

## 7.6: Strengths of Ionic and Covalent Bonds

### Learning Objectives

- Describe the energetics of covalent and ionic bond formation and breakage
- Use the Born-Haber cycle to compute lattice energies for ionic compounds
- Use average covalent bond energies to estimate enthalpies of reaction

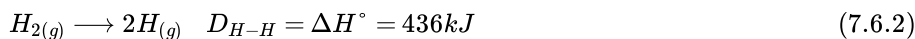
A bond's strength describes how strongly each atom is joined to another atom, and therefore how much energy is required to break the bond between the two atoms. In this section, you will learn about the bond strength of covalent bonds, and then compare that to the strength of ionic bonds, which is related to the lattice energy of a compound.

### 7.6.1: Bond Strength: Covalent Bonds

Stable molecules exist because covalent bonds hold the atoms together. We measure the strength of a covalent bond by the energy required to break it, that is, the energy necessary to separate the bonded atoms. Separating any pair of bonded atoms requires energy; *the stronger a bond, the greater the energy required to break it*. The energy required to break a specific covalent bond in one mole of gaseous molecules is called the bond energy or the bond dissociation energy. The bond energy for a diatomic molecule,  $D_{X-Y}$ , is defined as the standard enthalpy change for the endothermic reaction:

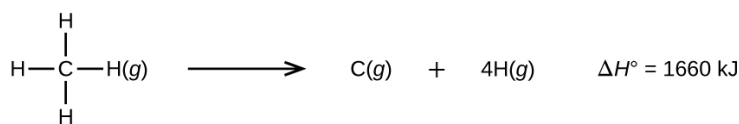


For example, the bond energy of the pure covalent H–H bond,  $\Delta_{H-H}$ , is 436 kJ per mole of H–H bonds broken:



*Breaking a bond **always** require energy to be added to the molecule. Correspondingly, making a bond **always** releases energy.*

Molecules with three or more atoms have two or more bonds. The sum of all bond energies in such a molecule is equal to the standard enthalpy change for the endothermic reaction that breaks all the bonds in the molecule. For example, the sum of the four C–H bond energies in CH<sub>4</sub>, 1660 kJ, is equal to the standard enthalpy change of the reaction:



A reaction is shown with Lewis structures. The first structure shows a carbon atom single bonded to four hydrogen atoms with the symbol, “( g )” written next to it. A right-facing arrow points to the letter “C” and the symbol “( g ),” which is followed by a plus sign. Next is the number 4, the letter “H” and the symbol, “( g ).” To the right of this equation is another equation: capital delta H superscript degree symbol equals 1660 k J.

The average C–H bond energy,  $D_{C-H}$ , is 1660/4 = 415 kJ/mol because there are four moles of C–H bonds broken per mole of the reaction. Although the four C–H bonds are equivalent in the original molecule, they do not each require the same energy to break; once the first bond is broken (which requires 439 kJ/mol), the remaining bonds are easier to break. The 415 kJ/mol value is the average, not the exact value required to break any one bond.

The strength of a bond between two atoms increases as the number of electron pairs in the bond increases. Generally, as the bond strength increases, the bond length decreases. Thus, we find that triple bonds are stronger and shorter than double bonds between the same two atoms; likewise, double bonds are stronger and shorter than single bonds between the same two atoms. Average bond energies for some common bonds appear in Table 7.6.2, and a comparison of bond lengths and bond strengths for some common bonds appears in Table 7.6.2. When one atom bonds to various atoms in a group, the bond strength typically decreases as we move down the group. For example, C–F is 439 kJ/mol, C–Cl is 330 kJ/mol, and C–Br is 275 kJ/mol.

Table 7.6.1: Bond Energies (kJ/mol)

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
H-H	436	C-S	260	F-Cl	255
H-C	415	C-Cl	330	F-Br	235
H-N	390	C-Br	275	Si-Si	230
H-O	464	C-I	240	Si-P	215
H-F	569	N-N	160	Si-S	225
H-Si	395	N = N	418	Si-Cl	359
H-P	320	N $\equiv$ N	946	Si-Br	290
H-S	340	N-O	200	Si-I	215
H-Cl	432	N-F	270	P-P	215
H-Br	370	N-P	210	P-S	230
H-I	295	N-Cl	200	P-Cl	330
C-C	345	N-Br	245	P-Br	270
C = C	611	O-O	140	P-I	215
C $\equiv$ C	837	O = O	498	S-S	215
C-N	290	O-F	160	S-Cl	250
C = N	615	O-Si	370	S-Br	215
C $\equiv$ N	891	O-P	350	Cl-Cl	243
C-O	350	O-Cl	205	Cl-Br	220
C = O	741	O-I	200	Cl-I	210
C $\equiv$ O	1080	F-F	160	Br-Br	190
C-F	439	F-Si	540	Br-I	180
C-Si	360	F-P	489	I-I	150
C-P	265	F-S	285		

Table 7.6.2: Average Bond Lengths and Bond Energies for Some Common Bonds

Bond	Bond Length (Å)	Bond Energy (kJ/mol)
C-C	1.54	345
C = C	1.34	611
C $\equiv$ C	1.20	837
C-N	1.43	290
C = N	1.38	615
C $\equiv$ N	1.16	891
C-O	1.43	350
C = O	1.23	741
C $\equiv$ O	1.13	1080

We can use bond energies to calculate approximate enthalpy changes for reactions where enthalpies of formation are not available. Calculations of this type will also tell us whether a reaction is exothermic or endothermic.

- An **exothermic reaction** ( $\Delta H$  negative, heat produced) results when the bonds in the products are stronger than the bonds in the reactants.
- An **endothermic reaction** ( $\Delta H$  positive, heat absorbed) results when the bonds in the products are weaker than those in the reactants.

The enthalpy change,  $\Delta H$ , for a chemical reaction is approximately equal to the sum of the energy required to break all bonds in the reactants (energy “in”, positive sign) plus the energy released when all bonds are formed in the products (energy “out,” negative sign). This can be expressed mathematically in the following way:

$$\Delta H = \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}} \quad (7.6.3)$$

In this expression, the symbol  $\Sigma$  means “the sum of” and  $D$  represents the bond energy in kilojoules per mole, which is always a positive number. The bond energy is obtained from a table and will depend on whether the particular bond is a single, double, or triple bond. Thus, in calculating enthalpies in this manner, it is important that we consider the bonding in all reactants and products. Because  $D$  values are typically averages for one type of bond in many different molecules, this calculation provides a rough estimate, not an exact value, for the enthalpy of reaction.

Consider the following reaction:



or



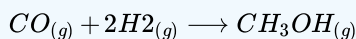
To form two moles of HCl, one mole of H–H bonds and one mole of Cl–Cl bonds must be broken. The energy required to break these bonds is the sum of the bond energy of the H–H bond (436 kJ/mol) and the Cl–Cl bond (243 kJ/mol). During the reaction, two moles of H–Cl bonds are formed (bond energy = 432 kJ/mol), releasing  $2 \times 432$  kJ; or 864 kJ. Because the bonds in the products are stronger than those in the reactants, the reaction releases more energy than it consumes:

$$\begin{aligned} \Delta H &= \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}} \\ &= [D_{\text{H-H}} + D_{\text{Cl-Cl}}] - 2D_{\text{H-Cl}} \\ &= [436 + 243] - 2(432) = -185 \text{ kJ} \end{aligned}$$

This excess energy is released as heat, so the reaction is exothermic. Table T2 gives a value for the standard molar enthalpy of formation of HCl(g),  $\Delta H_f^\circ$ , of  $-92.307$  kJ/mol. Twice that value is  $-184.6$  kJ, which agrees well with the answer obtained earlier for the formation of two moles of HCl.

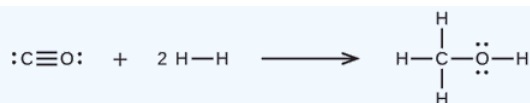
#### ✓ Example 7.6.1: Using Bond Energies to Approximate Enthalpy Changes

Methanol,  $\text{CH}_3\text{OH}$ , may be an excellent alternative fuel. The high-temperature reaction of steam and carbon produces a mixture of the gases carbon monoxide, CO, and hydrogen,  $\text{H}_2$ , from which methanol can be produced. Using the bond energies in Table 7.6.2, calculate the approximate enthalpy change,  $\Delta H$ , for the reaction here:



#### Solution

First, we need to write the Lewis structures of the reactants and the products:



A set of Lewis diagrams show a chemical reaction. The first structure shows a carbon atom with a lone pair of electrons triple bonded to an oxygen with a lone pair of electrons. To the right of this structure is a plus sign, then the number 2 followed by a hydrogen atom single bonded to a hydrogen atom. To the right of this structure is a right-facing arrow followed by a hydrogen atom single bonded to a carbon atom that is single bonded to two hydrogen atoms and an oxygen atom with two lone pairs of electrons. The oxygen atom is also single bonded to a hydrogen atom.

From this, we see that  $\Delta H$  for this reaction involves the energy required to break a C–O triple bond and two H–H single bonds, as well as the energy produced by the formation of three C–H single bonds, a C–O single bond, and an O–H single bond. We can express this as follows (via Equation 7.6.3):

$$\begin{aligned} \Delta H &= \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}} \\ \Delta H &= [D_{\text{C}\equiv\text{O}} + 2(D_{\text{H}-\text{H}})] - [3(D_{\text{C}-\text{H}}) + D_{\text{C}-\text{O}} + D_{\text{O}-\text{H}}] \end{aligned}$$

Using the bond energy values in Table 7.6.2, we obtain:

$$\begin{aligned} \Delta H &= [1080 + 2(436)] - [3(415) + 350 + 464] \\ &= -107 \text{ kJ} \end{aligned}$$

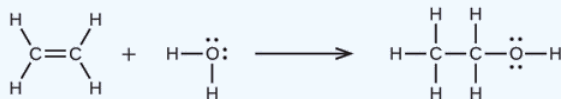
We can compare this value to the value calculated based on  $\Delta H_f^\circ$  data from Appendix G:

$$\begin{aligned} \Delta H &= [\Delta H_f^\circ \text{CH}_3\text{OH}(g)] - [\Delta H_f^\circ \text{CO}(g) + 2 \times \Delta H_f^\circ \text{H}_2] \\ &= [-201.0] - [-110.52 + 2 \times 0] \\ &= -90.5 \text{ kJ} \end{aligned}$$

Note that there is a fairly significant gap between the values calculated using the two different methods. This occurs because  $D$  values are the *average* of different bond strengths; therefore, they often give only rough agreement with other data.

### ? Exercise 7.6.1

Ethyl alcohol,  $\text{CH}_3\text{CH}_2\text{OH}$ , was one of the first organic chemicals deliberately synthesized by humans. It has many uses in industry, and it is the alcohol contained in alcoholic beverages. It can be obtained by the fermentation of sugar or synthesized by the hydration of ethylene in the following reaction:



A set of Lewis structures show a chemical reaction. The first structure shows two carbon atoms that are double bonded together and are each single bonded to two hydrogen atoms. This structure is followed by a plus sign, then an oxygen atom with two lone pairs of electrons single bonded to two hydrogen atoms. A right-facing arrow leads to a carbon atom single bonded to three hydrogen atoms and a second carbon atom. The second carbon atom is single bonded to two hydrogen atoms and an oxygen atom with two lone pairs of electrons. The oxygen atom is single bonded to a hydrogen atom as well.

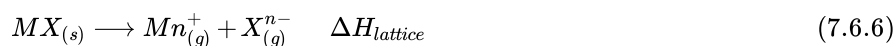
Using the bond energies in Table 7.6.2, calculate an approximate enthalpy change,  $\Delta H$ , for this reaction.

**Answer**

–35 kJ

## 7.6.2: Ionic Bond Strength and Lattice Energy

An ionic compound is stable because of the electrostatic attraction between its positive and negative ions. The lattice energy of a compound is a measure of the strength of this attraction. The lattice energy ( $\Delta H_{\text{lattice}}$ ) of an ionic compound is defined as the energy required to separate one mole of the solid into its component gaseous ions. For the ionic solid MX, the lattice energy is the enthalpy change of the process:



Note that we are using the convention where the ionic solid is separated into ions, so our lattice energies will be endothermic (positive values). Some texts use the equivalent but opposite convention, defining lattice energy as the energy released when separate ions combine to form a lattice and giving negative (exothermic) values. Thus, if you are looking up lattice energies in another reference, be certain to check which definition is being used. In both cases, a larger magnitude for lattice energy indicates a more stable ionic compound. For sodium chloride,  $\Delta H_{lattice} = 769$  kJ. Thus, it requires 769 kJ to separate one mole of solid NaCl into gaseous  $Na^{+}$  and  $Cl^{-}$  ions. When one mole each of gaseous  $Na^{+}$  and  $Cl^{-}$  ions form solid NaCl, 769 kJ of heat is released.

The lattice energy  $\Delta H_{lattice}$  of an ionic crystal can be expressed by the following equation (derived from Coulomb's law, governing the forces between electric charges):

$$\Delta H_{lattice} = \frac{C(Z^{+})(Z^{-})}{R_o} \quad (7.6.7)$$

in which

- $C$  is a constant that depends on the type of crystal structure;
- $Z^{+}$  and  $Z^{-}$  are the charges on the ions; and
- $R_o$  is the interionic distance (the sum of the radii of the positive and negative ions).

Thus, the lattice energy of an ionic crystal increases rapidly as the charges of the ions increase and the sizes of the ions decrease. When all other parameters are kept constant, doubling the charge of both the cation and anion quadruples the lattice energy. For example, the lattice energy of LiF ( $Z^{+}$  and  $Z^{-} = 1$ ) is 1023 kJ/mol, whereas that of MgO ( $Z^{+}$  and  $Z^{-} = 2$ ) is 3900 kJ/mol ( $R_o$  is nearly the same—about 200 pm for both compounds).

Different interatomic distances produce different lattice energies. For example, we can compare the lattice energy of  $MgF_2$  (2957 kJ/mol) to that of  $MgI_2$  (2327 kJ/mol) to observe the effect on lattice energy of the smaller ionic size of  $F^{-}$  as compared to  $I^{-}$ .

#### ✓ Example 7.6.2: Lattice Energy Comparisons

The precious gem ruby is aluminum oxide,  $Al_2O_3$ , containing traces of  $Cr^{3+}$ . The compound  $Al_2Se_3$  is used in the fabrication of some semiconductor devices. Which has the larger lattice energy,  $Al_2O_3$  or  $Al_2Se_3$ ?

#### Solution

In these two ionic compounds, the charges  $Z^{+}$  and  $Z^{-}$  are the same, so the difference in lattice energy will mainly depend upon  $R_o$ . The  $O^{2-}$  ion is smaller than the  $Se^{2-}$  ion. Thus,  $Al_2O_3$  would have a shorter interionic distance than  $Al_2Se_3$ , and  $Al_2O_3$  would have the larger lattice energy.

#### ? Exercise 7.6.2

Zinc oxide, ZnO, is a very effective sunscreen. How would the lattice energy of ZnO compare to that of NaCl?

#### Answer

ZnO would have the larger lattice energy because the  $Z$  values of both the cation and the anion in ZnO are greater, and the interionic distance of ZnO is smaller than that of NaCl.

### 7.6.3: The Born-Haber Cycle

It is not possible to measure lattice energies directly. However, the lattice energy can be calculated using the equation given in the previous section or by using a thermochemical cycle. The Born-Haber cycle is an application of Hess's law that breaks down the formation of an ionic solid into a series of individual steps:

- $\Delta H_f^{\circ}$ , the standard enthalpy of formation of the compound
- $IE_m$ , the ionization energy of the metal
- $EA_n$ , the electron affinity of the nonmetal
- $\Delta H_s^{\circ}$ , the enthalpy of sublimation of the metal
- $D$ , the bond dissociation energy of the nonmetal

- $\Delta H_{\text{lattice}}$ , the lattice energy of the compound

Figure 7.6.1 diagrams the Born-Haber cycle for the formation of solid cesium fluoride.

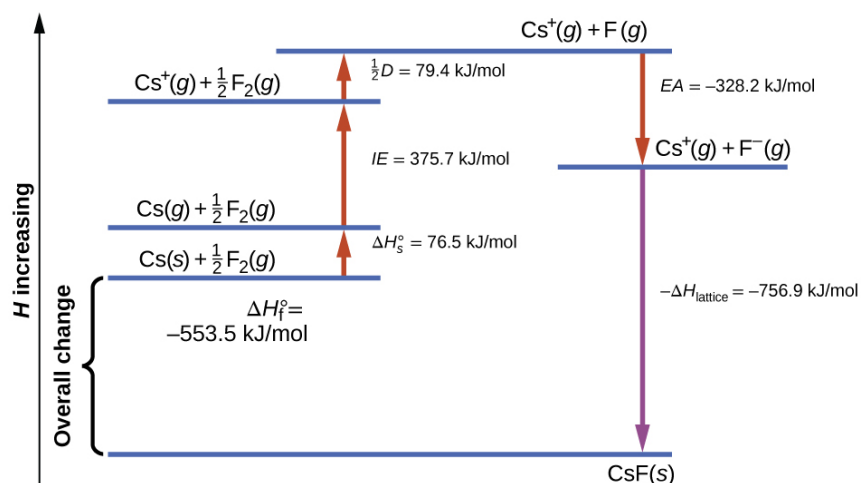


Figure 7.6.1: The Born-Haber cycle shows the relative energies of each step involved in the formation of an ionic solid from the necessary elements in their reference states.

A diagram is shown. An upward facing arrow is drawn to the far left of the chart and is labeled “H increasing.” A horizontal line is drawn at the bottom of the chart. A downward-facing, vertical arrow to the left side of this line is labeled, “Overall change.” Beside this arrow is another label, “capital delta H subscript f, equals negative 553.5 k J per mol, ( Enthalpy of formation ).” Three horizontal lines, one above the other, and all above the bottom line, are labeled, from bottom to top, as: “C s ( s ), plus sign, one half F subscript 2, ( g ),” “C s ( g ), plus sign, one half F subscript 2, ( g ),” and “C s, superscript positive sign, ( g ), plus sign, one half F subscript 2, ( g ).” Each of these lines is connected by an upward-facing vertical arrow. Each arrow is labeled, “capital delta H subscript 1, equals 76.5 k J per mol, ( Enthalpy of sublimation ),” “capital delta H subscript 2, equals 375.7 k J per mol, ( ionization energy ),” and “capital delta H subscript 3 equals 79.4 k J / mol ( one half dissociation energy ).” Another horizontal line is drawn in the center top portion of the diagram and is labeled “C s, superscript positive sign, ( g ), plus sign, F, ( g ).” There is one more horizontal line drawn to the right of the overall diagram and located halfway down the image. An arrow connects the top line to this line and is labeled, “capital delta H equals negative 328.2 k J / mol ( electron affinity ).” The line is labeled, “C s superscript positive sign ( g ) plus F superscript negative sign ( g ).” The arrow connecting this line to the bottom line is labeled, “negative capital delta H subscript lattice equals negative 756.9 k J / mol.” The arrow points to a label on the bottom line which reads, “C s F ( s ).”

We begin with the elements in their most common states,  $\text{Cs(s)}$  and  $\text{F}_2(\text{g})$ . The  $\Delta H_s^\circ$  represents the conversion of solid cesium into a gas, and then the ionization energy converts the gaseous cesium atoms into cations. In the next step, we account for the energy required to break the F–F bond to produce fluorine atoms. Converting one mole of fluorine atoms into fluoride ions is an exothermic process, so this step gives off energy (the electron affinity) and is shown as decreasing along the y-axis. We now have one mole of Cs cations and one mole of F anions. These ions combine to produce solid cesium fluoride. The enthalpy change in this step is the negative of the lattice energy, so it is also an exothermic quantity. The total energy involved in this conversion is equal to the experimentally determined enthalpy of formation,  $\Delta H_f^\circ$ , of the compound from its elements. In this case, the overall change is exothermic.

Hess’s law can also be used to show the relationship between the enthalpies of the individual steps and the enthalpy of formation. Table 7.6.3 shows this for cesium fluoride,  $\text{CsF}$ .

Table 7.6.3: Enthalpies of Select Transitions

Enthalpy of sublimation of $\text{Cs(s)}$	$\text{Cs(s)} \longrightarrow \text{Cs(g)} \quad \Delta H = \Delta H_s^\circ = 77 \text{ kJ/mol}$
One-half of the bond energy of $\text{F}_2$	$\frac{1}{2}\text{F}_2(\text{g}) \longrightarrow \text{F(g)} \quad \Delta H = \frac{1}{2}D = 79 \text{ kJ/mol}$
Ionization energy of $\text{Cs(g)}$	$\text{Cs(g)} \longrightarrow \text{Cs}^+(\text{g}) + \text{e}^- \quad \Delta H = IE = 376 \text{ kJ/mol}$
Negative of the electron affinity of F	$\text{F(g)} + \text{e}^- \longrightarrow \text{F}^-(\text{g}) \quad \Delta H = -EA = -328 \text{ kJ/mol}$
Negative of the lattice energy of $\text{CsF(s)}$	$\text{Cs}^+(\text{g}) + \text{F}^-(\text{g}) \longrightarrow \text{CsF(s)} \quad \Delta H = -\Delta H_{\text{lattice}} = ?$
Enthalpy of formation of $\text{CsF(s)}$ , add steps 1–5	$\Delta H = \Delta H_f^\circ = \Delta H_s^\circ + \frac{1}{2}D + IE + (-EA) + (-\Delta H_{\text{lattice}})$ $\text{Cs(s)} + \frac{1}{2}\text{F}_2(\text{g}) \longrightarrow \text{CsF(s)} = -554 \text{ kJ/mol}$

Thus, the lattice energy can be calculated from other values. For cesium chloride, using this data, the lattice energy is:

$$\Delta H_{\text{lattice}} = (411 + 109 + 122 + 496 + 368) \text{ kJ} = 770 \text{ kJ}$$

The Born-Haber cycle may also be used to calculate any one of the other quantities in the equation for lattice energy, provided that the remainder is known. For example, if the relevant enthalpy of sublimation  $\Delta H_s^\circ$ , ionization energy (IE), bond dissociation enthalpy (D), lattice energy  $\Delta H_{\text{lattice}}$ , and standard enthalpy of formation  $\Delta H_f^\circ$  are known, the Born-Haber cycle can be used to determine the electron affinity of an atom.

Lattice energies calculated for ionic compounds are typically much larger than bond dissociation energies measured for covalent bonds. Whereas lattice energies typically fall in the range of 600–4000 kJ/mol (some even higher), covalent bond dissociation energies are typically between 150–400 kJ/mol for single bonds. Keep in mind, however, that these are not directly comparable values. For ionic compounds, lattice energies are associated with many interactions, as cations and anions pack together in an extended lattice. For covalent bonds, the bond dissociation energy is associated with the interaction of just two atoms.

## Summary

The strength of a covalent bond is measured by its bond dissociation energy, that is, the amount of energy required to break that particular bond in a mole of molecules. Multiple bonds are stronger than single bonds between the same atoms. The enthalpy of a reaction can be estimated based on the energy input required to break bonds and the energy released when new bonds are formed. For ionic bonds, the lattice energy is the energy required to separate one mole of a compound into its gas phase ions. Lattice energy increases for ions with higher charges and shorter distances between ions. Lattice energies are often calculated using the Born-Haber cycle, a thermochemical cycle including all of the energetic steps involved in converting elements into an ionic compound.

### 7.6.3.1: Key Equations

- Bond energy for a diatomic molecule:  $\text{XY}(g) \longrightarrow \text{X}(g) + \text{Y}(g) \quad D_{\text{X-Y}} = \Delta H^\circ$
- Enthalpy change:  $\Delta H = \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}}$
- Lattice energy for a solid MX:  $\text{MX}(s) \longrightarrow \text{M}^{n+}(g) + \text{X}^{n-}(g) \quad \Delta H_{\text{lattice}}$
- Lattice energy for an ionic crystal:  $\Delta H_{\text{lattice}} = \frac{C(\text{Z}^+)(\text{Z}^-)}{R_o}$

## Footnotes

- This question is taken from the Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

## Glossary

### **bond energy**

(also, bond dissociation energy) energy required to break a covalent bond in a gaseous substance

### **Born-Haber cycle**

thermochemical cycle relating the various energetic steps involved in the formation of an ionic solid from the relevant elements

### **lattice energy ( $\Delta H_{\text{lattice}}$ )**

energy required to separate one mole of an ionic solid into its component gaseous ions

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