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.

\[
\ce{M_{a} L_{b} (s) \rightarrow a M^{b+} (g) + b X^{a-} (g) \label{eq1}}
\]

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, the lattice energy is positive, because energy is always required to separate the ions. For the reverse process of Equation \(\ref{eq1}\):

\[
\ce{a M^{b+} (g) + b X^{a-} (g) \rightarrow M_{a}L_{b}(s)}
\]

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

\[
U_{lattice} = -E_{\text{cryst}}
\]

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

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Solid & \(U\) & Solid & \(U\) & Solid & \(U\) \\
\hline
LiF & 1036 & LiCl & 853 & LiBr & 807 \\
NaF & 923 & NaCl & 786 & NaBr & 747 \\
KF & 821 & KCl & 715 & KBr & 682 \\
MgF\(_2\) & 2957 & MgCl\(_2\) & 2526 & MgBr\(_2\) & 2440 \\
\hline
\end{tabular}
\caption{Comparison of Lattice Energies \((U\ in \text{kJ/mol})\) of Some Salts}
\end{table}

The following trends are obvious at a glance of the data in Table \(\ref{PagelIndex{1}}\):

- 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.

\[
\begin{align*}
\text{Hsub of Na} &= 108 \text{ kJ/mol (Heat of sublimation)} \\
\text{D of Cl}_2 &= 244 \text{ (Bond dissociation energy)} \\
\text{IP of Na(g)} &= 496 \text{ (Ionization potential or energy)}
\end{align*}
\]
EA of Cl(g) = -349 (Electron affinity of Cl)
Hf of NaCl = -411 (Enthalpy of formation)

The Born-Haber cycle to evaluate \( E_{\text{lattice}} \) is shown below:

\[
\begin{align*}
\text{Na}(s) + 0.5 \text{Cl}_2(l) & \rightleftharpoons \text{NaCl}(s) & -411 \\
\text{Na}(g) & \rightleftharpoons \text{Na}(s) & -108 \text{ H}_{\text{sub}} \\
\text{Na}^+(g) + \text{e} & \rightleftharpoons \text{Na}(g) & -496 \text{ IP} \\
\text{Cl}(g) & \rightleftharpoons 0.5 \text{Cl}_2(g) & -0.5 \times 244 \text{ -0.5*D} \\
\text{Cl}^-(g) & \rightleftharpoons \text{Cl}(g) + 2 \text{e} & 349 \text{ -EA} \\
\end{align*}
\]

Add all the above equations leading to

\[
\text{Na}^+(g) + \text{Cl}^-(g) \rightleftharpoons \text{NaCl}(s) \quad -788 \text{ kJ/mol} = E_{\text{cryst}}
\]
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 repulsion from ions of opposite charge and ions of the same charge.

As an example, let us consider 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

\[
E = \frac{Z^2e^2}{4\pi\epsilon_or} M \tag{6.13.1}
\]

The Madelung constant, \( M \), is a poorly converging series of interaction energies:

\[
M= \frac{6}{1} - \frac{12}{2} + \frac{8}{3} - \frac{6}{4} + \frac{24}{5} ... \tag{6.13.2}
\]

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),
- \( \epsilon_o \) is \( 1.11265 \times 10^{-10} \) C\(^2/(\text{J m})\).

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 6.13.1: Madelung Constants**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal Lattice</th>
<th>M</th>
<th>A : C</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>NaCl</td>
<td>1.74756</td>
<td>6 : 6</td>
<td>Rock salt</td>
</tr>
<tr>
<td>CsCl</td>
<td>CsCl</td>
<td>1.76267</td>
<td>6 : 6</td>
<td>CsCl type</td>
</tr>
<tr>
<td>CaF(_2)</td>
<td>Cubic</td>
<td>2.51939</td>
<td>8 : 4</td>
<td>Fluorite</td>
</tr>
<tr>
<td>CdCl(_2)</td>
<td>Hexagonal</td>
<td>2.244</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgF(_2)</td>
<td>Tetragonal</td>
<td>2.381</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnS (wurtzite)</td>
<td>Hexagonal</td>
<td>1.64132</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO(_2) (rutile)</td>
<td>Tetragonal</td>
<td>2.408</td>
<td>6 : 3</td>
<td>Rutile</td>
</tr>
<tr>
<td>bSiO(_2)</td>
<td>Hexagonal</td>
<td>2.2197</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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 \(E_{\text{cryst}}\), for a mole of crystalline solid.

\[
E_{\text{cryst}} = \frac{N Z^2 e^2}{4\pi \epsilon_o r} \left( 1 - \frac{1}{n} \right)
\]

where \(N\) is the Avogadro's number \((6.022 \times 10^{-23})\), 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:

\[
\begin{array}{cccccc}
5 & 7 & 9 & 10 & 12 \\
e.c. & He & Ne & Ar & Kr & Xe \\
\end{array}
\]

The following values of \(n\) have been suggested for some common solids:

\[
\begin{array}{cccccc}
5.9 & 8.0 & 8.7 & 9.1 & 9.5 \\
e.c. & LiF & LiCl & LiBr & NaCl & NaBr \\
\end{array}
\]

Example 1

Estimate the energy of crystallization for NaCl.

\textbf{SOLUTION}

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

\[
E_{\text{cryst}} = \frac{(6.022 \times 10^{23} \text{ mol}) (1.6022 \times 10^{-19})^2 (1.747558)}{4\pi (8.854 \times 10^{-12} \text{ C}^2/\text{m}) (282 \times 10^{-12} \text{ m}) \left( 1 - \frac{1}{9.1} \right)}
\]

\[
[= - 766 \text{ kJ/mol}]
\]

\textbf{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.
Questions

1. Which one of the following has the largest lattice energy?
   LiF, NaF, CaF₂, AlF₃

2. Which one of the following has the largest lattice energy?
   LiCl, NaCl, CaCl₂, Al₂O₃

3. Lime, CaO, is known 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, \( E_{\text{cryst}} \) for CaO.

4. Assume the interionic distance for NaCl₂ to be the same as those of NaCl \( (r = 282 \text{ pm}) \), and assume the structure to be of the fluorite type \( (M = 2.512) \). Evaluate the energy of crystallization, \( E_{\text{cryst}} \).

Solutions

1. Hint: AlF₃, apply common sense.
   
   Skill -
   Explain the trend of lattice energy.

2. Hint: Al₂O₃
   
   Discussion -
   Corundum Al₂O₃ has some covalent character in the solid as well as the higher charge of the ions.

3. Hint: Energy of crystallization is -3527 kJ/mol
   
   Skill -
   Evaluate the lattice energy and know what values are needed.

4. Hint: -515 kJ/mol
   
   Discussion -
   This number has not been checked. If you get a different value, please let me know.

Contributors

- Chung (Peter) Chieh (Chemistry, University of Waterloo)