

# The reality of the lattice energy value<sup>1</sup>

The problem with the lattice energy value is it is only valid if the bond between the cation and the anion is purely ionic. There are very few pure ionic bonds. Most compounds have some percentage of covalent character. The addition of covalent character strengthens the bond and increases the lattice energy to a value larger than that calculated using Coulomb's law. A cation, such as transition elements, that does not have the electronic configuration of one of the noble gases, has empty valence atomic orbitals (p-orbitals) and is much more effective at pulling the electronic charged cloud of the anion into the region between the cation and anion nuclei and therefore of imparting covalent character to the bond, than is a cation that has a noble gas configuration (and filled p-orbitals) (groups 1A and 2A).

As an example, let us compare AgCl and NaCl. The value for the 'd' (distance of the radii) is 276pm for NaCl and 307pm for AgCl. Despite the somewhat larger 'd' for AgCl, the lattice energy for AgCl is larger than that of NaCl (904kJ/mol vs 788 kJ/mol)

While the sodium ion has the electronic configuration of neon, the silver ion does not have a noble gas configuration. There is significant covalent character to the bond in AgCl, while the bond in NaCl is essentially ionic. Because the bond in AgCl is ionic with partial covalent character, the lattice energy for AgCl is increased above that of NaCl. The greater cohesive forces in the AgCl crystal are largely responsible for the fact that AgCl has a very small solubility in water while NaCl is a soluble salt.

The larger the ion, the further its electron cloud extends out from its own nucleus, and the easier it is to pull the anionically charged cloud toward the cation. Larger anions are more polarizable than smaller anions. If we compare two crystals with the same cation but different anions, we can expect more covalent character in the cation-anion bond for the compound with the larger anion. Small highly charged cations are more effective polarizers of anions than larger, singly charged cations. For two cations of the same charge that do not have the electronic configuration of a rare gas (these are transition element) the smaller one has a greater charge density and is better polarizer of anions. Thus there is more covalent character to the bond in CuI than AgI. Because the copper(I) ion is smaller than the silver ion.

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<sup>1</sup> Segal, Bernice; chemistry page 82