# Preliminary Property Design for Ionic Solids and Liquids

### by Leslie Glasser

**In a recent Editorial in *IUCrJ*, Desiraju [1] characterised the three stages by which crystal engineering has developed: from crystal packing analysis, through crystal design strategies, to property design. He suggests that targeting properties has only recently come into its own, needing maturity at the earlier stages before its systematic development.**

However, there is one area of preliminary property design which has been available and active for many years and which is, in a sense, independent of structure. This is the prediction of the thermodynamic and thermomechanical properties of ionic materials (both solid and liquid), based upon their chemical composition and density alone—their very fundamentals! The utility of thermodynamic prediction is that it provides guidance for the direction of synthesis, suggesting when a proposed procedure might be viable, as compared to some pointless preparative process, and also that it provides a check on published values. These methods require minimal computation to add to their utility, nor do they require much expertise or experience in their successful operation. The methods are based on correlations with known values of the corresponding properties. Their independence of structure is both the best of procedures, since minimal information is required, while almost the worst of procedures, since no structural information results.

The initiating step in the development of these methods is due to A. F. Kapustinskii, [2] and is based upon the Born-Landé and Born-Mayer atomic interaction equations. Kapustinskii demonstrated that it is possible to estimate an ionic lattice energy, $U_{\mathrm{POT}}$, for a binary system using only the ionic charges and the cation-anion distance, <r>, computed as a sum of ion radii. To proceed to more complex ionic systems than binary, Glasser [3] introduced an ionic strength factor, *I*, to replace the Kapustinskii charge product,

$$|\nu z_+ z_-| \Rightarrow \sum_i n_i z_i^2 = 2I$$

and Jenkins, *et al.*, [4] (inspired by Mallouk, *et al.* [5]) further developed the procedure by replacing the cation-anion distance by the more general cube-root of formula volume, $V_m^{1/3}$ (which is derivable from density, available from X-ray structural determinations, or even estimated by ion volume summation). [6] The final result appears in the following equation:

$$U_{\mathrm{POT}} = \frac{A|\nu z_+ z_-|}{<r>}\left(1-\frac{\rho}{<r>}\right) \Rightarrow 2I\left(\frac{\alpha}{V_m^{1/3}}+\beta\right)$$

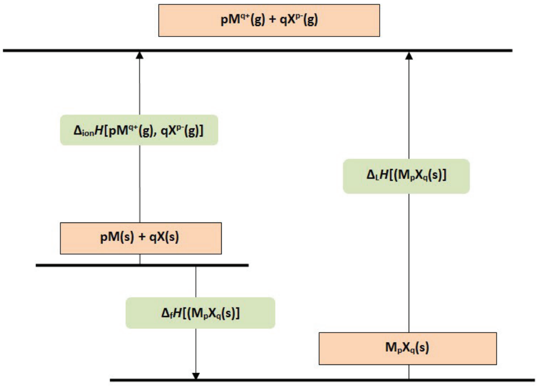
where *A* (= 121.4 kJ mol$^{-1}$ nm) is an electrostatic constant and ρ is a compressibility constant (usually chosen as ρ = 0.345 nm). The fitted constant α often approximates *A* while the fitted constant β approximates zero. The various fitted constants are listed in publications. [7]

For more complex materials, such as minerals, with lattice energies greater than ~5000 kJ mol$^{-1}$, an even more general expression was found: [8]

$$U_{\mathrm{POT}} = AI(2I/V_m)^{1/3}$$

This expression has the remarkable feature that it contains no adjustable constants whatsoever!

Once the lattice energy is determined (and trivially converted to a lattice enthalpy, $\Delta_L H$) [9], it becomes possible to complete a Born-Haber-Fajans thermochemical cycle, from which the thermodynamic quantities for the reaction are determined. This process has been termed "Volume-Based Thermodynamics" (VBT). [10]



Born-Haber-Fajans Thermochemical Cycle

We have further found that entropy, *S* [11], and heat capacity, $C_p$ [12], may be estimated using direct linear correlations:

$$S/\mathrm{JK^{-1}mol^{-1}} = kV_m + c$$

and

$$C_p/\mathrm{JK^{-1}mol^{-1}} = k'V_m + c'$$

$C_p$ has an upper limit of about 25$n$ J K$^{-1}$ mol$^{-1}$, where $n$ = number of atoms in the formula unit and 25 J K$^{-1}$ mol$^{-1}$ is the Dulong-Petit limiting heat capacity per atom.

Since the lattice energy calculation is independent of structure, it has been no great leap to apply the method to amorphous materials [13] and, indeed, to the increasingly important class of ionic liquids [14] with appropriate fitted constants for lattice energy and viscosity, $\eta$.

An important question to be considered is why these simple correlation methods work, independent of structure (although it must be recognised that density, or formula volume, already implicitly contains structural information). The predominant interactive force in ionic materials is the electrostatic (Coulombic or Madelung) interaction, [15] where the charges tend to group themselves so as to balance their overall charge locally, with repulsive van der Waals's forces acting over short distances preventing the collapse of the charge system. These repulsive forces are rather similar, even between different species, and so reflect volume changes rather similarly, leading to simple volume relationships.

## Acknowledgement

The correlations developed rely, of course, on the work of our predecessors in providing the data used to establish the thermodynamic parameters by their careful and laborious computations.

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