

Estimation of the Thermodynamics of Ionic Materials

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Thermodynamics provides the primary information regarding the feasibility of synthesis and stability of materials, principally through the quantities: heat capacity, C_p ; entropy, S ; enthalpy of formation, $\Delta_f H$; the Gibbs energy of formation, $\Delta_f G$, and amplified by lattice energy, $\Delta_L U$. Values of such properties for many materials are readily available from extensive tabulations, whether printed, [1,2] online [3] or from software [4]. However, experimental thermodynamics is currently unfashionable because it is difficult and requires advanced technical skills for its performance, so that the growth of such published values falls far behind the preparation of materials. Furthermore, such tabulations can inherently not list the properties of as-yet unsynthesised and hypothesised materials. For these reasons, there is an important and permanent place for estimation methods.

Simple estimation methods for gases based on the extensive database of known values have been established. These consist of the methods of group contributions [3] together with statistical mechanics, relying on the independence of the molecules from one another. The problem for condensed phases is more intractable because account must also be taken of the interactions between species. Molecular mechanics and quantum mechanics are available computational tools for estimation, but both are somewhat problematic for general use, because of the necessity to establish appropriate force fields (for the former) and their general complexity in operation.

However, it has been recognised over recent years that the properties of ionic materials are rather simple because they are dominated by the long-range coulombic (charge) and short-range repulsive forces present, with relatively minor contributions from other interactions. This implies that detailed consideration of the structures of ionic materials is unnecessary, so that simple relations may be expected between ionic materials, based solely on their charge identities and the closeness of packing of their charges - that is, on their formula volumes. This realisation has resulted in the preparation of tables of single-ion values for volume, [5] heat capacity, [6] entropy, [7] enthalpies of formation and Gibbs energies of formation [8] which are simply additive, yet yield reliable results. Furthermore, it has been demonstrated for numerous ionic solids and

even ionic liquids that there are excellent linear correlations between formula volume and these same thermodynamic properties; [9,10] we have named estimations by these means as "Volume-Based Thermodynamics" (VBT). This is a particularly valuable resource since the basic variable of formula volume is the most readily available thermodynamic quantity: through measurement of density; from structure by x-ray diffraction; through simple differences among related materials; or even simple estimation by single-ion addition. This additivity can even be taken further, through various "difference rules" [11-13] between related species and the "Simple Salt Approximation" (SSA), [14] whereby the properties of simple constituent salts are summed to yield the properties of a more complex salt (for example: $MgO \cdot Al_2O_3 \rightarrow MgAl_2O_4$; spinel). These methods are sufficiently simple to be used (with care and consideration) to yield reliable results even in unpracticed hands, and as a check on not-always reliable published values.

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