Lattice Energies and Unit Cell Volumes of Complex Ionic Solids

Leslie Glasser*,† **and H. Donald Brooke Jenkins‡**

Contribution from The Centre for Molecular Design, Department of Chemistry, University of the Witwatersrand, Johannesburg, P.O. WITS 2050, South Africa, and Department of Chemistry, University of Warwick, Coventry, CV4 7AL, West Midlands, U.K.

Received July 8, 1999

Abstract: We develop a powerful new limiting relation between lattice potential energy, U_{POT}, and unit cell volume, V (hence, also, density), applicable to some of the most complex ionic solids known (including minerals, and superconductive and even disordered, amorphous or molten materials). Our equation (which has a correlation coefficient, $R = 0.998$) possesses no *empirical* constants whatsoever, and takes the following form: $U_{\mathrm{POT}} = AI(2I/V_{\mathrm{m}})^{1/3}$. It is capable of estimating lattice energies in the range $5000 < U_{\mathrm{POT}}/\mathrm{kJ\ mol^{-1}} \leq 70\,000$ and extending toward 100 MJ mol^{-1}. The relation relies only on the following: (i) an ionic strength related term, I (defined as $^1/_2\sum n_i z_i^2$, where n_i is the number of ions of type i per formula unit, each bearing the charge z_i, with the summation extending over all ions of the formula unit); (ii) a standard electrostatic conversion term, $A/\mathrm{kJ\ mol^{-1}\ nm} = 121.39$ (the normal Madelung and electrostatic factor as found in the Kapustinskii equation, for example); and (iii) V_{m}, the volume of the formula unit (the "molar" or "molecular" volume). The equation provides estimates of U_{POT} to certainly within ±7%; in most cases, estimates are significantly better than this. Examples are provided to illustrate the uses of the equation in predicting lattice energies and densities; the calculations require minimal data and can be performed easily and rapidly, even on a pocket calculator. In the lower lattice energy range (i.e., $U_{\mathrm{POT}}/\mathrm{kJ\ mol^{-1}} < 5000$, corresponding to the simpler compounds and to many inorganic salts possessing complex ions), our recently published linear correlation is more accurate. The linear equation, though empirically developed, is consistent with and can be rationalized following the approach developed here.

Lattice potential energy (U_{POT}) is a dominant term in the thermodynamic analysis of the existence and stability of ionic solids. Direct experimental determination is generally not possible since, in practice, the crystalline solid dissociates into atoms and *not* into gaseous ions, as is required in the lattice energy evaluation. Therefore, its indirect experimental determination, computation, or estimation is of considerable interest in modern materials science; indeed, whenever the energetics of condensed-state materials are studied, the chemical processes under consideration may be rationalized if the appropriate lattice energy steps can be incorporated into the thermochemical cycle.

A variety of estimation methods for lattice energies is available. These include the Born−Haber−Fajans thermochemical cycle[1] (which requires ancillary thermodynamic data) and modern computational methods (which generally require knowledge of the lattice constants and the coordinates of the ions as well as needing an established force field). The computational methods range from direct energy calculational procedures[2] through to programs that produce lattice energies in the course of their modeling of the solid.[3−5] Quantum mechanical procedures are also available, but are highly computationally expensive and are generally applied only to the simpler systems.

By contrast, a few exceedingly rapid estimation methods based on ionic radii[6−8] or volume per formula unit ("molecular" volume)[9] have been developed. Originally only applicable to the simpler binary ionic solids (such as MX (with a 1:1 charge ratio)), the volume-based approach has recently been extended by us[10] to include MX_2 (2:1) and M_2X (1:2)) salts. It is our purpose in this paper to complete the extension of the range of these estimation methods, yielding very simple routes to lattice potential energies for essentially all ionic solids (whether crystalline, disordered, amorphous or even molten).

The earliest, and best-known, of the lattice energy estimation methods for binary ionic solids is due to Kapustinskii and Yatsimirskii:[6−8]

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

where z_+, z_-/electron units are the integer charges on cations and anions, respectively, ν is the number of ions per formula unit, ρ is a compressibility constant (derived from Born−Mayer theory[11]) describing the repulsions between the ions (usually

---

* Corresponding author: (e-mail) glasser@aurum.wits.ac.za; (tel) intl + 27 11 716-2070; (fax) intl + 27 11 339-7967.

† University of the Witwatersrand.

‡ University of Warwick.

(1) Waddington, T. C. *Adv. Inorg. Chem. Radiochem.* **1959**, *1*, 157.

(2) Pratt, K. F. Doctoral Thesis, University of Warwick, U.K., 1978.

(3) Busing, W. R., WMIN.; ORNL-5747; Oak Ridge National Laboratory; Oak Ridge, TN, April 1981 (revision of March 1984).

(4) Gale, J. D.; GULP−General Utility Lattice Program, Imperial College/Royal Institution of Great Britain; Gale, J. D. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 629.

(5) Catlow, C. R. A., Dixon, M., Mackrodt, W., Eds. *Computer Simulation of Solids*; Lecture Notes in Physics 166; Springer-Verlag: Berlin, 1982.

(6) Kapustinskii, A. F. *Q. Rev. Chem. Soc.* **1956**, *10*, 283.

(7) Kapustinskii, A. F.; Yatsimirskii, K. B. *Zh. Obshch. Khim.* **1956**, *26*, 941.

(8) Yatsimirskii, K. B. *Zh. Neorg. Khim.* **1961**, *6*, 518.

(9) Mallouk, T. E.; Rosenthal, G. L.; Muller, G.; Busasco, R.; Bartlett, N. *Inorg. Chem.* **1984**, *23*, 3167.

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

10.1021/ja992375u CCC: $19.00

chosen as $\rho = 0.0345$ nm), $\langle r \rangle$ is the sum of the cation and anion thermochemical radii (sometimes taken to correspond to the shortest anion−cation distance in the lattice), and A (= 121.4 kJ mol^{-1} nm) is the term $^1/_2 N_A M e^2/4\pi\epsilon_0$, where N_A/molecules mol^{-1} is Avogadro's number, M is the Madelung constant of the rock salt (sodium chloride)-type lattice (= 1.74756) on which the simplifications of the Kapustinskii equation are based, e/C is the charge on the electron and $4\pi\epsilon_0/C^2\ J^{-1}\ m^{-1}$ is the vacuum permittivity. This equation (quadratic in $1/\langle r \rangle$) is independent of the actual structure of the ionic solid; hence, it has the corresponding limitation of yielding the same lattice energy for all pleomorphic crystal structures and even amorphous materials. In its conventional usage, the Kapustinskii equation has served to yield lattice potential energy estimates even for inorganic complex salts by the device of developing thermochemical radii.[12] The previously limited range of thermochemical radii has recently been considerably extended by us[13,14] to include data for over 400 complex anions and cations.

In conventional electrochemical theory[15,16] the ionic strength term in solution, I, is defined by the equation

$$I/\text{mol kg}^{-1} = {}^1/_2 \sum m_i z_i^2 \qquad (2)$$

where m_i/mol kg^{-1} is the ionic molality and z_i/electron units is the charge on the ith ion; the summation is over all the ions in the formula unit of the electrolyte.

Recently, Glasser[17] demonstrated that the original Kapustinskii equation can be generalized beyond binary systems, to apply even to complex ionic solids, by substituting for the dimensionless quantity $|\nu z_+ z_-|$, the ionic strength-like term $\Sigma\, n_i z_i^2$ (where n_i is the number of ions with integer charge z_i; the summation is taken over all the types of ions, i, in the formula unit):

$$\sum n_i z_i^2 = 2I \qquad (3)$$

This substituted term describes the interactions among the complex of charges, but still simplifies to the original term for a binary system of charges.

Accordingly, the *generalized Kapustinskii equation* can be written, using this definition of I, as

$$U_{\text{POT}} = \frac{2AI}{\langle r \rangle}\left(1 - \frac{\rho}{\langle r \rangle}\right) \qquad (4)$$

where $\langle r \rangle$ is the weighted-mean cation−anion sum.

In a related development, a satisfactory linear correlation between lattice energy and the volume per formula unit ("molecular" volume, V_m) has been demonstrated for generalized binary ionic solids,[10] extending a similar relation for (1:1) binary salts published by Mallouk et al.:[9]

$$U_{\text{POT}} = |\nu z_+ z_-|\left(\frac{\alpha}{V_m^{1/3}} + \beta\right) = 2I\left(\frac{\alpha}{V_m^{1/3}} + \beta\right) \qquad (5)$$

where α (which has a value close to that of A) and β are empirical constants.

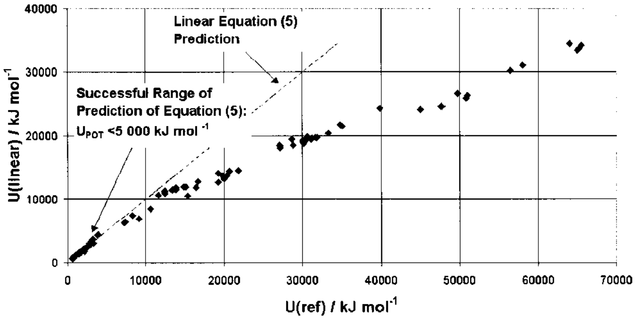

Figure 1. U_{POT} (linear) (from the linear eq 5, with[10] $\alpha = 138.7$ kJ mol^{-1} nm and $\beta = 27.6$ kJ mol^{-1}) versus U_{POT} (ref), showing unsuccessful prediction beyond values of U_{POT} greater than 5000 kJ mol^{-1}.

We now wish to apply the volume substitution for $\langle r \rangle$ more broadly, thus further generalizing and extending the equation to more complex ionic solids, such as minerals, magnetic and superconductor materials, and so forth. However, Figure 1 (using the extensive set of data in Table 1, encompassing over 120 ionic solids) shows that the linear relation is unsatisfactory for the more complex ionic solids. (The reference lattice energies in Table 1 are obtained from the literature or (for the minerals) from prior, independent (but unpublished[18]) calculations, using a value of 838 kJ mol^{-1} for the standard enthalpy of formation of the O^{2-}(g) ion, which is consistent with the lattice energies of many simpler materials.)

We therefore proceed by extending the generalized Kapustinskii eq 4 to more complex ionic materials, recognizing that the equation can be treated as a simple product of three terms: (i) a repulsion factor, $R = (1 - \rho/\langle r \rangle)$; (ii) a reciprocal of a cation−anion distance ($\langle r \rangle$); and (iii) a set of constant terms (= $2AI$).

$$U_{\text{POT}} = 2AI(1/\langle r \rangle)R \qquad (4a)$$

(i) The Repulsion Factor: *R*. In the early Born−Landé theory for the lattice energy of binary ionic solids, the repulsion factor, R, is formulated as $(1 - 1/n)$, where n is obtained from the compressibility of the crystalline material, having a value $n = 8$ for sodium chloride. This corresponds to the repulsion factor, R, having the fixed value 0.875. In Figure 2 we investigate the constancy of the Kapustinskii form of R (i.e., $1 - \rho/\langle r \rangle$); as may be seen from the figure, the function is rather variable for salts having small lattice energies (in the range $0.94 > R > 0.82$, and so neatly straddling the Born−Landé value). but for materials having lattice energies greater than 5000 kJ mol^{-1}, R reaches a limiting value of $R = \sim 0.84$. This limiting value of R is thus adopted as a constant in our extended expression.

(ii) The Cation−Anion Distance: ⟨*r*⟩. The sodium chloride lattice is face-centered cubic, with lattice constant a and four formula units per unit cell (i.e., $Z = 4$). The cation−anion distance, $\langle r \rangle$, is $a/2$. Hence, the relation between $\langle r \rangle$ and the molecular volume ($V_m = V/Z$) is precise, and is

$$\langle r \rangle = (4V_m)^{1/3}/2 = (V_m/2)^{1/3} \qquad (6)$$

If we are to treat more complex lattices, this expression needs to be normalized against sodium chloride lattices, since more complex materials will have less simple ionic formulas and correspondingly different charge densities. If a Boltzmann distribution of charge is assumed, then it follows (as in a Debye-

---

(11) Dasent, W. E. *Inorganic Energetics*, 2nd ed.; Cambridge University Press: Cambridge, U.K., 1982.

(12) Jenkins, H. D. B.; Thakur, K. P. *J. Chem. Educ.* **1979**, *56*, 576.

(13) Jenkins, H. D. B.; Roobottom, H. K.; Passmore, J.; Glasser, L. *J. Chem. Educ.* **1999**, *76*, 1570.

(14) Jenkins, H. D. B.; Roobottom, H. K. In *CRC Handbook of Chemistry and Physics, CRCnetBASE 1999*, 80th ed.; Lide, D. R., Ed.; Times Mirror Publications: New York, 1999.

(15) Lewis, G. N.; Randall, M. *J. Am. Chem. Soc.* **1921**, *43*, 1112.

(16) Lewis, G. N.; Randall, M. In Pitzer, K. S.; Brewer, L. *Thermodynamics*, 2nd ed.; McGraw Hill: New York, 1961.

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

(18) Jenkins, H. D. B. unpublished work, Warwick, U.K., 1990.

Table 1[a]

chemical formula	mineral name	ref	V_{cell}/nm^3	Z	$V_m = V_{cell} Z^{-1}$/nm^3	I	⟨r⟩/nm	U(ref) /kJ mol^{-1}	U(pred) /kJ mol^{-1}	U(pred)/ U(ref)
$SF_3 \cdot BF_4$		b	0.4394	4	0.1099	1	N/A	598	319	0.534
$KClO_4$			0.3627	4	0.0907	1	N/A	599	340	0.568
$KMnO_4$			0.3855	4	0.0964	1	N/A	607	334	0.550
RbI			0.3930	4	0.0983	1	0.372	617	331	0.537
$ClO_2 \cdot BF_4$		b	0.4514	4	0.1129	1	N/A	620	316	0.510
KI			0.3507	4	0.0877	1	0.358	632	344	0.545
RbBr			0.3228	4	0.0807	1	0.348	632	354	0.560
$CsClO_4$			0.4590	4	0.1148	1	N/A	636	315	0.495
KBr			0.2849	4	0.0712	1	0.334	671	369	0.550
RbCl			0.2823	4	0.0706	1	0.333	680	370	0.544
NaI			0.2698	4	0.0675	1	0.322	682	376	0.551
KCl			0.2492	4	0.0623	1	0.319	701	386	0.550
$LiClO_4$			0.2900	4	0.0725	1	N/A	709	367	0.517
LiI			0.2160	4	0.0540	1	0.296	730	405	0.554
NaBr			0.2106	4	0.0527	1	0.298	732	408	0.557
CsF			0.2171	4	0.0543	1	0.300	744	404	0.543
NaCl			0.1794	4	0.0449	1	0.283	769	430	0.560
$NaClO_3$			0.2842	4	0.0711	1	N/A	770	369	0.480
RbF			0.1785	4	0.0446	1	0.285	774	431	0.557
LiBr			0.1655	4	0.0414	1	0.272	788	442	0.561
KF			0.1514	4	0.0379	1	0.271	808	456	0.564
LiCl			0.1358	4	0.0340	1	0.257	834	472	0.566
NaF			0.0995	4	0.0249	1	0.235	910	524	0.576
LiF			0.0649	4	0.0162	1	0.209	1030	604	0.587
Cs_2MoCl_6			1.0834	4	0.2709	3	N/A	1347	1023	0.759
Cs_2GeCl_6			1.0704	4	0.2676	3	0.502	1375	1027	0.747
Cs_2CoCl_4			0.9336	4	0.2334	3	0.473	1391	1075	0.773
Cs_2CuCl_4			0.9196	4	0.2299	3	N/A	1393	1080	0.775
Rb_2MoCl_6			0.9969	4	0.2492	3	N/A	1399	1052	0.752
K_2MoCl_6			0.9556	4	0.2389	3	N/A	1418	1066	0.752
Cs_2ZnCl_4			0.9336	4	0.2334	3	N/A	1429	1075	0.752
Cs_2ZnBr_4			1.0709	4	0.2677	3	N/A	1454	1027	0.706
Cs_2GeF_6			0.7311	4	0.1828	3	N/A	1573	1166	0.741
K_2PtCl_4			0.2034	1	0.2034	3	N/A	1574	1125	0.715
$Ba(MnO_4)_2$			1.2893	8	0.1612	3	N/A	1778	1216	0.684
BaI_2			0.5060	4	0.1265	3	0.355	1831	1318	0.720
CaI_2			0.1210	1	0.1210	3	0.320	1905	1338	0.702
Rb_2S			0.4513	4	0.1128	3	0.336	1929	1369	0.710
MgI_2			0.1021	1	0.1021	3	0.292	1944	1416	0.728
$BaBr_2$			0.4290	4	0.1073	3	0.331	1950	1393	0.714
K_2S			0.3988	4	0.0997	3	0.322	1979	1427	0.721
$BaCl_2$			0.3506	4	0.0877	3	0.316	2033	1490	0.733
$MgBr_2$			0.0788	1	0.0788	3	0.268	2097	1544	0.736
$CaBr_2$			0.1965	2	0.0983	3	0.296	2132	1434	0.673
$Sr(ClO_3)_2$			1.0745	8	0.1343	3	N/A	2155	1292	0.600
Na_2S			0.2795	4	0.0699	3	0.286	2192	1607	0.733
$CaCl_2$			0.1685	2	0.0843	3	0.281	2223	1509	0.679
Na_2CO_3			0.2715	4	0.0679	3	N/A	2301	1622	0.705
$MgCl_2$			0.1965	3	0.0655	3	0.253	2326	1642	0.706
BaF_2			0.2378	4	0.0595	3	0.268	2341	1696	0.724
Li_2CO_3			0.2251	4	0.0563	3	N/A	2523	1727	0.684
CaF_2			0.1631	4	0.0408	3	0.233	2609	1923	0.737
$CaCO_3$	vaterite	c	0.7500	12	0.0625	4	N/A	2777	2447	0.881
$CaCO_3$	calcite	c	0.3678	6	0.0613	4	N/A	2814	2463	0.875
$CaCO_3$	aragonite	c	0.2267	4	0.0567	4	N/A	2820	2528	0.897
MgF_2			0.0659	2	0.0330	3	0.205	2913	2064	0.709
BaO			0.1682	4	0.0421	4	0.267	3029	2793	0.922
SrO			0.1350	4	0.0338	4	0.250	3217	3005	0.934
$BaLiF_3$		d	0.0638	1	0.0638	4	N/A	3361	2430	0.723
MgO			0.0785	4	0.0196	4	0.204	3795	3600	0.949
NiO			0.0727	4	0.0182	4	0.201	3908	3694	0.945
$AlAsO_4$			0.2458	3	0.0819	9	N/A	7255	6592	0.909
$AlPO_4$			0.2315	3	0.0772	9	N/A	7427	6725	0.906
Mg_2P2O_7		k	0.9598	8	0.1200	12	N/A	8275	8519	1.030
$Ca_2CuO_2Cl_2$		e	0.2260	2	0.1130	11	0.248	9162	7739	0.845
$Ca_3(PO_4)_2$		f	3.4200	21	0.1629	15	N/A	10602	10360	0.977
SiO_2	low quartz	l	0.1127	3	0.0376	12	0.172	11627	12546	1.079
TiO_2	anatase	f	0.1363	4	0.0341	12	0.196	12454	12961	1.041
TiO_2	brookite	f	0.2606	8	0.0326	12	N/A	12462	13156	1.056
TiO_2-II		f	0.1226	4	0.0307	12	N/A	12466	13426	1.077
TiO_2	rutile	f	0.0624	2	0.0312	12	N/A	12493	13347	1.068
$LaFeO_3$		g	0.0605	1	0.0605	15	0.227	13364	14412	1.078
$LaMnO_3$		g	0.0595	1	0.0595	15	0.225	13478	14492	1.075

Table 1 (Continued)

chemical formula	mineral name	ref	V_{cell}/nm^3	Z	$V_m = V_{cell}$ Z^{-1}/nm^3	I	$\langle r \rangle$/nm	U(ref) /kJ mol^{-1}	U(pred) /kJ mol^{-1}	U(pred)/ U(ref)
$LaCrO_3$		*g*	0.0581	1	0.0581	15	0.224	13678	14608	1.068
$LaCoO_3$		*g*	0.0559	1	0.0559	15	0.224	13805	14797	1.072
$NdFeO_3$		*h*	0.2366	4	0.0592	15	0.223	13854	14521	1.048
$LaAlO_3$		*h*	0.1090	2	0.0545	15	0.220	13856	14923	1.077
Ti_2O_3		*f*	0.1044	2	0.0522	15	0.201	14847	15139	1.020
Mn_2O_3			0.8386	16	0.0524	15	0.197	15146	15118	0.998
$HgBa_2CuO_4$		*d*	0.1458	1	0.1458	18	0.243	15398	13708	0.890
$CaSiO_3$	wollastonite		0.3978	6	0.0663	16	0.202	16439	15235	0.927
$MgSiO_3$	clinoenstatite		0.4181	8	0.0523	16	0.188	16725	16493	0.986
$MgAl2O_4$		*h*	0.5276	8	0.0660	19	0.192	19269	19192	0.996
Ba_2SiO_4			0.4434	4	0.1109	20	0.235	19300	17284	0.896
Ca_2SiO_4	larnite		0.3427	4	0.0857	20	0.212	19831	18834	0.950
Ca_2SiO_4			0.3926	4	0.0982	20	N/A	19980	18000	0.901
$Ba_2In_2O_5$		*i*	0.5923	4	0.1481	23	0.240	20065	18909	0.942
$CaMgSiO_4$	monticellite		0.3418	4	0.0855	20	0.203	20364	18851	0.926
Mg_2SiO_4	forsterite		0.2919	4	0.0730	20	0.183	20697	19869	0.960
$Ca_2Fe_2O_5$		*h*	0.4485	4	0.1121	23	0.216	21811	20746	0.951
Ti_3O_5	γ-Ti_3O5	*f*	0.3417	4	0.0854	27	0.199	27033	28129	1.041
Ti_3O_5	high Ti_3O_5	*f*	0.3700	4	0.0925	27	N/A	27159	27392	1.009
Ti_3O_5	low Ti_3O_5	*f*	0.3499	4	0.0875	27	N/A	27164	27907	1.027
Al_2SiO_5	kyanite		0.2932	4	0.0733	27	0.187	28687	29601	1.032
Al_2SiO_5	andalusite		0.3422	4	0.0856	27	N/A	28807	28115	0.976
$CsTiOAsO_4$		*i*	0.9890	8	0.1236	31	0.224	30020	29898	0.996
$RbTiOAsO_4$		*i*	0.9545	8	0.1193	31	0.219	30021	30254	1.008
Ba_2LaRuO_6		*m*	0.1553	1	0.1553	33	0.244	30134	30118	0.999
$KTiOAsO_4$		*i*	0.9328	8	0.1166	31	0.215	30334	30487	1.005
Sr_2ErRuO_6		*m*	0.2696	2	0.1348	33	0.231	30452	31573	1.037
Ba_2YRuO_6		*m*	0.2880	2	0.1440	33	0.236	30470	30886	1.014
Sr_2LuRuO_6		*m*	0.2638	2	0.1319	33	0.230	30640	31803	1.038
Sr_2YRuO_6		*m*	0.2720	2	0.1360	33	0.228	30686	31480	1.026
$KSnOPO_4$		*i*	0.9212	8	0.1152	31	0.214	31158	30614	0.983
$RbTiOPO_4$		*i*	0.8901	8	0.1113	31	0.217	31257	30967	0.991
$KVOPO_4$		*i*	0.8642	8	0.1080	31	0.210	31633	31273	0.989
$TlTiOPO_4$		*i*	0.8781	8	0.1098	31	0.216	31794	31107	0.978
$KTiOPO_4$		*i*	0.8682	8	0.1085	31	0.212	31850	31225	0.980
$CaMgSi_2O_6$	diopside		0.4388	4	0.1097	32	0.195	33324	32458	0.974
$LiAlSi_2O_6$	β-spodumene		0.3899	4	0.0975	33	0.184	34815	35176	1.010
$NaAlSi_2O_6$	jadeite		0.4012	4	0.1003	33	0.191	35020	34843	0.995
Ti_4O_7		*f*	0.4661	4	0.1165	39	0.199	39893	41413	1.038
$CaAl_2Si_2O_8$	anorthite		1.3363	8	0.1670	43	0.189	45005	41836	0.930
$KAlSi_3O_8$	microcline		0.7201	4	0.1800	45	0.194	47583	43354	0.911
$KAlSi_3O_8$	adularia		0.7150	4	0.1788	45	N/A	47626	43457	0.912
$KAlSi_3O_8$	low sandinite		0.7172	4	0.1793	45	N/A	47746	43413	0.909
$Ba_3NiSb_2O_9$		*j*	0.4210	2	0.2105	51	0.231	49757	48626	0.977
$Ba_3SrRu_2O_9$		*j*	0.9181	4	0.2295	51	0.238	50801	47244	0.930
$Ba_3CaRu_2O_9$		*j*	0.4379	2	0.2190	51	0.235	51007	47992	0.941
$Y_3Fe_5O_{12}$		*h*	1.8955	8	0.2369	60	0.208	56504	58056	1.027
$Y_3Al_5O_{12}$		*h*	1.7349	8	0.2169	60	0.199	58006	59795	1.031
Ti_6O_{11}		*f*	0.7160	4	0.1790	63	0.198	64051	68029	1.062
$Ba_4NaSb_3O_{12}$		*j*	0.5678	2	0.2839	70	0.235	64996	67133	1.033
$Ba_4LiSb_3O_{12}$		*j*	0.5548	2	0.2774	70	0.232	65181	67653	1.038
$Sr_4NaSb_3O_{12}$		*j*	0.5295	2	0.2648	70	0.226	65481	68714	1.049

[a] Crystal data from Donnay, J. D. H. *Crystal Data: Determinative Tables*, 2nd ed.; American Crystallographic Assoc.: Pittsburgh, PA, 1963, and U_{POT}(ref) from ref 14, or calculation (HDBJ), unless otherwise referenced. $\langle r \rangle$ is the mean cation−anion radius sum for use in the Kapustinskii eq 1. The table is sorted by ascending values of U_{POT}(ref). [b] Reference 9. [c] Jenkins, H. D. B.; Pratt, K. F.; Smith, B. T.; Waddington, T. C. J. *Inorg. Nucl. Chem.*, **1976**, *38*, 371. [d] Jackson, R. A.; Valerio, M. E. G.; de Lima, S. F. *J. Phys.: Condens Matter* **1996**, *8*, 10931. [e] Islam, M. S.; Read, M. S. D.; D'Arco, S. *Faraday Discuss.* **1997**, *106*, 367. [f] le Roux, H.; Glasser, L. *J. Mater. Chem.*, **1997**, *7*, 843. [g] Islam, M. S.; Cherry, M. *Solid State Ionics*, **1997**, *97*, 33−37. Data supplied to L.G. by M.S.I., in a personal communication. [h] Bush, T. S.; Gale, J. D.; Catlow, C. R. A.; Battle, P. D. *J. Mater. Chem.*, **1994**, 4, 831. [i] Fisher, C. A. J.; Islam, M. S. *Solid State Ionics* **1999**, *118*, 355. [j] Taylor, M. G.; Simkiss, K.; Drew, M. G. B.; Mitchell, P. C. G.; Leslie, M. *Mol. Simul.* **1992**, *9*, 129. [k] Post, J. E.; Burnham, C. W. *Am. Mineral.* **1986**, *71*, 142. [l] Glasser, L.; Catlow, C. R. A. *J. Mater. Chem.* **1997**, *7*, 2537. [m] Battle, P. D.; Bush, T. S.; Catlow, C. R. A. *J. Am. Chem. Soc.* **1995**, *117*, 6292.

type of analysis) that the charge density is proportional to the ionic strength, I. Thus, to extend the equation to these less simple cases, we need to normalize the volume in expression 6 by dividing the molecular volume by the ionic strength (which has the value $I = 1$ for sodium chloride), to yield a normalized molecular volume, V_{norm}:

$$\langle r \rangle = (V_m/2I)^{1/3} = V_{norm}{}^{1/3} \qquad (7)$$

Figure 3 demonstrates that, for situations where $U_{POT} > 5000$ kJ mol^{-1}, $\langle r \rangle$ is larger than $(V_m/2I)^{1/3}$ by a limiting factor (L) of value ∼1.7. The existence of this factor is easily rationalized since the cell volume is more closely packed in these more complex materials than it is in simpler salts; consider, for example, that in SiO_2 the Si^{4+} cation—lying within a tetrahedral cavity among four O^{2-} anions—contributes little (or nothing) to the cell volume. Hence, $1/L$ represents a packing factor, and

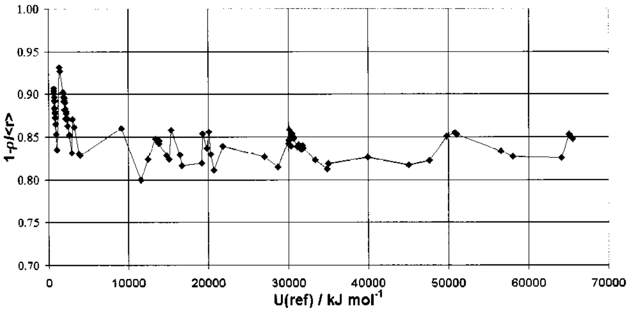

Figure 2. Repulsion factor, $R = 1 - \rho/\langle r\rangle$ versus U_{POT} (ref), showing that R reaches a limiting value of ~0.84 for lattice energies greater than 5000 kJ mol^{-1}. The data points are linked by straight lines in order to emphasize the systematic trends at small values of U_{POT} (ref).

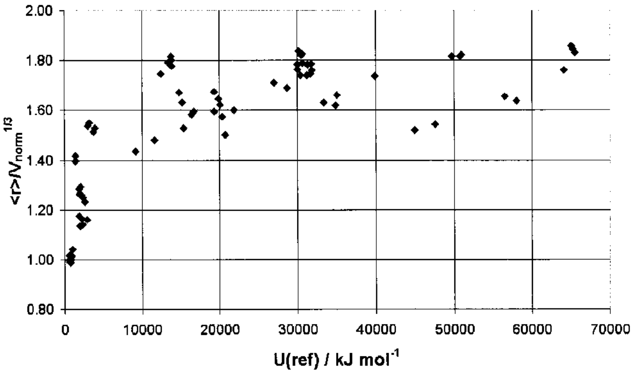

Figure 3. Ratio $L = \langle r\rangle/(V_m/2I)^{1/3}$, plotted versus U_{POT} (ref). The ratio reaches a limiting value of ~1.7 for lattice energies greater than 5000 kJ mol^{-1}. $1/L$ represents a packing factor.

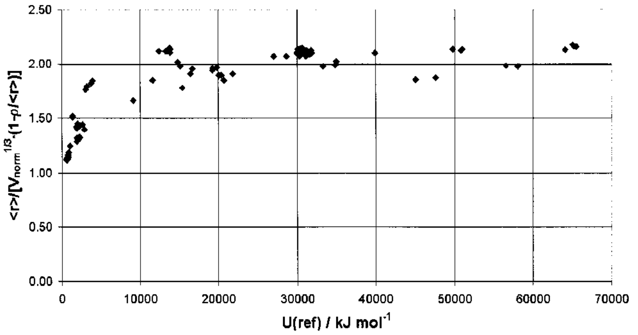

Figure 4. Ratio L/R, plotted versus U_{POT} (ref). The ratio reaches a limiting value close to 2 for lattice energies greater than 5000 kJ mol^{-1}.

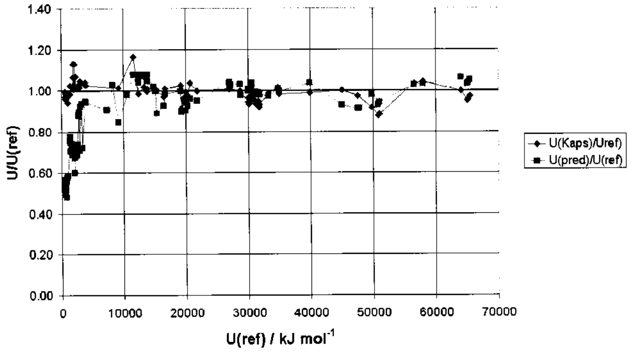

Figure 5. Comparison of U_{Kaps}/U(ref) and U(pred)/U(ref) versus U(ref). Perfect prediction would, in each case, yield a constant value of exactly 1. U_{Kaps} is calculated from eq 1, using the standard values, $A = 121.39$ kJ mol^{-1} nm and $\rho = 0.0345$ nm, and the mean cation−anion sums, $\langle r\rangle$, listed in Table 1.

we underestimate the cation−anion radius sum in expression 7 if this packing factor is ignored. The limiting relation between $\langle r\rangle$ and V_m can then be expressed in the form

$$\langle r\rangle = (V_m/2I)^{1/3}L \tag{7a}$$

and thus

$$1/\langle r\rangle = (2I/V_m)^{1/3}1/L \tag{7b}$$

(iii) The Constants: (2*AI*). These fundamental electrostatic-based constants remain unaffected by the increasing complexities of the lattice, being simply referred to the sodium chloride lattice by the above normalization of the cell volume.

The Extended, Generalized Equation. We now combine these modified expressions, (4a) and (7b), into a single, substituted, version of the generalized Kapustinskii equation, in the form

$$U_{POT} = 2AI(2I/V_m)^{1/3}(R/L) \tag{8}$$

From the values adopted for R and L for the more complex lattices, we anticipate that L/R will have a limiting value (≈1.7/0.84) close to 2; Figure 4 demonstrates that this is indeed the case. Thus, finally, the leading coefficient, 2, in eq 4a is canceled with the term R/L, to yield our limiting equation:

$$U_{POT} = AI(2I/V_m)^{1/3} = AI/V_{norm}^{\ 1/3} \quad \text{where} \quad V_{norm} = V_m/2I \tag{9}$$

Remarkably, this equation has no adjustable constants. Its success in the evaluation of lattice energies, and the closeness of the lattice energies that it yields to those of the generalized Kapustinskii equation, is shown in Figure 5. (A very slightly improved correlation may be obtained if the factor A is represented by a fitted constant, but its value will depend on the precise set of ionic solids selected for the fit.)

This result also explains the value of the constant, $\alpha = 138.7$ kJ mol^{-1} nm, previously obtained as an empirical constant for our generalized linear eq 5 for binary ionic solids;[10] that equation already allows in its formulation for the repulsion factor, R, so that the constant could be expected to have a value approximating to $2A/L$, i.e., 142.8 kJ mol^{-1} nm—a difference of only 3% from the value noted above.

The essential reason for the success of these charge- and repulsion-based formulas is, of course, that the contributions of the Coulombic interactions in ionic solids dominate the energy, constituting some *85%* of the total lattice potential energy, in close agreement with the above-mentioned Born−Landé factor. However, it is also clear from the process of derivation of eq 9, as a limiting equation, that it will not be successful for small lattice energies (see Figures 2−5); Figure 6 demonstrates that our earlier linear eq 5 is more successful for $U_{POT} < 5000$ kJ mol^{-1}.

We believe that eq 9 is an important generalization and extension, worthy of detailed theoretical analysis. It is one that will be of wide interest to materials scientists, inorganic chemists, solid-state chemists, and mineralogists alike and will allow the easy and reliable prediction of lattice energies, unit cell volumes, and densities of ionic solids (and even ionic melts). This is particularly true for minerals, complex oxides, and other complex inorganic solids (such as superconductors and magnetic materials) and will, in consequence, lead to an improved understanding of their stabilities and instabilities.

Advantages of the Extended, Generalized Equation. While the generalized Kapustinskii and our extended, generalized

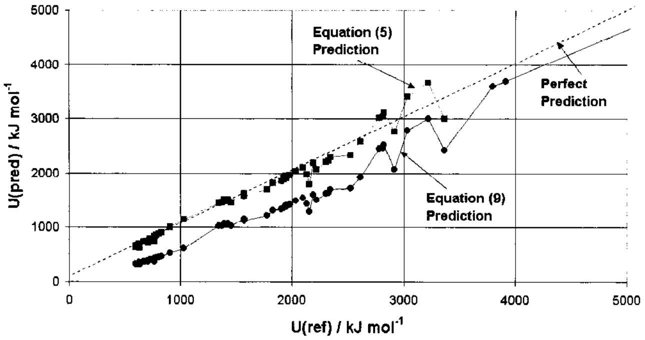

Figure 6. Prediction of lattice energy by the linear eq 5 and our extended, generalized eq 9 for $U_{\mathrm{POT}} < 5000$ kJ mol^{-1}. Perfect prediction would follow the diagonal line; hence, eq 5 is to preferred for the lower range of lattice energies.

equations are obviously very closely related, they are, in certain circumstances, also complementary. Nevertheless, the advantage of adopting eq 9 for most purposes is easily seen, for the following reasons:

(a) This volume-based equation uses an *experimental* molar/molecular volume for input, rather than tabulated and average ionic or thermochemical radii, which places it more directly in relation to experiment.

(b) Pleomorphic forms, while having the same chemical formula, will be predicted by eq 9 to have slightly differing lattice energies, in keeping with experiment, whereas the Kapustinskii equation generates identical lattice energies for all the pleomorphs.

(c) The effective packing volume is more realistic for complex ions than is the fictional, but simplifying, thermochemical radii which approximate the ions as being spherical.

(d) The Kapustinskii eq 4 and our generalized eq 9 are complementary in that it is possible to combine the two expressions to predict molar volumes (and, hence, densities)—which will, however, be identical for pleomorphic forms. The Kapustinskii equation yields a lattice energy, which can then be used for the purposes of a molar volume, V_m, estimation with the volume-based equation (see following section); it is also possible to use eq 9 to relate $\langle r \rangle$ and hence the shortest cation−anion distance in the lattice with V_m directly—no other method than these for estimation of V_m have before been proposed.

(e) Since lattice potential energies are so readily obtained by means of eq 9, they can be used in thermochemical cycle calculations for estimating otherwise unattainable enthalpies of formation of gaseous ions.

(f) Use of the factor $2I$ as a normalizing divisor for V_m has not previously been anticipated and, clearly, has important theoretical significance in the study of ionic solids.

The New Equation in Use. In calculation of lattice energies, there is a certain arbitrariness in the selection of the ions of which the lattice is conceived to be composed. Thus, for example, calcium carbonate can be treated as consisting of calcium and carbonate ions

$$\mathrm{CaCO_3(s)} \rightarrow \mathrm{Ca^{2+}(g)} + \mathrm{CO_3{}^{2-}(g)}$$

or as calcium, carbon, and oxide ions, as in

$$\mathrm{CaCO_3(s)} \rightarrow \mathrm{Ca^{2+}(g)} + \mathrm{C^{4+}(g)} + 3\mathrm{O^{2-}(g)}$$

The lattice energies obtained for these two complementary processes will be different (the energy will be larger when the structure is conceived as breaking up into single ions). In Table 1 we find some substances treated as consisting of complex ions, e.g., $CaCO_3$, while the complex minerals are treated as consisting of single ions; the choice made is consistent with that in the reference calculation of the lattice energy, U(ref).

We illustrate our prediction of the lattice potential energy of the mineral *larnite* or *β-calcium orthosilicate* (corresponding to the first "Ca_2SiO_4" entry in Table 1). The crystal structure determinations of this mineral by Midgley[19] and by Cruickshank[20] show the structure to be monoclinic, having the following crystal structure parameters: $a = 0.548$ nm, $b = 0.676$ nm, $c = 0.928$ nm, $\beta = 94°33'$, and $Z = 4$.

Unit cell volume is given by the generally applicable equation

$$V_m = (abc\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma})/Z \tag{10}$$

or, in simplified form (for all except the rhombohedral and triclinic crystal systems),

$$V_m = abc \sin\eta/Z \tag{10a}$$

where η is the unique oblique angle or, if there is no such unique angle, 90°, in which case

$$V_m = abc/Z \tag{10b}$$

We first establish the value of $V_m = V_{\mathrm{cell}}/Z = 0.3427/4 = 0.0857$ nm^3, employing eq 10b. Treating the oxide as composed of two Ca^{2+}, one Si^{4+}, and four O^{2-} ions leads, from eq 3, to a value for $I = 20$. Hence, using our extended generalized eq 9, $V_{\mathrm{norm}} = V_m/2I = 0.0857/40 = 0.002142$ nm^3. The term $AI/V_{\mathrm{norm}}^{1/3} = AI(2I/V_m)^{1/3} = 18\,834$ kJ mol^{-1}, which is our estimated lattice potential energy, U_{POT}, for the mineral, *larnite*. The full-scale lattice potential energy computation made using the program LATEN[21] gives a value 19 831 kJ mol^{-1} (prediction error 5.0%) while the Born−Fajans−Haber cycle value is calculated to be 19 949 kJ mol^{-1} (prediction error 5.6%).

Alternatively, were we to regard the mineral as consisting of two Ca^{2+} and one complex $SiO_4{}^{4-}$ ion, for which $I = 12$, then eq 9 leads *to* $V_{\mathrm{norm}} = V_m/2I = 0.0857/24 = 0.0035708$ nm^3. Then: $U_{\mathrm{POT}} = AI/V_{\mathrm{norm}}^{1/3} = AI(2I/V_m)^{1/3} = 9530$ kJ mol^{-1}. The difference (9304 kJ mol^{-1}) between these two lattice energies corresponds to the self-energy of formation of the complex ion, $SiO_4{}^{4-}$(g), from its constituent gaseous atomic ion counterparts:

$$\mathrm{Si^{4+}(g)} + 4\mathrm{O^{2-}(g)} \rightarrow \mathrm{SiO_4{}^{4-}(g)}$$

If we have ancillary data for $\Delta_f H^{\ominus}(\mathrm{Si^{4+}}, \mathrm{g})$ and $\Delta_f H^{\ominus}(\mathrm{O^{2-}}, \mathrm{g})$, then we can, as the closing loop of an appropriate thermochemical cycle, estimate a value for the standard enthalpy of formation of the gaseous $SiO_4{}^{4-}$ ion, $\Delta_f H^{\ominus}(\mathrm{SiO_4{}^{4-}}, \mathrm{g})$, using the self-energy above (suitably corrected to an enthalpy change by subtraction of $4RT$).

We illustrate the estimation of density, ρ, using magnetite, Fe_3O_4, as our example, for which the literature value is 5.18 g

---

[19] Midgley, C. M. *Acta Crystallogr.* **1952**, *5*, 307.

[20] Cruickshank, D. W. J. *Acta Crystallogr.* **1964**, *17*, 685.

[21] Jenkins, H. D. B.; Pratt, K. F. *Prog. Solid State Chem.* **1979**, *12*, 125.

cm^{-3}. Equation 9, solved for density, has the form

$$\rho/\text{g cm}^{-3} = \frac{10^{21}}{N_A}\frac{M_m}{2I^4}\left(\frac{U_{POT}}{A}\right)^3$$

where the factor 10^{21} converts nm^3 to cm^3, while Avogadro's number, N_A, is required to convert between molar mass, M_m, and molecular mass.

The lattice potential energy of magnetite was previously estimated by Glasser[17] from his generalized Kapustinskii equation as $U_{Kaps}(Fe_3O_4) = 18\,788$ kJ mol^{-1}, with $I = 19$. Hence, $\rho = 5.46$ g cm^{-3}, which is within 5% of the literature value.

Similar calculations on a range of materials (results not given here) show that the error is quite generally within 30% of literature densities (which often cover a somewhat wide range and sometimes differ considerably from the X-ray-calculated value). It is hardly surprising that our predicted densities have a large error range relative to the predicted lattice energy since our density calculation relies on the cube of U_{POT}. Conversely, the fact that U_{POT} depends on the cube root of V_m renders the lattice potential energies the more reliable.

JA992375U