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# LATTICE ENERGIES: CALCULATIONS FROM PRESSURE–VOLUME DATA, AND UNCERTAINTIES IN THE RESULTS

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## ABSTRACT

A method of calculating lattice energies is developed, which reproduces directly the observed pressure–volume curve of some simple ionic solids. The results in general are close to the experimental values, and show deviations usually between 5 and 10 kJ mole$^{-1}$. The calculated values are not systematically too high or too low. Some estimates are made of the effect of errors in the P–V curve on the calculated lattice energies.

## INTRODUCTION

In earlier papers[1], the present author attempted to develop equations which would reproduce the observed variation of compressibility of a simple ionic crystal with pressure. The compressibility was fitted to an empirical equation

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

where $\beta$ is the compressibility at a pressure $P$. The coefficients $\beta_0$, $\beta_1$ and $\beta_2$ were obtained by the method of least squares. Various equations, relating the crystal energy to distance between neighbouring ions, were investigated. Of these, the most successful was

$$E = \frac{-M}{r} - \frac{C'}{r^6} + \left(B + \frac{G}{r} + \frac{H}{r^2}\right) e^{-\sigma r} \qquad (1)$$

where, $M = NAe^2Z_+Z_-$, $A$ = Madelung constant, $Z_+$,$Z_-$ = charges on cations and anions, $C'$ = van der Waal's constant, $r$ = distance between neighbours. The quantities $B$, $G$, $H$ and $\sigma$ are adjustable constants. If $G$ and $H$ are omitted, eqn. (1), of course, reduces to the Born–Mayer equation[2]. The Born–Mayer equation, and the earlier Born equation, contain two adjustable constants, which are usually evaluated from the equilibrium distance between ions, and the compressibility of the crystal at a fairly low pressure. In effect this method adjusts the constants to give the correct values of d$E$/d$r$ and d$^2E$/d$r^2$ at $r = r_e$, the equilibrium distance. The method used earlier in applying eqn. (1) was to adjust the constants so that in addition

$d^3E/dr^3$ and $d^4E/dr^4$ at $r = r_e$ agreed with experiment. This allows an equation relating $B$, $G$, $H$ and $\sigma$ to $\beta_0$, $\beta_1$, $\beta_2$ and $r_e$ to be developed, and solved to give values of the adjustable constants. Once these constants are known, the lattice energy, $U$, is easily calculated. This procedure gave, in general, larger absolute values for the lattice energy than those calculated from simpler equations such as the Born–Mayer equation. These larger values were usually in better agreement with experimental values, obtained indirectly from a thermodynamic cycle (the "Born–Haber" cycle).

This method rests on the assumption that the best method of fitting the constants is by means of various $d^nE/dr^n$ at $r = r_e$. This is not the only possible approach, and the present paper treats the data somewhat differently, as follows. The primary data in measurements of compressibilities are values of $\Delta V/V_0$ at various pressures, where $\Delta V$ is the change in volume of the sample at some higher pressure from its volume, $V_0$, at zero (or very low) pressure. Hence the constants in eqn. (1) were adjusted to give the experimental curve for $\Delta V/V_0$ plotted against $P$. The details of the method will be described in the next section. The main purpose of this paper is to discover how well this method agrees with results from the earlier treatments, and with experiment. Similar calculations were also made using an equation like eqn. (1), but with fewer constants, and a second object of this paper is to explore the relation between the number of constants and the calculated lattice energies. In addition some values of $P$ for various $\Delta V/V_0$ were calculated, using the constants obtained from the earlier paper[1], and these can also be compared with experiments.

It became apparent in the course of these calculations that the constants in eqn. (1) and, to a considerably lesser extent, the lattice energies were very sensitive to the exact values of $\Delta V/V_0$ that were used. Values of $\Delta V/V_0$ are, of course, subject to experimental error, and their measurement is not easy. Consequently the effect of possible errors in $\Delta V/V_0$ on the calculated results, particularly lattice energies, was also investigated to some extent.

In general, the conclusion cannot be avoided that there is some degree of arbitrariness in lattice energy calculations. This arises, in part, because the equation relating $E$ to $r$ is in effect extrapolated from distances equal to the equilibrium distance, or somewhat less out to $r = \infty$. This is not quite as bad as it sounds, because for distances a few (perhaps 3–4) times the equilibrium distance or larger, the only term in $E$ of any importance is the electrostatic one, and this can presumably be calculated fairly accurately. Some indication of the extent of this arbitrariness will be seen below.

## TREATMENT OF DATA

Equation (1) above contains four constants (it is assumed that $C'$ is known, as values appear in the literature[3]), and in theory it should be possible to take the values of $\Delta V/V_0$ for four different pressures, substitute in eqn. (1), and solve the resulting four equations for $B$, $G$, $H$ and $\sigma$. In practice this approach runs into two difficulties: firstly, the four pressures must be selected somewhat arbitrarily; secondly, the resulting equations are not easy to solve explicitly, as they contain a polynomial multiplied by an exponential term.

A rather different procedure was therefore adopted. Three values of the pressure were selected, and a guessed value of the constant $\sigma$. The resulting three equations were solved for $B$, $G$, and $H$. The pressures were then calculated for the other observed values of $\Delta V/V_0$, and the deviations of these from the observed pressure were also obtained. The average value of these deviations was calculated, with the use of all the observed values of $\Delta V/V_0$, except those for the three initially selected pressures for which the deviation is necessarily zero. The whole calculation was repeated with various values of $\sigma$, and it was found, as might be expected, that the average deviation went through a minimum for some value of $\sigma$. This was taken to be the best value of $\sigma$, and as the relevant $B$, $G$ and $H$ are now known, the lattice energy could be easily calculated.

This procedure has the advantage that it makes use of all the data. It still suffers from some arbitrariness in the selection of the three pressures. In practice the lower and highest pressures were used, and an intermediate one with $\Delta V/V_0$ about half the largest value. It is also arbitrary whether the average deviation in the calculated pressure, or the average fractional deviation is minimised. It was found, fortunately, that this did not make much difference. The same applied to the use of the root mean square deviation. The results reported below come from minimum absolute deviations.

Equation (1) above leads to the following equation for the pressure

$$\frac{\mathrm{d}E}{\mathrm{d}r} = \frac{NAe^2}{r} + \frac{6C'}{r^6} - \left[B\sigma r + G\left(\sigma + \frac{1}{r}\right) + \frac{H}{r}\left(\sigma + \frac{2}{r}\right)\right] \mathrm{e}^{-\sigma r}$$

$$= 3CN_r^3\,(T\alpha_0/\beta_0 - P) \qquad (2)$$

where $C$ is a number such that the volume of one mole of the compound is $CN\mathrm{r}^3$. $\alpha_0$ and $\beta_0$ are, respectively, the coefficient of thermal expansion, and the compressibility,

TABLE 1

CONSTANTS, LATTICE ENERGIES, AND AVERAGE DEVIATIONS IN PRESSURE, CALCULATED FROM EQNS, (1) AND (2)

| *Compound* | $\sigma$ | $B$ | $G$ | $H$ | *Lattice energy* | *Average deviations in P (atm)* |
|---|---|---|---|---|---|---|
| NaCl | 3.00 | $-1.165 \times 10^7$ | $2.068 \times 10^9$ | $-1.777 \times 10^9$ | −777.0 | 372 |
| NaBr | 5.82 | $6.604 \times 10^{13}$ | $-3.240 \times 10^{14}$ | $4.042 \times 10^{14}$ | −754.5 | 196 |
| NaI | 4.52 | $2.351 \times 10^{12}$ | $-11.534 \times 10^{12}$ | $14.652 \times 10^{12}$ | −692.9 | 90 |
| CsCl | 5.78 | $1.710 \times 10^{15}$ | $-10.185 \times 10^{15}$ | $15.344 \times 10^{15}$ | −663.5 | 97 |
| CsBr | 5.10 | $2.211 \times 10^{14}$ | $-13.014 \times 10^{14}$ | $19.442 \times 10^{14}$ | −637.5 | 265 |
| CsI | 4.40 | $3.504 \times 10^{13}$ | $-21.156 \times 10^{13}$ | $32.686 \times 10^{13}$ | −598.3 | 88 |

both at low pressure. The term $T\alpha_0/\beta_0$ allows for the fact that the crystal is not at absolute zero, and has expanded somewhat between 0 K and the temperature of the compressibility measurements (20°C for the data used).

Equation (2) was used either to obtain linear equations in $B$, $G$ and $H$, if $r$ and $P$ are known and a value of $\sigma$ is assumed; or to calculate $P$ at various $r$ after all the constants had been evaluated.

The results for eqn. (1) are given in Table 1. The constants were fixed by the distances observed at pressures of 0, 40 000, and 100 000 atm. Table 1 gives the values of $B$, $G$, and $H$ for the best value of $\sigma$. The average deviations of calculated from observed pressures are also given. These are for the pressures other than 0, 40 000 and 100 000 atm. at which measurements were made: these in general were at multiples of 10 000 atm. up to 90 000. The calculated lattice energies in Table 1 are in kJ mole$^{-1}$. The units of $\sigma$ are Å$^{-1}$, and $B$, $G$ and $H$ are the values if energy is in J mole$^{-1}$ and distance in Å.

Before the results in Table 1 are considered, attention should be drawn to Table 2, which shows how the average deviations varied with different values of $\sigma$. To comment on Table 2, we may note that the calculated pressure for any given interionic distance always drifted steadily as the value of $\sigma$ was increased. This drift might be either up or down, and, of course, the calculated and observed pressures did not all coincide at the same value of $\sigma$. However, the net effect was that the average deviation went through a minimum at some value of $\sigma$. When the observed and calculated pressures coincide at similar values of $\sigma$, the average deviations went through a relatively sharp minimum, and the lowest average deviation was relatively small.

If we look at Table 1, it is hard to see any pattern in the values of $\sigma$. This may arise in part from experimental errors in $\Delta V/V_0$. The observed values of these quantities run from about 0.05 (at $10^4$ atm) to nearly 0.3 (at $10^5$ atm). They are reported

TABLE 2

AVERAGE DEVIATIONS IN CALCULATED PRESSURE FOR DIFFERENT VALUES OF $\sigma$

| *NaCl* | | *NaBr* | | *NaI* | | *CsCl* | | *CsBr* | | *CsI* | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\sigma$ (Å$^{-1}$) | *Dev.* (*atm*) | $\sigma$ (Å$^{-1}$) | *Dev.* (*atm*) | $\sigma$ (Å$^{-1}$) | *Dev.* (*atm*) | $\sigma$ (Å$^{-1}$) | *Dev.* (*atm*) | $\sigma$ (Å$^{-1}$) | *Dev.* (*atm*) | $\sigma$ (Å$^{-1}$) | *Dev.* (*atm*) |
| 2.6 | 374.5 | 4.0 | 557.5 | 4.0 | 125.6 | 5.0 | 630.0 | 5.0 | 297.6 | 4.0 | 333.1 |
| 2.9 | 372.6 | 5.0 | 318.2 | 4.4 | 92.0 | 5.7 | 147.8 | 5.08 | 271.4 | 4.3 | 132.7 |
| 3.0 | 372.4 | 5.5 | 224.6 | 4.48 | 90.9 | 5.76 | 104.8 | 5.10 | 265.1 | 4.38 | 92.7 |
| 3.1 | 372.6 | 5.7 | 199.2 | 4.50 | 90.6 | 5.77 | 98.5 | 5.11 | 266.2 | 4.40 | 88.1 |
| 3.2 | 374.5 | 5.8 | 197.6 | 4.52 | 90.3 | 5.78 | 97.4 | 5.12 | 267.4 | 4.42 | 89.5 |
| | | 5.81 | 196.4 | 4.54 | 91.3 | 5.79 | 98.4 | 5.2 | 277.4 | 4.5 | 98.0 |
| | | 5.82 | 196.1 | 4.58 | 105.0 | 5.8 | 99.4 | 5.4 | 429.9 | 4.6 | 155.0 |
| | | 5.83 | 197.0 | 4.6 | 112.1 | 5.9 | 124.6 | | | | |
| | | 5.9 | 204.5 | | | | | | | | |

TABLE 3

EFFECT OF POSSIBLE ERRORS IN $\Delta V/V_0$ FOR NaBr

| $-\Delta V/V_0$ *for* $P = 4 \times 10^4$ | $\sigma$ | *Average deviation in* $P$ *(atm)* | *Lattice energy (kJ)* |
|---|---|---|---|
| 0.130 | 5.89 | 517 | −756.2 |
| 0.131 | 5.50 | 281 | −751.9 |
| 0.132 | 5.82 | 196 | −754.5 |
| 0.133 | 5.01 | 355 | −745.3 |
| 0.134 | 4.10 | 557 | −732.0 |

to three decimal places, and a change of 0.001 in $\Delta V/V_0$ changed the calculated pressures by about 250 atm at low pressures, and by about 900 atm at high pressures. Consequently a small error in $\Delta V/V_0$ could lead to an appreciable change in the average deviation, and to a lesser extent in the best value of $\sigma$.

This is illustrated by some calculations for sodium bromide in Table 3. The reported value of $\Delta V/V_0$ is $-0.132$ at $4 \times 10^4$ atm. If slightly different values are used in the calculations, the best values of $\sigma$, the average deviations, and the lattice energies are as shown. Note that $\sigma$ does not vary in a monotonic manner, and also that the reported $\Delta V/V_0$ does in fact give the lowest average deviation. The calculated lattice energy changes quite considerably for the small changes in $\Delta V/V_0$.

Another general trend is that the larger the values of $\sigma$, the larger is the absolute value for the lattice energy, as can be seen, for example, from these calculated results for sodium bromide

| | | | | |
|---|---|---|---|---|
| $\sigma$ (Å$^{-1}$) | 4.0 | 5.0 | 5.5 | 6.0 |
| $U$ (kJ mole$^{-1}$) | −733.7 | −745.9 | −751.3 | −756.3 |

The change in $U$ is not large, but it is appreciable.

It seems necessary to conclude that relatively small errors in $\Delta V/V_0$ could lead to moderate sized errors (perhaps 5–10 kJ mole$^{-1}$) in the lattice energy. In spite of this in every case the calculated curve of $\Delta V/V_0$ against $P$ closely reproduced the experimental points. This is true even of sodium chloride, which gave the poorest agreement.

In the earlier paper[1] on this type of calculation, the variation of compressibility with pressure was allowed for, as mentioned above, by fitting $d^3E/dr^3$ and $d^4E/dr^4$ at $r = r_e$. This gives values for $B$, $G$, $H$ and $\sigma$, and so allows pressures to be calculated at various $r$. It was found that the pressures calculated in this way deviated quite seriously from the observed pressures, and it is evident that the earlier method is not nearly as satisfactory in reproducing the $P$–$V$ curve.

The types of calculation involved in eqns. (1) and (2) were also applied to similar equations, but with fewer constants: firstly an equation containing only $B$, $G$ and $\sigma$; and secondly one containing only $B$ and $\sigma$, which is in fact the Born–Mayer

TABLE 4

EFFECT OF NUMBER OF ADJUSTABLE CONSTANTS ON LATTICE ENERGIES

| | *$\sigma$* | | | *Average deviation* | | | *Absolute lattice energies* | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | *4* | *3* | *2* | *4* | *3* | *2* | *4* | *3* | *2* | *Obs.* |
| NaCl | 3.00 | 3.26 | 3.20 | 372 | 327 | 383 | 777.0 | 777.3 | 776.8 | 783.5 |
| NaBr | 5.82 | 2.85 | 3.16 | 196 | 360 | 1302 | 754.5 | 740.1 | 739.4 | 757.5 |
| NaI | 4.52 | 2.57 | 2.81 | 90 | 667 | 452 | 692.9 | 682.0 | 683.1 | 699.5 |
| CsCl | 5.70 | 2.79 | 3.05 | 97 | 644 | 1481 | 663.8 | 648.6 | 648.0 | 655.5 |
| CsBr | 5.10 | 3.30 | 2.78 | 265 | 607 | 998 | 637.5 | 624.4 | 618.8 | 632 |
| CsI | 4.40 | 2.98 | 2.69 | 88 | 473 | 619 | 598.3 | 588.5 | 585.7 | 598.5 |

equation. The results are collected in Table 4. The columns indicate at the top the number of adjustable constants; the column headed "4" repeats part of Table 1, which is included for easy comparison. Also in the last column, observed lattice energies are given (to the nearest 0.5 kJ), obtained in effect from a Born–Haber cycle. These experimental numbers differ slightly from those in ref. 1, being based on slightly revised data (mostly available in ref. 4).

The results in Table 4 show, as might be expected, generally lower deviations with more adjustable constants. However, there are some slight exceptions to this, which arise because the calculated pressure is constrained to agree with the observed pressure at more points in the equations with more constants. This may not reproduce the other pressures quite as well, probably because of some experimental error in observed $P$–$V$ results.

The last section of Table 4 gives absolute lattice energies in kJ mole$^{-1}$. The equation with most constants agrees best with experiment, though the improvement is not very great. The agreement with experiment is, however, definitely better than with the earlier method of obtaining the adjustable constants (from $d^3E/dr^3$, etc.). Also by the earlier method all the calculated results were absolutely too large; by the newer method some are too large and some too small. At the best the calculated results can still differ from experiment by 5–10 kJ. This seems to be the inevitable result of trying to fit the repulsive energy between ions at short distances to a fairly simple formula, and then to extrapolate the equation to an infinite distance. At present, also, a gross repulsive energy for the whole crystal is considered without taking into account differences between cation–anion, cation–cation, and anion–anion repulsions. However, it is doubtful whether these differences could be included in the calculations without either introducing very many adjustable constants, or making fairly extensive assumptions about the relative sizes of the repulsions.

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