6.4.5: Kapustinskii Equation

From the discussion above, it is clear that the lattice energy, E_L, of an ionic crystal can be calculated with reasonable accuracy if the structure is known. But how can we calculate E_L for a new or hypothetical compound of unknown structure? Recall that the reduced Madelung constant is about the same for different crystal structures. Russian chemist A. F. Kapustinskii recognized this fact and devised a formula that allows one to calculate E_L for any compound if we know the univalent radii of the constituent ions. [5]

The Madelung constant, A, is proportional to the number of ions (n) in formula unit, so dividing by the n gives similar values as shown in the table below:

A/n ~ invariant

Structure	A/n
NaCl	0.874
CsCl	0.882
Rutile	0.803
Fluorite	0.800

Kapustinskii noticed that the difference in ionic radii between M^+ and M^{2+} (the monovalent vs. divalent radius) largely compensates for the differences in A/n between monovalent (NaCl, CsCl) and divalent (rutile, CaF_2) structures. He thus arrived at a lattice energy formula using an average Madelung constant, corrected to monovalent radii. In the **Kapustinskii formula**, the lattice energy (kJ/mol) is given by:

$$E_L = \frac{1213.8 z_+ z_- n}{r_+ + r_-}\left(1 - \frac{0.345}{r_+ + r_-}\right) \tag{6.4.5.1}$$

Here the sum of the monovalent radii is used in place of r_o, the bond distance in the Born-Mayer equation. The beauty of this formula is that it requires no knowledge of the structure of the compound. Therefore it can be used, in combination with Born-Haber cycles, to predict the stability of unknown compounds. As we show below, this is a broadly useful tool in guiding syntheses and predicting the reactivity of inorganic solids.