Inorg. Chem. **2002**, *41*, 4378–4388

Inorganic Chemistry

Article

Ionic Hydrates, $M_pX_q \cdot nH_2O$: Lattice Energy and Standard Enthalpy of Formation Estimation

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Received March 21, 2002

This paper is one of a series (see: *Inorg. Chem*. **1999**, *38*, 3609; *J. Am. Chem. Soc*. **2000**, *122*, 632; *Inorg. Chem*. **2002**, *41*, 2364) exploring simple approaches for the estimation of lattice energies of ionic materials, avoiding elaborate computation. Knowledge of lattice energy can lead, *via thermochemical cycles*, to the evaluation of the underlying thermodynamics involving the preparation and subsequent reactions of inorganic materials. A simple and easy to use equation for the estimation of the lattice energy of hydrate salts, $U_{POT}(M_pX_q \cdot nH_2O)$ (and therefore for solvated salts, $M_pX_q \cdot nS$, in general), using either the density or volume of the hydrate, or of another hydrate, or of the parent anhydrous salt or the volumes of the individual ions, is derived from first principles. The equation effectively determines the hydrate lattice energy, $U_{POT}(M_pX_q \cdot nH_2O)$, from a knowledge of the (estimated) lattice energy, $U_{POT}(M_pX_q)$, of the parent salt by the addition of $n\theta_U$ where $\theta_U(H_2O)/kJ\ mol^{-1} = 54.3$ and n is the number of water molecules. The average volume of the water molecule of hydration, $V_m(H_2O)/nm^3 = 0.0245$, has been determined from data on a large series of hydrates by plotting hydrate/parent salt volume differences against n. The enthalpy of incorporation of a gaseous water molecule into the structure of an ionic hydrate, $[\Delta_f H^\circ (M_pX_q \cdot nH_2O,s) - \Delta_f H^\circ (M_pX_q,s) - n\Delta_f H^\circ (H_2O,g)]$, is shown to be a constant, -56.8 kJ (mol of $H_2O)^{-1}$. The physical implications with regard to incorporation of the water into various types of solid-state structures are considered. Examples are given of the use of the derived hydrate lattice energy equation. Standard enthalpies of formation of a number of hydrates are thereby predicted.

Introduction

Considerable progress has recently been made[1-4] in providing a convenient and easy to use, yet reliable, set of equations for the estimation of lattice energy, U_{POT}, of ionic materials. These equations apply for both ionic salts (with simple or complex ions),[1,3] M_pX_q, for which $U_{POT}(M_pX_q)/kJ\ mol^{-1} < 5000$ (eqs 1 and 2, Scheme 1A) as well[2] as for minerals and complex chalcogenides, $M_pX_qZ_z$..., for which[5] $U_{POT}(M_pX_qZ_z...)/kJ\ mol^{-1} > 5000$ (eqs 3 and 4, Scheme 1B).

Scheme 1 provides a schematic summary of these equations and the input data[6] that can be utilized to obtain an estimate of the lattice energy. Such equations make the underlying thermochemistry much more accessible (espe-

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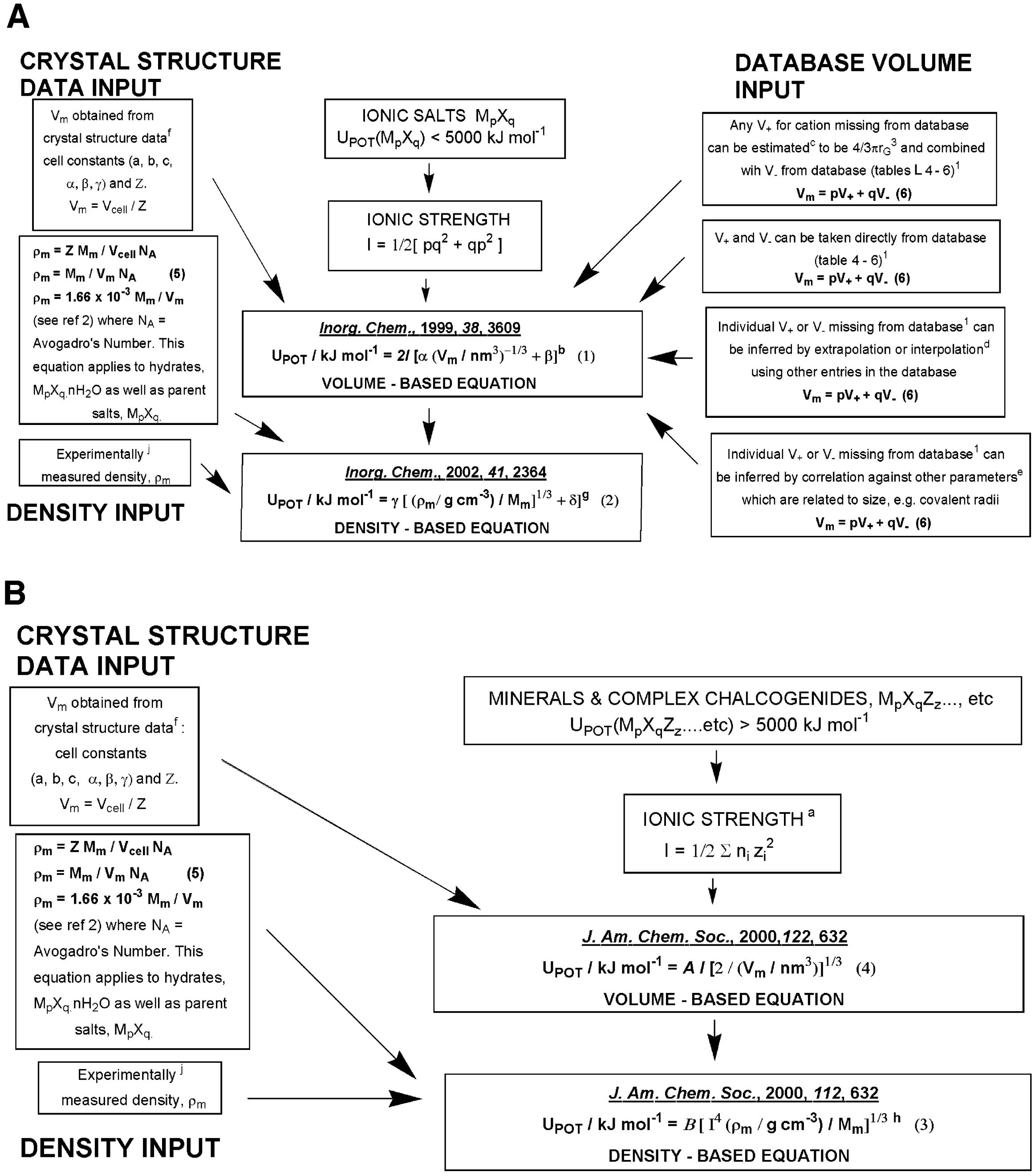
(5) Division of ionic materials into those for which $U_{POT} < 5000$ kJ mol^{-1} and for which $U_{POT} > 5000$ kJ mol^{-1} does not present a problem in practice. The former condition applies to most inorganic salts, M_pX_q, while the latter condition applies generally to minerals and complex chalcogenides, $M_pX_qZ_z$..., etc.

(6) Since the equations require no structural detail as input, they apply not only to crystalline solids but even to amorphous solids and ionic liquids.

10.1021/ic020222t CCC: $22.00

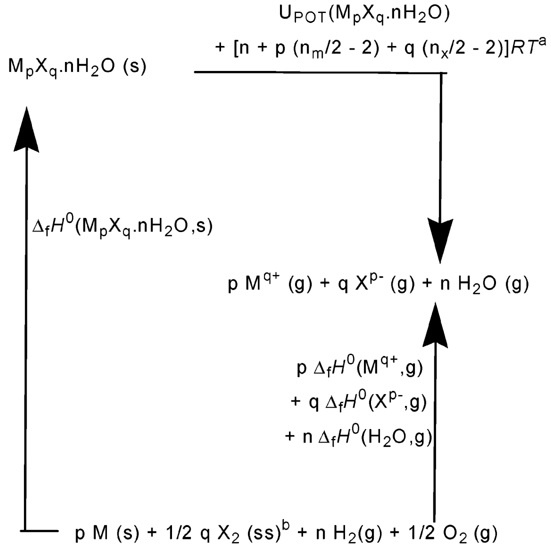
Scheme 1. Summary of Equations and Their Relations for Lattice Energy Evaluations. (A) Ionic Salts with Lattice Energies < 5000 kJ mol^{-1}. (B) Minerals and Complex Chalcogenides with Lattice Energies > 5000 kJ mol^{-1}



[a] $I = {}^1/_2\sum n_i z_i^2$ where n_i = number of ions of type i in formula unit bearing charge z_i and the summation is extended over all ions in the unit cell (see ref 4). [b]Applicable to salts with U_{POT}/kJ mol^{-1} < 5000[5] where α and β are constants. For MX salts, charge ratio (1:1): α/kJ mol^{-1} nm = 117.3; β/kJ mol^{-1} = 51.9; for MX_2 salts, charge ratio (2:1): α/kJ mol^{-1} nm = 133.5; β/kJ mol^{-1} = 60.9; for M_2X salts, charge ratio (1:2): α/kJ mol^{-1} nm = 165.3; β/kJ mol^{-1} = −29.8; for MX salts, charge ratio (2:2): α/kJ mol^{-1} nm = 101.6; β/kJ mol^{-1} = 91.5; and for general salts, M_pX_q, charge ratio (q:p): α/kJ mol^{-1} nm = 138.6; β/kJ mol^{-1} = 27.6. (see ref 1 and Table 1, ref 2). [c]r_G = Goldschmidt radius of cation, directly leads to V_+. [d]For an example of inferences which can be made about V_+ by this approach, see footnotes 176 and 177 in ref 7a and footnotes 121 and 129 in ref 7b. [e]See, for example, estimation of $V_m(S_4^{2+})$ discussed in ref 1, page 3618. [f]a, b, and c represent unit cell lengths; α, β, and γ represent unit cell angles; Z = number of molecules per unit cell. $V_m = abc(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)^{1/2}$ (see also footnote 2 in ref 2). [g]Applicable to salts with U_{POT}/kJ mol^{-1} < 5000[5] where γ and δ are constants. For MX salts, charge ratio (1:1): γ/kJ mol^{-1} cm = 1981.2; δ/kJ mol^{-1} = 103.8; for MX_2 salts, charge ratio (2:1): γ/kJ mol^{-1} cm = 6764.3; δ/kJ mol^{-1} = 365.4; for M_2X salts, charge ratio (1:2): γ/kJ mol^{-1} cm = 8375.6; δ/kJ mol^{-1} = 178.8; for MX salts, charge ratio (2:2): γ/kJ mol^{-1} cm = 6864.0; δ/kJ mol^{-1} = 732.0; and for general salts, M_pX_q, charge ratio (q:p): γ/kJ mol^{-1} cm = 2342.6 I; δ/kJ mol^{-1} = 55.2 I; where I is the ionic strength term[a] $[= {}^1/_2(pq^2 + qp^2)]$. [h]B/kJ mol cm = 1291.7; ρ_m is density (Mg m^{-3}, or g cm^{-3}). I is ionic strength.[a] [i]A/kJ mol^{-1} = 121.4. This equation contains no adjustable constants. [j]The experimental value of ρ_m may differ from that calculated from crystallographic data using V_{cell} and Z.

cially for the occasional user). They possess a number of advantages not previously available.[7] First, they link the thermodynamics (via lattice potential energies) *directly* to experimentally accessible quantities of the ionic material which are relatively easy to measure. These include molecular (formula unit) volume, V_m/nm^3; density, ρ_m/g cm^{-3}; and crystal structure or powder diffraction data (unit cell lengths, a, b, c; angles, α, β, γ; and the number of molecules per unit cell, Z; see Scheme 1, footnote f). Second, because of their dependence on ion volume (eqs 1 and 4), they provide a more satisfactory and a generalizable model of the ionic state than do equations using thermochemical radii. Thus, ions need no longer be modeled as possessing a notional (thermochemical) radius and thereby be regarded as being *spherical* (which most ions of topical interest are certainly not). This new approach, based on volume (or density), therefore supersedes the traditional approach of Kapustinskii,[8] which has served chemistry well for over four decades. Third, as we have earlier demonstrated,[3] there is the possibility of estimating *unknown* ion volumes and so expanding the scope of the application. By use of extrapolative or interpolative techniques (see Scheme 1, footnote d) or else by correlation of ion volumes with other relevant size parameters (see Scheme 1, footnote e), U_{POT} can be estimated for speculative as well as for new and novel inorganic ionic materials. In this way it becomes possible to examine the thermodynamics of such materials about which little or nothing may (or, indeed, can) be known. Fourth, the volume-based equations (1 and 4) require much less detailed structural information than has previously been the case,[9] and, in the case of the density-based equations (Scheme 1, eqs 2 and 3), *none* is required. Since its publication, eq 1 has been employed by a number of workers in studying the energetics of a range of new inorganic materials. These have included high-energy-density materials (HEDM),[12] haloorganostannates(IV),[13] salts containing the newly synthesized N_5^+ cation,[14] studies related to aspects of hydrogen bonding,[15] fluoride ion affinities,[16a] the first donor-free salt of the $Sb(OTeF_5)_6^-$ anion,[16b] and the degree of hydration in dinuclear oxalato-bridged nickel(II) complexes[16c] and the stability of $N_5^+ N_5^-$,[16d] and the coordination of silver cations.[16e] Care[16e,f] must, however, be taken to ensure that the equations *are* used in the appropriate context.

Scheme 2. Born−Fajans−Haber Cycle for Hydrates and Parent Salts ($n = 0$)



[a] The lattice enthalpy, $\Delta H^{(n)}{}_{hydrate}$/kJ mol^{-1} = $U_{POT}(M_pX_q{\cdot}nH_2O) + [n + p(n_M/2 - 2) + q(n_x/2 - 2)]RT$ where n_M and n_X refer to the ions M^{q+} and X^{p-}. If the ion is monatomic, n_M or $n_X = 3$; if the ion is nonlinear polyatomic, n_M or $n_X = 5$; and if the ion is polyatomic, n_M or $n_X = 6$. For the anhydrous parent salt ($n = 0$): $\Delta H^{(0)}{}_{parent}$/kJ mol^{-1} = $U_{POT}(M_pX_q) - [p(n_M/2 - 2) + q(n_x/2 - 2)]RT$ (see Appendix 1 of this paper). [b](ss) = standard state: e.g., (ss) = l for $X_2 = Br_2$; (ss) = g for $X_2 = F_2$, Cl_2; etc.

Absent from Scheme 1 is an equation appropriate for estimating the lattice energy, $U_{POT}(M_pX_q{\cdot}nH_2O)$, of a hydrated salt,[17] $M_pX_q{\cdot}nH_2O$, an absence which we here remedy. We first note that our equations developed so far refer to *ionic* materials, which hydrates are manifestly not[18] and so we can conclude that an equation of the analytical form of eq 1 would not be appropriate for the estimation of hydrate lattice energies. In this paper we derive from first principles, and test, an equation which is both simple in form and applicable to ionic hydrates.

Theory

Consider the thermochemical cycle shown in Scheme 2. For the anhydrous parent salt, M_pX_q, we have (cf. Appendix

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(7) (a) For a practical example, see the quantification made possible for ionic salts containing homopolyatomic cations of group 16 and 17 as treated in the following: Brownridge, S.; Krossing, I.; Passmore, J.; Jenkins, H. D. B.; Roobottom, H. K. *Coord. Chem. Rev.* **2000**, *197*, 397. (b) Cameron, T. S.; Deeth, R. J.; Dionne, I.; Du, H.; Jenkins, H. D. B.; Passmore, J.; Roobottom, H. K. *Inorg. Chem.* **2000**, *39*, 5614.

(8) Kapustinskii, A. F. *Q. Rev., Chem. Soc.* **1956**, *10*, 283. It should be noted that our eq 1, which is linear in reciprocal distance (equivalent to $V^{-1/3}$) is not of Kapustinskii type (as stated in ref 16a), since the latter is quadratic in reciprocal distance.

(9) Consider for example, the use of the Kapustinskii[8] model over the past four and more decades. Successful use of the equation $U_{POT} = 121.4|\nu z_+ z_-|[1 - \rho/(r_+ + r_-)]/(r_+ + r_-)$ was initially hampered by the nonavailability of thermochemical radii, r_+ and r_-, for many ions of interest. Although the additive term $(r_+ + r_-)$ for complex salts could be equated to the shortest anion−cation distance in the lattice, such information was not always available and, for newer materials, normally not at all. Although the original set of thermochemical radii was extended,[10] it is only relatively recently that we have been able to produce a database[11] of thermochemical radii that encompasses a wider range of ions of topical interest. Determination of internal distances within crystals usually demands more detailed examination than that simply required to determine the unit cell volume, V_{cell}, which, since $V_m = V_{cell}/Z$, is all that is required to use eqs 1 and 4.

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(17) Lattice energies of $M_pX_q{\cdot}nH_2O$ salts are usually less than 5000 kJ mol^{-1}.

(18) See: Jenkins, H. D. B.; Hirst, D. M.; Lagadianou, E.; Patel, M.; Herzig, P.; Brown, I. D. *J. Chem. Soc., Faraday Trans 2* **1985**, *81*, 1607 which shows that $U_{POT}(CaCl_2{\cdot}6H_2O) > U_{POT}(CaCl_2{\cdot}4H_2O) > U_{POT}(CaCl_2{\cdot}2H_2O) > U_{POT}(CaCl_2)$, i.e., as the molar volumes of the hydrates increase, so do the lattice energies.

Table 1. Sample of Dataset[19] for Anhydrous Parent, M_pX_q, and Hydrate, $M_pX_q\cdot nH_2O$, Salts Used To Obtain the Rectilinear Fit of $[\Delta_f H°(M_pX_q\cdot nH_2O,s) - \Delta_f H°(M_pX_q,s)]$/kJ mol^{-1} against n[a]

anhydrous parent M_pX_q	$\Delta_f H°$/ kJ mol^{-1}	hydrate $M_pX_q\cdot nH_2O$	n	$\Delta_f H°$/ kJ mol^{-1}	$[\Delta_f H°(M_pX_q\cdot nH_2O,s) - \Delta_f H°(M_pX_q, s)]/n$/kJ mol^{-1}	predicted $\Delta_f H°(M_pX_q\cdot nH_2O,s)$/ kJ mol^{-1}	% diff
LiOH	−484.93	$LiOH\cdot H_2O$	1	−788.01	−303.1	−783.5	0.6
LiCl	−408.61	$LiCl\cdot 3H_2O$	3	−1311.3	−300.9	−1304.4	0.1
		$LiCl\cdot 2H_2O$	2	−1012.65	−302.0	−1005.8	0.7
		$LiCl\cdot H_2O$	1	−712.58	−304.0	−707.2	0.8
Li_2SO_4	−1436.49	$Li_2SO_4\cdot H_2O$	1	−1735.5	−299.0	−1735.1	0.0
Li_2Se	−419.2	$Li_2Se\cdot 9H_2O$	9	−3089.5	−296.7	−3106.6	0.6
NaHS	−237.23	$NaHS\cdot 2H_2O$	2	−838.47	−300.6	−834.4	0.5
Na_2Se	−341.4	$Na_2Se\cdot 16H_2O$	16	−5091.9	−296.9	−5119.0	0.5
		$Na_2Se\cdot 9H_2O$	9	−3040.1	−299.9	−3028.8	0.4
		$Na_2Se\cdot 4.5H_2O$	4.5	−1741.0	−311.0	−1685.1	3.2
$K_2S_2O_5$	−1173.6	$K_2S_2O_5\cdot H_2O$	1	−1464.8	−291.2	−1472.2	0.5
$K_2Zn(SO_4)_2$	−2434.3	$K_2Zn(SO_4)_2\cdot 6H_2O$	6	−4234.2	−300.0	−4225.9	0.2
		$K_2Zn(SO_4)_2\cdot 2H_2O$	2	−3037.6	−301.7	−3031.5	0.2
RbF	−557.7	$RbF\cdot 1.5H_2O$	1.5	−1013.8	−304.1	−1005.6	0.8
Cs_2CO_3	−1139.7	$Cs_2CO_3\cdot 3H_2O$	3	−2048.1	−302.8	−2035.5	0.6
$Ca(IO_3)_2$	−1002.5	$Ca(IO_3)_2\cdot 6H_2O$	6	−2780.7	−296.3	−2794.1	0.5
		$Ca(IO_3)_2\cdot H_2O$	1	−1293.3	−290.3	−1301.1	0.6
$Sr(HCO_2)_2$	−1393.3	$Sr(HCO_2)_2\cdot 2H_2O$	2	−1990.7	−298.7	−1990.2	0.0
BaO_2	−634.3	$BaO_2\cdot 8H_2O$	8	−3006.6	−296.5	−3023.1	0.5

[a] The table also shows back-predictions made from eq 11 and the % difference found using the correlation $[\Delta_f H°(M_pX_q\cdot nH_2O,s) - \Delta_f H°(M_pX_q,s)]$/kJ mol^{-1} = −298.6 n with correlation coefficient 0.999_1. Data range of experimental difference per mole of H_2O: $-288 \le \theta_{Hf}(H_2O)/\text{kJ mol}^{-1} \le -329$.

1)and for the hydrated salt, $M_pX_q\cdot nH_2O$,

$$U_{POT}(M_pX_q) + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT = p\Delta_f H°(M^{q+},g) + q\Delta_f H°(X^{p-},g) - \Delta_f H°(M_pX_q,s) \quad (7)$$

$$U_{POT}(M_pX_q\cdot nH_2O) + [n + p(n_M/2 - 2) + q(n_X/2 - 2)]RT = p\Delta_f H°(M^{q+},g) + q\Delta_f H°(X^{p-},g) + n\Delta_f H°(H_2O,g) - \Delta_f H°(M_pX_q\cdot nH_2O,s) \quad (8)$$

Subtraction of eq 7 from eq 8 leads to

$$[U_{POT}(M_pX_q\cdot nH_2O) - U_{POT}(M_pX_q)] = -[\Delta_f H°(M_pX_q\cdot nH_2O,s) - \Delta_f H°(M_pX_q,s)] + n\Delta_f H°(H_2O,g) - nRT \quad (9)$$

At 298 K and 1 atm (bar) pressure, $\Delta_f H°(H_2O,g)/\text{kJ mol}^{-1} = -241.8$[19] and $RT/\text{kJ mol}^{-1} = 2.5$ so that we can write

$$U_{POT}(M_pX_q\cdot nH_2O)/\text{kJ mol}^{-1} = U_{POT}(M_pX_q) - [\Delta_f H°(M_pX_q\cdot nH_2O,s) - \Delta_f H°(M_pX_q,s)] + n\Xi \quad (10)$$

where $\Xi/\text{kJ mol}^{-1} = -244.3$.

Figure 1 displays a plot of $[\Delta_f H°(M_pX_q\cdot nH_2O,s) - \Delta_f H°(M_pX_q,s)]$/kJ mol^{-1} versus n (constrained through zero) for the 342 hydrate salts for which $\Delta_f H°$ data appears[19] for both hydrate $M_pX_q\cdot nH_2O$ and parent M_pX_q salts ($^1/_4 \le n \le 19$). A small sample of the dataset used for this plot is shown in Table 1. The plot is rectilinear with a correlation coefficient of almost unity ($r^2 = 0.999_1$) and a gradient, $\theta_{Hf}(H_2O)$/kJ mol^{-1} = − 298.6 (with the intercept constrained to zero).

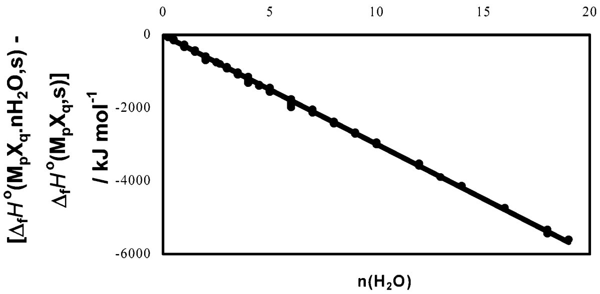

Figure 1. Plot of "difference" function: $[\Delta_f H°(M_pX_q\cdot nH_2O,s) - \Delta_f H°(M_pX_q,s)]$/kJ mol^{-1} versus n for a series of hydrates.

The estimated uncertainty in prediction of data using this equation is ± 20.5 kJ mol^{-1}. Thus:[20]

$$[\Delta_f H°(M_pX_q\cdot nH_2O,s) - \Delta_f H°(M_pX_q,s)] = n\theta_{Hf}(H_2O) \quad (11)$$

where $\theta_{Hf}(H_2O)/\text{kJ mol}^{-1}(H_2O\text{ molecule})^{-1} = -298.6$, and hence we can write

$$U_{POT}(M_pX_q\cdot nH_2O) = U_{POT}(M_pX_q) + n\theta_U(H_2O) \quad (12)$$

where

$$\theta_U(H_2O)/\text{kJ mol}^{-1}(H_2O\text{ molecule})^{-1} = \Xi - \theta_{Hf}(H_2O) = 54.3 \quad (13)$$

Equation 12 is our new equation for the estimation of the lattice energy of a hydrate salt. $U_{POT}(M_pX_q\cdot nH_2O)$/kJ mol^{-1} can thus be derived from the lattice energy of the parent

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(20) This relationship seems first to have been noted by Le Van My, *C.R. Seances Acad. Sci., Ser. C* **1971**, *272*, 125. A lattice energy difference between hydrate and parent salt for the incorporation of a water molecule into a salt lattice of −54 ± 63 kJ mol^{-1} was there reported, which may be compared with our present value (eq 13) of −54.3 kJ mol^{-1}.

Table 2. Comparison of Born−Fajans−Haber Thermochemical Cycle Values of Lattice Energies of Hydrate Salts, with Values Predicted for $U_{POT}(M_pX_q{\cdot}nH_2O)$/kJ mol^{-1} Using Eq 12, with $\theta_U(H_2O)$/kJ mol^{-1} = 54.3

anhydrous parent salt	Born−Fajans−Haber cycle value $U_{POT}(M_pX_q)$/kJ mol^{-1}	salt hydrate	Born−Fajans−Haber cycle value $U_{POT}(M_pX_q{\cdot}nH_2O)$/kJ mol^{-1}	est value of $U_{POT}(M_pX_q{\cdot}nH_2O)$/ kJ mol^{-1}, eq 12	% diff
$CaCl_2$	2232[a]	$CaCl_2{\cdot}2H_2O$	2352[a]	2341	−0.5
		$CaCl_2{\cdot}4H_2O$	2470[a]	2449	−0.8
		$CaCl_2{\cdot}6H_2O$	2575[a]	2558	−0.7
NaCl	790	$NaCl{\cdot}2H_2O$	895[b]	899	0.4
NaBr	754	$NaBr{\cdot}2H_2O$	869[c]	863	−0.7
NaI	705	$NaI{\cdot}2H_2O$	824[c]	814	−1.2
LiI	764	$LiI{\cdot}3H_2O$	914[d]	927	1.4

[a] Table 8, ref 18. [b] In the absence of experimental data for $\Delta_fH°(NaCl{\cdot}2H_2O,s)$/kJ mol^{-1} this quantity is estimated to be −1008.3 (see Table 10: this value has earlier[22] been estimated to be −1071 kJ mol^{-1}) using eq 11 and the data[19] $\Delta_fH°$ (NaCl,s)/kJ mol^{-1} = − 411.153. Then: $U_{POT}(NaCl{\cdot}2H_2O,s)$/kJ mol^{-1} = $\Delta_fH°(Na^+,g) + \Delta_fH°(Cl^-,g) + 2\Delta_fH°(H_2O,g) - \Delta_fH°(NaCl{\cdot}2H_2O,s) - RT$ = 895 kJ mol^{-1}. [c] Table 1, ref 22. [d] The value for $U_{POT}(LiI{\cdot}3H_2O)$ quoted in ref 19 is incorrectly stated as 972 kJ mol^{-1}, but should be 914 kJ mol^{-1} from standard thermodynamic cycle calculations.

anhydrous ($n = 0$) salt by the addition[21] of the appropriate number (=n) of constant terms or, correspondingly, the lattice energy difference between pairs of hydrate salts (with differing n values) can similarly be found.

More generally, once suitably parametrized, an equation of the form of 12 can be anticipated to predict the lattice energy, $U_{POT}(M_pX_q{\cdot}nS)$, of solvated salts of the type $M_pX_q{\cdot}nS$, where solvate, S, for example, might be D_2O, SO_2, NH_3, N_2H_4, CH_3OH, AsF_3, HCl, HNO_3, H_2SO_4, etc.

Equation 12 can, in view of eqs 1 and 2 (Scheme 1), be written

$$U_{POT}(M_pX_q{\cdot}nH_2O)/\text{kJ mol}^{-1} = 2I[\alpha V_m(M_pX_q)^{-1/3} + \beta] + n\theta_U(H_2O) \quad (14)$$

where I is the ionic strength of the *parent* salt, M_pX_q, of formula unit volume $V_m(M_pX_q)/nm^3$, and α and β are defined as in footnote *b* of Scheme 1. Alternatively,

$$U_{POT}(M_pX_q{\cdot}nH_2O)/\text{kJ mol}^{-1} = \gamma[\rho_m(M_pX_q)/M_m(M_pX_q)]^{1/3} + \delta + n\theta_U(H_2O) \quad (15)$$

where $\rho_m(M_pX_q)$/g cm^{-3} is the density of the *anhydrous* salt of chemical formula mass $M_m(M_pX_q)$, and γ and δ are as defined in footnote *g* of Scheme 1. Thus, eqs 14 and 15 permit the evaluation of the lattice energy, $U_{POT}(M_pX_q{\cdot}nH_2O)$/kJ mol^{-1}, of a hydrate *without reference to any hydrate data* (see Table 2) apart from the chemical formula.

In order to extend the use and scope of the above equations, we have also plotted (Figure 2) the function $[V_m(M_pX_q{\cdot}nH_2O) - V_m(M_pX_q)]/nm^3$ against n for a series of 34 hydrates (Table 3). We find that

$$[V_m(M_pX_q{\cdot}nH_2O) - V_m(M_pX_q)]/nm^3 = n\theta_V(H_2O) \quad (16)$$

with a correlation coefficient $r^2 = 0.988_1$ and a constant value of θ_V/nm^3:

$$\theta_V(H_2O)/nm^3\,(H_2O\text{ molecule})^{-1} = 0.0245 \quad (17)$$

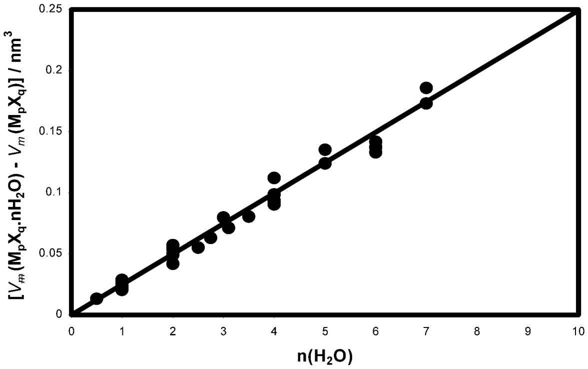

Figure 2. Plot of "difference" function: $[V_m(M_pX_q{\cdot}nH_2O,s) - V_m(M_pX_q,s)]/nm^3$ versus n for a series of hydrates.

Volume is related to density by the equation[1]

$$V_m/nm^3 = 1.66 \times 10^{-3}\,(M_m/g)/(\rho_m/g\text{ cm}^{-3}) \quad (18)$$

so that we can transform eq 16 into the form

$$[M_m(M_pX_q{\cdot}nH_2O)/\rho_m(M_pX_q{\cdot}nH_2O)]/cm^3 = [M_m(M_pX_q)/\rho_m(M_pX_q)] + n\theta_V(H_2O)/1.66 \times 10^{-3} \quad (19)$$

which, rearranging, gives

$$\{([M_m(M_pX_q{\cdot}nH_2O)/\rho_m(M_pX_q{\cdot}nH_2O)] - [M_m(M_pX_q)/\rho_m(M_pX_q)])/n\} = \theta_{M/\rho}(H_2O)/cm^3\,(H_2O\text{ molecule})^{-1} = 14.8 \quad (20)$$

an equation which can be used to interconvert hydrate and parent densities.

Rearranging eq 16 and substituting into eq 14 leads to

$$U_{POT}(M_pX_q{\cdot}nH_2O)/\text{kJ mol}^{-1} = 2I[\alpha\{V_m(M_pX_q{\cdot}nH_2O) - nV_m(H_2O)\}^{-1/3} + \beta] + n\theta_U(H_2O) \quad (21)$$

and, since the modulus $|nV_m(H_2O)/V_m(M_pX_q{\cdot}nH_2O)| < 1$, we can use the binomial theorem[23] to expand the volume term

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(21) The fact that lattice energies of hydrates, $U_{POT}(M_pX_q{\cdot}nH_2O)$/kJ mol^{-1}, and their parent salts, $U_{POT}(M_pX_q)]$/kJ mol^{-1}, differ by a constant term multiplied by n was noted earlier by one of us[22] (where the value of the constant is reported to be slightly higher (in the range $67 < \theta_U(H_2O)/\text{kJ mol}^{-1} < 84$) than discussed herein.

(22) Brink, G.; Glasser, L. *J. Phys. Chem.* **1990**, *94*, 981.

(23) Selby, S. M. *Standard Mathematical Tables*, 19th ed.; Chemical Rubber Co.: Cleveland, OH, 1971.

Table 3. Molar Volumes of Anhydrous Parents [$V_m(0)$] and of Hydrates [$V_m(n)$]/nm^3

anhydrous parent salt	$V_m(0)$/ nm^3	salt hydrate	n	$V_m(n)$/ nm^3	[$V_m(n) - V_m(0)$]/nm^3
LiI	0.0547	$LiI\cdot 3H_2O$	3	0.1344	0.0797
LiI		$LiI\cdot 2H_2O$	2	0.1082	0.0535
LiI		$LiI\cdot H_2O$	1	0.0805	0.0258
LiI		$LiI\cdot 0.5H_2O$	0.5	0.0678	0.0131
NaCl	0.0449	$NaCl\cdot 2H_2O$	2	0.0948	0.0499
NaBr	0.0527	$NaBr\cdot 2H_2O$	2	0.1069	0.0542
NaI	0.0675	$NaI\cdot 2H_2O$	2	0.1245	0.0570
LiOH	0.0273	$LiOH\cdot H_2O$	1	0.0485	0.0212
NaOH	0.0329	$NaOH\cdot 7H_2O$	7	0.2060	0.1731
		$NaOH\cdot 5H_2O$	5	0.1568	0.1239
		$NaOH\cdot 4H_2O$	4	0.1316	0.0987
		$NaOH\cdot 3.5H_2O$	3.5	0.1134	0.0805
		$NaOH\cdot 3.1H_2O$	3.1	0.1041	0.0712
		$NaOH\cdot 2.75H_2O$	2.75	0.0959	0.0630
		$NaOH\cdot 2.5H_2O$	2.5	0.0880	0.0551
		$NaOH\cdot H_2O$	1	0.0550	0.0221
$NaClO_4$	0.0924	$NaClO_4\cdot H_2O$	1	0.1154	0.0230
KVO_3	0.0800	$KVO_3\cdot H_2O$	1	0.1024	0.0224
Na_2CO_3	0.0695	$Na_2CO_3\cdot 10H_2O$	10	0.3299	0.2604
		$Na_2CO_3\cdot 7H_2O$	7	0.2552	0.1857
		$Na_2CO_3\cdot H_2O$	1	0.0915	0.0220
Li_2SO_4	0.0832	$Li_2SO_4\cdot H_2O$	1	0.1036	0.0204
Na_2SO_4	0.1088	$Na_2SO_4\cdot 10H_2O$	10	0.3650	0.2562
$MgCl_2$	0.0782	$MgCl_2\cdot 6H_2O$	6	0.2154	0.1372
$BaBr_2$	0.1017	$BaBr_2\cdot H_2O$	1	0.1251	0.0234
$BaCl_2$	0.0890	$BaCl_2\cdot 2H_2O$	2	0.1309	0.0419
$SrCl_2$	0.0849	$SrCl_2\cdot 6H_2O$	6	0.2265	0.1416
$CoCl_2$	0.0732	$CoCl_2\cdot 6H_2O$	5	0.2085	0.1353
$CaCl_2$	0.0835	$CaCl_2\cdot 6H_2O$	6	0.2165	0.1330
		α-$CaCl_2\cdot 4H_2O$	4	0.1740	0.0905
		β-$CaCl_2\cdot 4H_2O$	4	0.1772	0.0937
		γ-$CaCl_2\cdot 4H_2O$	4	0.1956	0.1121
		$CaCl_2\cdot 2H_2O$	2	0.1326	0.0491
		$CaCl_2\cdot {}^1/_3H_2O$	1/3	0.0823	(−0.0012)[a]
PbO	0.0397	$PbO\cdot H_2O$	1	0.0684	0.0287

[a] The one-third hydrate, $CaCl_2\cdot {}^1/_3H_2O$, is the subject of a patent (Sinke, G. C. High-density calcium chloride 1/3 hydrate. US patent 1975, 3878295 19750415, 1975; *Chem. Abstr.* **1975**, *83*, 45397) and has been reported in the literature (Sinke, G. C.; Mossner, E. H.; Curnutt, J. L. *J. Chem. Thermodynam.* **1985**, *17*, 893), with a density of 2.36 g cm^{-3}. However, this density (as the table shows) would result in a negative volume for the water of hydration. If the chemical formula and density are correct, the bonding in the crystal would be most unusual.

(see Appendix 2), leading to

$$U_{POT}(M_pX_q\cdot nH_2O)/\text{kJ mol}^{-1} = 2I[\alpha V_m(M_pX_q\cdot nH_2O)^{-1/3}\{1 + \sum A_i[n/V_m(M_pX_q)]^i\} + \beta] + n\theta_U(H_2O) \quad (22)$$

where the summation is from $n = 1$ to ∞, and where A_1/nm^3 = 8.167×10^{-3}, A_2/nm^6 = 1.334×10^{-4}, A_3/nm^9 = 2.542×10^{-6}, A_4/nm^{12} = 5.189×10^{-8}, A_5/nm^{15} = 1.102×10^{-9}, A_6/nm^{18} = 2.400×10^{-11}, ..., etc., obtained by substituting eq 17 into eq A2.4 and hence into eq A2.5. This equation is really of academic interest only since it contains the term $\sum A_i[n/V_m(M_pX_q)]^i$, which represents a slowly convergent series. If sufficient terms are taken to obtain convergence, it *does* offer a means of obtaining $U_{POT}(M_pX_q\cdot nH_2O)$ *directly* from $V_m(M_pX_q\cdot nH_2O)$, the molecular (formula unit) volume of the hydrate, although this is not a recommended approach.

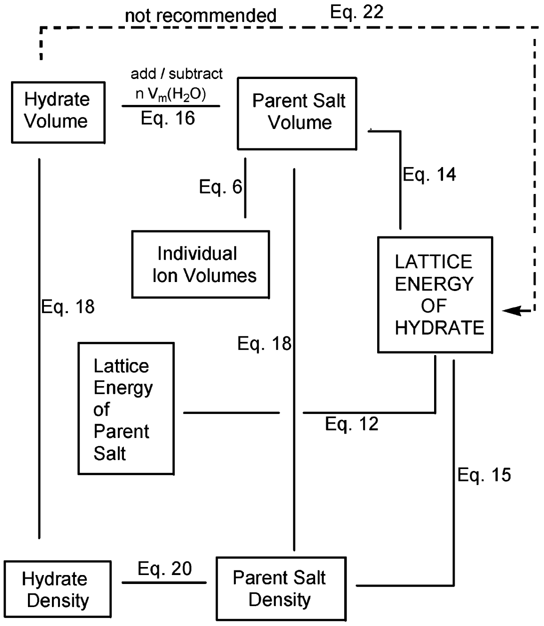
By analogy with eqs 14 and 15, eqs 23 and 24 offer a means of evaluating the lattice energies of the hydrates of minerals and complex chalcogenides, $M_pX_qZ_z...\cdot nH_2O$, having $U_{POT}(M_pX_qZ_z...\cdot nH_2O)$/kJ mol^{-1} > 5000 kJ mol^{-1}. These equations are not developed further in this paper.where the

$$U_{POT}(M_pX_qZ_z...\cdot nH_2O)/\text{kJ mol}^{-1} = AI[2I/\{V_m(M_pX_qZ_z.../\text{nm}^3)\}]^{1/3} + n\theta_U(H_2O) \quad (23)$$

$$U_{POT}(M_pX_qZ_z...\cdot nH_2O)/\text{kJ mol}^{-1} = B[I^4\rho_m(M_pX_qZ_z.../\text{g cm}^{-3})/M_m(M_pX_qZ_z...)]^{1/3} + n\theta_U(H_2O) \quad (24)$$

symbols, *I*, *A*, and *B*, on the right-hand side, apply to *parent* minerals (chalcogenides) and *A* and *B* have the values defined in footnotes *h* and *i* of Scheme 1.

Scheme 3. Flow Scheme Showing Interconnections among Various Input Parameters and the Target Ionic Hydrate Lattice Energy[a]



[a] Lines indicate variables connected by an equation. Conversions can go in either direction. (Note: Dotted line indicates a conversion that is not reversible.)

Practical Use of the Equations

Scheme 3 summarizes how the various equations listed in this paper can be used to interconvert between parameters and obtain a target value for $U_{POT}(M_pX_q\cdot nH_2O)$.

Starting from a knowledge of the density of either parent, $\rho_m(M_pX_q)$, or of hydrate $\rho_m(M_pX_q\cdot nH_2O)$, or of the molecular (formula unit) volume of the parent, $V_m(M_pX_q)$, or of the hydrate, $V_m(M_pX_q\cdot nH_2O)$, or from individual ion volumes, $V_m(M^{q+})$, $V_m(X^{p-})$, we follow the various lines indicated in the Scheme to estimate $U_{POT}(M_pX_q\cdot nH_2O)$. Tables 4−8 give typical results obtained by using eqs 12−15 for a series of hydrates, selected because they have already been extensively studied by traditional computational routes.[18,22,24] It will be noted that differences between the differently computed energies range between 1% and 10%, in most cases being less than 5%. Routes starting from density data tend to give slightly better results than those from volume sources. The

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(24) Herzig, P.; Jenkins, H. D. B.; Pritchett, M. S. F. *Solid State Commun.* **1984**, *15*, 397.

Table 4. Computation of Hydrate Lattice Energy, $U_{POT}(M_pX_q{\cdot}nH_2O)$/kJ mol^{-1}, Using $V_m(M_pX_q)$/nm^3 for the Parent Salt, as Obtained from the Crystal Structure Data, and using Eq 14 (Values Are Compared to Computational Results[19,21])

salt hydrate	$V_m{}^a$/nm^3	I, ionic strength	$U_{POT}(M_pX_q)$/ kJ mol^{-1} using eq 1 or 14	$U_{POT}(M_pX_q{\cdot}nH_2O)$ using eq 14 with $\theta_U(H_2O) = 54.3$/ kJ mol^{-1} and % difference		$U_{POT}(M_pX_q{\cdot}nH_2O)$/ kJ mol^{-1} and % difference from full-scale computational result		$U_{POT}(M_pX_q{\cdot}nH_2O)$/ kJ mol^{-1} Born−Fajans−Haber cycle
$NaCl{\cdot}2H_2O$	0.0449	1	764	873	3%	956[b]	6%	898
$NaBr{\cdot}2H_2O$	0.0533	1	727	836	2%	914[b]	7%	856
$NaI{\cdot}2H_2O$	0.0679	1	679	788	3%	874[b]	8%	809
$LiI{\cdot}3H_2O$	0.0543	1	723	886	4%	977[b]	6%	920
$CaCl_2{\cdot}2H_2O$	0.0828	3	2203	2312	2%	2320[d]	1%	2352
$CaCl_2{\cdot}4H_2O$[c]	0.0828	3	2203	2420	2%	2349[d]	5%	2470
$CaCl_2{\cdot}6H_2O$	0.0828	3	2203	2529	2%	2481[d]	4%	2575

[a] Volume derived from V_{cell}/Z for M_pX_q from crystal structure data. [b] Reference 22. [c] Averaged value for the three pleomorphs of the tetrahydrate. [d] Reference 18.

Table 5. Computation of Hydrate Lattice Energy, $U_{POT}(M_pX_q{\cdot}nH_2O)$/kJ mol^{-1}, Using $V_m(M^{q+})$ and $V_m(X^{p-})$ Obtained from Single Ion Volume Database for Parent Salt (Tables 4 and 5, Ref 3) and Eqs 6 and 14

salt hydrate	$V_m(M^{q+})$/ nm^3	$V_m(X^{p-})$/ nm^3	$V_m(M_pX_q)$/nm^3 using eq 6	I, ionic strength	$U_{POT}(M_pX_q)$/ kJ mol^{-1} using eq 1 or 14	$U_{POT}(M_pX_q{\cdot}nH_2O)$ using eq 14 with $\theta_U(H_2O) = 54.3$/ kJ mol^{-1} and % difference		$U_{POT}(M_pX_q{\cdot}nH_2O)$/ kJ mol^{-1} Born−Fajans−Haber cycle
$NaCl{\cdot}2H_2O$	0.0039	0.047	0.0509	1	737	845	6%	898
$NaBr{\cdot}2H_2O$	0.0039	0.056	0.0599	1	703	812	5%	856
$NaI{\cdot}2H_2O$	0.0039	0.072	0.0759	1	657	766	5%	809
$LiI{\cdot}3H_2O$	0.0020	0.072	0.0740	1	663	826	10%	920
$CaCl_2{\cdot}2H_2O$	0.0050	0.047	0.0990	3	2097	2206	6%	2352
$CaCl_2{\cdot}4H_2O$	0.0050	0.047	0.0990	3	2097	2314	6%	2470
$CaCl_2{\cdot}6H_2O$	0.0050	0.047	0.0990	3	2097	2423	6%	2575

Table 6. Computation of Hydrate Lattice Energy, $U_{POT}(M_pX_q{\cdot}nH_2O)$/kJ mol^{-1}, Using $V_m(M_pX_q{\cdot}nH_2O)$ Obtained from Crystal Structure Data for the Hydrate and Eqs 18 and 14 (Recommended Alternative to the Use of Eq 22)

salt hydrate	$V_m(M_pX_q{\cdot}nH_2O)$/ nm^3	$V_m(M_pX_q) = V_m(M_pX_q{\cdot}nH_2O) - nV_m(H_2O)^a$/nm^3	I	$U_{POT}(M_pX_q)$/ kJ mol^{-1} using eq 1 or 14	$U_{POT}(M_pX_q{\cdot}nH_2O)$ using eq 14 with $\theta_U(H_2O) = 54.3$/ kJ mol^{-1} and % difference		$U_{POT}(M_pX_q{\cdot}nH_2O)$/ kJ mol^{-1} Born −Fajans−Haber cycle
$NaCl{\cdot}2H_2O$	0.0948	0.0458	1	760	869	3%	898
$NaBr{\cdot}2H_2O$	0.1069	0.0579	1	710	820	4%	856
$NaI{\cdot}2H_2O$	0.1148	0.0658	1	685	794	2%	809
$LiI{\cdot}3H_2O$	0.131	0.0575	1	712	876	5%	920
$CaCl_2{\cdot}2H_2O$	0.1328	0.0838	3	2197	2304	2%	2352
$CaCl_2{\cdot}4H_2O$	0.1794	0.0814	3	2216	2431	2%	2470
$CaCl_2{\cdot}6H_2O$	0.2124	0.0654	3	2354	2680	4%	2575

[a] $V_m(H_2O)$ taken to be 0.0245 nm^3 from equation 17.

Table 7. Computation of Hydrate Lattice Energy, $U_{POT}(M_pX_q{\cdot}nH_2O)$/kJ mol^{-1}, from Measured Density, $\rho(M_pX_q)$/g cm^{-3}, of Parent Salt Using Eq 18 To Convert to $V_m(M_pX_q)$ and Eq 14 or Directly from Eq 15

salt hydrate	density,[25] $\rho_m(M_pX_q)$/ g cm^{-3}	$M_m(M_pX_q)$/ g	I	$U_{POT}(M_pX_q)$/ kJ mol^{-1} using eq 2 or 15	$U_{POT}(M_pX_q{\cdot}nH_2O)$/ kJ mol^{-1} using eq 1 or 14 and % difference		$U_{POT}(M_pX_q{\cdot}nH_2O)$/ kJ mol^{-1} Born−Fajans−Haber cycle
$NaCl{\cdot}2H_2O$	2.1678	58.44	1	764	873	3%	898
$NaBr{\cdot}2H_2O$	3.464	102.89	1	743	852	0%	856
$NaI{\cdot}2H_2O$	3.67	149.89	1	679	788	3%	809
$LiI{\cdot}3H_2O$	4.061	133.85	1	721	885	4%	920
$CaCl_2{\cdot}2H_2O$	2.174	110.99	3	2189	2298	2%	2352
$CaCl_2{\cdot}4H_2O$	2.174	110.99	3	2189	2406	2%	2470
$CaCl_2{\cdot}6H_2O$	2.174	110.99	3	2189	2515	2%	2575

[a] Using coefficients γ and δ as defined in footnote g, Scheme 1.

simplicity and value of the present approach are obvious by comparison with those of large-scale computational approaches.

Discussion: Thermodynamic and Physical Relationships

The theory developed above has yielded a plethora of forms of the basic eq 12, which gives the lattice potential energy of a hydrate or of its parent salt. Experimentally, salts can often only be crystallized in their hydrated (or solvated) form. In order to access the energetics in diverse situations, the various forms of equation are needed. This was illustrated recently in an application to HEDM materials (Appendix 3).

There is undoubtedly error in the experimental data used to obtain the rectilinear fits displayed by eq 11. Typically,

Table 8. Computation of Hydrate Lattice Energy, $U_{POT}(M_pX_q \cdot nH_2O)$/kJ mol^{-1}, Using Measured Density, $\rho_m(M_pX_q \cdot nH_2O)$/g cm^{-3}, of Hydrate and Eqs 5, 18, and 14

salt hydrate	density, $\rho(M_pX_q \cdot nH_2O)$/ g cm^{-3}	$M_m(M_pX_q \cdot nH_2O)$/ g	I	$V_m(M_pX_q)$/nm^3 using eq 5 [subtract $nV_m(H_2O)$]^a	$U_{POT}(M_pX_q)$/ kJ mol^{-1} using eq 2 or 15	$U_{POT}(M_pX_q \cdot nH_2O)$/ kJ mol^{-1} using eq 1 or 14 and % difference		$U_{POT}(M_pX_q \cdot nH_2O)$/ kJ mol^{-1} Born−Fajans−Haber cycle
$NaBr \cdot 2H_2O$	2.34	138.92	1	0.0496	743	851	0%	856
$NaI \cdot 2H_2O$	2.67	185.92	1	0.0666	683	792	2%	809
$LiI \cdot 3H_2O$	2.37^b	187.89	1	0.0627	694	857	7%	920
$CaCl_2 \cdot 2H_2O$	1.85	147.01	3	0.0827	2204	2313	2%	2352
$CaCl_2 \cdot 4H_2O$	1.836	183.05	3	0.0760	2256	2473	0%	2470
$CaCl_2 \cdot H_2O$	1.71	219.07	3	0.0651	2357	2683	8%	2575

[a] $V_m(M_pX_q \cdot nH_2O)$ calculated using eq 5. $V_m(M_pX_q)$ obtained by subtraction of $nV_m(H_2O)$. [b] The density of 3.86 g cm^{-3} quoted in ref 26 does not accord with the X-ray data[27] and is incorrect.

Table 9. Comparison of Parameters for Water Molecules in Various Solid-State Environments

solid phase	V_m/nm^3	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}
ice (0 °C)	0.0307	−51.14	−140.8
metastable ice^a (25 °C)		−50	−188.3
hydrates	0.0245	−56.8	−147.7
minerals^a ("structural" water)	0.0137		
zeolites^a (water in channels)	0.008		

[a] Helgeson, H. C.; Delany, J. M.; Nesbitt, H. W.; Bird, D. K. *Am. J. Sci.* **1978**, *278A*, 1. See p 49.

Table 10. Predicted Thermodynamic Data Using the Rectilinear Relationship, Eq 11

anhydrous salt	hydrate	predicted $\Delta_fH°$/ kJ mol^{-1}	comparison with sources other than ref 19
$RaCl_2$		−867	−887,^{a} −870^b
	$LiClO_3 \cdot {}^1/_4H_2O$	−444	
	$NaCl \cdot 2H_2O^c$	−1008.3	
	$NaIO_4 \cdot 3H_2O$	−1287	
	$NaNbO_3 \cdot 3.5H_2O$	−2361	
	$MgC_2O_4 \cdot 2H_2O$	−1866	
	$MgCO_3 \cdot 3H_2O$	−1992	
	$MgCO_3 \cdot 5H_2O$	−2589	
	$MgCO_3 \cdot 7H_2O$	−1866	
	$ZnCO_3 \cdot 2H_2O$	−1111	

[a] Brewer, L. L.; Bromley, L.; Gilles, P. W.; Lofgren, N. L. in *Chemistry and Metallurgy of Miscellaneous Materials*; Quill, L. L., Ed.; Natl. Nuclear Energy Ser. Div IV, 19B; McGraw Hill: New York, Toronto, London, 1950; p 76. [b] (a) Karapet'yants, M. Kh. *Zh. Fiz. Khim.* **1956**, *30*, 293. (b) Wilcox, D. E.; Bromley, L. A. *Ind. Eng.Chem.* **1963**, *55*, 32. [c] Required for Table 2, see footnote *b*.

the uncertainty in the *experimental* enthalpy of formation of a parent or a hydrate salt can range from a few kilojoules per mole to as much as 25 kJ mol^{-1} (see Table 2, ref 18). This uncertainty is of the *same order of magnitude* as the estimated uncertainty expressed above for predictions made by using eq 11. This fact elevates the significance of this relationship in thermodynamic terms.

The correlation parameters which are reported in this paper, viz., $\theta_U(H_2O)$/kJ mol^{-1} = 54.3 and $\theta_V(H_2O) = V_m(H_2O)$/nm^3 = 0.0245, are important physical quantities in their own right. $[\theta_{Hf}(H_2O) - \Delta_fH°(H_2O,g)]$ represents the enthalpy of incorporation of a mole of gaseous water molecules into a hydrate, and the value, −56.8 kJ mol^{-1}, may be compared with the enthalpy of incorporation of a mole of water molecules into ice, which is −51.13 kJ mol^{-1} (Table 9). Similarly, $[\theta_{Sf}(H_2O) - \Delta_fS°(H_2O,g)]$ represents the entropy of incorporation of a mole of gaseous water molecules into a hydrate. We have established (in work to be submitted) that $\theta_{Sf}(H_2O)$/J K^{-1} mol^{-1} (H$_2$O molecule)$^{-1}$ = −192.4, and thus, since $\Delta_fS°(H_2O,g)$/J K^{-1} mol^{-1} = −44.5, the entropy of incorporation of a gaseous water molecule into a hydrate is −147.9 J K^{-1} mol^{-1},

It is apparent that the water molecule is more strongly held in the hydrate than it is in ice. This conclusion is corroborated by the fact that the molar volume of water in a hydrate, 0.0245 nm^3, is about 20% smaller than in ice, at 0.0307 nm^3. This is itself consistent with the longer hydrogen bonds observed in the open structure of ice (177 pm) compared to the normal length of a covalent O−H bond (94 pm).

We have used eq 11 to predict 11 $\Delta_fH°$ values for hydrates or their parents which were missing from ref 19, in cases where $\Delta_fH°$ for either the corresponding parent or hydrate salts were listed. The values predicted are listed in Table 10. In work in preparation, we have also established the entropy change on incorporating a water molecule into a hydrate.

Conclusion and Future Work

This suite of work (i.e., refs 1−4, work already submitted,[28] and work currently in progress) has, as its mission, to provide the widest group of chemists with new, modern thermodynamic approaches. These are designed to considerably extend the range of predictive thermodynamic methods, particularly for the benefit of materials, inorganic synthetic, and physical chemists. The result has been the creation of reliable and simple tools to attack problems which have been quite beyond reach with the procedures available hitherto. The simple methods that have evolved are capable of assessing the thermodynamics of a range of ionic materials: from simple binary systems to complex minerals and, now, their hydrates or solvates. These methods are almost trivial in their application. They utilize readily available physical information (the effects of whose errors are often minimized

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(25) Note that this is not the same as the X-ray density, ρ_X, often cited, which is another form of V_m since they are related by eq 20 ($\rho = \rho_X$). ρ_m experimental would be expected to be close in value to ρ_X, however.

(26) Lide, D. R., Ed. *Handbook of Chemistry and Physics*, 82nd ed.; CRC Press: Boca Raton, 2001−2002; pp 4−66.

(27) Donnay, J. D. H.; Ondik, H. M. *Crystal Data: Determinative Tables*, 3rd ed.; National Bureau of Standards: Washington, DC, 1973; Vol. 2.

(28) Jenkins, H. D. B.; Glasser, L. *J. Am. Chem. Soc.* **2002**, submitted for publication.

by cube-root dependency in the equations) and thus are easily accessible to both specialists and nonspecialists. Thermodynamic stabilities of materials for synthesis can now be assessed thus directing chemists toward practicable procedures or suggesting reasons for lack of success in other procedures.

In order to complete the scope of the predictions, it is necessary to be able to provide *entropic* information, as well as the enthalpic information provided based on lattice potential energies. We have already succeeded in developing very successful entropic predictions,[28] which apply almost equally well to organic as to inorganic materials.

By far the most significant development, to be reported in the longer term, arises directly from the present work and from the functional form of the equations typified by eqs 11 and 12 and by the plot in Figure 1. These are part of a fundamental, *hitherto unreported and unrecognized*, extra-thermodynamic rule (which is of much greater generality than, but of a type similar to that of Trouton). Definition and use of this rule, in areas we have researched to date, will provide (with high precision) much of the missing thermodynamic information that currently hampers progress right across the discipline from inorganic chemistry through to mineralogy and geology.

Acknowledgment. H.D.B.J. thanks the EPSRC for support in the form of a ROPA (Realising Our Potential Award), the Canadian Institute of Chemistry for travel money to visit Montreal, and the University of Warwick for facilities for carrying out this work. Prof. T. M Klapötke is thanked for his contribution to the discussion of HEDM materials and for his hospitality during a visit by H.D.B.J. to the University of Munich.

Appendix 1

The lattice energy, $U_{\mathrm{POT}}(\mathrm{M}_p\mathrm{X}_q\cdot n\mathrm{H_2O})$ of a hydrate is defined by the process

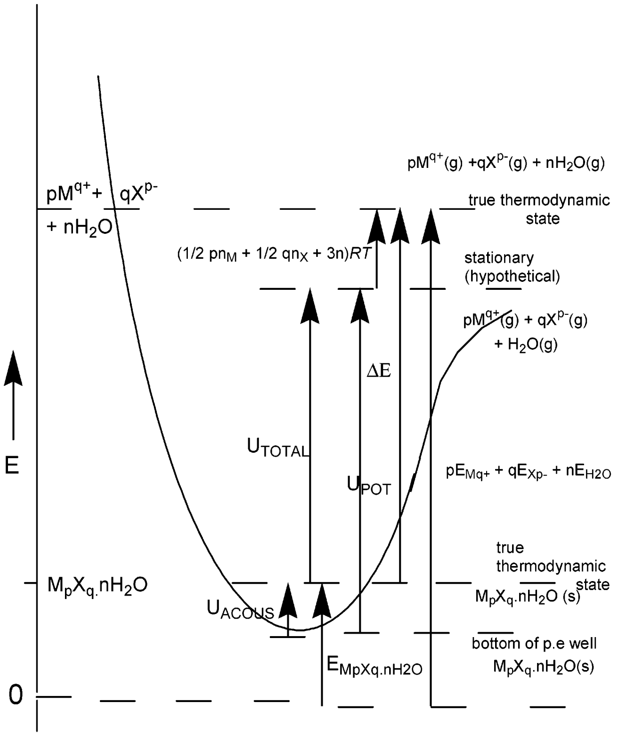
$$\mathrm{M}_p\mathrm{X}_q\cdot n\mathrm{H_2O(s)} \rightarrow p\mathrm{M}^{q+}(\mathrm{g}) + q\mathrm{X}^{p-}(\mathrm{g}) + n\mathrm{H_2O(g)} \quad \text{(A1.1)}$$

If we assume that the ions in the crystal are static in their positions on their lattice points and that the gaseous ions and the n water molecules produced are also stationary (and, in this sense, in a hypothetical state), then we can define (see Scheme A1.1) $E(\mathrm{M}^{q+})$, $E(\mathrm{X}^{p-})$, $E(\mathrm{H_2O})$, and $E(\mathrm{M}_p\mathrm{X}_q\cdot n\mathrm{H_2O})$ to be the absolute total internal energies of the species indicated. ΔE, the total internal energy change in going from the true thermodynamic state of the crystalline hydrate to the true thermodynamic state of the gaseous species M^{q+}, X^{p-}, and $\mathrm{H_2O}$ (possessing, as they variously do, translational, rotational, and vibrational energy), can be written

$$\Delta E = pE(\mathrm{M}^{q+}) + qE(\mathrm{X}^{p-}) + nE(\mathrm{H_2O}) - E(\mathrm{M}_p\mathrm{X}_q\cdot n\mathrm{H_2O}) \quad \text{(A1.2)}$$

If M^{q+} and X^{p-} are monatomic ions, they each possess only translational degrees of freedom (i.e., a kinetic energy of $3RT/2$ per ion), while if they are linear polyatomic ions, they possess rotational and translational degrees of freedom ($=5RT/2$ per ion) (any vibrational modes are assumed to be equally excited in the crystal and in the gaseous phase). For nonlinear polyatomic ions these will possess rotational and translational degrees of freedom yielding a kinetic energy of $6RT/2 = 3RT$ per ion. We generalize this by writing the number of degrees of freedom n_{M} (and n_{X}) = 3, 5, or 6 so as to apply to a general hydrate. The gaseous water molecules each possess rotational and translational kinetic energy of $3RT$ per ion, it being again assumed that the vibrationalmodes are equally excited in the crystal and in the gas. Hence,

Scheme A1.1 Potential Energy Diagram for Reactions in Ionic Hydrate Systems



$$\Delta E = (\tfrac{1}{2}pn_{\mathrm{M}} + \tfrac{1}{2}qn_{\mathrm{X}} + (\tfrac{1}{2})6n)RT + U_{\mathrm{TOTAL}} \quad \text{(A1.3)}$$

where

$$U_{\mathrm{TOTAL}} = U_{\mathrm{POT}} - U_{\mathrm{ACOUS}} \quad \text{(A1.4)}$$

in which U_{ACOUS} is the acoustic potential energy of the lattice, correcting for the fact that the ions actually vibrate on their lattice points and are not stationary. Thus,

$$\Delta E = (\tfrac{1}{2}pn_{\mathrm{M}} + \tfrac{1}{2}qn_{\mathrm{X}} + 3n)RT + U_{\mathrm{POT}} - U_{\mathrm{ACOUS}} \quad \text{(A1.5)}$$

We can estimate U_{ACOUS} for a crystal lattice, either from knowledge of specific heat capacities as a function of temperature and from the zero-point energy of the lattice or by means of either the Einstein or Debye theory of specific heat capacities. However, for the purposes of the present work, we simply assume 3 degrees of vibrational freedom per species in the solid state so that

$$U_{\mathrm{ACOUS}} = 3(p + q + n)RT \quad \text{(A1.6)}$$

and hence

$$\Delta E = [p(^1/_2 n_\mathrm{M} - 3\ ) + q(^1/_2 n_\mathrm{X} - 3)]RT + U_\mathrm{POT} \qquad \text{(A1.7)}$$

The standard enthalpy change, $\Delta H^{(n)}{}_\mathrm{hydrate}$, for the process involved in the lattice energy step (A1.1) is related, by standard thermodynamics, to the internal energy change, ΔE, by the equation

$$\Delta H^{(n)}{}_\mathrm{hydrate} = \Delta E + P\Delta V \qquad \text{(A1.8)}$$

If we ignore the volume of the crystal compared to the volume occupied by the gaseous ions, assumed to be ideal, we have

$$P\Delta V = (p + q + n)RT \qquad \text{(A1.9)}$$

and, hence,

$$\Delta H^{(n)}{}_\mathrm{hydrate} = [p(^1/_2 n_\mathrm{M} - 3) + q(^1/_2 n_\mathrm{X} - 3) + (p + q + n)]RT + U_\mathrm{POT} \qquad \text{(A1.10)}$$

leading to

$$\Delta H^{(n)}{}_\mathrm{hydrate} = U_\mathrm{POT} + [p(^1/_2 n_\mathrm{M} - 2) + q(^1/_2 n_\mathrm{X} - 2) + n]RT \qquad \text{(A1.11)}$$

Appendix 2

$$U_\mathrm{POT}(\mathrm{M}_p\mathrm{X}_q\cdot n\mathrm{H_2O})/\mathrm{kJ\ mol^{-1}} = 2I[\alpha\{V_\mathrm{m}(\mathrm{M}_p\mathrm{X}_q\cdot n\mathrm{H_2O}) - nV_\mathrm{m}(\mathrm{H_2O})\}^{-1/3} + \beta] + n\theta_\mathrm{U}(\mathrm{H_2O}) \qquad \text{(A2.1)}$$

Since $V_\mathrm{m}(\mathrm{M}_p\mathrm{X}_q\cdot n\mathrm{H_2O})$ will always be greater than $nV_\mathrm{m}(\mathrm{H_2O})$, we can use the binomial expansion:[24]

$$U_\mathrm{POT}(\mathrm{M}_p\mathrm{X}_q\cdot n\mathrm{H_2O})/\mathrm{kJ\ mol^{-1}} = 2I[\alpha V_\mathrm{m}(\mathrm{M}_p\mathrm{X}_q\cdot n\mathrm{H_2O})^{-1/3}\{1 - nV_\mathrm{m}(\mathrm{H_2O})/V_\mathrm{m}(\mathrm{M}_p\mathrm{X}_q\cdot n\mathrm{H_2O})\}^{-1/3} + \beta] + n\theta_\mathrm{U}(\mathrm{H_2O}) \qquad \text{(A2.2)}$$

When eq A2.2 is combined with

$$\Omega = nV_\mathrm{m}(\mathrm{H_2O})/V_\mathrm{m}(\mathrm{M}_p\mathrm{X}_q\cdot n\mathrm{H_2O}) \qquad \text{(A2.3)}$$

and expanded, we obtain the slowly convergent series shown in the equation

$$U_\mathrm{POT}(\mathrm{M}_p\mathrm{X}_q\cdot n\mathrm{H_2O})/\mathrm{kJ\ mol^{-1}} = 2I[\alpha V_\mathrm{m}(\mathrm{M}_p\mathrm{X}_q\cdot n\mathrm{H_2O})^{-1/3}\{1 + {}^1/_3\Omega + {}^2/_9\Omega^2 + {}^{14}/_{81}\Omega^3 + {}^{35}/_{243}\Omega^4 + {}^{91}/_{729}\Omega^5 + {}^{728}/_{6561}\Omega^6 + {}^{1976}/_{19683}\Omega^7 + {}^{5434}/_{59049}\Omega^8 + ...\} + \beta] + n\theta_\mathrm{U}(\mathrm{H_2O}) \qquad \text{(A2.4)}$$

Consider the use of eq A2.4 to estimate the lattice energy of $\mathrm{CaCl_2\cdot 6H_2O}$, $U_\mathrm{POT}(\mathrm{CaCl_2\cdot 6H_2O})$, for which $V_\mathrm{m}(\mathrm{CaCl_2\cdot 6H_2O})/\mathrm{nm^3} = 0.2124$, thus $\Omega = 0.692$; for the parent $\mathrm{CaCl_2}$, $I = 3$, $\alpha/\mathrm{kJ\ mol^{-1}\ nm} = 133.5$, and $\beta/\mathrm{kJ\ mol^{-1}} = 60.9$. Hence,

$$U_\mathrm{POT}(\mathrm{CaCl_2\cdot 6H_2O})/\mathrm{kJ\ mol^{-1}} = 6\{223.8(1 + 0.231 + 0.106 + 0.057 + 0.033 + 0.020 + 0.012 + 0.008 + 0.004 + ...) + 60.9\} + 6(54.3) = 1342.5(1 + 0.231 + 0.106 + 0.057 + 0.033 + 0.020 + 0.012 + 0.008 + 0.004 + ...) + 691.2 \qquad \text{(A2.5)}$$

Table A2.1 Cumulative Value of $U_\mathrm{POT}(\mathrm{CaCl_2\cdot 6H_2O})$ Obtained by Evaluating Successive Terms of the Series in Eq A2.6

no. of terms taken in series	cumulative value of $U_\mathrm{POT}(\mathrm{CaCl_2\cdot 6H_2O})/\mathrm{kJ\ mol^{-1}}$
1	2034
2	2344
3	2486
4	2563
5	2607
6	2634
7	2650
8	2661
9	2666
converged result (after 11 terms)	2669
Born−Fajans−Haber cycle value	2575

Scheme A3.1 Thermodynamic Cycle for HEDM Synthesis

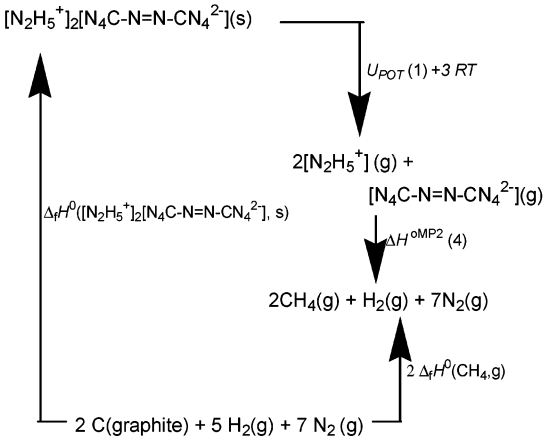


Table A2.1 shows how the convergence progresses as the terms in the inner bracket of eq 15 are successively evaluated, resulting in the converged result (after evaluating 11 terms) that

$$U_\mathrm{POT}(\mathrm{CaCl_2\cdot 6H_2O})/\mathrm{kJ\ mol^{-1}} = 2669 \qquad \text{(A2.6)}$$

Appendix 3

Application to High-Energy-Density Materials (HEDM). A recent study has reported[12] on 5,5′-azotetrazolate high-energy-density materials based on the 5,5′-azotetrazolate anion, $[\mathrm{N_4C{-}N{=}N{-}C_4N}]^{2-}$. Synthesis produced the yellow dihydrazinium salt in the form of dihydrate needles, $[\mathrm{N_2H_5}]_2{}^+[\mathrm{N_4C{-}N{=}N{-}C_4N}]^{2-}\cdot 2\mathrm{H_2O}$, which were shown to be monoclinic, crystallizing in space group $P2/c$ and having lattice constants $a/\mathrm{nm} = 0.8958(2)$, $b/\mathrm{nm} = 0.36596(7)$, $c/\mathrm{nm} = 1.6200(3)$, and $\beta = 96.834(3)°$ with a unit cell volume $V/\mathrm{nm^3} = 0.5273(2)$ and number of molecules per formula unit $Z = 2$; hence, the formula unit volume of the dihydrate is $V_\mathrm{m}([\mathrm{N_2H_5}]_2{}^+[\mathrm{N_4C{-}N{=}N{-}C_4N}]^{2-}\cdot 2\mathrm{H_2O})/\mathrm{nm^3} = 0.2636$. The enthalpy of combustion of the parent salt, $[\mathrm{N_2H_5}]_2{}^+[\mathrm{N_4C{-}N{=}N{-}C_4N}]^{2-}$, measured experimentally, corresponded to a standard enthalpy of formation of the parent salt, $\Delta_\mathrm{f}H°([\mathrm{N_2H_5}]_2{}^+[\mathrm{N_4C{-}N{=}N{-}C_4N}]^{2-},\mathrm{s})/\mathrm{kJ\ mol^{-1}} = 858$. Using the cycle in Scheme A3.1 we have

$$\Delta_f H°([N_2H_5]_2{}^+[N_4C-N{=}N-C_4N]^{2-},s) = 2\Delta_f H°(CH_4,g) - \Delta H^{°MP2} - U_{POT}([N_2H_5]_2{}^+[N_4C-N{=}N-C_4N]^{2-}) - 3RT \quad (A3.1)$$

where $\Delta_f H°(CH_4,g)$/kJ mol^{-1} = −74.81.[19] For the reaction (A3.2),

$$2N_2H_5{}^+(g) + [N_4C-N{=}N-CN_4]^{2-}(g) \rightarrow 2CH_4(g) + H_2(g) + 7N_2(g) \quad (A3.2)$$

the reaction enthalpy, $\Delta H^{°MP2}$/kJ mol^{-1}, is calculated[12] to be − 2506.

By estimating a value of $U_{POT}([N_2H_5]_2{}^+[N_4C-N{=}N-C_4N]^{2-})$, we can test our procedures by then estimating the corresponding $\Delta_f H°([N_2H_5]_2{}^+[N_4C-N{=}N-C_4N]^{2-},s)$, using eq A3.1.

Taking $V_m([N_2H_5]_2{}^+[N_4C-N{=}N-C_4N]^{2-}\cdot 2H_2O)$/nm^3 to be 0.2636, and using eq 16, we have

$$V_m([N_2H_5]_2{}^+[N_4C-N{=}N-C_4N]^{2-})/\mathrm{nm}^3 = 0.2636 - 2V_m(H_2O) = 0.2146 \quad (A3.3)$$

Using eq 1 (Scheme 1) with the appropriate values of I (=3) and α and β (footnote *b*, Scheme 1) leads to

$$U_{POT}([N_2H_5]_2{}^+[N_4C-N{=}N-C_4N]^{2-})/\mathrm{kJ\ mol^{-1}} = 1478 \quad (A3.4)$$

and, from eq 25, we predict

$$\Delta_f H°([N_2H_5]_2{}^+[N_4C-N{=}N-C_4N]^{2-},s)/\mathrm{kJ\ mol^{-1}} = 871 \quad (A3.5)$$

which differs by only 1.5% from the experimental value reported.[12] It is also clear that had these workers also measured the experimental density[25] of their material, eq 15 could then have been used to give a second estimate of U_{POT}-$([N_2H_5]_2{}^+[N_4C-N{=}N-C_4N]^{2-})$.

Crystallographers should be encouraged to make *independent* measurements of density for new materials, which is easily done and requires miniscule amounts of material.

IC020222T