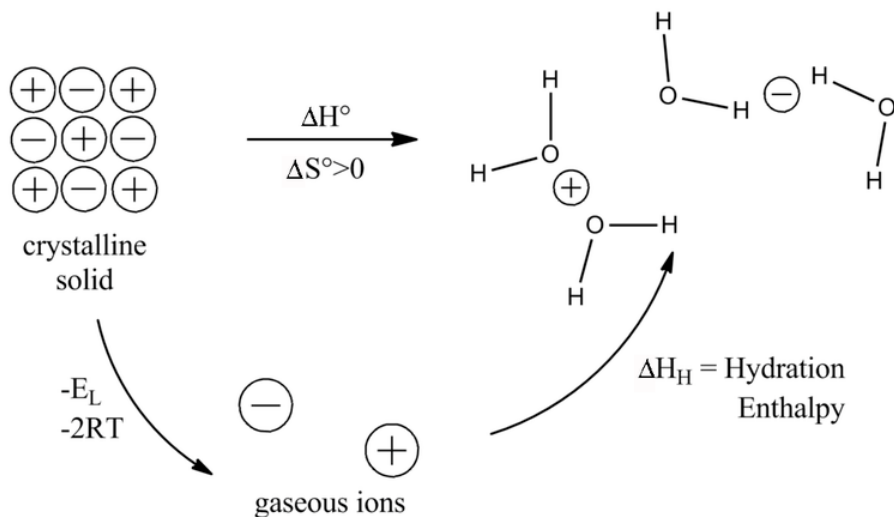


## 9.12: Lattice Energies and Solubility

Lattice energies can also help predict compound solubilities. Let's consider a Born-Haber cycle for dissolving a salt in water. We can imagine this as the sum of two processes: (1) the vaporization of the salt to produce gaseous ions, characterized by the lattice enthalpy, and (2) the hydration of those ions to produce the solution. The enthalpy change for the overall process is the sum of those two steps. We know that the entropy change for dissolution of a solid is positive, so the solubility depends on the enthalpy change for the overall process.



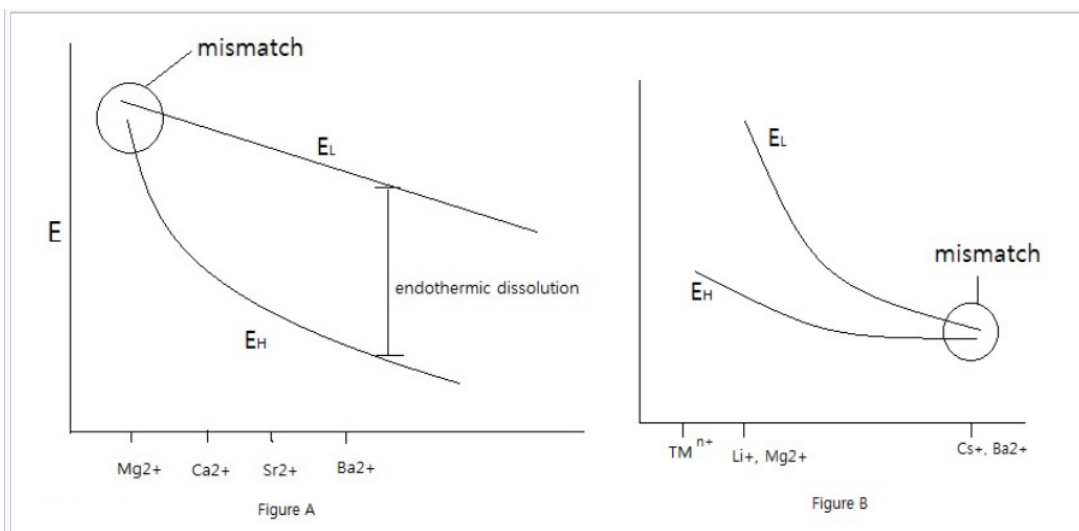
Here we need to consider the trends in both the lattice energy  $E_L$  and the hydration energy  $E_H$ . The lattice energy depends on the sum of the anion and cation radii ( $r_+ + r_-$ ), whereas the hydration energy has separate anion and cation terms. Generally the solvation of small ions (typically cations) dominates the hydration energy because of the  $1/r^2$  dependence.

$$E_L \propto \frac{1}{r_+ + r_-} \quad (9.12.1)$$

$$E_H \propto \frac{1}{r_+^2} + \frac{1}{r_-^2} \quad (9.12.2)$$

For salts that contain large anions,  $E_L$  doesn't 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.

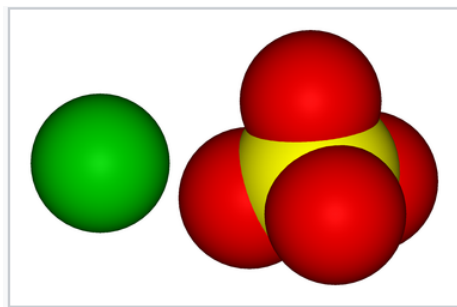
As a result, sulfate salts of small divalent cations, such as  $\text{MgSO}_4$  (epsom salts), are soluble, whereas the lower hydration energy of  $\text{Ba}^{2+}$  in  $\text{BaSO}_4$  makes that salt insoluble ( $K_{sp} = 10^{-10}$ ).



Left:  $E_L$  diagram for sulfate salts. The large  $\text{SO}_4^{2-}$  ion is size-mismatched to small cations such as  $\text{Mg}^{2+}$ , which have large hydration energies, resulting soluble salts. With larger cations such as  $\text{Ba}^{2+}$ , 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  $\text{F}^-$  and  $\text{OH}^-$ , the lattice energy dominates with small cations such as transition metal ions ( $\text{TM}^{n+}$ ),  $\text{Mg}^{2+}$ , and  $\text{Li}^+$ . Anion-cation size mismatch occurs with larger cations, such as  $\text{Cs}^+$  and  $\text{Ba}^{2+}$ , 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,  $\text{LiF}$  is slightly soluble whereas  $\text{CsF}$  is very soluble, and  $\text{Mg}(\text{OH})_2$  is insoluble whereas  $\text{Ba}(\text{OH})_2$  is very soluble.

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**.



Space-filling models showing the van der Waals surfaces of  $\text{Ba}^{2+}$  and  $\text{SO}_4^{2-}$ . The similarity in size of the two ions contributes to the low solubility of  $\text{BaSO}_4$  in water.

Combining all our conclusions about solubility, we note the following trends:

- 1) Increasing **size mismatch** between the anion and cation leads to greater solubility, so  $\text{CsF}$  and  $\text{LiI}$  are the most soluble alkali halides.
- 2) Increasing **covalency** leads to lower solubility in the salts (due to larger  $E_L$ ). For example,  $\text{AgF}$ ,  $\text{AgCl}$ ,  $\text{AgBr}$ , and  $\text{AgI}$  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  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{PF}_6^-$ , and acetate.

**Examples:** Salts of transition metal and lanthanide ions

- $\text{Ln}^{3+}$ : Nitrate salts are soluble, but oxides and hydroxides are insoluble.
- $\text{Fe}^{3+}$ : Perchlorate is soluble, but sulfate is insoluble.

5) Multiple charged anions such as  $\text{O}^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{PO}_4^{3-}$ , and  $\text{SO}_4^{2-}$  make insoluble salts with most  $\text{M}^{2+}$ ,  $\text{M}^{3+}$ , and  $\text{M}^{4+}$  metals.

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