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Predictive thermodynamics for ionic solids and liquids†

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The application of thermodynamics is simple, even if the theory may appear intimidating. We describe tools, developed over recent years, which make it easy to estimate often elusive thermodynamic parameter values, generally (but not exclusively) for ionic materials, both solid and liquid, as well as for their solid hydrates and solvates. The tools are termed volume-based thermodynamics (VBT) and thermodynamic difference rules (TDR), supplemented by the simple salt approximation (SSA) and single-ion values for volume, V_m, heat capacity, C_p°, entropy, S_{298}°, formation enthalpy, $\Delta_f H^\circ$, and Gibbs formation energy, $\Delta_f G^\circ$. These tools can be applied to provide values of thermodynamic and thermomechanical properties such as standard enthalpy of formation, $\Delta_f H^\circ$, standard entropy, S_{298}°, heat capacity, C_p, Gibbs function of formation, $\Delta_f G^\circ$, lattice potential energy, U_{POT}, isothermal expansion coefficient, α, and isothermal compressibility, β, and used to suggest the thermodynamic feasibility of reactions among condensed ionic phases. Because many of these methods yield results largely independent of crystal structure, they have been successfully extended to the important and developing class of ionic liquids as well as to new and hypothesised materials. Finally, these predictive methods are illustrated by application to K_2SnCl_6, for which known experimental results are available for comparison. A selection of applications of VBT and TDR is presented which have enabled input, usually in the form of thermodynamics, to be brought to bear on a range of topical problems. Perhaps the most significant advantage of VBT and TDR methods is their inherent simplicity in that they do not require a high level of computational expertise nor expensive high-performance computation tools – a spreadsheet will usually suffice – yet the techniques are extremely powerful and accessible to non-experts. The connection between formula unit volume, V_m, and standard thermodynamic parameters represents a major advance exploited by these techniques.

Introduction

Consider what obliges one to attempt to estimate the properties of a known inorganic material or predict the properties of an as-yet unprepared material. Examine the complexities! There are about 100 chemical elements, which combine to form about 100 million already-known compounds, of which some 10% could be classified as inorganic/mineral.[1] There remains an almost limitless range of possible combinations as yet unexplored. By contrast, the most comprehensive current crystallographic databases report data on only about one million of these organic compounds and on only about one-quarter of a million inorganic compounds.[2] Ionic liquids are combinations of such a broad range of cations and anions so that the in-principle possible number of such liquids is of the order of 10^{18} (although the realistically possible number is orders of magnitude smaller) – already, some 1000 have been reported in the literature.[3] On the other hand, thermodynamic data is available for only some 30 000 compounds, of which about 60% (20 000) are inorganic (see ESI† for a list of thermodynamic data compendia). Thus, the chance of finding the property data one seeks is miniscule; add to this, the need to obtain data on as-yet unprepared material, such as might be required for a proposed synthesis. As a consequence, a number of simple empirical rules have been developed for a variety of thermodynamic properties (see Table 1).

The most basic data that needs to be obtained for this essentially unlimited set of materials is thermodynamic because such data informs us of the stability of the materials, our ability to synthesise them, and to maintain their integrity. In the absence of published data, the question then arises as to how one should proceed in order to obtain that data.

The most fundamental approach would be through quantum mechanical (QM) calculation,[10] where one considers in detail

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how the fundamental particles of which a material consists, such as atoms and electrons, interact with one another through electrostatic forces, charge transfer, van der Waals (dispersion) interactions, electron correlation, and so forth. While such an approach has yielded important results, it is complex, uses expensive computation facilities, and requires considerable expertise in both application and interpretation. At a somewhat simpler level, density functional theory (DFT)[11] has reduced the complexity of QM methods and, hence, their cost by relating the energetics to the more readily computable electron density of the material and using functions of the electron density function (that is, functionals) to derive experimentally observable results. DFT has found increasing favour in recent years in providing useful results but difficulties remain in dealing with dispersion and electron correlation. Thus, in stark contrast to the VBT approach, these QM approaches require considerable expertise to execute and interpret reliably.

A rational response has been to collect data on related materials and use that data to extrapolate (or interpolate) in order to estimate the properties of the material under investigation. We illustrate this approach in some general terms first, and then focus on an approach which we have termed volume-based thermodynamics (VBT)[12,13] together with the thermodynamic difference rule (TDR),[9,14–16] both of which we and colleagues have developed and fostered over the last two decades. These empirical procedures have proven to have great generality and utility, and have been widely implemented for ionic solids and liquids,[17] as also illustrated in a list of applications in the final section of this paper. One further very successful method is the "Simple Sum Approximation" (SSA)[18] where the thermodynamic properties of a complex ionic, such as $MgSiO_3$, is treated as a sum of its components, being the oxides MgO and SiO_2 in this case.

Prediction basically relies on the combination, through the Gibbs relation, of enthalpy, H, and entropy, S, contributions:[19]

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

VBT and TDR provide estimates of values of standard enthalpy, $\Delta_f H^\circ$, standard entropy, S°_{298}, and hence, *via* eqn (1) lead to the prediction of $\Delta_f G^\circ$ for individual materials as well as $\Delta_r G^\circ$ for a reaction of interest. It is often of little concern that such estimates may not be highly precise, since the purpose of thermodynamic prediction may, in many instances, simply be one of assessing synthetic feasibility or otherwise, *i.e.*, simply whether $\Delta_r G$ is negative (feasible) or positive (infeasible in principle, although a small positive value, say $\sim$20 kJ mol^{-1}, does not preclude formation of useful proportions of product which can be extracted from the reaction system).[20] Furthermore, experimentally-derived thermodynamic values themselves can have considerable uncertainties.[21–23] The actual mathematics required is minimal yet quantitative interpretation results. This review summarises VBT, TDR, SSA, and single-ion additivity, and highlights many of their successes – indeed, the scope of their application has proved to be quite remarkable – and directs the reader to numerous applications where these procedures have played a significant role in yielding the thermodynamics.

In essence, VBT [together with its isomegethic ("equal size") rule,[24] which vastly extends its application to new and hypothesised materials] relates the formula unit volumes, V_m, of materials, however measured or estimated, to their thermodynamic quantities, thereby leading to practical prediction. TDR uses the differences between related materials to predict values for other similar materials, while the additive SSA and single-ion values (and also TDR, in a slightly more complex way) demonstrate that the properties of complex materials may be estimated by summing the corresponding properties of their component parts.

Group additivity methods

Group methods operate by assuming that a material (typically, but not exclusively, an organic molecule) contains independent entities (such as single bonds, double bonds, alcohol, amine, *etc.*) whose thermodynamic property values can be summed to produce a property value for the whole material, but supplemented

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Table 1 Some empirical thermodynamic and volume rules

Rule	Thermodynamic property	Value	Ref.
Dulong and Petit and Neumann–Kopp summation: heat capacity	C_p, per mole for atoms in solids	$\approx 3R \approx 25$ J K^{-1} mol^{-1} where R is gas constant	4
Trouton: vaporization	$\Delta_{vap}S^\circ$ for organic molecules and non-polar liquids $\Delta_{vap}H^\circ$ for organic molecules and non-polar liquids For hydrogen bonding in liquids	$\Delta_{vap}S^\circ$/J K^{-1} mol^{-1} $\approx$ 85 $\Delta_{vap}H^\circ$/kJ mol^{-1} $\approx 85T_b$/K T_b = boiling point $\Delta_{vap}H^\circ$/kJ mol^{-1} $> 85T_b$/K	
Walden: fusion	$\Delta_{fus}S^\circ$ for rigid non-spherical molecules	$\approx$20–60 J K^{-1} mol^{-1}	
Richards: fusion	$\Delta_{fus}S^\circ$ for rigid spherical molecules	$\approx$7–14 J K^{-1} mol^{-1}	5
Glasser & Jenkins: C_p, for silicate anions	Single ion heat capacity, C_p, for silicate anions	$\approx 13.8n$ where n is the number of atoms contained within the silicate anion	6
Glasser & Jenkins: C_p for general anions	Single ion heat capacity, C_p for general anions	$\approx 17n$ where n is the number of atoms contained within the anion	6
Westwell, Searle, Wales & Williams: sublimation enthalpy from melting point	$\Delta_{subl}H^\circ$ for molecules that do not possess internal rotors, such as long chain organic molecules	$\Delta_{subl}H^\circ$/kJ mol^{-1} = 0.188T_m/K + 0.522 T_m = melting point R^2 = 0.90	7
Westwell, Searle, Wales & Williams: sublimation enthalpy from boiling point	$\Delta_{subl}H^\circ$ for molecules that do not possess internal rotors, such as long chain organic molecules	$\Delta_{subl}H^\circ$/kJ mol^{-1} = 0.119T_b/K + 1.38 T_b = boiling point R^2 = 0.96	
Westwell, Searle, Wales & Williams: vaporization enthalpy of solids	$\Delta_{vap}H^\circ$ for molecules that do not possess internal rotors, such as long chain organic molecules	$\Delta_{vap}H^\circ$/kJ mol^{-1} = 0.166T_m/K − 3.99 T_m = melting point R^2 = 0.86	
Westwell, Searle, Wales & Williams: vaporization enthalpy of liquids	$\Delta_{vap}H^\circ$ for molecules that do not possess internal rotors, such as long chain organic molecules	$\Delta_{vap}H^\circ$/kJ mol^{-1} = 0.108T_b/K − 5.08 T_b = boiling point R^2 = 0.98	
Westwell, Searle, Wales & Williams: T_b from T_m	T_b from T_m for molecules that do not possess internal rotors, such as long chain organic molecules	T_b/K = 1.52T_m/K + 14.5 T_b = boiling point T_m = melting point R^2 = 0.86	
Westwell, Searle, Wales & Williams: vaporization and sublimation enthalpies	$\Delta_{vap}H^\circ$ for molecules that do not possess internal rotors, such as long chain organic molecules	$\Delta_{vap}H^\circ$/kJ mol^{-1} = 0.889$\Delta_{subl}H^\circ$/kJ mol^{-1} − 4.75 R^2 = 0.98	
Kempster & Lipson; Glasser & Jenkins: formula unit volume	V_m mainly for organic solids V_m for water	$V_m \approx 0.018$ nm^3 per atom $V_m \approx 0.0245$ nm^3	8 (see Table 3)[9]

by other terms to allow for the interactions between and among groups. (An extensive list of group methods is presented in our ESI.†) The most developed of these are termed Benson group methods.[25] In order to permit broad application of the methods, it has been necessary to develop hundreds of group terms, with the further complication of the necessity for the user to identify suitable groups within the material under consideration. Many computer programs incorporate these methods, often as preliminary steps to a more complex analysis. The NIST WebBook[26] provides a free service which implements the Benson group additivity scheme for gas-phase organic molecules.

Group methods have also been developed for ionic systems, by identifying constituent cations and anions whose properties are summed to provide the overall property value sought. The results are most reliable when based on related materials. In general, these methods have not received wide acceptance.

Volume-based thermodynamics

Early thermodynamic property-size relations were generally based upon ion radii since the alkali metal and halide monatomic ions of the most important alkali halides are spherical and radius, which could be quite readily established from X-ray data, was the most obvious measure of relative ion size. An important equation in this context was the Kapustinskii relation[27] for lattice potential energy, U_{POT}:

$$U_{POT} = \frac{A|\nu z_+ z_-|}{\langle r \rangle}\left(1 - \frac{\rho}{\langle r \rangle}\right) \quad (2)$$

where z_+, z_-/electron units are the integer charges on the cations and anions, respectively, ν is the number of ions per formula unit, ρ is a compressibility constant (usually chosen as ρ = 0.345 nm), $\langle r \rangle$ is the sum of the cation and anion radii (which is often equated to the shortest cation–anion distance found in the lattice), and A (=121.4 kJ mol^{-1} nm) is an electrostatic constant. While the contact distance, $\langle r \rangle$, between cation and anion is a straightforward sum for simple ions, it becomes ill-defined when complex ions are present. In addition to this conceptual problem, the Kapustinskii equation cannot be applied beyond binary materials because (i) there is no

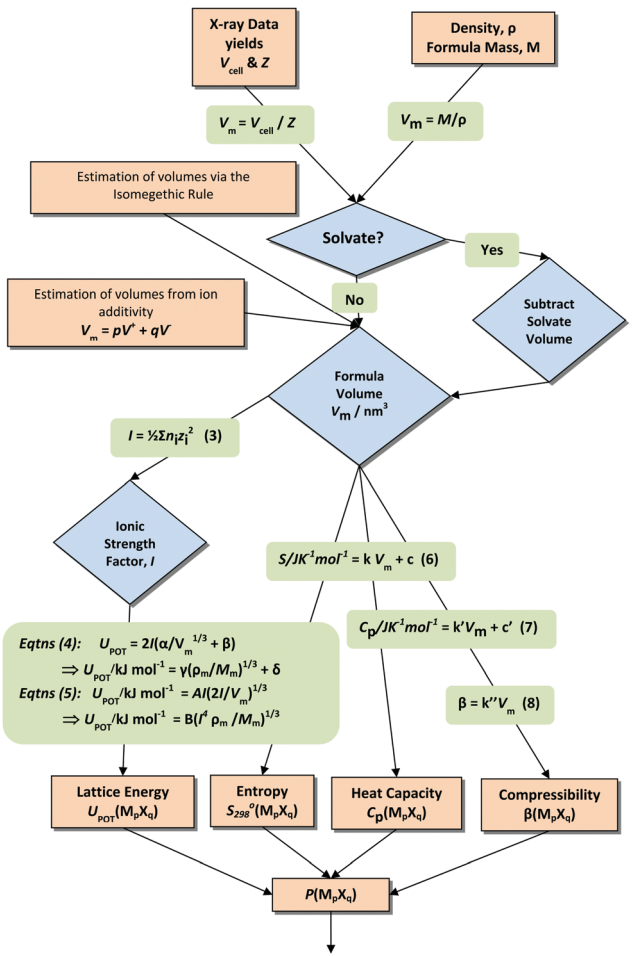
provision for more than one type of cation–anion contact, nor (ii) can more than a pair of charge types be accommodated.

Mallouk, Bartlett and coworkers[28–31] presented some relationships between formula unit volume, V_m and thermodynamic properties (notably lattice energy, U_{POT}, as a function of $V_m^{-1/3}$) and standard entropy, S°_{298} (as a function of V_m) but only for a handful of MX (1 : 1) simple salts. Jenkins, Roobottom, Passmore and Glasser[32] explored these relationships further, by (i) replacing the distance sum with the equivalently-dimensioned cube-root of the formula unit volume, $V_m^{1/3}$, and (ii) using a generalisation of the charge product[33] into an ionic strength factor-type summation, I:

$$|\nu z_+ z_-| \Rightarrow \sum_i n_i z_i^2 = 2I \qquad (3)$$

where n_i = number of ions of type i in the formula unit.

Scheme 1 summarises the processes and equations which use material volumes to produce thermodynamic values.



Scheme 1 Volume-based thermodynamics (VBT) flowchart. Data sources of various kinds are used to generate a formula unit volume, V_m, from which thermodynamic properties are estimated. $P(M_pX_q)$ represents any thermodynamic property, P, of the material M_pX_q. α, β, γ, δ, A, B, k, c, c', k' and k'' represent various constants obtained by fitting to experimental data. Eqn (4)–(8) appear in this scheme.

Lattice energies for a large database of simple ionic solids could be reliably correlated using this linear VBT function:[34]

$$U_{POT} = 2I\left(\frac{\alpha}{V_m^{1/3}} + \beta\right) \qquad (4, \text{Scheme1})$$

where α and β are empirical constants which differ depending on stoichiometry, and have been determined by fitting to extensive experimental data.[32] It is noteworthy that the fitted constant, α, is found always to be close in value to the electrostatic factor, A, in eqn (2), above.

Equivalent equations may be couched in terms of density, ρ_m, and formula mass, M_m:

$$U_{POT}/\text{kJ mol}^{-1} = \gamma(\rho_m/M_m)^{1/3} + \delta \qquad (4, \text{Scheme 1})$$

$$U_{POT}/\text{kJ mol}^{-1} = B(I^4\rho_m/M_m)^{1/3} \qquad (5, \text{Scheme 1})$$

where B is a combined constant.

For lattice energies greater than 5000 kJ mol^{-1}, which includes most minerals, a limiting version[35] of this equation exists which contains no empirical constants whatsoever and yet satisfactorily predicts lattice energies up to 70 000 kJ mol^{-1} and probably beyond:

$$U_{POT} = AI(2I/V_m)^{1/3} \qquad (5, \text{Scheme 1})$$

Lattice energy is readily converted to lattice enthalpy[36] (as it needs to be if it is to be included in an enthalpy-based thermochemical cycle such as that in Fig. 1 below) using the equation:

$$\Delta_L H = U_{POT} + \sum_{i=1}^{n} s_i\left(\frac{c_i}{2} - 2\right)RT \qquad (9)$$

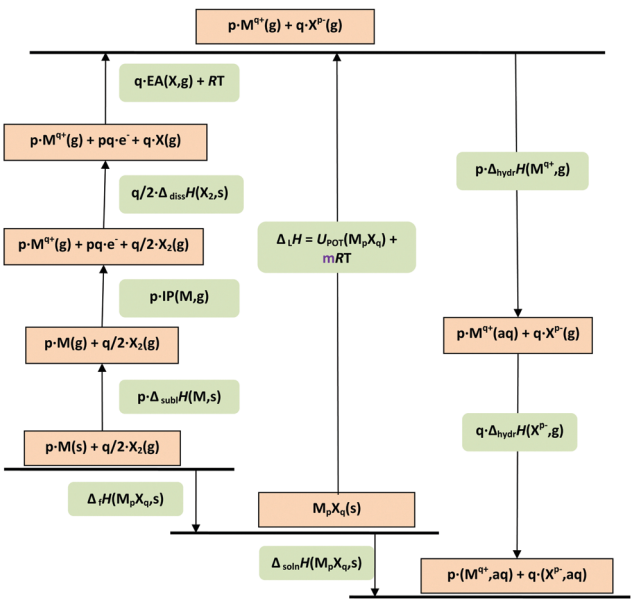
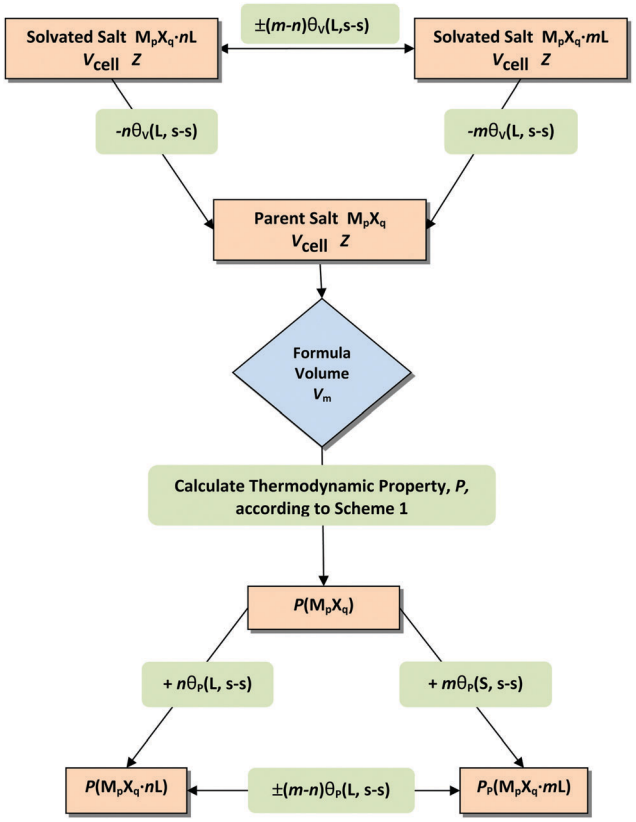


Fig. 1 Born–Haber–Fajans cycle for solids and aqueous solutions of formula M_pX_q. IP = ionisation potential; EA = electron affinity; lattice enthalpy ($\Delta_L H$) and enthalpies of formation ($\Delta_f H$), sublimation ($\Delta_{subl}H$), dissociation ($\Delta_{diss}H$), hydration ($\Delta_{hydr}H$), and solution ($\Delta_{soln}H$) are involved. U_{POT} represents the lattice potential energy. In the formula for $\Delta_L H$, m depends on p and q and the nature of the ions M^{q+} and X^{q-} (see eqn (9) in text).[36]



Scheme 2 Thermodynamic difference rule (TDR) flowchart. The volume of addend or solvate, *L*, is subtracted to generate the volume of the parent material:

$$V(M_pX_q{\cdot}nL) - nV(L) = V(M_pX_q) \qquad (10)$$

from which the thermodynamic property, *P*, is calculated. Finally, the thermodynamic property value, $\theta_P(L, s{-}s)$, of the addend or solvent (which may be water) is added (where "s–s" represents that the difference, θ_P, between materials each in the same phase, often solid).

where $\Delta_L H$ is the lattice enthalpy, n is the number of ion types in the formula unit, s_i is the number of ions of type i, and c_i is defined according to whether ion i is monatomic ($c_i = 3$), linear polyatomic ($c_i = 5$), or nonlinear polyatomic ($c_i = 6$).

Using these approaches, it becomes simple to evaluate the lattice energies, U_{POT} (and enthalpies of formation, $\Delta_f H^\circ$, *via* the Born–Haber–Fajans relation) of ionic solids.

Thermodynamic difference rule (TDR)

The thermodynamic difference rule, TDR, is a complementary set of procedures which utilizes additive connections among related materials.[9,12–16] Scheme 2 shows the steps by which TDR is usually applied. The technique is extremely powerful as a result of its ability to enable estimates to be made of thermodynamic data not otherwise available.

$$P(M_pX_q{\cdot}nL,s) - P(M_pX_q,s) = n\theta_P(L, s{-}s) \qquad (11a)$$

$$P(M_pX_q{\cdot}mL,s) - P(M_pX_q{\cdot}nL,s) = (m - n)\theta_P(L, s{-}s) \qquad (11b)$$

Thus, various thermodynamic state properties may be estimated as, for example, the lattice energies of hydrates using the thermodynamic difference rule relation:

$$U_{POT}(M_pX_q{\cdot}nH_2O,c) - U_{POT}(M_pX_q,c) = n\theta_U(H_2O) \qquad (12)$$

with $\theta_U(H_2O)$ = 54.3 kJ mol^{-1}, as empirically determined. Table 2 lists values for the fitted constants for various groups of materials, while Table 3 lists values pertaining to the hydrate TDR rules. TDR constants for other solvates may be found in Table 1 in the literature referenced.[9] An important recent paper considers the thermodynamics of hydration in minerals.[37]

Room-temperature ionic liquids

Room-temperature ionic liquids (RTILs)[38–41] can replace organic solvents used for the dissolution of both polar and non-polar solutes and for processing or extraction of materials, while also having useful catalytic features.[42] ILs are low-polluting, with low combustibility, good thermal stability and low vapour pressures. They have high viscosities, and their liquid range can often cover several hundred degrees. The range of their applications has been extended by use of mixtures of IL's[43] and as supercritical fluids.[44]

As their name implies, they are usually liquid at ambient temperatures and consist solely of ionic species. In order to reduce the lattice energy of their crystalline state and hence their melting point, one or sometimes both of their cations and anions need to be large and their cations also often have low symmetry. The cations are generally organic with long-chain features and buried charges, such as the pyrollidinium, methylimidazolium and pyridinium cations (see Fig. 2) while the anions, such as BF_4^-, PF_6^-, or NTf_2^- [formula: $(CF_3SO_2)_2N^-$] have diffuse charges.

Since there are, as noted above, many possible combinations of cation and anion, it becomes possible to consider designing ionic liquids to purpose. Although early QSAR predictions[45–47] were not always regarded as satisfactory,[48] molecular volume[49] has emerged as an important observable. Thus, Glasser[38] has estimated a VBT-based entropy for ionic liquids, derived from correlations for both inorganic solids and organic liquids:

$$S\ (J\ K^{-1}\ mol^{-1}) = 1246.5(V_m/nm^3) + 29.5 \qquad (13)$$

Similarly, Gutowski, *et al.*,[50–52] have developed a lattice energy correlation for 1 : 1 ionic liquids, with amended constants (eqn (4), Scheme 1): I = 1, α = 8326 kJ nm mol^{-1} and β = 157 kJ mol^{-1}.

VBT relations have now been used to establish other physical thermodynamic properties, independent of crystal structure, such as liquid entropy,[53] melting point,[54–56] heat capacity[57] and critical micelle concentration (c.m.c.).[58] A recent review by Beichel[59] cites relevant literature from the Krossing laboratory; in order to emphasize lack of reliance on any experimental input at all, this group has introduced the term "augmented volume-based thermodynamics".

An explanation for the simple volume relations

The striking simple relations to volume involved in VBT, almost independent of structure, upon which we have reported invite some explanation. We suggest that the bulk thermodynamic

Table 2 Constants for a selection of volume-based thermodynamic relations

Material	Ionic strength factor, I	α/kJ mol^{-1} (nm^3 formula unit^{-1})$^{-1/3}$	β/kJ mol^{-1}	Mean absolute error (%)
Lattice energy from volume data, U_{POT}/kJ mol^{-1} = $2I(\alpha/V_m^{1/3} + \beta)$ (4)				
MX (1 : 1)	1	117	52	4
MX_2 (2 : 1)	3	134	61	
M_2X (1 : 2)	3	165	−30	
MX (2 : 2)	4	119	60	
M_pX_q	$\frac{1}{2}(pq^2 + qp^2)$	139	28	

Material	Ionic strength factor, I	γ/kJ mol^{-1} cm^{-1}	δ/kJ mol^{-1}	Mean absolute error (%)
Lattice energy from density data, U_{POT}/kJ mol^{-1} = $\gamma(\rho/M)^{1/3} + \delta$ (5)				
MX (1 : 1)	1	1981.2	103.8	4
MX_2 (2 : 1)	3	8375.6	−178.8	
M_2X (1 : 2)	3	6764.3	365.4	
MX (2 : 2)	4	6864.0	732.0	
M_pX_q	$\frac{1}{2}(pq^2 + qp^2)$	2347.6 × I	55.2 × I	

	k/J K^{-1} mol^{-1} (nm^{-3} formula unit)	c/J K^{-1} mol^{-1}	Mean absolute error (%)
Entropy, S/J K^{-1} mol^{-1} = $kV_m + c$ (6)			
Anhydrous ionic salts	1360 ± 56	15 ± 6	12
Hydrated ionic salts	1579 ± 30	6 ± 6	7.4
Organic liquids	1133 ± 7	44 ± 2	5.7
Organic solids	774 ± 21	57 ± 6	10.4

	k'/J K^{-1} mol^{-1} (nm^{-3} formula unit)	c'/J K^{-1} mol^{-1}	Mean absolute error (%)
Heat capacity, C_p/J K^{-1} mol^{-1} = $k'V_m + c'$ (7)			
Non-framework silicates	1465	11	
General ionic solids[a]	1322	−0.8	24.5
Ionic liquids	1037	45	

	k''/GPa^{-1} (nm^{-3} formula unit)	Mean absolute error (%)
Isothermal compressibility, β/GPa^{-1} = $k''V_m$ (8)		
General ionic solids (no alkali halides)	0.634	12
Perovskites	0.472	7

[a] C_p values have been estimated for 799 materials, ranging from small ionics to large mineral structures. Poor outliers may be avoided by using the lesser of the calculated value from eqn (7) and the approximate limiting Dulong–Petit value of 25 × m J K^{-1} mol^{-1}, where m = number of atoms in the formula unit (*cf.* Table 1).

Table 3 Thermodynamic difference values, θ_P, for hydrates for property P: $P(M_pX_q{\cdot}nH_2O) - P(M_pX_q) = n\theta_P(H_2O,s\text{–}s)$[a]

Thermodynamic property, P	θ_P[9]
V_m/nm^3 (mol of H_2O)$^{-1}$	0.0245
U_{POT}/kJ (mol of H_2O)$^{-1}$	54.3
$\Delta_f H$/kJ (mol of H_2O)$^{-1}$	−298.6
$\Delta_f S$/J K^{-1} (mol of H_2O)$^{-1}$	−192.4
$\Delta_f G$/kJ (mol of H_2O)$^{-1}$	−242.4
S°_{298}/J K^{-1}(mol of H_2O)$^{-1}$	40.9
C°_{p298}/J K^{-1}(mol of H_2O)$^{-1}$	42.8[16]

[a] A more complete table, including values of θ_P for solvates other than H_2O, has been published.[16]

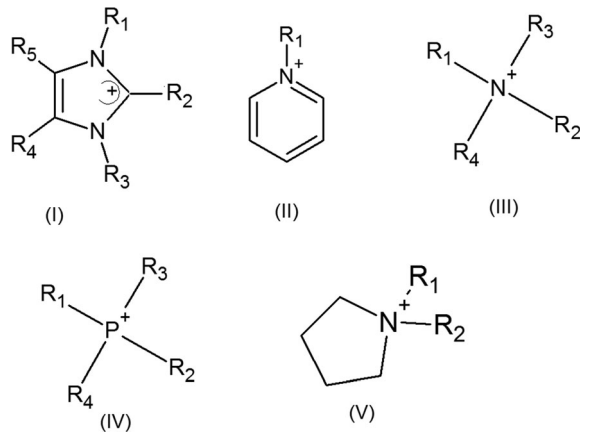


Fig. 2 Principal cations involved in important ionic liquids. (I) Imidazolium cations, (II) pyridinium cations, (III) tetraalkylammonium cations, (IV) tetraalkylphosphonium cations, and (V) pyrollidinium cations.

properties derive from the interactions between the particles involved (complex ions or even molecules) rather than within those particles.[60] For ionic materials, the interactions are largely coulombic (electrostatic or Madelung energies) with lesser contributions from specific repulsion and van der Waals-type interactions so that (to the approximation inherent in our correlations) the interactions are similar, independent of the specific species involved and also independent of structure. At this level of approximation we have found that the thermodynamic values that emerge prove adequate, in the majority of cases, for deciding questions of alternative synthetic routes for the preparation of inorganic materials.

Table 4 Single-ion additive volumes, entropies and heat capacities for a range of inorganic cations and anions. Note that the values listed for H_2O were used as reference values in the optimizations to generate these single-ion values

Cation	Volume/ nm^3	S°_{ion}/J K^{-1} mol^{-1}	$C_p(298)_{ion}$/ J K^{-1} mol^{-1}	$-\Delta_f H(298)$/ kJ mol^{-1}	$-\Delta_f G(298)$/kJ mol^{-1}	Anion	Volume/ nm^3	S°_{ion}/J K^{-1} mol^{-1}	$C_p(298)_{ion}$/ J K^{-1} mol^{-1}	$-\Delta_f H(298)$/ kJ mol^{-1}	$-\Delta_f G(298)$/ kJ mol^{-1}
NH_4^+	0.0356	67.0				F^-	0.014	20.6		5	5.0
Li^+	0.0067	19.4	21.1	308.7	259.8	Cl^-	0.0298	36.1	23.5	110.8	113.7
Na^+	0.0158	37.2	29.7	278.3	232.2	Br^-	0.0363	48.6	26.6	66.3	70.6
K^+	0.0277	50.5	31.4	316	258.7	I^-	0.0488	56.8	28.3	−8.2	0.0
Rb^+	0.0341	63.1	31.3	311.7	257.4	N_3^-	0.0416	54.8			
Cs^+	0.042	69.2	31.7	315.4	260.4	O^{2-}	0.0134	7.4			
Ag^+			29.9			OH^-	0.0184	20.7	21.2	228.6	247.9
Mg^{2+}	0.0049	20.5	26.1	491.4	374	S^{2-}	0.032	22.1			
Ca^{2+}	0.0201	32.5	28.9	579.8	468.2	ClO_3^-			70.1	68.5	
Sr^{2+}	0.0213	37.9	30.3	627.2	558.7	BrO_3^-			76.1	39.7	
Ba^{2+}	0.027	55.1	30.2	655	570.1	CO_3^{2-}	0.0426	52.6	57.5	594.3	582.7
Mn^{2+}			30.4	262.9	161.3	NO_3^-	0.0492	78.5			
Fe^{2+}	0.0067	38.6	31.8	138.5	32.3	PO_4^{3-}	0.057	71.8			
Zn^{2+}	0.0125	37.3				SO_4^{2-}	0.0611	74.3	71.5	812.2	802.3
Cu^{2+}	0.0053	33.5				ClO_4^-	0.0619	105.8	134.9		
Ni^{2+}	0.0004	29.6		126.7		MnO_4^-	0.0665				
Co^{2+}	0.0019	39.5	32.0	161.8		AsO_4^{3-}	0.0658				
Fe^{3+}	0.0061	28.2		208.2	60.0	VO_4^{3-}	0.0663				
Al^{3+}		17.3	20.9	630.1	462.5	$Fe(CN)_6^{4-}$			219.8		
La^{3+}			28.8	785.9	595.3						
Cr^{3+}			31.0	282.1	85.6						
Fe^{3+}			30.7			SiO_3^{2-}			57.58	1056.9	1090.1
Sc^{3+}	0.0035					SiO_4^{4-}			68.93	1198.5	1300.8
Lu^{3+}	0.0102					SiO_5^{6-}			82.18	1344.4	1520.9
Yb^{3+}	0.0111					$Si_2O_5^{2-}$			101.86	1962.7	1920.0
Tm^{3+}	0.011					$Si_2O_7^{6-}$			127.4	2246.4	2361.2
Er^{3+}	0.0126					$Si_2O_{10}^{12-}$			162.2		
Y^{3+}	0.0131					$Si_3O_{10}^{8-}$			182.77	3315.1	3476.7
Dy^{3+}	0.0137					$Si_5O_{18}^{16-}$			317.21	5660.3	6050.0
Tb^{3+}	0.0148					$Si_4O_{11}^{6-}$			213.09	4098.6	4108.7
Gd^{3+}	0.0133										
Eu^{3+}	0.0146										
Sm^{3+}	0.0164										
Si^{4+}		24.5									
Ti^{4+}		35.2				**H_2O**	**0.0245**	**40.9**	**41.3**	**285.8**	**237.1**

As we have noted above, an important consequence of the independence of structure is that these relations apply equally to pure liquids as to solids, so that they can be applied to the increasingly important class of ionic liquids.[38]

Madelung energies – for known structures

The coulombic (or Madelung) energy, E_M, of a material of known structure is readily calculated by means of standard computer programs, such as GULP[61] and EUGEN.[62] This energy corresponds to separating the constituent ions into independent gas phase ions against coulombic forces only. We have observed[63] that the resulting Madelung energy is closely related to the corresponding lattice energy, in the form

$$U_{POT}/\text{kJ mol}^{-1} = 0.8518E_M + 293.9 \quad (14)$$

Eqn (14) thus provides a further simple direct means for obtaining lattice energies, apart from VBT. However, the Madelung calculation comes into its own when applied to an ionic system with structures containing covalently-bonded complexes, such as K_2SnCl_6. If the complex ion, $SnCl_6^{2-}$ in this case, is treated as a "condensed ion", with all the ion charge placed on the central atom (thus Sn^{2-}) and the ligands given zero charge (Cl^0), then we are effectively dealing with a system which decomposes to $2K^+(g) + Sn^{2-}(g)$ when the Madelung energy, now E_M', is supplied. For this system

$$U_{POT}/\text{kJ mol}^{-1} = 0.963E_M' \quad (15)$$

From these values, we can determine a formation energy for the "condensed ion" complex (see example below).

Isomegethic rule

Our isomegethic ("equal size") rule[24] states that "ionic salts of the same empirical chemical formula having identical charge states (*i.e.*, lattice ionic strength factors, I) will have approximately equal formula unit volumes, V_m." Since I, V_m and stoichiometry are then approximately identical, isomegethic compounds will have almost identical lattice potential energies too.

As an illustration, consider the relation:

$$V_m(NO^+ClO_4^-) \approx V_m(NO_2^+ClO_3^-) \approx V_m(ClO_2^+NO_3^-) \quad (14a)$$

and hence:

$$U_{POT}(NO^+ClO_4^-) \approx U_{POT}(NO_2^+ClO_3^-) \approx U_{POT}(ClO_2^+NO_3^-) \quad (14b)$$

Good examples of the scope of the isomegethic rule in providing multiple estimates for the volumes of ions are given in detail in ref. 24 and 64. Relations of this kind provide enormous scope for estimation of formula unit volumes and lattice energies, which is especially useful for hypothesised materials. If the enthalpies of formation of the individual gaseous component ions are known[65,66] then the enthalpy of formation of the isomegethic compound may usually be estimated, thus taking us into the full compass of the thermodynamics of the material concerned.

Single-ion values

Since it is seldom that all the desired thermodynamic values are available to generate the desired data, we have prepared sets of internally consistent single-ion values which may be used additively to generate otherwise absent data, collected in Table 4. An early example of this procedure is provided by the work of Latimer[67,68] in developing single ion entropy estimates.

An example set of predictive thermodynamic calculations: K_2SnCl_6

We here provide a set of results for the material dipotassium hexachlorostannate, K_2SnCl_6, where we have deliberately selected the difficult case of a partially covalent material for which experimental thermodynamic values are available for comparison. This demonstrates some of the weaknesses of these predictive methods against some of their strengths in that they may provide a wide range of otherwise unavailable thermodynamic values.

Simple salt approximation (SSA). Table 5 demonstrates the features of the "Simple Salt Approximation" in generating results by combining reaction components.

For the SSA to be accurate, it is necessary that the reaction to form product should yield zero (or small) thermodynamic differences. As may be seen from the final column in Table 5, the reaction $2KCl + SnCl_4 \rightarrow K_2SnCl_6$ produces non-zero differences, so that the SSA results (3rd last column) are not accurate, but may be useful as a general guide when the thermodynamic values are unknown.

Volume-based thermodynamics (VBT). VBT is a specifically ionic-based set of empirical procedures, correlated against strongly ionic materials such as simple halides and more complex oxides. We examine its application to K_2SnCl_6 with its covalent central ion, $SnCl_6^{2-}$.

The constants used in the following calculations are selected from Table 2.

(a) Formula unit volume,[70] $V_m/\text{nm}^3 = V_{cell}/Z = 1.0057/4 = 0.2514$

(b) Ionic strength factor, $I = 1/2\sum n_i z_i^2 = 3$ (eqn (3))

(c) Lattice (potential) energy, $U_{POT}/\text{kJ mol}^{-1} = 2I(\alpha/V_m^{1/3} + \beta)$ (eqn (4)) $= 2 \times 3\,(165/0.2514^{1/3} - 30) = 1389$ (*cf.* Born–Haber–Fajans cycle value[71] = 1390, Fig. 3)

Table 5 Additive thermodynamic values for K_2SnCl_6, following the "Simple Salt Approximation".[18] Data (columns 2, 3, 4 and 7) from HSC Chemistry 8[69]

	KCl	$SnCl_4$	K_2SnCl_6	$2KCl + SnCl_4$	% Diff	$2KCl + SnCl_4 \rightarrow K_2SnCl_6$
$\Delta_f H°(25\ °C,s)/\text{kJ mol}^{-1}$	−436.7	−517.0	−1482.0	−1390.4	−6.2	−91.6
$S°(25\ °C,s)/\text{J K}^{-1}\text{ mol}^{-1}$	82.7	265.0	371.0	430.4	16.0	−59.4
$\Delta_f G°(25\ °C,s)/\text{kJ mol}^{-1}$	−461.3	−596.0	−1592.6	−1518.7	−4.6	−73.9
$C_p(25\ °C,s)/\text{J K}^{-1}\text{ mol}^{-1}$	51.4	157.2	221.1	260.1	17.6	−39.0

(d) Standard entropy, S/J K^{-1} mol^{-1} = $kV_m + c$ (eqn (6)) = 1360 × 0.2514 + 15 = 356.9 (*cf.* 371.0, diff. 3.9%, Table 5)

(e) Heat capacity, C_p/J K^{-1} mol^{-1} = $k'V_m + c'$ (eqn (7)) = 1322 × 0.2514 − 0.8 = 331.6 (*cf.* 221.1, diff. −33%, Table 5) (Neumann–Kopp atom additive value[6] for 9 atoms = 25 × 9 = 225: diff. 1.7%)

Comment: the VBT value calculated for C_p considerably exceeds the 9-atom limiting Neumann–Kopp value, which we propose is a preferred value (see Table 2). This suggests that the rigid covalent $SnCl_6^{2-}$ structure corresponds to too-large a volume compared with a close-packed strictly ionic system. Correspondingly, the predicted entropy is also too large. By contrast, in calculating the lattice energy, any volume error is minimised by the use of a cube-root volume.

(f) $\Delta_fH(SnCl_6^{2-},g)$/kJ mol^{-1} = $U_{POT}(K_2SnCl_6,s)$[71] + $\Delta_fH(K_2SnCl_6,s)$[69] − $2\Delta_fH(K^+,g)$[71] = (1390) + (−1482) − 2(514) = −1120 (*cf.*[65] −1156, diff. 3.1%)

(g) Madelung energy[72] for K_2SnCl_6(s), E_M/kJ mol^{-1} = 9322 converted to U_M/kJ mol^{-1} = 0.8518 × 9322 + 293.9 = 8234

Comment: see Born–Haber–Fajans cycle, Fig. 3.

(h) Madelung energy, assuming the "condensed ion"[72] $SnCl_6^{2-}$, E_M'/kJ mol^{-1} = 1613.7 converted to U_{POT}/kJ mol^{-1} = 0.963 × 1614 = 1554

Comment: this result may be compared with the value noted in (c) above of 1390 kJ mol^{-1} (+11%).

Comment: see Born–Haber–Fajans cycle, Fig. 3.

(i) By difference, dissociation energy to independent ions, $\Delta_{diss}H(SnCl_6^{2-},g)$ = 5199 kJ mol^{-1}

Comment: this is a "new" value, not previously reported.

(j) Lattice energy/kJ mol^{-1} to form independent gaseous ions 2 × K^+ (Δ_fH = 2 × 541.0),[69] 6 × Cl^- (Δ_fH = 6 × −227.6),[69] and Sn^{4+} (Δ_fH = 9320.7)[65] = 7501, diff. 10% from (g).

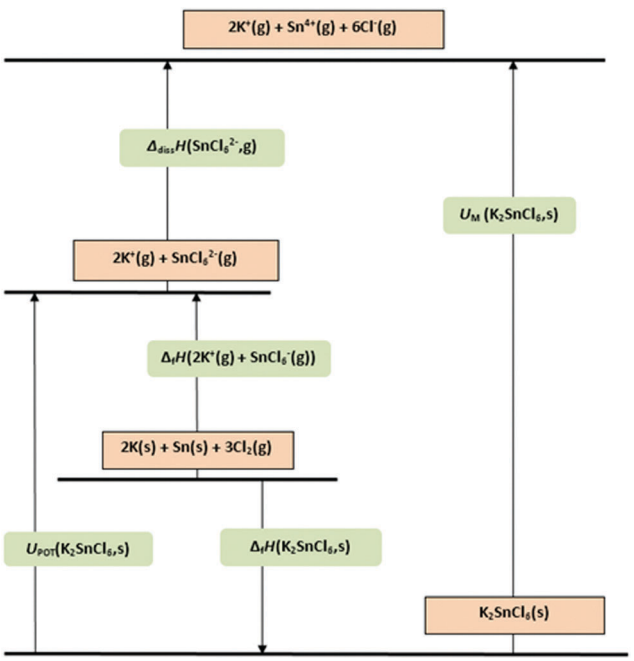


Fig. 3 Born–Haber–Fajans cycle for K_2SnCl_6.

Table 6 Applications of volume-based thermodynamics, VBT, and the thermodynamic difference rule, TDR

Volume Based Thermodynamics (VBT) or Difference Rule (TDR) specific application	Topic treated	Ref.
Thermodynamics of new homopolyatomic cation salts of sulfur and selenium.	A study designed to investigate hitherto unknown homopolyatomic cation species of sulfur and selenium (*e.g.*, S_8^{2+} and Se_8^{2+}). The crystalline salt, $S_8(AsF_6)_2$ and its selenium analogue were predicted, *prior to synthesis*, to be lattice-stabilised in the solid state relative to the corresponding AsF_6^- salts of their stoichiometrically possible dissociation.	73
The fluoride ion affinity of AsF_5 and standard enthalpy of formation, $\Delta_fH(AsF_6^-,g)$.	Two different values for $\Delta_fH'(AsF_6^-,g)$ had been published in the literature at the time of our investigation. The first estimate was made by Bartlett, *et al.* Jenkins, Krossing, Passmore and co-workers estimated $\Delta_fH(AsF_6^-,g)$ using the thermochemical data for the salts $[NF_4^+][BF_4^-]$, $[NF_4^+][SbF_6^-]$, and $[NF_4^+][AsF_6^-]$, obtaining a value which was lower than Bartlett *et al.*'s value. This lower standard enthalpy of formation implied a lower fluoride ion affinity of AsF_5. In order to decide which value (433 or 467 kJ mol^{-1}) is likely to be the more accurate, we modelled the fluoride ion affinity using *ab initio* methods and concluded a most likely value to be: 430.5 ± 5.5 kJ mol^{-1}. In a further, later, study further FIA values were assigned.	74–76
Thermodynamics of stabilisation of S^{2+}, Se^{2+} and Te^{2+} ions in the solid state.	In a study on the solvated salt $S_4(AsF_6)_2{\cdot}AsF_3$ we found, using the TDR, that the solvated salt: $S_4(AsF_6)_2{\cdot}AsF_3$ was more stable than the unsolvated salt, $S_4(AsF_6)_2$ or more stable than the decomposition products of $S_4(AsF_6)_2{\cdot}AsF_3$ (which are $2S_2AsF_6$ (c) and AsF_3(l)). Such systems could not have been examined thermodynamically in this way other than by using VBT and TDR because of the complexity of the lattices involved.	77
Study of fluoride ion donor ability.	Here was studied the ability of fluoride ion donors, C^+F^-(s), to donate a fluoride ion to an acceptor, A(g). The trend among experimentalists attempting to synthesise increasingly more effective fluoride ion donors: $C^+F^-(s) + A(g) \rightarrow C^+AF^-(g)$ had been to increase the cation size further and further but this study, guided by VBT, showed that there was very little gained by size increases beyond a critical level. Here VBT played a defining role in that it led to an abortion of certain synthetic work which was taking a particular (unfruitful) avenue of development.	78 and 79

Table 6 (*continued*)

Volume Based Thermodynamics (VBT) or Difference Rule (TDR) specific application	Topic treated	Ref.
Application of VBT and TDR to assessment of the relative stabilities of bisulfite (HSO_3^-) and meta-bisulfite ($S_2O_5^{2-}$) salts.	Although the bisulfites, $MHSO_3$ (M = Li, Na, and K), are widely believed to be stable compounds, they have never been obtained as solids. VBT suggests that the cation volumes, $V_m(M^+)$ are insufficiently large to stabilize the HSO_3^- ion relative to the metabisulfite, $S_2O_5^{2-}$ ion. Crystalline compounds, originally thought to be $NaHSO_3$ and $KHSO_3$, were eventually identified to be metabisulfites, $Na_2S_2O_5$ and $K_2S_2O_5$. The fact that $RbHSO_3$ and $CsHSO_3$ can be isolated, whilst attempts to crystallize $MHSO_3$ (M = Li, Na, K) lead to the formation of $M_2S_2O_5$: $2MHSO_3(s) \rightarrow M_2S_2O_5(s) + H_2O(l)$ has been explained using volume-based thermodynamics, VBT.	80
Use of VBT to identify thermodynamics of complex reactions and to assist in discerning the probable synthetic route of formation of products.	This application illustrates the level of sophistication of the thermochemistry that can be dealt with using VBT. Here the synthesis of the salts $NO[Al(OR)_4]$, R = $C(CF_3)_2Ph$ and $C(CF_3)_3$ by metathesis reaction of $NO[SbF_6]$ and the corresponding $Li[Al(OR)_4]$ salts in liquid sulfur dioxide solution were studied and the complete thermodynamics involved in the reaction (in the liquid sulfur dioxide medium): $3NO(g) + NO_2(g) + Li[Al(OR)_4](s) \rightarrow NO[Al(OR)_4](s) + LiNO_3(s) + N_2O(g)$ was analysed using VBT, whereupon it was seen that an unfavourable disproportionation reaction: $2NO_2(g) \rightarrow NO^+(g) + NO_3^-(g)$ is more than compensated for by the disproportionation enthalpy of the reaction: $3NO(g) \rightarrow N_2O(g) + NO_2(g)$ and the lattice energy of $LiNO_3(s)$. Evidence is presented that the reaction proceeds *via* a complex of Li^+ with NO, NO_2 (or their dimers) and N_2O.	81
Assessment of the stability of N_5^+ salts.	The nitrogen-rich energetic salts, $N_5^+N_3^-$ and $N_5^+N_5^-$ were initially seen as having enormous potential as environmentally clean (friendly) rocket propellants and aircraft fuels offering the possibility of cheap travel. Their potential captured the excitement of the media. However, in a theoretical study, VBT coupled with *ab initio* calculations for the species N_3, N_3^-, N_5^+ and N_5^- showed that neither $N_5^+N_3^-$ or $N_5^+N_5^-$ could be stabilised thermodynamically and that they would decompose instantaneously into N_3 radicals and nitrogen gas.	82 and 83
VBT and Prussian blue – a contribution to evolving technology.	This study examined the solid-state thermodynamics of the cation exchanges that occur in electrochromic reactions of Prussian Blue. These electrochemically induced changes of valence that result in striking color changes constitute the process of electrochromism, a modern evolving technology in which final ''best formulations'' are yet being sought. Our study provided an incisive thermodynamic clarification of an ill-understood ion exchange that accompanies the early electrochromic cycles. The results showed by how much the exchange of interstitial Fe^{3+} ions by alkali metal ions, as exemplified by K^+, is thermodynamically favoured.	84
Use of VBT to investigate the thermodynamics of a new binary fluoro metal dianion $[Ti_4F_{19}]^{2-}$ prepared by autoionisation of TiF_4 by cation complexation with crown ethers.	This application of VBT shows how the methodology can be applied to investigate new and complex problems in thermodynamics. Following the successful preparation of the new $Ti_4F_{19}^{2-}$ anion, this application was used to guide synthetic endeavour by studying whether the $Ti_4F_{19}^{2-}$ anion is more able to form salts with mono or dications. To investigate this we considered two reactions: $2MTi_2F_9(s) \rightarrow M_2Ti_4F_{18}(s)$ (the target reaction, for which we needed to estimate $\Delta H \approx \Delta G$) and the gas phase dimerisation reaction: $2Ti_2F_9^-(g) \rightarrow Ti_4F_{18}^{2-}(g)$.	85
Hypothetical compounds – nitryl chlorate and its possible preparation.	Volume-based thermodynamics (VBT) has examined the attempted preparation of the salt, nitryl chlorate: $[NO_2][ClO_3]$. Nitrosyl perchlorate, $[NO][ClO_4]$, is a known and stable salt which provoked attempts to synthesize the isomeric nitryl chlorate, $[NO_2][ClO_3]$. Our isomegethic rule assigns these two materials to have similar lattice potential energies. Silver chlorate, $Ag[ClO_3]$, was reacted with nitryl hexafluoroantimonate, $[NO_2][SbF_6]$ (in nitromethane) at room temperature. Silver hexafluoroantimonate, $Ag[SbF_6]$ was identified as one of the reaction products but no $[NO_2][ClO_3]$ was detected. Nitric acid, HNO_3, was found as a side product and it was concluded that this was possibly caused by the presence of traces of water within the nitromethane solvent employed. After three attempts, we failed to prepare the target material, $[NO_2][ClO_3]$. However VBT calculations tend to confirm that $[NO_2][ClO_3]$ is formed but then decomposes in neat $Ag[ClO_3]$ and $[NO_2][SbF_6]$.	86
Novel, state-of-the-art, selenium chemistry	This study represents state of the art chemistry and an extremely complex problem. Here ^{77}Se NMR spectroscopy, DFT and MO computations, coupled with VBT and TDR estimations, were utilised to investigate the reversible dissociation of solid $Se_6I_2(AsF_6)_2{\cdot}2SO_2$ in liquid SO_2 into solutions containing 1,4-$Se_6I_2^{2+}$ in equilibrium with Se_4^{2+}, Se_8^{2+} and Se_{10}^{2+} and seven binary selenium–iodine cations. The study also provided preliminary evidence for the existence and stability of the 1,1,4,4-$Se_4Br_4^{2+}$ and cyclo-Se_7Br^+ cations.	87

Table 6 (*continued*)

Volume Based Thermodynamics (VBT) or Difference Rule (TDR) specific application	Topic treated	Ref.
Predicted stabilities for noble-gas fluorocation salts using VBT.	In the few situations in noble gas (Ng) chemistry where thermochemical facts are known, VBT can be used to validate and confirm these. This provides further evidence that, in predictive mode, results from VBT can provide a reliable guide to thermodynamic possibilities. The lattice energies, standard enthalpies, and Gibbs energies of formation for salts containing the NgF^+, $Ng_2F_3^+$, XeF_3^+, XeF_5^+, $Xe_2F_{11}^+$, and $XeOF_3^+$ (Ng = Ar, Kr, Xe) cations were estimated using crystallographic and estimated ion volumes. VBT was able, in this way, to provide estimates and predict stabilities – albeit sometimes with quite large uncertainties in the estimated data. While, for example, the stabilities of $[XeF_n][Sb_2F_{11}]$ (n = 2, 3) and $[XeF][AsF_6]$ were confirmed with respect to dissociation to the xenon fluoride and the pnictogen pentafluoride, the stabilities of $[XeF_3][AsF_6]$ and $[XeF_3][As_2F_{11}]$ were shown to be marginal under standard conditions.	88
The thermodynamic hydrate difference rule (HDR) applied to materials at the inorganic–organic interface.	The thermodynamic hydrate difference rule (HDR) is shown here also to apply equally well to formate, carbonate, acetate, glycolate and oxalate salts and their hydrates.	89
The thermodynamic difference rule and the thermodynamics of hydration (and solvation) of inorganic solids and the existence/absence of certain hydrates.	The thermodynamics of the formation of solid and liquid inorganic hydrates and ammoniates was examined in this application, suggesting that hydration is always marginally thermodynamically favourable. More detailed consideration further demonstrated that the mean value of $\Delta_r G$ per mole of water addition, from anhydrous parent to hydrate within a sequence, increases consistently toward zero, becoming progressively less favorable as the degree of hydration, n, increases, and is also broadly independent of any structural features of the materials.	90
VBT determination of ionicity or covalency within structures.	The question as to why $[P(C_6H_5)_4]^+N_3^-$ and $[As(C_6H_5)_4]^+N_3^-$ exist as ionic salts whilst $[Sb(C_6H_5)_4]^+N_3^-$ and $[Bi(C_6H_5)_4]^+N_3^-$ are covalent solids was examined. The estimations provided an unexpected answer!	91
Interpolation of thermodynamic data for sulfur compounds and use of VBT to examine possible synthetic routes and subsequent stability.	Using VBT the values of $\Delta_f G$ led us to a tentative proposal for the synthesis of Na_2SO_2. The stability of Na_2SO_2 however raises doubts and Na_2SeO_2 emerges as a more attractive target material for synthesis. We predict its synthesis will be easier and that it is stable to disproportionation into Na_2Se and Na_2SeO_4. (Subsequently to the publication of this paper it was preliminarily reported to Vegas verbally that Na_2SO_2 has indeed been possibly identified in aqueous solution).	92
Tetraanionic nitrogen-rich tetrazole-based salts (TDAE)(O_2SSSSO_2)(s) examined using VBT and containing the very first polythionite anion, $OSSSSO_2^{2-}$.	Study of energetics using VBT Synthesis of (TDAE)(O_2SSSSO_2).	93 94
Examination of VBT in respect of estimation of lattice energies of salts containing the 5,5′-(tetrazole-1*N*-oxide)$^{2-}$ anion.	Investigation of energetics of defence materials.	95
Use of TDR to examine thermochemical data for arsenic and phosphorus compounds.	Arsenic oxides/hydrates conform exactly to the TDR whilst analogous phosphorus oxides/hydrates do not. Comments on enthalpies of formation of phosphates.	96 and 97

Conclusion

Neither volume-based thermodynamics (VBT) nor the thermodynamic difference rule (TDR), together with their supporting quantities, require a high level of computational expertise nor expensive high-performance computation tools – a spreadsheet will usually suffice – yet the techniques are extremely powerful and accessible to non-experts. Table 2 summarises correlation equations between formula unit volume, V_m, and various thermodynamic properties, together with measures of anticipated errors. These correlation equations provide ready access to otherwise unavailable thermodynamic data, as also rapid checks of published data. The results should always be treated with appropriate caution by checking against known values for related materials.

Applications of volume-based thermodynamics, VBT, and the thermodynamic difference rule, TDR

In rough chronological order, we present a selection of applications of VBT and TDR which have enabled input, usually in the form of thermodynamics, to be brought to bear on a range of topical problems, often ''state of the art''. These present a diverse range of applications for our techniques. The message for the reader is that:

- VBT and TDR can be applied in numerous situations;
- Their application can lead to surprising new results as well as confirmatory ones;
- The basic application is usually very straightforward (Table 6).

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