Haber value with one calculated from a purely ionic model shows how ionic a compound really is.
- **Dissolving.** Whether a salt dissolves, and whether its solution warms or cools, depends on the balance between lattice enthalpy and the hydration of the ions (see [Electrolytes and Dissolving](#)).
- **Why formulas are what they are.** Born–Haber cycles explain why magnesium forms MgCl_2 , not MgCl , even though removing a second electron costs a lot of energy.

How does it work?

1. The steps

Every step is per mole of the compound, under standard conditions:

Step	Name	Sign
$\text{Na(s)} \longrightarrow \text{Na(g)}$	enthalpy of sublimation of the metal	+
$\frac{1}{2} \text{Cl}_2(\text{g}) \longrightarrow \text{Cl(g)}$	enthalpy of atomization of the non-metal (half the bond enthalpy)	+
$\text{Na(g)} \longrightarrow \text{Na}^+(\text{g}) + \text{e}^-$	first ionization energy (IE)	+
$\text{Cl(g)} + \text{e}^- \longrightarrow \text{Cl}^-(\text{g})$	first electron affinity (EA)	-
$\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \longrightarrow \text{NaCl(s)}$	lattice enthalpy	-
$\text{Na(s)} + \frac{1}{2} \text{Cl}_2(\text{g}) \longrightarrow \text{NaCl(s)}$	enthalpy of formation	usually -

- The metal step is **sublimation**: solid sodium is a metallic lattice of ions held by delocalized electrons, so energy is needed to turn it directly into free gaseous atoms.
- Enthalpies of atomization of the non-metal are always **per mole of atoms formed**, so for Cl it is **half** the Cl-Cl bond enthalpy ($242.6 \text{ kJ/mol} \div 2 = 121.3 \text{ kJ/mol}$).
- A first electron affinity is usually **exothermic**: the nucleus attracts the incoming electron. A **second** electron affinity ($\text{O}^- + \text{e}^- \longrightarrow \text{O}^{2-}$) is **endothermic**: the electron is pushed away by the negative ion.

2. Using the cycle

By Hess's law, the direct route (formation) equals the indirect route (all the other steps):

$$\begin{aligned}\Delta H_{\text{f}}^{\circ} &= \Delta H_{\text{sub}}(\text{metal}) \\ &+ \Delta H_{\text{atom}}(\text{non-metal}) \\ &+ \text{IE} + \text{EA} + \Delta H_{\text{latt}}^{\circ}\end{aligned}$$

Rearrange to find whichever value is unknown, usually the lattice enthalpy:

$$\begin{aligned}\Delta H_{\text{latt}}^{\circ} &= \Delta H_{\text{f}}^{\circ} \\ &- (\Delta H_{\text{sub}} + \Delta H_{\text{atom}} \\ &+ \text{IE} + \text{EA})\end{aligned}$$

Multiply each step by the number of times it happens: for MgCl_2 , Mg loses **two** electrons ($\text{IE}_1 + \text{IE}_2$), and **two** Cl atoms each form and each gain an electron.

3. What makes a lattice strong?

The attraction between two ions follows Coulomb's law, so the lattice enthalpy gets more negative with:

- **Higher charges** on the ions (the product of the charges).
- **Smaller ions** (the ions can get closer together).

Compound	Ions	$\Delta H_{\text{latt}}^\circ$ (kJ/mol, approx.)
NaF	Na^+, F^-	-923
NaCl	Na^+, Cl^-	-787
NaBr	Na^+, Br^-	-747
NaI	Na^+, I^-	-704
MgCl_2	$\text{Mg}^{2+}, 2 \text{Cl}^-$	-2522
MgO	$\text{Mg}^{2+}, \text{O}^{2-}$	about -3800

Down Group 17 the halide ion gets bigger, so the lattice enthalpy gets less negative. MgO, with 2+ and 2- ions that are both small, has a lattice enthalpy almost five times that of NaCl.

THINK OF IT LIKE THIS

Think of a Born-Haber cycle as working out the cost of one item on a shopping receipt when only the total is printed. You know the total (the enthalpy of formation) and the price of every other item (sublimation, atomization, ionization, electron affinity), so the missing price (the lattice enthalpy) is the total minus everything else.

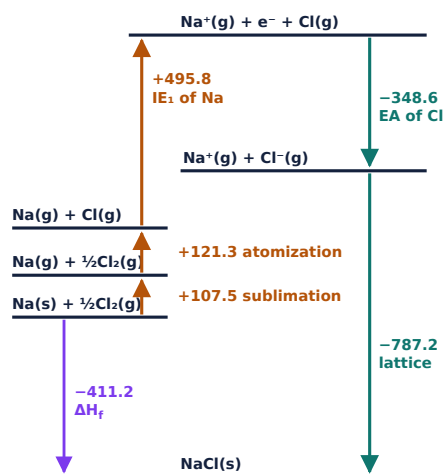
MORE PRECISELY

Lattice enthalpy can also be calculated from a model that treats the solid as perfect spherical ions (the Born-Landé equation). For the alkali metal halides, the model and the Born-Haber values agree within a few percent, so these compounds are close to purely ionic. For silver halides such as AgI, the Born-Haber value is noticeably **more negative** than the model predicts: the large, polarizable iodide ion shares some electron density with Ag^+ , so the bonding has partial **covalent character**. The cycle is named after Max Born and Fritz Haber, who devised it in 1919.

Visualise it

Born-Haber cycle for sodium chloride

Enthalpy levels drawn to scale (kJ/mol).



$$\begin{aligned} \text{Lattice enthalpy} &= -411.2 - (107.5 + 121.3 + 495.8 - 348.6) \\ &= -411.2 - 376.0 = -787.2 \text{ kJ/mol} \end{aligned}$$

Up arrows are endothermic steps, down arrows exothermic. The lattice enthalpy is the biggest step of all.

Worked example

WORKED EXAMPLE: The lattice enthalpy of sodium chloride

Question: Use the data to calculate the lattice enthalpy of NaCl.

$$\Delta H_f^\circ(\text{NaCl}) = -411.2 \text{ kJ/mol} \cdot \text{sublimation of Na} = +107.5 \text{ kJ/mol} \cdot \text{atomization of } \frac{1}{2}\text{Cl}_2 = +121.3 \text{ kJ/mol} \cdot \text{IE}_1(\text{Na}) = +495.8 \text{ kJ/mol} \cdot \text{EA}_1(\text{Cl}) = -348.6 \text{ kJ/mol}$$

Step 1 Add the steps that turn the elements into gaseous ions:

$$\begin{aligned} &107.5 \text{ kJ/mol} \\ &+ 121.3 \text{ kJ/mol} \\ &+ 495.8 \text{ kJ/mol} \\ &- 348.6 \text{ kJ/mol} \\ &= +376.0 \text{ kJ/mol} \end{aligned}$$

Step 2 Subtract this from the enthalpy of formation:

$$\begin{aligned} &\Delta H_{\text{latt}}^\circ \\ &= -411.2 \text{ kJ/mol} \\ &- 376.0 \text{ kJ/mol} \\ &= -787.2 \text{ kJ/mol} \end{aligned}$$

 WORKED EXAMPLE: A 2+ ion: magnesium chloride

Question: Calculate the lattice enthalpy of MgCl_2 .

$$\Delta H_f^\circ(\text{MgCl}_2) = -641.3 \text{ kJ/mol} \cdot \text{sublimation of Mg} = +147.1 \text{ kJ/mol} \cdot \text{IE}_1(\text{Mg}) = +737.7 \text{ kJ/mol} \cdot \text{IE}_2(\text{Mg}) = +1450.7 \text{ kJ/mol} \cdot \text{atomization of } \frac{1}{2}\text{Cl}_2 = +121.3 \text{ kJ/mol} \cdot \text{EA}_1(\text{Cl}) = -348.6 \text{ kJ/mol}$$

Step 1 Count each step: one Mg atom loses **two** electrons; **two** Cl atoms form, and each gains one electron.

Step 2 The two chlorine steps:

$$2 \times (+121.3 \text{ kJ/mol})$$

$$= +242.6 \text{ kJ/mol}$$

$$2 \times (-348.6 \text{ kJ/mol})$$

$$= -697.2 \text{ kJ/mol}$$

Step 3 All the steps to the gaseous ions:

$$147.1 + 737.7 + 1450.7$$

$$+ 242.6 - 697.2 \text{ (kJ/mol)}$$

$$= +1880.9 \text{ kJ/mol}$$

Step 4 Lattice enthalpy:

$$\Delta H_{\text{latt}}^\circ$$

$$= -641.3 \text{ kJ/mol}$$

$$- 1880.9 \text{ kJ/mol}$$

$$= -2522.2 \text{ kJ/mol}$$

Removing the second electron from Mg costs 1450.7 kJ/mol, but the lattice with Mg^{2+} ions is so much stronger that MgCl_2 is still very stable.

Common mistake

 COMMON MISTAKE: Mixing up the sign conventions

This lesson defines lattice enthalpy as **forming** the lattice from gaseous ions (negative). Some books define it as **breaking** the lattice into gaseous ions (positive, the “lattice dissociation enthalpy”). The size is the same; check which definition a question uses before writing the sign.

 COMMON MISTAKE: Using the whole bond enthalpy

Atomization makes **one mole of atoms**. For NaCl you need only one Cl atom, so use **half** the Cl-Cl bond enthalpy (121.3 kJ/mol, not 242.6 kJ/mol). For MgCl₂ you need two Cl atoms: 2 × 121.3 kJ/mol, which equals the full bond enthalpy.

 COMMON MISTAKE: Forgetting the second ionization energy

To make Mg²⁺ you need IE₁ **and** IE₂. To make O²⁻ you need the first electron affinity (exothermic) **and** the second (endothermic).

 NOTATION NOTE

- $\Delta H_{\text{latt}}^\circ$ is the standard lattice enthalpy; $\Delta H_{\text{f}}^\circ$ the standard enthalpy of formation; ΔH_{sub} the enthalpy of sublimation (of the metal); ΔH_{atom} the enthalpy of atomization (of the non-metal).
- IE and EA values are per mole of atoms or ions, in kJ/mol.
- In the figure, up arrows are endothermic (+) and down arrows are exothermic (-).

Remember this

 REMEMBER THIS

- Lattice enthalpy: 1 mol of ionic solid from its gaseous ions; exothermic; more negative = stronger lattice.
- Born-Haber cycle: $\Delta H_{\text{f}}^\circ = \text{sublimation} + \text{atomization} + \text{IEs} + \text{EAs} + \Delta H_{\text{latt}}^\circ$ (Hess's law).
- Count every step: half the bond enthalpy per non-metal atom; IE₁ + IE₂ for a 2+ ion.
- Higher ion charges and smaller ions give more negative lattice enthalpies.

References

1. Brown, T. L.; LeMay, H. E., Jr.; Bursten, B. E.; Murphy, C. J.; Woodward, P. M.; Stoltzfus, M. W. Chemistry: The Central Science, 15th ed.; Pearson, 2022.

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