# 10.11: Lattice Energy

**Discussion Questions**

- How is lattice energy estimated using Born-Haber cycle?
- How is lattice energy related to crystal structure?

The Lattice energy, $U$, is the amount of energy required to separate a mole of the solid (s) into a gas (g) of its ions.

$$\mathrm{M_aL_b(s) \rightarrow aM^{b^+}(g) + bX^{a^-}(g)} \tag{10.11.1}$$

This quantity cannot be experimentally determined directly, but it can be estimated using a Hess Law approach in the form of *Born-Haber cycle*. It can also be calculated from the electrostatic consideration of its crystal structure. As defined in Equation 10.11.1, the lattice energy is positive, because energy is always required to separate the ions. For the reverse process of Equation 10.11.1:

$$\mathrm{aM^{b^+}(g) + bX^{a^-}(g) \rightarrow M_aL_b(s)} \tag{10.11.2}$$

the energy released is called **energy of crystallization** ($E_{cryst}$). Therefore,

$$U_{lattice} = -E_{cryst} \tag{10.11.3}$$

Values of lattice energies for various solids have been given in literature, especially for some common solids. Some are given here.

Table 10.11.1: Comparison of Lattice Energies (U in kJ/mol) of Some Salts

| Solid | $U$ | Solid | $U$ | Solid | $U$ | Solid | $U$ |
|---|---|---|---|---|---|---|---|
| LiF | 1036 | LiCl | 853 | LiBr | 807 | LiI | 757 |
| NaF | 923 | NaCl | 786 | NaBr | 747 | NaI | 704 |
| KF | 821 | KCl | 715 | KBr | 682 | KI | 649 |
| $MgF_2$ | 2957 | $MgCl_2$ | 2526 | $MgBr_2$ | 2440 | $MgI_2$ | 2327 |

The following trends are obvious at a glance of the data in Table 10.11.1:

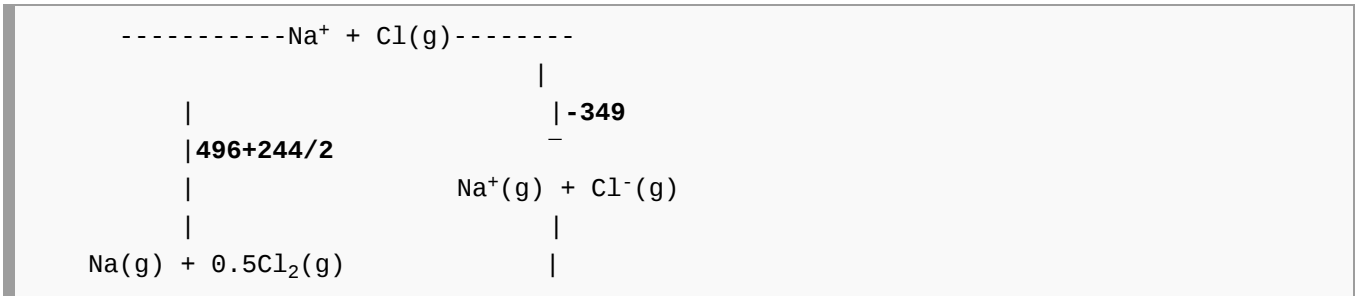
- As the ionic radii of either the cation or anion increase, the lattice energies decrease.
- The solids consists of divalent ions have much larger lattice energies than solids with monovalent ions.

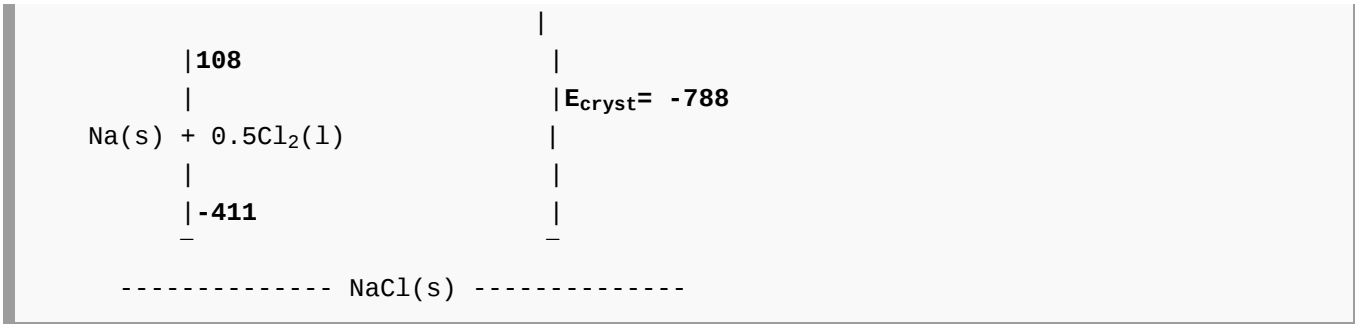
## How is lattice energy estimated using Born-Haber cycle?

Estimating lattice energy using the Born-Haber cycle has been discussed in Ionic Solids. For a quick review, the following is an example that illustrate the estimate of the energy of crystallization of NaCl.

Hsub of Na = 108 kJ/mol (Heat of sublimation)
D of Cl2 = 244 (Bond dissociation energy)
IP of Na(g) = 496 (Ionization potential or energy)
EA of Cl(g) = -349 (Electron affinity of Cl)
Hf of NaCl = -411 (Enthalpy of formation)

The Born-Haber cycle to evaluate $E_{lattice}$ is shown below:






$E_{cryst}$ = -411-(108+496+244/2)-(-349) kJ/mol
= -788 kJ/mol.

***Discussion***

The value calculated for $U$ depends on the data used. Data from various sources differ slightly, and so is the result. The lattice energies for NaCl most often quoted in other texts is about 765 kJ/mol.

Compare with the method shown below

| | | |
|---|---|---|
| Na(s) + 0.5 $Cl_2$(l) ® NaCl(s) | - 411 | $H_f$ |
| Na(g) ® Na(s) | - 108 | -$H_{sub}$ |
| $Na^+$(g) + e ® Na(g) | - 496 | -*IP* |
| Cl(g) ® 0.5 $Cl_2$(g) | - 0.5 * 244 | -0.5*$D$ |
| $Cl^-$(g) ® Cl(g) + 2 e | 349 | -*EA* |
| Add all the above equations leading to | | |
| $Na^+$(g) + $Cl^-$(g) ® NaCl(s) | -788 kJ/mol = $E_{cryst}$ | |

## Lattice Energy is Related to 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 repulson 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 $Na^+$ and $Cl^-$ ions. The nearest neighbors of $Na^+$ are 6 $Cl^-$ ions at a distance 1$r$, 12 $Na^+$ ions at a distance 2$r$, 8 $Cl^-$ at 3$r$, 6 $Na^+$ at 4$r$, 24 $Na^+$ at 5$r$, and so on. Thus, the energy due to one ion is

$$E = \frac{Z^2 e^2}{4\pi\epsilon_o r} M \tag{10.11.4}$$

The Madelung constant, $M$, is a poorly converging series of interaction energies:

$$M = \frac{6}{1} - \frac{12}{2} + \frac{8}{3} - \frac{6}{4} + \frac{24}{5} \ldots \tag{10.11.5}$$

with

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

The above discussion is valid only for the sodium chloride (also called rock salt) structure type. This is a geometrical factor, depending on the arrangement of ions in the solid. The Madelung constant depends on the structure type, and its values for several structural types are given in Table 6.13.1.

*A* is the number of anions coordinated to cation and *C* is the numbers of cations coordinated to anion.

Table 10.11.2: Madelung Constants

| Compound | Crystal Lattice | M | A : C | Type |
|---|---|---|---|---|
| NaCl | NaCl | 1.74756 | 6 : 6 | Rock salt |
| CsCl | CsCl | 1.76267 | 6 : 6 | CsCl type |
| $CaF_2$ | Cubic | 2.51939 | 8 : 4 | Fluorite |
| $CdCl_2$ | Hexagonal | 2.244 | | |
| $MgF_2$ | Tetragonal | 2.381 | | |
| ZnS (wurtzite) | Hexagonal | 1.64132 | | |
| $TiO_2$ (rutile) | Tetragonal | 2.408 | 6 : 3 | Rutile |
| $bSiO_2$ | Hexagonal | 2.2197 | | |
| $Al_2O_3$ | Rhombohedral | 4.1719 | 6 : 4 | Corundum |
| *A* is the number of anions coordinated to cation and *C* is the numbers of cations coordinated to anion. | | | | |

Madelung constants for a few more types of crystal structures are available from the Handbook Menu. There are other factors to consider for the evaluation of energy of crystallization, and the treatment by *M. Born* led to the formula for the evaluation of crystallization energy $E_{cryst}$, for a mole of **crystalline solid**.

$$E_{cryst} = \frac{NZ^2e^2}{4\pi\epsilon_o r}\left(1 - \frac{1}{n}\right) \tag{10.11.6}$$

where *N* is the Avogadro's number (6.022x10$^{-23}$), and *n* is a number related to the electronic configurations of the ions involved. The *n* values and the electronic configurations (e.c.) of the corresponding inert gases are given below:

| *n* = | 5 | 7 | 9 | 10 | 12 |
|---|---|---|---|---|---|
| e.c. | He | Ne | Ar | Kr | Xe |

The following values of *n* have been suggested for some common solids:

| *n* = | 5.9 | 8.0 | 8.7 | 9.1 | 9.5 |
|---|---|---|---|---|---|
| e.c. | LiF | LiCl | LiBr | NaCl | NaBr |

**Example 10.11.1**

Estimate the energy of crystallization for NaCl.

**Solution**

Using the values giving in the discussion above, the estimation is given by Equation 10.11.6

$$E_cryst = \frac{(6.022\times10^{23}/mol(1.6022\times10^{-19})^2(1.747558)}{4\pi\,(8.854\times10^{-12}C^2/m)(282\times10^{-12}\ m}\left(1-\frac{1}{9.1}\right)$$

$$= -766kJ/mol$$

**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-Haber cycle to evaluate other chemical properties, for example the electron affinity, which is really difficult to determine directly by experiment.

### Exercise 10.11.1

Which one of the following has the largest lattice energy? LiF, NaF, $CaF_2$, $AlF_3$

**Answer**

**Skill:** Explain the trend of lattice energy.

### Exercise 10.11.2

Which one of the following has the largest lattice energy? LiCl, NaCl, $CaCl_2$, $Al_2O_3$

**Answer**

Corrundum $Al_2O_3$ has some covalent character in the solid as well as the higher charge of the ions.

### Exercise 10.11.3

Lime, CaO, is know to have the same structure as NaCl and the edge length of the unit cell for CaO is 481 pm. Thus, Ca-O distance is 241 pm. Evaluate the energy of crystallization, $E_{cryst}$ for CaO.

**Answer**

**Energy of crystallization is -3527 kJ/mol**

**Skill:** Evaluate the lattice energy and know what values are needed.

### Exercise 10.11.4

Assume the interionic distance for $NaCl_2$ to be the same as those of NaCl ($r$ = 282 pm), and assume the structure to be of the fluorite type ($M$ = 2.512). Evaluate the energy of crystallization, $E_{cryst}$ .

**Answer**

**-515 kJ/mol**

**Discussion:** This number has not been checked. If you get a different value, please let me know.

## Contributors and Attributions

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