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Lattice Potential Energy Estimation for Complex Ionic Salts from Density Measurements

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This paper is one of a series exploring simple approaches for the estimation of lattice energy of ionic materials, avoiding elaborate computation. The readily accessible, frequently reported, and easily measurable (requiring only small quantities of inorganic material) property of density, ρ_m, is related, as a rectilinear function of the form $(\rho_m/M_m)^{1/3}$, to the lattice energy U_{POT} of ionic materials, where M_m is the chemical formula mass. Dependence on the cube root is particularly advantageous because this considerably lowers the effects of any experimental errors in the density measurement used. The relationship that is developed arises from the dependence (previously reported in Jenkins, H. D. B.; Roobottom, H. K.; Passmore, J.; Glasser, L. *Inorg. Chem.* **1999**, *38*, 3609) of lattice energy on the inverse cube root of the molar volume. These latest equations have the form $U_{POT}/\text{kJ mol}^{-1} = \gamma(\rho_m/M_m)^{1/3} + \delta$, where for the simpler salts (i.e., $U_{POT}/\text{kJ mol}^{-1} < 5000$ kJ mol^{-1}), γ and δ are coefficients dependent upon the stoichiometry of the inorganic material, and for materials for which $U_{POT}/\text{kJ mol}^{-1} > 5000$, $\gamma/\text{kJ mol}^{-1}\text{ cm} = 10^{-7}\, AI(2IN_A)^{1/3}$ and $\delta/\text{kJ mol}^{-1} = 0$ where A is the general electrostatic conversion factor ($A = 121.4$ kJ mol^{-1}), I is the ionic strength $= \frac{1}{2}\sum n_i z_i^2$, and N_A is Avogadro's constant.

Introduction

Recently, a new approach has been proposed[1] for the estimation of the lattice potential energy, U_{POT}/kJ mol^{-1}, of ionic materials. The equation developed uses the molecular (formula unit) volume,[2] V_m/nm^3 molecule^{-1}, and the ionic strength,[3] I, of the lattice (I can be simply calculated, as $I = {}^1/_2\sum n_i\, z_i^2$, where n_i is the number of ions of type i in the formula unit with charge z_i, and the summation extends over all ions in the formula unit). Applicable for lattice energies up to 5000 kJ mol^{-1}, the equation has the form

$$U_{POT}/\text{kJ mol}^{-1} = 2I[\alpha\, (V_m)^{-1/3} + \beta] \qquad (1a)$$

where α and β are appropriate fitted coefficients (see Table 1) chosen according to the stoichiometry of the salt.[4] The coefficient α is close in value[1] to the general electrostatic conversion factor, $A = 121.4$ kJ mol^{-1}.

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(1) Jenkins, H. D. B.; Roobottom, H. K.; Passmore, J.; Glasser, L. *Inorg. Chem.* **1999**, *38*, 3609.

(2) V_m can be obtained (a) directly from crystal structure or powder diffraction data using the unit cell parameters (a, b, c, α, β, γ) in eq 4 of ref 1 (anorthic/triclinic lattices). Specifically, for individual lattice types: $V_m = a^3/Z$ (cubic); $V_m = abc/Z$ (orthorhombic); $V_m = a^2c/Z$ (tetragonal); $V_m = abc{\cdot}\sin\beta/Z$ (monoclinic); $V_m = 0.86602\ a^2c/Z$ (hexagonal), where sin 60° = 0.86602; $V_m = a^3(1 - 3\cos^2\alpha + 2\cos^3\alpha)^{1/2}/Z$ (rhombohedral), where Z is the number of molecules in the unit cell; (b) from tabulated ion volumes.

(3) Glasser, L. *Inorg. Chem.* **1995**, *34*, 4935.

(4) Generalised parameters α and β for salts (p:q) and values specific for charge ratios of (1:1), (1:2), and (2:1) are from ref 1. Additionally, parameters for use in the case of MX (2:2) salts, containing a divalent anion and cation, are: α/kJ mol^{-1} nm = 101.6 and β/kJ mol^{-1} = 91.5. Note: In ref 1, the ratios (*1:1*), etc., are used to represent ion ratios, not charge ratios as in the present paper.

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Table 1. Constants for Use in Equations 1a (α, β) and 1b (γ, δ)

salt (charge ratio)	I, ionic strength	α^a/kJ mol^{-1} nm	β^a/kJ mol^{-1}	γ^c/kJ mol^{-1} cm	δ^c/kJ mol^{-1}
MX (1:1)	1	117.3	51.9	1981.2	103.8
M_2X (1:2)	3	165.3	−29.8	8375.6	−178.8
MX_2 (2:1)	3	133.5	60.9	6764.3	365.4
MX (2:2)	4	101.6^b	91.5^b	6864.0	732.0
		General Formula			
M_pX_q (q:p)	$I = {}^1/_2(pq^2 + qp^2)$	138.7	27.6	2342.6·I	55.2·I

[a] Values from ref 1. [b] Values reported here. [c] $\gamma = 2 \times 10^{-7} I\alpha N_A{}^{1/3}$; $\delta = 2I\beta$.

Table 2. U_{POT}(pred) Predicted from ρ_m, Calculated Using Equation 1b or 2b, and Compared with Reference Values

salt	experimental density ρ_m/g cm^{-3}	formula mass, M_m	U_{POT}(pred)/kJ mol^{-1}	U_{POT}(ref)^a/kJ mol^{-1}
	$U_{POT} < 5000$ kJ mol^{-1} (using eq 1b)			
	z_+:$z_- = 1$:1			
$NaClO_3$	2.49	106	670	770
$KClO_4$	2.52	139	625	599
LiF	2.635	25.9	1028	1030
KI	3.13	166	631	632
$CsICl_2$	3.86	331	553	555^b
TlCN	6.528	230	708	690^b
	z_+:$z_- = 1$:2			
Li_2S	1.66	45.9	2590	2464
Na_2SiF_6	2.679	188	1852	1832^b
K_2CrO_4	2.732	194	1843	1849^b
$Rb_2Cr_2O_7$	3.02, 3.125^c	387	1482, 1502	1532^b
K_2PtCl_4	3.38	415	1506	1574
Rb_2SeO_4	3.9	314	1761	1686
Cs_2SO_4	4.243	362	1724	1596
	z_+:$z_- = 2$:1			
$CaCl_2$	2.15	111	2182	2223
$Ca(ClO_2)_2$	2.71	175	2051	2003^b
$Ca(PO_3)_2$	2.82	198	2005	1912^b
$CuCl_2$	3.386	134	2348	2774
CaI_2	3.956	294	1974	1905
BaI_2	5.15	391	1963	1831
	z_+:$z_- = 2$:2			
$CaCO_3$	2.71	100	2793	2814
$BaSiF_6$	4.29	279	2438	2362^b
BaO	5.72	153	3026	3029
	$U_{POT} > 5000$ kJ mol^{-1} (using eq 2b)			
Mg_2SiO_4 (forsterite)	3.222	141	19899	20697^d
Al_2SiO_5 (kyanite)	3.247	162	28421	28687^d
$KAlSi_3O_8$ (microcline)	2.56	278	43335	47583^d

[a] Jenkins, H. D. B. Lattice Energies. In *Handbook of Chemistry and Physics*, 79th ed.; Lide, D. R. Ed.; CRC Press: Boca Raton, FL, 1998; Chapter 9, p 1222. [b] Calculated using tabulated ion volumes, Table 3. [c] Monoclinic, triclinic rubidium dichromate, respectively. [d] See ref 9.

Equation 1a has rapidly been adopted to study energetics in areas as diverse as haloorganostannate(IV) thermochemistry,[5] hydrogen bonding,[6] and high-energy-density materials (HEDM)[7] and in the study of polynitrogen chemistry and the thermochemistry of new N_5^+ salts.[8]

Table 3. U_{POT} Calculated Using Tabulated Ion Volumes[1]

salt	cation volume, V_+/nm^3	anion volume, V_-/nm^3	V_m/nm^3	U_{POT}/kJ mol^{-1}
		z_+:$z_- = 1$:1		
$CsICl_2$	0.01882	0.122	0.141	555
TlCN	0.014	0.050	0.064	690
		z_+:$z_- = 1$:2		
Na_2SiF_6	0.00394	0.112	0.120	1832
K_2CrO_4	0.00986	0.097	0.117	1849
$Rb_2Cr_2O_7$	0.01386	0.167	0.195	1532
		z_+:$z_- = 2$:1		
$Ca(ClO_2)_2$	0.00499	0.056	0.117	2003
$Ca(PO_3)_2$	0.00499	0.067	0.139	1912
		z_+:$z_- = 2$:2		
$BaSiF_6$	0.01225	0.112	0.124	2362

We have also developed[9] a generalized, limiting version of the equation, suitable for ionic materials with lattice energies greater than 5000 kJ mol^{-1} (such as minerals):

$$U_{POT}/\text{kJ mol}^{-1} = AI(2I/V_m)^{1/3} \tag{2a}$$

It is noteworthy that this limiting equation contains *no* adjustable constants whatsoever, because A is the previously mentioned electrostatic conversion factor with a fixed value ($A = 121.4$ kJ mol^{-1}). Furthermore, because no structural detail is required, the equations are applicable not only to crystalline ionic solids but also to amorphous ionic solids and ionic liquids.

The attraction of this volume-based approach to lattice potential energy lies in its extreme simplicity, its ability to provide data for new and complex ionic materials (and even hypothetical ones) for which no prior thermodynamic information is available, and in its ability to link energetics (via volume data) *directly* to the formula unit. The dependence on volume data, rather than on more traditional thermochemical radii (via the Kapustinskii equation and its generalization[10]), is also inherently more appropriate for lattices containing ions which are often patently nonspherical.

Theory

Molar volume, V_m, is nowadays often found by X-ray crystallographic studies, which yield lattice constants together with Z, the number of formula units per cell: $V_m = V_{cell}/Z$. But density, ρ_m, is also a readily measurable property[11,12] of ionic solids, conveniently made on small quantities of material, widely reported, and directly related to V_m. Measured values of ρ_m can be compared to the calculated X-ray density, ρ_{calcd}, using the equation

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(5) Tudela, D.; Diaz, M.; Alvaro, D. A.; Ignacio, J.; Seijo, L.; Belsky, V. K. *Organometallics*. **2001**, *20*, 654.

(6) Fortes, A. D.; Brodholt, J. P.; Wood, I. G.; Vočadlo, L.; Jenkins, H. D. B. *J. Chem. Phys*. **2001**, *115*, 7006.

(7) Hammerl, A.; Klapötke, T. M.; Noth, H.; Warchhold, M.; Holl, G.; Kaiser, M.; Ticnaris, U. *Inorg. Chem*. **2001**, *40*, 3570.

(8) Vij, A.; Wilson, W. W.; Vij, V.; Tham, F. S.; Sheehy, J. A.; Christe, K. O. *J. Am. Chem. Soc*. **2001**, *123*, 6308.

(9) Glasser, L.; Jenkins, H. D. B. *J. Am. Chem. Soc*. **2000**, *122*, 632.

(10) (a) Kapustinskii, A. F. *Q. Rev. Chem. Soc. (London)* **1956**, *10*, 283. (b) Jenkins, H. D. B.; Thakur, K. P. *J. Chem. Educ*. **1979**, *56*, 576. (c) Roobottom, H. K.; Jenkins, H. D. B.; Passmore, J.; Glasser, L. *J. Chem. Educ.* **1999**, *76*, 1570.

(11) Richards, F. M. In *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic: Dordrecht, 1995; Vol C, p 141.

(12) Density, ρ_m/Mg m^{-3} (or g cm^{-3}), is related to V_m/m^3 molecule^{-1} by the equation $\rho_m = M_m/N_AV_m$ where M_m is the chemical formula weight and N_A is Avogadro's number (6.02245×10^{23} molecule mol^{-1}). Converting V_m into units of nm^3 molecule^{-1} (as required in eq 1), $V_m = 10^{21}\ M_m/N_A\ \rho_m$, and substituting for V_m in eq 1 leads to the form $U_{POT}/\text{kJ mol}^{-1} = 2I[10^{-7}\alpha N_A{}^{1/3}(\rho_m/M_m)^{1/3} + \beta] = \gamma(\rho_m/M_m)^{1/3} + \delta$ which enables the lattice energy to be obtained directly from ρ_m measurements made in g cm^{-3} (Mg m^{-3}).

Table 4. U_{POT} Predicted for Anhydrous Salts, from Hydrate Densities and Volumes. Assumed Value of $V(H_2O)$: 0.02496 nm^3

salt·nH$_2$O	n(H$_2$O)	formula mass/g	density/g cm^{-3}	formula volume/nm^3	predicted volume: V(anhyd) = V(hydrate) − nV(H$_2$O)/nm^3				
LiI·3H$_2$O	3	187.88	2.32[a]	0.1344	0.1344				
LiI·2H$_2$O	2	169.87	2.607	0.1082		0.1082			
LiI·H$_2$O	1	151.86	3.13	0.0805			0.0805		
LiI·$^1/_2$H$_2$O	0.5	142.86	3.5	0.0678				0.0678	
LiI	0	133.85	4.061	0.0547	0.0596	0.0582	0.0556	0.0553	
% vol error					9	6	2	1	
U_{POT}(anhyd)[b]	ref	730		722	705	709	719	720	
Na$_2$CO$_3$·10H$_2$O	10	286.14	1.44	0.3299	0.3299				
Na$_2$CO$_3$·7H$_2$O	7	232.1	1.51	0.2552		0.2552			
Na$_2$CO$_3$·H$_2$O	1	124	2.25	0.0915			0.0915		
Na$_2$CO$_3$	0	105.99	2.532	0.0695	0.0803	0.0804	0.0665		
% vol error					15	16	−4		
U_{POT}(anhyd)[b]	ref	2301		2234	2361	2380	2420		
CaCl$_2$·6H$_2$O	6	219.08	1.68	0.2165	0.2165				
CaCl$_2$·2H$_2$O	2	147.02	1.86[a]	0.1312		0.1312			
CaCl$_2$	0	110.99	2.174	0.0847	0.0667	0.0813			
% vol error					−21	−4			
U_{POT}(anhyd)[b]	ref	2223		2189	2340	2214			
Using X-ray Volumes[c]									
CaCl$_2$·6H$_2$O	6	219.08		0.2124	0.2124				
α-CaCl$_2$·4H$_2$O (alpha)	4	183.1		0.1740		0.1740			
β-CaCl$_2$·4H$_2$O (beta)	4	183.1		0.1772			0.1772		
γ-CaCl$_2$·4H$_2$O (gamma)	4	183.1		0.1956				0.1956	
CaCl$_2$·2H$_2$O	2	147.02		0.1328					0.1328
CaCl$_2$	0	110.99		0.0835	0.0626	0.0742	0.0773	0.0957	0.0829
% vol error					−25	−11	−7	15	−1
U_{POT}(anhyd)[b]	ref	2223		2198	2382	2272	2246	2116	2203

[a] *Landolt-Börnstein Tables*, 6th ed.; Borchers, H., Hausen., H., Hellwege, K.-H., Schäfer, K. L., Schmidt, E., Eds.; Springer-Verlag: Berlin, 1971; vol. II, part 1. Values in *Handbook of Chemistry and Physics*, 79th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1998; Chapter 9, p 1222 are incorrect. [b] Reference and predicted lattice energies of the anhydrous salt. [c] Lattice constants for CaCl$_2$ and its hydrates are collated in ref 13.

$$\begin{aligned}\rho_{calcd}/\text{g cm}^{-3} &= (M_m/\text{g})/((V_m/\text{cm}^3)N_A)\\ &= 1.66\times10^{-3}(M_m/\text{g})/(V_m/\text{nm}^3)\\ &= 1.66\times10^{-3}Z(M_m/\text{g})/(V_{cell}/\text{nm}^3) \qquad (3)\end{aligned}$$

where N_A = Avogadro's constant, 6.02245×10^{23} molecule mol^{-1}.

The purpose of this paper is to introduce density, ρ_m, into eqs 1a and 2a, giving a method of estimating lattice energy *directly* from experimental density measurements. The results obtained by volume or density routes are essentially the same (because they are related by the exact eq 3), and it will be a matter of choice, on the basis of the available data, which route will be the more convenient.

In terms of density, ρ_m/g cm^{-3} (or Mg m^{-3}), eqs 1a and 2a take the forms

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

$$\begin{aligned}U_{POT}/\text{kJ mol}^{-1} &= AI(2I/V_m)^{1/3} = 10^{-7}\times AI(2IN_A\rho_m/M_m)^{1/3}\\ &= B(I^4\rho_m/\text{M}_m)^{1/3} = 1291.7(I^4\rho_m/M_m)^{1/3} \qquad (2b)\end{aligned}$$

where M_m is the chemical formula mass of the ionic material, g (or Mg) and the coefficients γ/kJ mol^{-1} cm ($= 2 \times 10^{-7}I\alpha N_A^{1/3}$) and δ/kJ mol^{-1} ($= 2I\beta$) take the values listed in Table 1 for various stoichiometries. B is the collected constant for eq 2b, with the value 1291.7 kJ mol^{-1} cm. It is noteworthy that these equations depend on only the cube root of density, thus considerably dampening the effects of any errors in the experimentally determined density value (such as may be caused by the presence of vacancies, interstitials, and other defects of various kinds). The corresponding lattice enthalpy, ΔH_L for salt M_pX_q (required when lattice energy is incorporated into a thermochemical cycle), is derived from U_{POT} using eq 4:

$$\Delta H_L = U_{POT} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \qquad (4)$$

where n_M and n_X depend on the nature of the ions, M^{q+} and X^{p-}, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions.

In addition, where a salt crystallizes as its hydrate (or solvate) rather than as the preferred anhydrous (unsolvated) parent material, it is possible still to use these equations to estimate the lattice energy of the anhydrous material by subtracting the estimated volume contribution of the water (solvate) molecules, without ever having prepared the material! An additive volume may be assigned for each water molecule of crystallization.[13]

Results and Discussion

Table 2 lists salts of varying charge ratios, showing how lattice potential energy, U_{POT}, can be estimated using eqs 1b and 2b (for lattice energies lower and higher, respectively, than 5000 kJ mol^{-1}). These results are compared to U_{POT} obtained by thermodynamic methods or from our ion volume database (combining the ion volumes according to eq 5 of

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(13) 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.

ref 1; see Table 3). Good agreement is obtained for the salts listed, with U_{POT} differing by small percentages in most cases.

Table 4 demonstrates the possibility of determining lattice energies of anhydrous salts from their hydrated salts. In this table, the experimental densities of the salts are listed followed by the calculated (using eq 3) unit formula volume. In the final set of *columns*, the volume of the anhydrous salt is predicted by subtracting the assigned volume per water molecule of crystallization from that of the hydrated salt. (The value assigned for $V(H_2O)$ in Table 4 has been obtained by us as a "best fit" from a range of hydrate/anhydrous salt pairs.) Finally, in the lower set of *rows*, the percent error in the volume prediction is listed, followed by the predicted value of the lattice energy, U_{POT}. As can be seen, the results are very acceptable, especially in view of the fact that lattice energies can be predicted in this way even for unknown or hypothetical anhydrous materials whose solvates are known.

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