Lattice energies can also help predict compound solubilities.

Here we need to consider the trends in both the lattice energy \( \langle E_L \rangle \) and the hydration energy \( \langle E_H \rangle \). The lattice energy depends on the sum of the anion and cation radii \( (r_+ + r_-) \):

\[
\langle E_L \rangle \propto \dfrac{1}{r_+ + r_-}
\]

whereas the hydration energy has separate anion and cation terms

\[
\langle E_H \rangle \propto \dfrac{1}{r_+^2} + \dfrac{1}{r_-^2}
\]

Generally the solvation of small ions (typically cations) dominates the hydration energy because of the \( 1/r^2 \) dependence.

For salts that contain large anions, \( E_L \) does not change much as \( r_+ \) changes. That is because the anion dominates the \( r_+ + r_- \) term in the denominator of the formula for \( E_L \). On the other hand, \( E_H \) changes substantially with \( r_+ \), especially for small cations. As a result, sulfate salts of small divalent cations, such as MgSO\(_4\) (epsom salts), are soluble, whereas the lower hydration energy of Ba\(^{2+}\) in BaSO\(_4\) makes that salt insoluble (\( K_{sp} = 10^{-10} \)).

Figure: Left: \( E_L \) diagram for sulfate salts. The large SO\(_4^{2-}\) ion is size-mismatched to small cations such as Mg\(^{2+}\), which have large hydration energies, resulting soluble salts. With larger cations such as Ba\(^{2+}\), which have lower \( E_H \), the lattice energy exceeds the solvation enthalpy and the salts are insoluble. Right: In the case of small anions such as F\(^-\) and OH\(^-\), the lattice energy dominates with small cations such as transition metal ions (TM\(^{n+}\)), Mg\(^{2+}\), and Li\(^+\). Anion-cation size mismatch occurs with larger cations, such as Cs\(^+\) and Ba\(^{2+}\), which make soluble fluoride salts.
For small anions, $E_L$ is more sensitive to $r_+$, whereas $E_H$ does not depend on $r_+$ as strongly. For fluorides and hydroxides, LiF is slightly soluble whereas CsF is very soluble, and Mg(OH)$_2$ is insoluble whereas Ba(OH)$_2$ is very soluble.

Note

Putting both trends together, we see that low solubility is most often encountered when the anion and cation match well in their sizes, especially when one or both are multiply charged.

Combining the trends noted above:

1. Increasing size mismatch between the anion and cation leads to greater solubility, so CsF and LiI are the most soluble alkali halides.
2. Increasing covalency leads to lower solubility in the salts (due to larger $E_L$). For example, AgF, AgCl, AgBr, and AgI exhibit progressively lower solubility because of increasing covalency. $\{\text{AgF} > \text{AgCl} > \text{AgBr} > \text{AgI}\}$
3. Increasing the charge on the anion lowers the solubility because the increase in $E_L$ is large relative to the increase in $E_H$.
4. Small, polyvalent cations (having large $E_H$) make soluble salts with large, univalent anions such as $I^-$, NO$_3^-$, ClO$_4^-$, PF$_6^-$, and acetate. **Examples:** Salts of transition metal and lanthanide ions
   - Ln$^{3+}$: Nitrate salts are soluble, but oxides and hydroxides are insoluble.
   - Fe$^{3+}$: Perchlorate is soluble, but sulfate is insoluble.
5. Multiple charged anions such as $O^{2-}$, $S^{2-}$, PO$_4^{3-}$, and SO$_4^{2-}$ make insoluble salts with most M$^{2+}$, M$^{3+}$, and M$^{4+}$ metals.

**Contributors**

- Adapted from the Wikibook constructed by [Chemistry 310](https://www.pennstate.edu) students at [Penn State University](https://www.pennstate.edu).