SOME ASPECTS OF THE CALCULATION OF LATTICE ENERGIES. II

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ABSTRACT

Calculations of the lattice energies, which incorporate the variation of compressibility with pressure, have been extended to a wider range of alkali halides. The present calculations deal with compounds for which the data only justify a linear relation between compressibility and pressure, and consequently equations have been used with one fewer adjustable constant than those used in an earlier paper.

In general, the calculated lattice energies are larger (absolutely) than those from equations which ignore the variation of compressibility; and these larger values are usually in better agreement with the experiment.

INTRODUCTION

In a recent paper[1], the present author pointed out that calculated values of lattice energies differed considerably, depending on whether the variation of compressibility with pressure was taken into account or not. In general, inclusion of this variation led to a somewhat better agreement between observed and calculated values. In this earlier paper, the compressibilities, β, were fitted to an empirical equation:

$$\beta = \beta_0 + \beta_1 P + \beta_2 P^2$$

which, in fact, reproduces very exactly the observed variation of volume with pressure. However, extensive data are available only for sodium and cesium chloride, bromide and iodide[2,3]. Other data [2,3] of a less extensive kind are also available for some other alkali halides; namely, sodium and cesium fluorides, the potassium halides, and rubidium bromide and iodide. These data have been fitted by Bridgman[3] to an equation for β containing two terms; that is,

$$\beta = \beta_0 + \beta_1 P$$

It is the object of the present paper to apply the above expression for the compressibility to the calculation of lattice energies and to compare the results with experiment. This will be done both for the alkali halides for which the less extensive data are available (sodium fluoride, etc.) and also for the salts that were considered earlier[1], since the effect of curtailing the series for β is of considerable interest.

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The experimental values, obtained as usual through a Born–Haber cycle, are available from a variety of sources, some of which differ somewhat, especially in their estimates of electron affinity. For present purposes, the values of Dasent[4], which were used earlier[1], will again be used.

EQUATIONS FOR COMPRESSIBILITY

Since we only have two terms in the expression for the compressibility, we can only employ equations with three adjustable constants, which can be fitted to the observed values of β_0, β_1 and r_e (the equilibrium distance of neighbours in the crystal). Hence, somewhat abbreviated forms of the earlier[1] eqns (5)–(7) must be used, which are as follows:

$$E = -\frac{M}{r} - \frac{C'}{r^6} + (B+Gr)\,e^{-r/\rho} \tag{5a}$$

$$E = -\frac{M}{r} - \frac{C'}{r^6} + \left\{B + \frac{G}{r}\right\} e^{-r/\rho} \tag{6a}$$

$$E = -\frac{M}{r} - \frac{C'}{r^6} + \frac{B}{r^x} + \frac{G}{r^{x+w}} \tag{7a}$$

where B, G, and ρ or n are adjustable constants, and w (as before) is some arbitrarily selected small integer. The expressions for $\frac{dE}{dr}$, $\frac{d^2E}{dr^2}$, $\frac{d^3E}{dr^3}$ at $r = r_e$ used earlier, are still valid; and applying these, the above equations give:

Equation (5a)

$$\mu - v = Xe^u$$

$$\mu u - 2vu = Ye^u$$

$$\mu u^2 - 3vu^2 = Ze^u$$

where

$$u = r_e/\rho$$

$$\mu = Bu + Gr_e u$$

$$v = Gr_e$$

$$X = \frac{M+6D}{r_e}$$

$$Y = \frac{2M+42D+Q}{r_e}$$

$$Z = \frac{6M + 336D}{r_e} - 27V_0 \frac{(\beta_0^2 - \beta_1)}{\beta_0}$$

$$Q = \frac{9V_0 r_e}{\beta_0}$$

$$D = \frac{C'}{r_e^5}$$

X, Y, Z, Q, and D are as defined in the earlier paper, and can be found from the experimental data. If we eliminate μ and v, we get

$$Xu^2 - 2Yu + Z = 0$$

which can be solved to give u. The lattice energy is

$$U = -\frac{(M+D)}{r_e} + \frac{(2Xu - Y)}{u^2}$$

which can be evaluated, once u is known.

Equation (6a)

Similar treatment gives

$$\mu + v = Xe^u$$
$$\mu u + v(2u + 2) = Ye^u$$
$$\mu u^2 + v(3u^2 + 6u + 6) = Ze^u$$

where we now define

$$\mu = Bu + Gu/r_e$$
$$v = G/r_e$$

Elimination of μ and v gives

$$Xu^3 + (4X - 2Y)u^2 + (6X - 6Y + Z)u - 6Y + 2Z = 0$$

which can be solved numerically for u. The lattice energy is

$$U = -\frac{(M+D)}{r_e} + \frac{2X(u+1) - Y}{u(u+2)}$$

Equation (7a)

Similar treatment gives

$$\mu + v = X$$

$$(n+1)\mu + (n + w + 1)v = Y$$

$$(n+1)(n+2)\mu + (n + w + 1)(n + w + 2)v = Z$$

where we now define

$$\mu = \frac{nB}{r_c^n}$$

$$\nu = \frac{(n+w)G}{r_c^{n+w}}$$

Elimination of μ and ν gives

$$Xn^2 + [(w+2)X - 2Y]n + (w+1)X - 3Y + Z = 0$$

and the lattice energy is

$$U = -\frac{(M+D)}{r_e} + \frac{(2n+2w+1)X-Y}{n(n+w)}$$

which can be evaluated once n is known.

DATA AND NUMERICAL RESULTS

The values of X, Y, Z, Q, and D for sodium and cesium chloride, bromide and iodide were evaluated earlier. Table 1 gives the values of β_0 and β_1 reported for the compressibilities of the other salts. Table 1 also gives the calculated values of Q and D, which incorporate data on Van der Waal's constants[5] and distances[6]. Table 2 gives the values of X, Y, and Z calculated from the data in Table 1 and the r_e values.

The calculated lattice energies are presented in the following way. Equations (5) and (6), or (5a) and (6a), if reduced to two adjustable constants would both become

$$E = -\frac{M}{r} - \frac{C'}{r^6} + Be^{-r/\rho} \tag{4}$$

or eqn (4) of the earlier paper[1]. Consequently, Table 3 gives the results for sodium and cesium chloride, bromide, and iodide for two, three, and four adjustable constants; the results for two and four adjustable constants were calculated earlier.

TABLE 1

COMPRESSIBILITIES AND VALUES OF Q AND D FOR SOME ALKALI HALIDES

Compound	$10^6 \beta_0$ (atm^{-1})	$10^{12} \beta_1$ (atm^{-2})	$10^3 Q$ $(Jm\ mol^{-1})$	$10^6 D$ $(Jm\ mol^{-1})$
NaF	2.07	−17.7	1.503	4.24
KF	3.24	−32.0	1.708	7.50
KCl	5.52	−73.5	1.932	8.93
KBr	6.57	−102.5	1.966	9.41
KI	8.37	−150.7	2.029	10.21
RbBr	7.78 -	−133.4	1.963	11.33
RbI	9.38	−197.7	2.108	12.15
CsF	4.155	−57.9	2.156	12.17

TABLE 2

VALUES OF X, Y, AND Z FOR SOME ALKALI HALIDES (kJ mol^{-1})

Compound	X	Y	Z
NaF	1162.6	9392	73680
KF	1080.2	9414	54310
KCl	944.2	8897	40280
KBr	908.7	8645	38650
KI	862.3	8346	33730
RbBr	904.9	8516	35970
RbI	861.8	8474	36650
CsF	1050.9	10490	69110

TABLE 3

LATTICE ENERGIES (kJ mol^{-1}) CALCULATED WITH VARIOUS NUMBERS OF ADJUSTABLE CONSTANTS

	Number of constants	Eqn (4) 2	Eqn (5a) 3	Eqn (6a) 3	Eqn (5) 4	Eqn (6) 4	Observed —
NaCl		−769.3	−778.8	−778.4	−792.9	−792.5	−783
NaBr		−734.3	−749.4	−749.1	−759.0	−760.7	−747
NaI		−681.3	−696.3	−696.1	−704.7	−704.4	−698.5
CsCl		−645.5	−660.2	−660.0	−668.6	−667.4	−654.5
CsBr		−624.2	−639.5	−643.4	−646.2	−646.1	−631.5
CsI		−585.6	−603.0	−602.9	−609.4	−611.4	−597

TABLE 4

LATTICE ENERGIES (kJ mol^{-1}) CALCULATED WITH VARIOUS NUMBERS OF ADJUSTABLE CONSTANTS

	Number of constants	Eqn (4) 2	Eqn (5a) 3	Eqn (6a) 3	Observed —
NaF		−926.4	−929.8	−929.6	−914
KF		−816.1	−832.3	−831.9	−812
KCl		−700.4	−719.3	−718.9	−712
KBr		−670.1	−687.3	−687.1	−683
KI		−628.9	−645.1	−644.9	−642
RbBr		−644.8	−661.3	−660.4	−656
RbI		−609.0	−624.4	−624.2	−618
CsF		−743.1	−757.4	−757.2	−725

Inspection of Table 3 leads to certain conclusions. Firstly, it makes very little difference whether eqn (5) or (6) or (5a) or (6a) is used. Secondly, the main difference arises from the number of adjustable constants. The trend to larger (absolute) U with more adjustable constants comes, in part, from the fact that β_1 is invariably negative. Thirdly, the experimental results seem, on the whole, and somewhat surprisingly, to agree best with eqn (5a) or (6a).

Table 4 gives similar results for the other alkali halides, except that data for eqns (5) or (6) are not available. On the whole, the same conclusions apply, except that the observed lattice energies for the fluorides always seem to be lower than expected. Equation (7) similarly reduces to

$$E = \frac{M}{r} - \frac{C'}{r^6} + \frac{B}{r^n} \tag{3}$$

if only two adjustable constants are included. This is the earlier eqn (3). The results are presented in a similar way. Table 5 gives the results for sodium and cesium chloride, bromide, and iodide with two, three or four adjustable constants using eqns (3), (7a), and (7). Equations (7a) and (7) were employed with $w = 1$, 2 or 4. The results are not very different, though a trend to smaller (absolute) lattice energies with larger w is consistently followed. Much the same comments can be made as before, except that the effect of increasing w is more marked in eqn (7a) than in eqn (7). Agreement with eqn (7) is better on the whole, except for cesium bromide and iodide.

TABLE 5

LATTICE ENERGIES (kJ mol⁻¹) CALCULATED WITH VARIOUS NUMBERS OF ADJUSTABLE CONSTANTS

	Eqn (3)	Eqn (7a)			Eqn (7)			Observed
Number of adjustable constants	2	3			4			
w	—	1	2	4	1	2	4	
NaCl	−754.2	−766.8	−758.9	—	−788.3	−788.2	−787.7	−783
NaBr	−721.8	−736.9	−736.4	−726.3	−755.7	−755.6	−755.3	−747
NaI	−669.9	−689.1	−686.1	−677.5	−701.7	−701.7	−701.4	−698.5
CsCl	−637.1	−655.0	−652.6	−647.0	−655.3	−655.3	−655.1	−654.5
CsBr	−616.2	−634.8	−633.1	−628.8	−644.2	−644.2	−644.1	−631.5
CsI	−581.2	−598.6	−597.0	−593.0	−607.5	−607.1	−607.1	−597

Table 6 contains similar results for the other alkali halides. Equation (7a) undoubtedly leads to better agreement with experiment, usually with a small value of w. The sole exception is cesium fluoride, where eqn (3) is better; there is no obvious reason for this.

TABLE 6

LATTICE ENERGIES (kJ mol^{-1}) CALCULATED WITH VARIOUS NUMBERS OF ADJUSTABLE CONSTANTS

	Eqn (3)				Observed
Number of adjustable constants	2		3		
w	—	1	2	4	
NaF	−905.9	−910.8	—	—	−914
KF	−800.2	−821.4	−816.2	−798.8	−812
KCl	−688.2	−712.1	−709.3	−701.8	−712
KBr	−658.9	−680.6	−678.0	−671.0	−683
KI	−618.7	−640.2	−636.9	−631.2	−642
RbBr	−633.7	−654.5	−651.9	−645.1	−656
RbI	−599.2	−618.5	−616.3	−610.6	−618
CsF	−731.4	−749.5	−745.8	−734.8	−725

The general conlusions of the earlier paper[1] seem to be reinforced by the present calculations. Equations with more adjustable constants, fitted to the variation of compressibility with pressure give better agreement with experiment for the lattice energies as might be expected. It was noted earlier that eqn (3) must give a smaller (absolute) value of the lattice energy than eqn (4). The same is true of eqn (7a), as opposed to eqns (5a) or (6a), but the difference is now smaller. This difference is reduced still further if equations with four adjustable constants are used. A choice between the various equations with three adjustable constants is difficult to make, since no equation is consistently the best.

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