

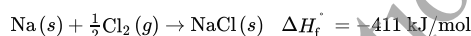
9.11: Lattice Energies for Ionic Compounds

As we discussed in [Section 4.5](#), the formation of an ionic compound from its constituent elements is usually quite exothermic because of lattice energy—the energy associated with the formation of a crystalline lattice of alternating cations and anions from the gaseous ions (see [Figure 4.5](#)). In this section of the chapter we examine how to calculate lattice energy for an ionic compound and two trends in lattice energy.

Calculating Lattice Energy: The Born–Haber Cycle

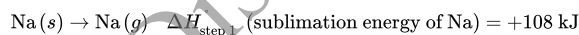
The **Born–Haber cycle** is a hypothetical series of steps that represents the formation of an ionic compound from its constituent elements. The steps are chosen so that the change in enthalpy of each step is known except for that of the last step, which is the lattice energy. The change in enthalpy for the overall process is also known. Using Hess's law (see [Section 9.8](#)), we can determine the enthalpy change for the unknown last step, the lattice energy.

Consider the formation of NaCl from its constituent elements in their standard states. The enthalpy change for the overall reaction is the standard enthalpy of formation of NaCl(s).



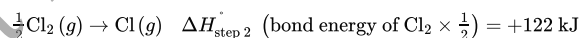
Consider the following set of steps—the Born–Haber cycle—from which NaCl(s) can also be made from Na(s) and Cl₂(g):

- Step 1 is the formation of gaseous sodium from solid sodium.

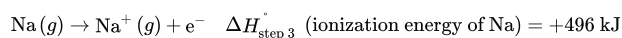


The sublimation energy is the energy required to convert 1 mol of substance from a solid to gas.

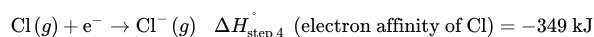
- Step 2 is the formation of a chlorine atom from a chlorine molecule.



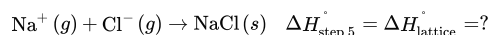
- Step 3 is the ionization of gaseous sodium. The enthalpy change for this step is the ionization energy of sodium.



- Step 4 is the addition of an electron to gaseous chlorine. The enthalpy change for this step is the electron affinity of chlorine.



- Step 5 is the formation of the crystalline solid from the gaseous ions. The enthalpy change for this step is the lattice energy, the unknown quantity.

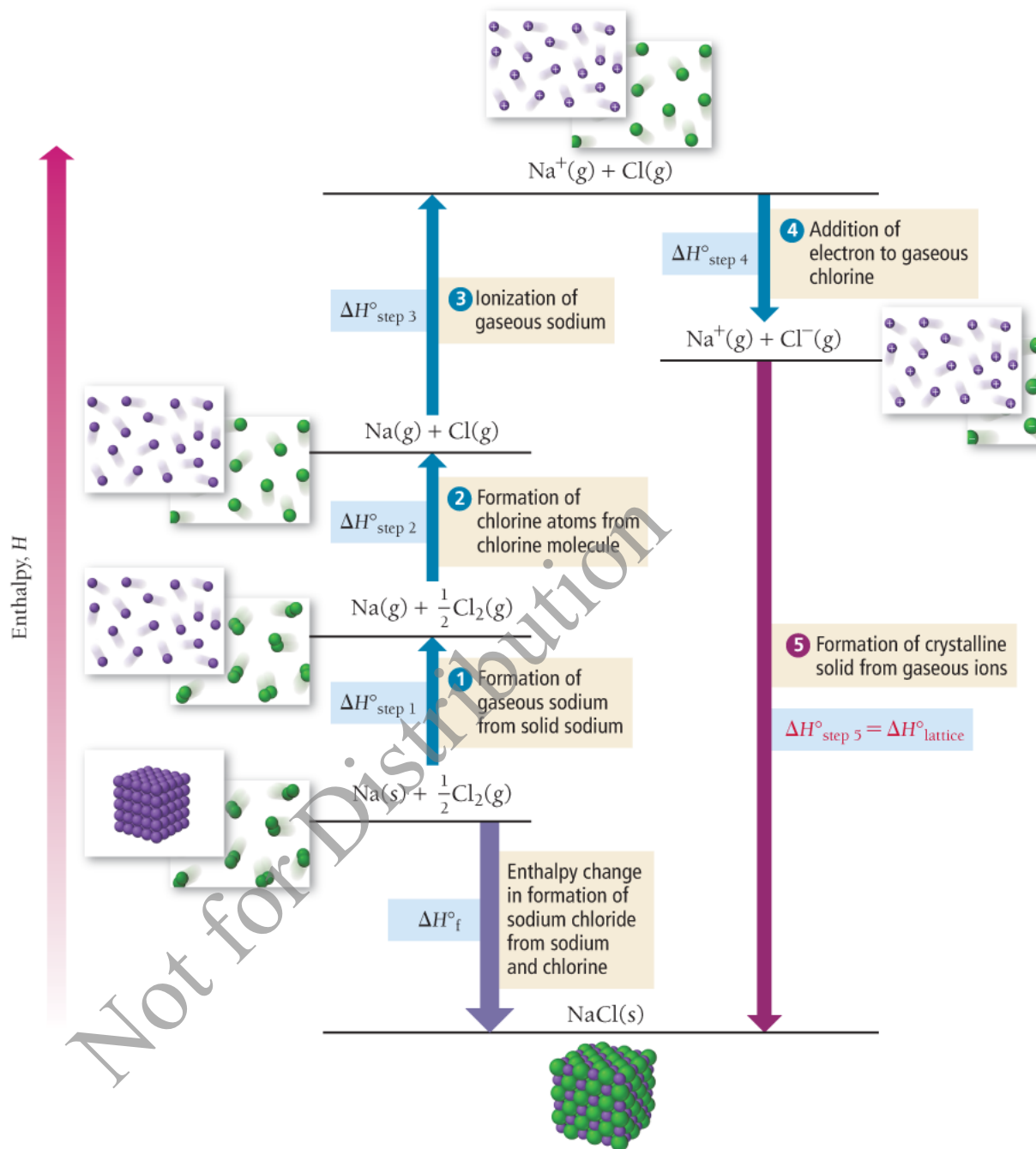


[Figure 9.12](#) illustrates the entire Born–Haber cycle for NaCl.

Figure 9.12 Born–Haber Cycle for Sodium Chloride

The sum of the steps is the formation of NaCl from elemental Na and Cl. The enthalpy change of the last step (5) is the lattice energy.

Born–Haber Cycle for Production of NaCl from Na(s) and Cl₂(g)



Because the overall reaction obtained by summing the steps in the Born–Haber cycle is equivalent to the formation of NaCl from its constituent elements, we use Hess's law to set the overall enthalpy of formation for NaCl(s) equal to the sum of the steps in the Born–Haber cycle:

$$\Delta H^\circ_f = \Delta H^\circ_{\text{step 1}} + \Delta H^\circ_{\text{step 2}} + \Delta H^\circ_{\text{step 3}} + \Delta H^\circ_{\text{step 4}} + \Delta H^\circ_{\text{step 5}}$$

Lattice energy
↓

We then solve this equation for $\Delta H^\circ_{\text{step 5}}$, which is $\Delta H^\circ_{\text{lattice}}$, and substitute the appropriate values to calculate the lattice energy:

$$\begin{aligned}
 \Delta H_{\text{lattice}}^{\circ} = \Delta H_{\text{step 5}}^{\circ} &= \Delta H_{\text{f}}^{\circ} - (\Delta H_{\text{step 1}}^{\circ} + \Delta H_{\text{step 2}}^{\circ} + \Delta H_{\text{step 3}}^{\circ} + \Delta H_{\text{step 4}}^{\circ}) \\
 &= -411 \text{ kJ} - (+108 \text{ kJ} + 122 \text{ kJ} + 496 \text{ kJ} - 349 \text{ kJ}) \\
 &= -788 \text{ kJ}
 \end{aligned}$$

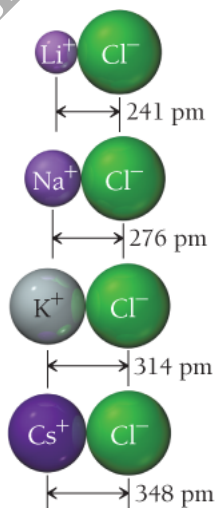
The value of the lattice energy is a large negative number. The formation of the crystalline NaCl lattice from sodium cations and chloride anions is highly exothermic and more than compensates for the endothermicity of the electron transfer process. In other words, the formation of ionic compounds is not exothermic because sodium “wants” to lose electrons and chlorine “wants” to gain them; rather, it is exothermic because of the large amount of heat released when sodium and chlorine ions coalesce to form a crystalline lattice.

Trends in Lattice Energies: Ion Size

Consider the lattice energies of the following alkali metal chlorides:

Metal Chloride	Lattice Energy (kJ/mol)
LiCl	−834
NaCl	−788
KCl	−701
CsCl	−657

Why does the magnitude of the lattice energy decrease as we move down the column? We know from the periodic trends discussed in [Chapter 3](#) that the ionic radius increases as we move down a column in the periodic table (see [Section 3.7](#)). We also know, from the discussion of Coulomb’s law in [Section 3.3](#), that the potential energy of oppositely charged ions becomes less negative (or more positive) as the distance between the ions increases. As the size of the alkali metal ions increases down the column, so does the distance between the metal cations and the chloride anions. The magnitude of the lattice energy of the chlorides decreases accordingly, making the formation of the chlorides less exothermic. In other words, *as the ionic radii increase as we move down the column, the ions cannot get as close to each other and therefore do not release as much energy when the lattice forms.*

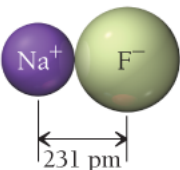
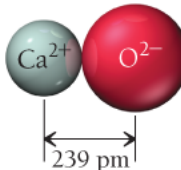


Bond lengths of the group 1A metal chlorides.

Trends in Lattice Energies: Ion Charge

Consider the lattice energies of the following two compounds:

Compound	Lattice Energy (kJ/mol)
NaF	−910
CaO	−3414

Why is the magnitude of the lattice energy of CaO so much greater than the lattice energy of NaF? Na^+ has a radius of 95 pm and F^- has a radius of 136 pm, resulting in a distance between ions of 231 pm. Ca^{2+} has a radius of 99 pm and O^{2-} has a radius of 140 pm, resulting in a distance between ions of 239 pm. Even though the separation between calcium and oxygen is slightly greater (which would tend to lower the lattice energy), the lattice energy for CaO is almost four times *greater*. The explanation lies in the charges of the ions. Recall from Coulomb's law that the magnitude of the potential energy of two interacting charges depends not only on the distance between the charges, but also on the product of the charges:

$$E = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r}$$

For NaF, E is proportional to $(1+)(1-) = 1-$, while for CaO, E is proportional to $(2+)(2-) = 4-$, so the relative stabilization for CaO relative to NaF is roughly four times greater, as observed in the lattice energy.

Summarizing Trends in Lattice Energies:

- Lattice energies become less exothermic (less negative) with increasing ionic radius.
- Lattice energies become more exothermic (more negative) with increasing magnitude of ionic charge.

Example 9.14 Predicting Relative Lattice Energies

Arrange these ionic compounds in order of increasing *magnitude* of lattice energy: CaO, KBr, KCl, SrO.

SOLUTION

KBr and KCl should have lattice energies of smaller magnitude than CaO and SrO because of their lower ionic charges ($1+$, $1-$ compared to $2+$, $2-$). When you compare KBr and KCl, you expect KBr to have a lattice energy of lower magnitude due to the larger ionic radius of the bromide ion relative to the chloride ion. Between CaO and SrO, you expect SrO to have a lattice energy of lower magnitude due to the larger ionic radius of the strontium ion relative to the calcium ion.

Order of increasing *magnitude* of lattice energy:

$\text{KBr} < \text{KCl} < \text{SrO} < \text{CaO}$

Actual lattice energy values:

Compound	Lattice Energy (kJ/mol)
KBr	−671
KCl	−701
SrO	−3217
CaO	−3414

FOR PRACTICE 9.14 Arrange these ionic compounds in order of increasing magnitude of lattice energy: LiBr, KI, and CaO.

FOR MORE PRACTICE 9.14 Which compound has a higher magnitude lattice energy: NaCl or MgCl_2 ?

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