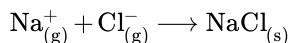


9.4: Born-Haber Cycles for NaCl and Silver Halides

Now that we have an equation for the lattice energy of an ionic crystal, we can ask the question of how accurate it is. Remember, we made several approximations in arriving at this formula. We assumed that the lattice was completely ionic, we ignored the van der Waals attractive energy of the ions, and we assumed that there was no covalent contribution to the bonding.

Let's consider the lattice energy of table salt (NaCl)



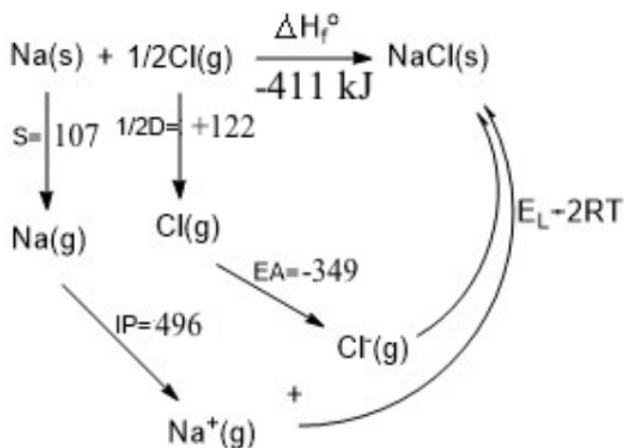
To calculate the lattice energy, we lump together the physical constants:

$$E_L \left(\frac{\text{kJ}}{\text{mol}} \right) = (1389.3) \frac{Aq_1q_2}{r_o} \left(1 - \frac{.345}{r_o} \right) \quad (9.4.1)$$

where r_o is expressed in Å. Now we can calculate the lattice energy for NaCl using $r_o = 2.814$ Å, as:

$$E_L = -(1389.3) \frac{1.7476}{2.814} \left(1 - \frac{.345}{2.814} \right) = -766.5 \frac{\text{kJ}}{\text{mol}} \quad (9.4.2)$$

We can alternatively construct a **Born-Haber cycle** for the formation of NaCl from the elements and calculate the lattice energy as the "missing" term in the cycle.



S= Sublimation energy of Na(s)

IP= Ionization potential of Na(g)

D= Bond dissociation energy of $\text{Cl}_2(\text{g})$

EA= Electron affinity of $\text{Cl}(\text{g})$

E_L =Lattice energy of NaCl

R= Gas constant

T= Absolute temperature

From **Hess' Law**: $\Delta H_f = s + \frac{1}{2}D + IP + EA + E_L - 2RT = -396 \frac{\text{kJ}}{\text{mol}}$

Here we have to subtract $2RT$ to convert our cycle of energies to a cycle of enthalpies, because we are compressing two moles of gas in making $\text{NaCl}(\text{s})$ and $P\Delta V = \Delta nRT$, where $\Delta n = -2$.

Experimentally ΔH_f for NaCl is **-411 kJ/mol**

Because all the other numbers in the cycle are known accurately, the error in our calculation is only about 15 kJ (about 2% of E_L). The result is promising because we neglected the van der Waals term.

But....how did we get away with neglecting the van der Waals term?

This is because we used **energy minimization** to obtain the repulsion energy in the Born-Mayer equation. If we underestimate the attractive energy of the crystal lattice, the energy minimization criterion ensures that the repulsion energy is underestimated as well. The two errors partially compensate, so the overall error in the calculation is small.

We can do better by explicitly including the short-range van der Waals attractive energy between ions. The table below shows results of more detailed lattice energy calculations for ionic fluorides in which the van der Waals term is explicitly included. The errors in this case are only about 1% of E_L .

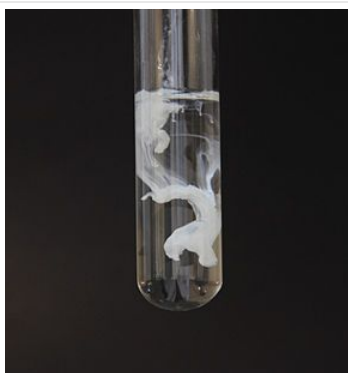
Compound	Calculated Lattice Energy (kJ/mol)	Experimental E_L from Born-Haber Cycle
MgF ₂ (rutile structure)	-2,920	-2,908
CaF ₂ (fluorite structure)	-2,586	-2,611
BaF ₂ (fluorite structure)	-2,326	-2,368

Silver Halides

It is interesting to repeat this exercise for the silver halides, which have either the NaCl structure (AgF, AgCl, AgBr) or zincblende structure (AgI).

Silver Halide	Calculated	Cycle	Difference (kJ/mol)
AgF	-920	-954	34
AgCl	-833	-908	75
AgBr	-816	-900	84
AgI	-778	-883	105

Looking at the table, we see that the error is small for AgF and becomes progressively larger for the heavier silver halides. However we are still obtaining answers within about 12% error even for AgI. Should we interpret the good agreement with values calculated from the ionic model to mean that these compounds are ionic? Clearly, this description is inappropriate for AgI, where the electronegativity difference $\Delta\chi$ is only 0.6 (compare this value to 0.4 for a C-H bond, which we typically view as non-polar).



A drop of silver nitrate solution, when added to a dilute hydrochloric acid solution, results in the immediate formation of a white silver chloride precipitate. This reaction is used as a qualitative test for the presence of halide ions in solutions. The covalent bonding contribution to the lattice energies of AgCl, AgBr, and AgI makes these salts sparingly soluble in water.

Again, we can interpret the fortuitous agreement between the calculated and experimentally obtained energies in terms of compensating errors. Our lattice energy calculation *overestimates* the ionic contribution in the case of the heavier silver halides, but *underestimates* the covalent contribution. Of these compounds, only AgF is soluble in water and should be thought of as an ionic compound. The others are progressively more insoluble in water (K_{sp} is 10^{-10} , 10^{-13} , and 10^{-16} for AgCl, AgBr, and AgI), reflecting increasing covalency as $\Delta\chi$ decreases.

The moral of the story is that simple lattice energy calculations based on the ionic model work well, but *they do not necessarily imply that the compounds are ionic!*

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