

## 21.5: Lattice Energies of Crystals

### Learning Objectives

- To understand the relationship between the lattice energy and physical properties of an ionic compound.
- To use the Born–Haber cycle to calculate lattice energies.

Recall that the reaction of a metal with a nonmetal usually produces an ionic compound; that is, electrons are transferred from the metal (the *reductant*) to the nonmetal (the *oxidant*). Ionic compounds are usually rigid, brittle, crystalline substances with flat surfaces that intersect at characteristic angles. They are not easily deformed, and they melt at relatively high temperatures. NaCl, for example, melts at 801°C. These properties result from the regular arrangement of the ions in the crystalline lattice and from the strong electrostatic attractive forces between ions with opposite charges.

While formation of ion pairs from isolated ions releases large amounts of energy, even more energy is released when these ion pairs condense to form an ordered three-dimensional array. In such an arrangement each cation in the lattice is surrounded by more than one anion (typically four, six, or eight) and vice versa, so it is more stable than a system consisting of separate pairs of ions, in which there is only one cation–anion interaction in each pair. Note that  $r_0$  may differ between the gas-phase dimer and the lattice.

An ionic lattice is more stable than a system consisting of separate ion pairs.

### Calculating (Ionic) Lattice Energies

The lattice energy of nearly any ionic solid can be calculated rather accurately using a modified form of **Coulomb's law**:

$$U = -\frac{k'Q_1Q_2}{r_0} \quad (21.5.1)$$

where  $U$ , which is always a positive number, represents the amount of energy required to dissociate 1 mol of an ionic solid into the gaseous ions. The proportionality constant in Equation 21.5.1 is expanded below, but it is worthwhile to discuss its general features first.

If we assume that  $\Delta V = 0$ , then the lattice energy,  $U$ , is approximately equal to the change in enthalpy,  $\Delta H$ :



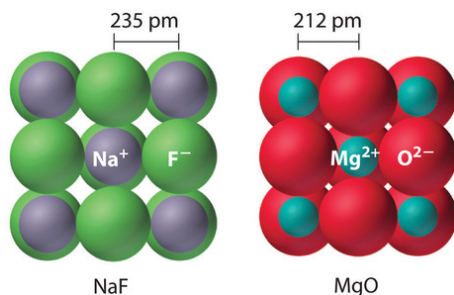
As before,  $Q_1$  and  $Q_2$  are the charges on the ions and  $r_0$  is the internuclear distance. We see from Equation 21.5.1 that lattice energy is directly related to the product of the ion charges and inversely related to the internuclear distance. The value of the constant  $k'$  depends on the specific arrangement of ions in the solid lattice and their valence electron configurations. Representative values for calculated lattice energies, which range from about 600 to 10,000 kJ/mol, are listed in Table 21.5.1. Energies of this magnitude can be decisive in determining the chemistry of the elements.

Table 21.5.1: Representative Calculated Lattice Energies

Substance	U (kJ/mol)
NaI	682
CaI <sub>2</sub>	1971
MgI <sub>2</sub>	2293
NaOH	887
Na <sub>2</sub> O	2481
NaNO <sub>3</sub>	755
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	10,602
CaCO <sub>3</sub>	2804

Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

Because the lattice energy depends on the *product* of the charges of the ions, a salt having a metal cation with a +2 charge ( $M^{2+}$ ) and a nonmetal anion with a -2 charge ( $X^{2-}$ ) will have a lattice energy four times greater than one with  $M^+$  and  $X^-$ , assuming the ions are of comparable size (and have similar internuclear distances). For example, the calculated value of  $U$  for NaF is 910 kJ/mol, whereas  $U$  for MgO (containing  $Mg^{2+}$  and  $O^{2-}$  ions) is 3795 kJ/mol.



Because lattice energy is *inversely* related to the internuclear distance, it is also inversely proportional to the size of the ions. This effect is illustrated in Figure 21.5.1, which shows that lattice energy decreases for the series LiX, NaX, and KX as the radius of  $X^-$  increases. Because  $r_0$  in Equation 21.5.1 is the sum of the ionic radii of the cation and the anion ( $r_0 = r^+ + r^-$ ),  $r_0$  increases as the cation becomes larger in the series, so the magnitude of  $U$  decreases. A similar effect is seen when the anion becomes larger in a series of compounds with the same cation.

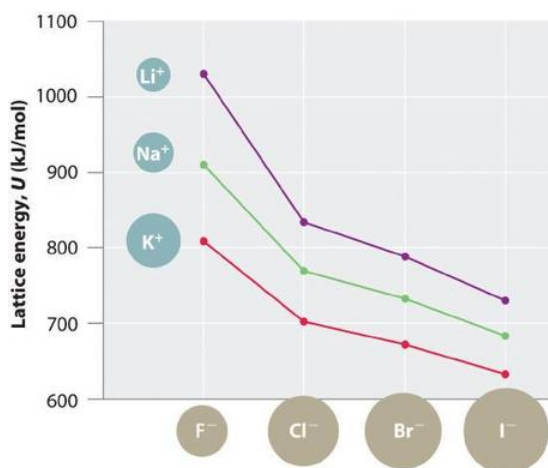


Figure 21.5.1: A Plot of Lattice Energy versus the Identity of the Halide for the Lithium, Sodium, and Potassium Halides

Because the ionic radii of the cations decrease in the order  $K^+ > Na^+ > Li^+$  for a given halide ion, the lattice energy decreases smoothly from  $Li^+$  to  $K^+$ . Conversely, for a given alkali metal ion, the fluoride salt always has the highest lattice energy and the iodide salt the lowest.

*Lattice energies are highest for substances with small, highly charged ions.*

#### ✓ Example 21.5.1

Arrange GaP, BaS, CaO, and RbCl in order of increasing lattice energy.

**Given:** four compounds

**Asked for:** order of increasing lattice energy

**Strategy:**

Using Equation 21.5.1, predict the order of the lattice energies based on the charges on the ions. For compounds with ions with the same charge, use the relative sizes of the ions to make this prediction.

**Solution:**

The compound GaP, which is used in semiconductor electronics, contains  $Ga^{3+}$  and  $P^{3-}$  ions; the compound BaS contains  $Ba^{2+}$  and  $S^{2-}$  ions; the compound CaO contains  $Ca^{2+}$  and  $O^{2-}$  ions; and the compound RbCl has  $Rb^+$  and  $Cl^-$  ions. We know from

Equation 21.5.1 that lattice energy is directly proportional to the product of the ionic charges. Consequently, we expect RbCl, with a  $(-1)(+1)$  term in the numerator, to have the lowest lattice energy, and GaP, with a  $(+3)(-3)$  term, the highest. To decide whether BaS or CaO has the greater lattice energy, we need to consider the relative sizes of the ions because both compounds contain a  $+2$  metal ion and a  $-2$  chalcogenide ion. Because  $\text{Ba}^{2+}$  lies below  $\text{Ca}^{2+}$  in the periodic table,  $\text{Ba}^{2+}$  is larger than  $\text{Ca}^{2+}$ . Similarly,  $\text{S}^{2-}$  is larger than  $\text{O}^{2-}$ . Because the cation and the anion in BaS are both larger than the corresponding ions in CaO, the internuclear distance is greater in BaS and its lattice energy will be lower than that of CaO. The order of increasing lattice energy is  $\text{RbCl} < \text{BaS} < \text{CaO} < \text{GaP}$ .

### ? Exercise 21.5.1

Arrange InAs, KBr, LiCl, SrSe, and ZnS in order of decreasing lattice energy.

#### Answer

$\text{InAs} > \text{ZnS} > \text{SrSe} > \text{LiCl} > \text{KBr}$

## Lattice Energy also Depends on Crystal Structure

There are many other factors to be considered such as covalent character and electron-electron interactions in ionic solids. But for simplicity, let us consider the ionic solids as a collection of positive and negative ions. In this simple view, appropriate number of cations and anions come together to form a solid. The positive ions experience both attraction and repulsion from ions of opposite charge and ions of the same charge.

As an example, let us consider the the NaCl crystal. In the following discussion, assume  $r$  be the distance between  $\text{Na}^+$  and  $\text{Cl}^-$  ions. The nearest neighbors of  $\text{Na}^+$  are 6  $\text{Cl}^-$  ions at a distance  $1r$ , 12  $\text{Na}^+$  ions at a distance  $2r$ , 8  $\text{Cl}^-$  at  $3r$ , 6  $\text{Na}^+$  at  $4r$ , 24  $\text{Na}^+$  at  $5r$ , and so on. Thus, the electrostatic potential of a single ion in a crystal by approximating the ions by point charges of the surrounding ions:

$$E_{\text{ion-lattice}} = \frac{Z^2 e^2}{4\pi\epsilon_0 r} M \quad (21.5.3)$$

The **Madelung constant**  $M$  - named after Erwin Madelung - is a geometrical factor that depends on the arrangement of ions in the solid. For example,  $M$  for NaCl is a poorly converging series of interaction energies:

$$M = \frac{6}{1} - \frac{12}{2} + \frac{8}{3} - \frac{6}{4} + \frac{24}{5} \dots \quad (21.5.4)$$

with

- $Z$  is the number of charges of the ions, (e.g., 1 for NaCl),
- $e$  is the charge of an electron ( $1.6022 \times 10^{-19} \text{ C}$ ),
- $4\pi\epsilon_0$  is  $1.11265 \times 10^{-10} \text{ C}^2/(\text{J m})$ .

The Madelung constant depends on the structure type and Equation 21.5.4 is applicable only for the sodium chloride (e.g., rock salt) lattice geometry. Other values for other structural types are given in Table 21.5.2

Table 21.5.2: Madelung Constants. A is the number of anions coordinated to cation and C is the numbers of cations coordinated to anion.

Compound	Crystal Lattice	M	A : C	Type
NaCl	NaCl	1.74756	6 : 6	Rock salt
CsCl	CsCl	1.76267	6 : 6	CsCl type
$\text{CaF}_2$	Cubic	2.51939	8 : 4	Fluorite
$\text{CdCl}_2$	Hexagonal	2.244		
$\text{MgF}_2$	Tetragonal	2.381		
ZnS (wurtzite)	Hexagonal	1.64132		
$\text{TiO}_2$ (rutile)	Tetragonal	2.408	6 : 3	Rutile

Compound	Crystal Lattice	M	A : C	Type
bSiO <sub>2</sub>	Hexagonal	2.2197		
Al <sub>2</sub> O <sub>3</sub>	Rhombohedral	4.1719	6 : 4	Corundum

There are other factors to consider for the evaluation of lattice energy and the treatment by Max Born and Alfred Landé led to the formula for the evaluation of lattice energy for a mole of **crystalline solid**. The Born–Landé equation (Equation 21.5.5) is a means of calculating the lattice energy of a crystalline ionic compound and derived from the electrostatic potential of the ionic lattice and a repulsive potential energy term

$$U = \frac{N_A M z^+ z^- e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right) \quad (21.5.5)$$

where

- $N_A$  is Avogadro constant
- $M$  is the Madelung constant for the lattice
- $z^+$  is the charge number of cation
- $z^-$  is the charge number of anion
- $e$  is elementary charge ( $1.6022 \times 10^{-19} C$ )
- $\epsilon_0$  is the permittivity of free space ( $8.854 \times 10^{-12} C^2/m$ )
- $r_0$  is the distance to closest ion
- $n$  is the **Born exponent** that is typically between 5 and 12 and is determined experimentally.  $n$  is a number related to the electronic configurations of the ions involved (Table 21.5.3).

Table 21.5.3:  $n$  values for select solids

Atom/Molecule	$n$
He	5
Ne	7
Ar	9
Kr	10
Xe	12
LiF	5.9
LiCl	8.0
LiBr	8.7
NaCl	9.1
NaBr	9.5

### ✓ Example 21.5.2

Estimate the lattice energy for NaCl.

#### Solution

Using the values giving in the discussion above, the estimation is given by Equation 21.5.5

$$\begin{aligned}
 U_{NaCl} &= \frac{(6.022 \times 10^{23} / mol)(1.74756)(1)(1)(1.6022 \times 10^{-19} C)^2}{4\pi (8.854 \times 10^{-12} C^2/m)(282 \times 10^{-12} m)} \left(1 - \frac{1}{9.1}\right) \\
 &= -756 \text{ kJ/mol}
 \end{aligned}$$

#### Discussion

Much more should be considered in order to evaluate the lattice energy accurately, but the above calculation leads you to a good start. When methods to evaluate the energy of crystallization or lattice energy lead to reliable values, these values can be used in the Born-Hable cycle to evaluate other chemical properties, for example the electron affinity, which is really difficult to determine directly by experiment.

## The Relationship between Lattice Energies and Physical Properties

The magnitude of the forces that hold an ionic substance together has a dramatic effect on many of its properties. The melting point, for example, is the temperature at which the individual ions have enough kinetic energy to overcome the attractive forces that hold them in place. At the melting point, the ions can move freely, and the substance becomes a liquid. Thus melting points vary with lattice energies for ionic substances that have similar structures. The melting points of the sodium halides (Figure 21.5.2), for example, decrease smoothly from NaF to NaI, following the same trend as seen for their lattice energies (Figure 21.5.1). Similarly, the melting point of MgO is 2825°C, compared with 996°C for NaF, reflecting the higher lattice energies associated with higher charges on the ions. In fact, because of its high melting point, MgO is used as an electrical insulator in heating elements for electric stoves.

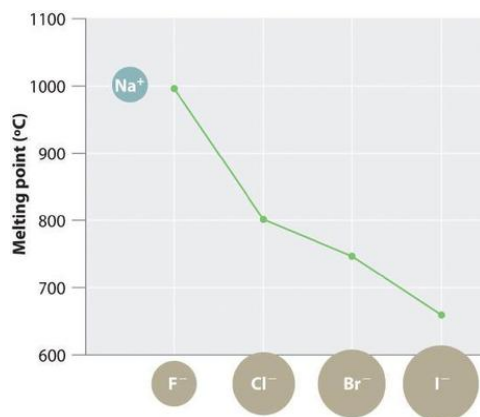


Figure 21.5.2: A Plot of Melting Point versus the Identity of the Halide for the Sodium Halides. The melting points follow the same trend as the magnitude of the lattice energies in Figure 21.5.1.

The hardness of ionic materials—that is, their resistance to scratching or abrasion—is also related to their lattice energies. Hardness is directly related to how tightly the ions are held together electrostatically, which, as we saw, is also reflected in the lattice energy. As an example, MgO is harder than NaF, which is consistent with its higher lattice energy.

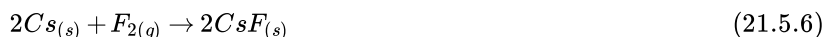
In addition to determining melting point and hardness, lattice energies affect the solubilities of ionic substances in water. In general, *the higher the lattice energy, the less soluble a compound is in water*. For example, the solubility of NaF in water at 25°C is 4.13 g/100 mL, but under the same conditions, the solubility of MgO is only 0.65 mg/100 mL, meaning that it is essentially insoluble.

*High lattice energies lead to hard, insoluble compounds with high melting points.*

## The Born–Haber Cycle

In principle, lattice energies could be measured by combining gaseous cations and anions to form an ionic solid and then measuring the heat evolved. Unfortunately, measurable quantities of gaseous ions have never been obtained under conditions where heat flow can be measured. Instead, lattice energies are found using the experimentally determined enthalpy changes for other chemical processes, Hess's law, and a *thermochemical cycle* called the [Born–Haber cycle](#). Developed by Max Born and Fritz Haber in 1919, the Born–Haber cycle describes a process in which an ionic solid is conceptually formed from its component elements in a stepwise manner.

Let's use the Born–Haber cycle to determine the lattice energy of CsF(s). CsF is a nearly ideal ionic compound because Cs is the least electronegative element that is not radioactive and F is the most electronegative element. To construct a thermochemical cycle for the formation of CsF, we need to know its enthalpy of formation,  $\Delta H_f$ , which is defined by the following chemical reaction:



Because enthalpy is a state function, the overall  $\Delta H$  for a series of reactions is the sum of the values of  $\Delta H$  for the individual reactions. We can therefore use a thermochemical cycle to determine the enthalpy change that accompanies the formation of solid

CsF from the parent *elements* (not ions). The Born–Haber cycle for calculating the lattice energy of cesium fluoride is shown in Figure 21.5.1. This particular cycle consists of six reactions, Equation 21.5.6 plus the following five reactions:

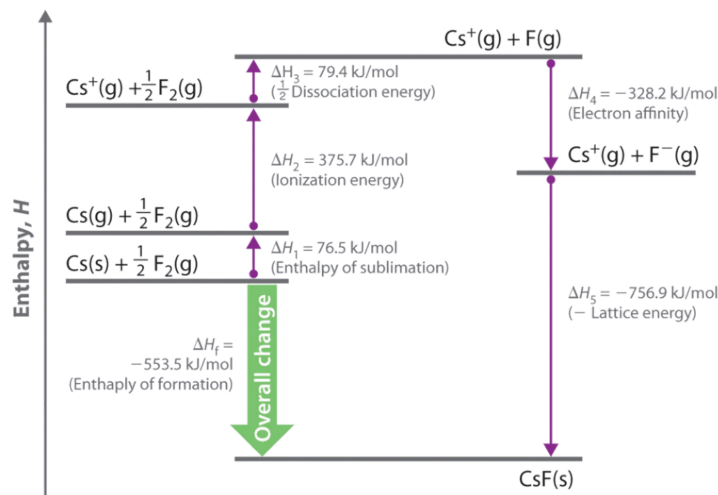
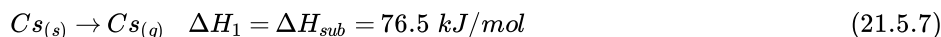


Figure 21.5.3: The Born–Haber Cycle Illustrating the Enthalpy Changes Involved in the Formation of Solid Cesium Fluoride from Its Elements

### Reaction 1



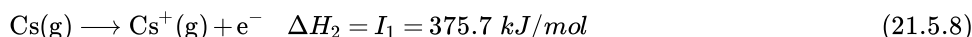
This equation describes the sublimation of elemental cesium, the conversion of the solid directly to a gas. The accompanying enthalpy change is called the enthalpy of sublimation ( $\Delta H_{\text{sub}}$ ) (Table 21.5.4) and is *always* positive because energy is required to sublime a solid.

Table 21.5.4: Selected Enthalpies of Sublimation at 298 K

Substance	$\Delta H_{\text{sub}}$ (kJ/mol)
Li	159.3
Na	107.5
K	89.0
Rb	80.9
Cs	76.5
Be	324.0
Mg	147.1
Ca	177.8
Sr	164.4
Ba	180.0

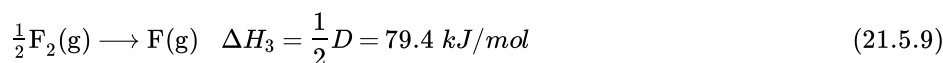
Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

### Reaction 2:



This equation describes the ionization of cesium, so the enthalpy change is the first ionization energy of cesium. Recall that energy is needed to ionize any neutral atom. Hence, regardless of the compound, the enthalpy change for this portion of the Born–Haber cycle is always positive.

### Reaction 3:



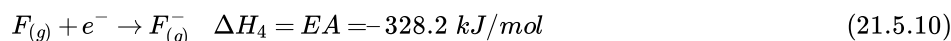
This equation describes the dissociation of fluorine molecules into fluorine atoms, where  $D$  is the energy required for dissociation to occur (Table 21.5.5). We need to dissociate only  $\frac{1}{2}$  mol of  $\text{F}_{2(\text{g})}$  molecules to obtain 1 mol of  $\text{F}_{(\text{g})}$  atoms. The  $\Delta H$  for this reaction, too, is **always** positive because energy is required to dissociate any stable diatomic molecule into the component atoms.

Table 21.5.5: Selected Bond Dissociation Enthalpies at 298 K

Substance	$D$ (kJ/mol)
$\text{H}_2(\text{g})$	436.0
$\text{N}_2(\text{g})$	945.3
$\text{O}_2(\text{g})$	498.4
$\text{F}_2(\text{g})$	158.8
$\text{Cl}_2(\text{g})$	242.6
$\text{Br}_2(\text{g})$	192.8
$\text{I}_2(\text{g})$	151.1

Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

#### Reaction 4:



This equation describes the formation of a gaseous fluoride ion from a fluorine atom; the enthalpy change is the electron affinity of fluorine. Recall that **electron affinities** can be positive, negative, or zero. In this case,  $\Delta H$  is negative because of the highly negative electron affinity of fluorine.

#### Reaction 5:



This equation describes the formation of the ionic solid from the gaseous ions. Because Reaction 5 is the reverse of the equation used to define lattice energy and  $U$  is defined to be a *positive* number,  $\Delta H_5$  is always *negative*, as it should be in a step that forms bonds.

If the enthalpy of formation of  $\text{CsF}$  from the elements is known ( $\Delta H_f = -553.5 \text{ kJ/mol}$  at 298 K), then the thermochemical cycle shown in Figure 21.5.3 has only one unknown, the quantity  $\Delta H_5 = -U$ . From Hess's law, we can write

$$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 \quad (21.5.12)$$

We can rearrange Equation 21.5.12 to give

$$-\Delta H_5 = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 - \Delta H_f \quad (21.5.13)$$

Substituting for the individual  $\Delta H$ s, we obtain

$$U = \underbrace{\Delta H_{\text{sub}}(\text{Cs})}_{-\Delta H_5} + \underbrace{I_1(\text{Cs})}_{\Delta H_1} + \underbrace{\frac{1}{2}D(\text{F}_2)}_{\Delta H_3} + \underbrace{EA(\text{F})}_{\Delta H_4} - \underbrace{H_f(\text{CsF})}_{\Delta H_f}$$

Substituting the appropriate values into this equation gives

$$\begin{aligned} U &= 76.5 \text{ kJ/mol} + 375.7 \text{ kJ/mol} + 79.4 \text{ kJ/mol} + (-328.2 \text{ kJ/mol}) - (-553.5 \text{ kJ/mol}) \\ &= 756.9 \text{ kJ/mol} \end{aligned} \quad (21.5.14)$$

$U$  is larger in magnitude than any of the other quantities in Equation 21.5.1. The process we have used to arrive at this value is summarized in Table 21.5.6

Table 21.5.6: Summary of Reactions in the Born–Haber Cycle for the Formation of  $\text{CsF}(\text{s})$

Reaction	
(1)	$\text{Cs(s)} \rightarrow \text{Cs(g)}$
(2)	$\text{Cs(g)} \rightarrow \text{Cs} + (\text{g}) + \text{e}^-$
(3)	$\frac{1}{2}\text{F}_2(\text{g}) \rightarrow \text{F(g)}$

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4



(4)	$\text{F(g)} + \text{e}^- \rightarrow \text{F}^-\text{(g)}$	$E_A = -328 \text{ kJ mol}^{-1}$
(5)	$\text{Cs} + \text{F}^-\text{(g)} \rightarrow \text{CsF(s)}$	$U = -756 \text{ kJ mol}^{-1}$
total	$\text{Cs(s)} + \frac{1}{2}\text{F}_2\text{(g)} \rightarrow \text{CsF(s)}$	$\Delta H_f = -553 \text{ kJ mol}^{-1}$

### Predicting the Stability of Ionic Compounds

Equation 21.5.12 may be used as a tool for predicting which ionic compounds are likely to form from particular elements. As we have noted,  $\Delta H_1$  ( $\Delta H_{\text{sub}}$ ),  $\Delta H_2$  ( $I$ ), and  $\Delta H_3$  ( $D$ ) are always positive numbers, and  $\Delta H_2$  can be quite large. In contrast,  $\Delta H_4$  ( $EA$ ) is comparatively small and can be positive, negative, or zero. Thus the first three terms in Equation 21.5.12 make the formation of an ionic substance energetically unfavorable, and the fourth term contributes little either way. The formation of an ionic compound will be exothermic ( $\Delta H_f < 0$ ) if and only if  $\Delta H_5$  ( $-U$ ) is a large negative number. This means that *lattice energy is the most important factor in determining the stability of an ionic compound*. Another example is the formation of BaO:



The enthalpy change is just the enthalpy of formation (e.g.,  $\Delta H = \Delta H_f$ ) with a Born–Haber cycle is compared with that for the formation of CsF in Figure 21.5.4

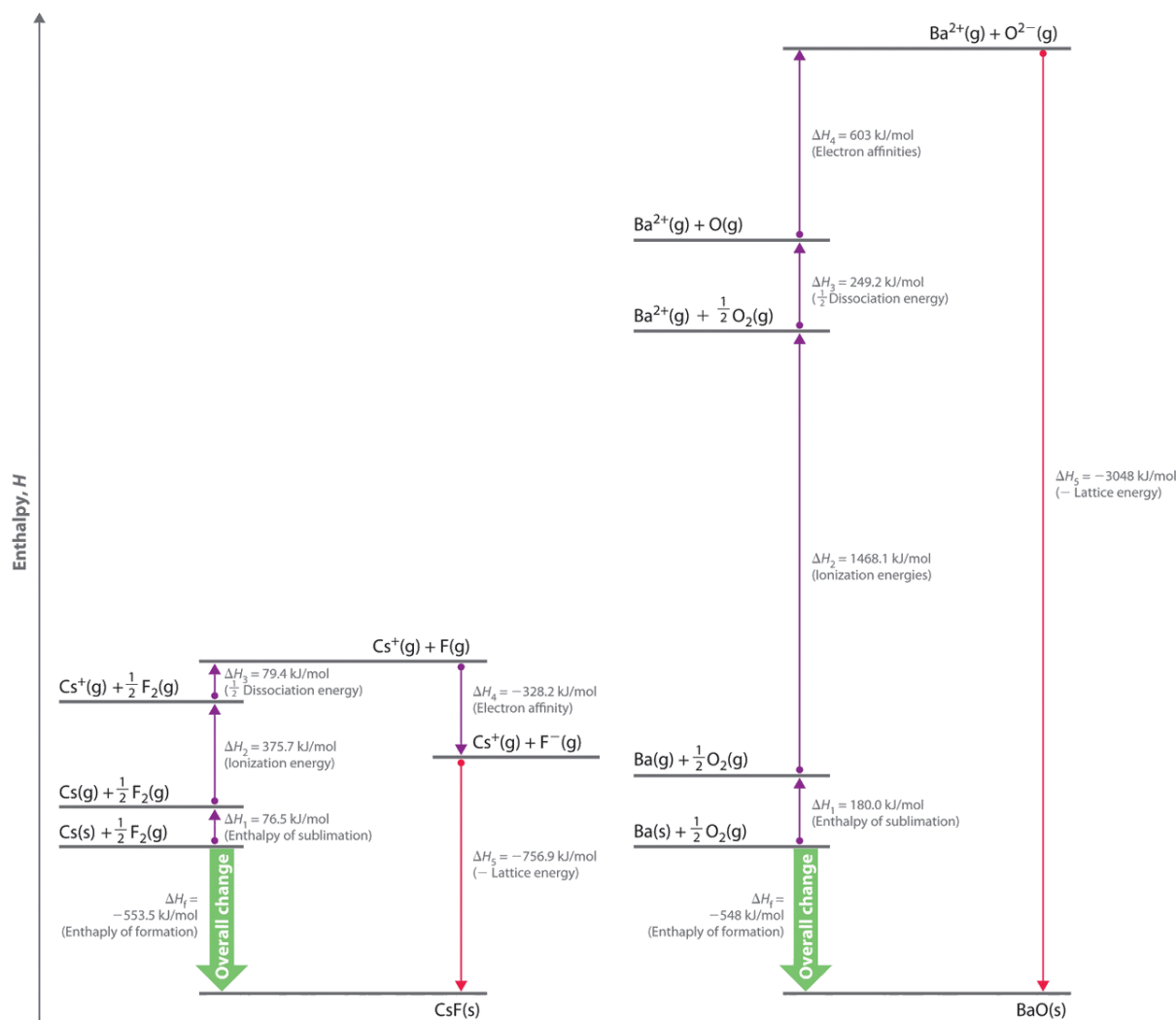
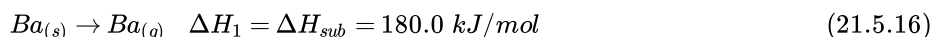


Figure 21.5.4: Comparison of the Enthalpy Changes Involved in the Formation of Solid CsF and BaO from Their Elements. (CC BY-SA-NC; anonymous)

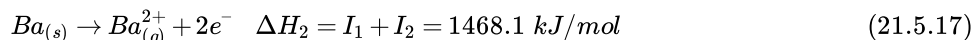
The lattice energy of BaO, with a di-positive cation and a di-negative anion, dominates the Born–Haber cycle.

- Reaction 1:



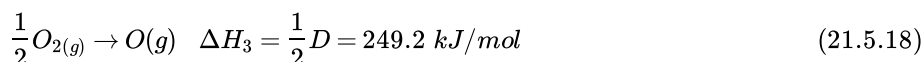
More than twice as much energy is required to sublime barium metal (180.0 kJ/mol) as is required to sublime cesium (76.5 kJ/mol).

- Reaction 2:



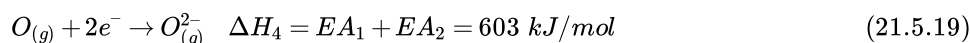
Nearly four times the energy is needed to form  $\text{Ba}^{2+}$  ions ( $I_1 = 502.9 \text{ kJ/mol}$ ,  $I_2 = 965.2 \text{ kJ/mol}$ ,  $I_1 + I_2 = 1468.1 \text{ kJ/mol}$ ) as  $\text{Cs}^+$  ions ( $I_1 = 375.7 \text{ kJ/mol}$ ).

- Reaction 3:



Because the bond energy of  $\text{O}_{2(g)}$  is 498.4 kJ/mol compared with 158.8 kJ/mol for  $\text{F}_{2(g)}$ , more than three times the energy is needed to form oxygen atoms from  $\text{O}_2$  molecules as is required to form fluorine atoms from  $\text{F}_2$ .

- Reaction 4:



Forming gaseous oxide ( $O^{2-}$ ) ions is energetically unfavorable. Even though adding one electron to an oxygen atom is exothermic ( $EA_1 = -141 \text{ kJ/mol}$ ), adding a second electron to an  $O^-(g)$  ion is energetically unfavorable ( $EA_2 = +744 \text{ kJ/mol}$ )—so much so that the overall cost of forming  $O^{2-}(g)$  from  $O(g)$  is energetically prohibitive ( $EA_1 + EA_2 = +603 \text{ kJ/mol}$ ). If the first four terms in the Born–Haber cycle are all substantially more positive for BaO than for CsF, why does BaO even form? The answer is the formation of the ionic solid from the gaseous ions (Reaction 5):

- *Reaction 5:*



Remember from Equations 21.5.1 and 21.5.5 that lattice energies are directly proportional to the product of the charges on the ions and inversely proportional to the internuclear distance. Although the internuclear distances are not significantly different for BaO and CsF (275 and 300 pm, respectively), the larger ionic charges in BaO produce a much higher lattice energy. Substituting values for BaO ( $\Delta H_f = -548.0 \text{ kJ/mol}$ ) into the equation and solving for  $U$  gives:

$$\begin{aligned} U &= \Delta H_{sub}(Ba) + [I_1(Ba) + I_2(Ba)] + \frac{1}{2}D(O_2) + [EA_1(O) + EA_2(O)] - \Delta H_f(BaO) \\ &= 180.0 \text{ kJ/mol} + 1468.1 \text{ kJ/mol} + 249.2 \text{ kJ/mol} + 603 \text{ kJ/mol} - (-548.0 \text{ kJ/mol}) \\ &= 3048 \text{ kJ/mol} \end{aligned}$$

If the formation of ionic lattices containing multiple charged ions is so energetically favorable, why does CsF contain  $Cs^+$  and  $F^-$  ions rather than  $Cs^{2+}$  and  $F^{2-}$  ions? If we assume that  $U$  for a  $Cs^{2+}F^{2-}$  salt would be approximately the same as  $U$  for BaO, the formation of a lattice containing  $Cs^{2+}$  and  $F^{2-}$  ions would release  $2291 \text{ kJ/mol}$  ( $3048 \text{ kJ/mol} - 756.9 \text{ kJ/mol}$ ) more energy than one containing  $Cs^+$  and  $F^-$  ions. To form the  $Cs^{2+}$  ion from  $Cs^+$ , however, would require removing a  $5p$  electron from a filled inner shell, which calls for a great deal of energy:  $I_2 = 2234.4 \text{ kJ/mol}$  for Cs. Furthermore, forming an  $F^{2-}$  ion is expected to be even more energetically unfavorable than forming an  $O^{2-}$  ion. Not only is an electron being added to an already negatively charged ion, but because the  $F^-$  ion has a filled  $2p$  subshell, the added electron would have to occupy an empty high-energy  $3s$  orbital. Cesium fluoride, therefore, is not  $Cs^{2+}F^{2-}$  because the energy cost of forming the doubly charged ions would be greater than the additional lattice energy that would be gained.

*Lattice energy is usually the most important energy factor in determining the stability of an ionic compound.*

### ✓ Example 21.5.3

Use the thermodynamics data in the reference tables to calculate the lattice energy of  $MgH_2$ .

**Given:** chemical compound and data from figures and tables

**Asked for:** lattice energy

**Strategy:**

**A** Write a series of stepwise reactions for forming  $MgH_2$  from its elements via the gaseous ions.

**B** Use [Hess's law](#) and data from the specified figures above and tables to calculate the lattice energy.

**Solution:**

**A** Hess's law allows us to use a thermochemical cycle (the Born–Haber cycle) to calculate the lattice energy for a given compound. We begin by writing reactions in which we form the component ions from the elements in a stepwise manner and then assemble the ionic solid:

(1)	$Mg_{(s)} \rightarrow Mg_{(g)}$	$\Delta H_1 =$	$\Delta H = \Delta H_{sub}(Mg)$
(2)	$Mg_{(g)} \rightarrow Mg_{(g)}^{2+} + 2e^-$	$\Delta H_2 =$	$I_1(Mg) + I_2(Mg)$
(3)	$H_{2(g)} \rightarrow 2H_{(g)}$	$\Delta H_3 =$	$D(H_2)$
(4)	$2H_{(g)} + 2e^- \rightarrow 2H_{(g)}^-$	$\Delta H_4 =$	$2EA(H)$
(5)	$Mg_{(g)}^{2+} + 2H_{(g)}^- \rightarrow MgH_{2(s)}$	$\Delta H_5 =$	$-U$

total	$Mg_{(s)} + H_{2(g)} \rightarrow MgH_{2(s)}$	$\Delta H =$	$\Delta H_f$
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**B** Table A6 lists the first and second ionization energies for the period 3 elements [ $I_1(\text{Mg}) = 737.7 \text{ kJ/mol}$ ,  $I_2(\text{Mg}) = 1450.7 \text{ kJ/mol}$ ]. First electron affinities for all elements are given in Figure 21.5.1 [ $EA(\text{H}) = -72.8 \text{ kJ/mol}$ ]. Table 21.5.4 lists selected enthalpies of sublimation [ $\Delta H_{\text{sub}}(\text{Mg}) = 147.1 \text{ kJ/mol}$ ]. Table 21.5.5 lists selected bond dissociation energies [ $D(\text{H}_2) = 436.0 \text{ kJ/mol}$ ]. Enthalpies of formation ( $\Delta H_f = -75.3 \text{ kJ/mol}$  for  $\text{MgH}_2$ ) are listed in Table T2. From Hess's law,  $\Delta H_f$  is equal to the sum of the enthalpy changes for Reactions 1–5:

For  $\text{MgH}_2$ ,  $U = 2701.2 \text{ kJ/mol}$ . Once again, lattice energy provides the driving force for forming this compound because  $\Delta H_1$ ,  $\Delta H_2$ ,  $\Delta H_3 > 0$ . When solving this type of problem, be sure to write the chemical equation for each step and double-check that the enthalpy value used for each step has the correct sign *for the reaction in the direction it is written*.

### ? Exercise 21.5.3

Use data from the reference tables to calculate the lattice energy of  $\text{Li}_2\text{O}$ . Remember that the second electron affinity for oxygen [ $\text{O}^-(\text{g}) + \text{e}^- \rightarrow \text{O}^{2-}(\text{g})$ ] is *positive* (+744 kJ/mol).

#### Answer

2809 kJ/mol

## Summary

Ionic compounds have strong electrostatic attractions between oppositely charged ions in a regular array. The lattice energy ( $U$ ) of an ionic substance is defined as the energy required to dissociate the solid into gaseous ions;  $U$  can be calculated from the charges on the ions, the arrangement of the ions in the solid, and the internuclear distance. Because  $U$  depends on the product of the ionic charges, substances with di- or tripositive cations and/or di- or trinegative anions tend to have higher lattice energies than their singly charged counterparts. Higher lattice energies typically result in higher **melting points** and increased **hardness** because more thermal energy is needed to overcome the forces that hold the ions together. Lattice energies cannot be measured directly but are obtained from a thermochemical cycle called the **Born–Haber cycle**, in which Hess's law is used to calculate the lattice energy from the measured enthalpy of formation of the ionic compound, along with other thermochemical data. The Born–Haber cycle can be used to predict which ionic compounds are likely to form. **Sublimation**, the conversion of a solid directly to a gas, has an accompanying enthalpy change called the **enthalpy of sublimation**.

## Key Takeaway

- The lattice energy is usually the most important energy factor in determining the stability of an ionic compound.

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