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SOME ASPECTS OF THE CALCULATION OF LATTICE ENERGIES

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ABSTRACT

Some relations between lattice energies calculated from various simple equations are pointed out. It is found that these equations give values of the variation of compressibility with pressure that agree poorly with experiments, at least for sodium and cesium chloride, bromide, and iodide. Equations which take this variation into account are developed, and it is found that calculated values of the lattice energy vary very little with the exact equation used. On the whole these extended equations give better agreement between the calculated and observed lattice energies.

INTRODUCTION

It has been common, since the problem was first formulated by Born[1], to suppose that the lattice energy of an ionic crystal is given by

$$E = \frac{-NAe^2 z_+ z_-}{r} + \text{(repulsive energy)}$$

where the first term represents the electrostatic attractions and repulsions of ions, and the second arises from the repulsion of ions at short distances. N is Avogadro's number, A the Madelung constant, and r the distance between neighbouring ions of charge $+ez_+$ and $-ez_-$. At the equilibrium distance $r = r_e$, E becomes the lattice energy U. Somewhat more sophisticated treatments contain other terms, particularly the Van der Waals attraction. These calculated values can be compared with experimental values, obtained indirectly by some thermodynamic cycle (the "Born–Haber" cycle), which involve the combination of a number of experimental results.

The repulsive energy is usually assumed to be given by some largely empirical expression, particularly B/r^n or $B'e^{-r/\rho}$ (ref. 2). These contain two adjustable constants, which are generally chosen to agree with the observed values of the equilibrium distance, r_e, and the compressibility.

The first object of this paper is to point out that the lattice energies calculated from these two expressions (with or without Van der Waals energy) are necessarily related to each other by certain simple equations; relations that have probably been noted before, but do not seem to have been commented on explicitly. As will be seen, the differences in lattice energy are sufficiently small to make choice, on the basis of experiment, difficult.

Treatments of this type, with only two adjustable constants, only use the value of the compressibility at low pressure. However, compressibility, in general, falls with increasing pressure; and, at least for certain alkali halides, fairly extensive data on this exist. Two approaches are possible: either the simple equations can be used to predict the variation of compressibility with pressure, and the results compared with experiment; or equations with more adjustable constants can be fitted to the compressibilities observed. These will then give lattice energies which can be compared with experiment. The second and main part of this paper will deal with these aspects of the problem.

DATA ON COMPRESSIBILITY

Data on the compressibility of the alkali halides have been collected in Landolt–Börnstein[3] from various workers[4]. Unfortunately data on lithium halides are inadequate, and potassium and rubidium chloride, bromide and iodide undergo a phase change at moderately high pressures which limits the data applicable to the present problem. In fact extensive data are only available for sodium and cesium chloride, bromide and iodide, and the present paper will therefore deal with these compounds.

For these compounds, values of $-\Delta V/V_0$ (where V_0 is the volume at zero pressure) are available for pressures up to 100,000 atmospheres. Inspection of these values suggested that they might reasonably fit an empirical equation for the compressibility, β, at constant T:

$$\beta = -\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}P} = \beta_0 + \beta_1 P + \beta_2 P^2 .$$

This gives on integration

$$-\frac{1}{P}\ln\left(\frac{V}{V_0}\right) = \beta_0 + \frac{\beta_1 P}{2} + \frac{\beta_2 P^2}{3} .$$

Values of $-(1/P)\ln(V/V_0)$ were calculated from the data for various values of P (usually multiples of 10^4 atm, up to 10^5 atm), and the coefficients β_0, β_1 and β_2 were obtained by the method of least squares. Table 1 gives these values, all at 20 °C.

In calculating lattice energies, it is much more convenient to have the compressibility expressed as a function of the volume. If V is not very different from V_0, this can be done by the empirical equation:

$$\beta = Y_0 + Y_1\left(\frac{V-V_0}{V_0}\right) + Y_2\left(\frac{V-V_0}{V_0}\right)^2 .$$

The relations between the two sets of coefficients can easily be shown to be:

$$Y_0 = \beta_0; \quad Y_1 = -\beta_1/\beta_0; \quad \text{and} \quad Y_2 = \frac{\beta_0\beta_1 - \beta_1^2/\beta_0 - 2\beta_2}{2\beta_0^2}.$$

Hence Table 1 also includes values of Y_1 and Y_2.

TABLE 1

COEFFICIENTS FOR COMPRESSIBILITIES OF SOME ALKALI HALIDES

Pressures are in atmospheres.

Compound	$10^6 \beta_0$	$10^{12} \beta_1$	$10^{18} \beta_2$	$10^6 Y_1$	$10^6 Y_2$
NaCl	4.133	−64.51	440.9	15.61	−11.47
NaBr	4.694	−66.64	347.7	14.20	−12.78
NaI	6.200	−108.89	715.9	17.56	−14.65
CsCl	5.278	−79.98	415.9	15.15	−14.40
CsBr	5.808	−83.91	477.3	14.45	−11.04
CsI	7.267	−133.50	886.4	18.37	−15.62

FUNCTIONS WITH TWO ADJUSTABLE CONSTANTS

When the function for the repulsive part of the energy contains two adjustable constants, it is usual to fit these to give the correct distance at the minimum energy, and the compressibility at low pressure. In a plot of E against r, this fixes the minimum or the correct place on the r axis, and gives the correct radius of curvature at that minimum. This radius of curvature is given by $(\mathrm{d}^2E/\mathrm{d}r^2)^{-1}$, which equals $\beta_0/9CNr_e$, where C is a numerical factor, depending on the lattice, such that the molar volume equals CNr_e^3.

It is useful here to introduce two quantities, M and Q, defined by:

$$M = NAe^2 z_+ z_- \quad \text{and} \quad Q = \frac{9CNr_e^4}{\beta_0} = \frac{9V_0 r_e}{\beta_0}.$$

Then if the repulsive energy is f, so that

$$E = -\frac{M}{r} + f$$

and if f_0, f_0', f_0'', etc. indicate the values at $r = r_e$ of f, $\mathrm{d}f/\mathrm{d}r$, $\mathrm{d}^2f/\mathrm{d}r^2$, etc., then

$$f_0' = -M/r_e^2 \quad \text{and} \quad f_0'' = (Q+2M)/r_e^3.$$

M can be calculated, and Q can be found from experimental data, and hence the two adjustable constants are found from these two equations. If we apply this to the commonly used forms for the repulsive energy, we get the following.

(*1*) *Born equation*

Here $f = B/r^n$, and this gives

$$n = 1 + Q/M.$$

As is well known, the lattice energy is

$$U_1 = -\frac{M}{r_e}\left(1 - \frac{1}{n}\right) = -\frac{M}{r_e}\left(\frac{Q}{Q+M}\right).$$

(*2*) *Born–Mayer equation*

Here $f = B'e^{-r/\rho}$, and this gives

$$r_e/\rho = 2 + Q/M = n + 1.$$

The lattice energy is

$$U_2 = -\frac{M}{r_e}\left(1 - \frac{\rho}{r_e}\right) = -\frac{M}{r_e}\left(\frac{Q+M}{Q+2M}\right).$$

Hence the ratio U(Born)/U(Born–Mayer) is $1 - 1/n^2$, where U(Born) is invariably a smaller (absolute) quantity. As n is in general between 6 and 12, the difference is 0.7 to 2.8%.

(*3*) *Born equation with Van der Waals term*

Here we take

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

with B'' and q as the adjustable constants. C' is assumed to be known, and values are found in the literature, for instance by Mayer[5]. If we write $D = C'/r_e^5$, we find

$$q = \frac{Q+M+36D}{M+6D}$$

and the lattice energy is

$$U_3 = \frac{M}{r_e}\left\{\frac{Q + \dfrac{DQ}{M} + 25D}{Q+M+36D}\right\}.$$

Compounds with the NaCl structure have $M = 2.42787 \times 10^{-4}$ Jm; for the CsCl structure, $M = 2.44886 \times 10^{-4}$ Jm. Values of Q and D for the compounds being considered are given in Table 2. With these values of Q and D, the lattice energy is a larger (absolute) quantity than on the simple Born equation, but the difference ranges from only 0.15% for NaCl up to 1.85% for CsI.

TABLE 2

VALUES OF Q AND D FOR SOME ALKALI HALIDES

Compound	$10^{+3}\times Q$ *(Jm)*	$10^{+6}\times D$ *(Jm)*
NaCl	1.667	6.144
NaBr	1.848	6.933
NaI	1.931	8.244
CsCl	2.574	16.11
CsBr	2.767	17.67
CsI	2.833	18.60

(4) Born–Mayer equation with Van der Waals term

Here we take

$$E = -\frac{M}{r} - \frac{C'}{r^6} + B''' \mathrm{e}^{-r/\sigma}$$

with B''' and σ as adjustable constants. The same treatment gives

$$\frac{r_e}{\sigma} = \frac{Q+2M+42\,D}{M+6\,D}$$

and the lattice energy is

$$U = -\frac{M}{r_e}\left\{\frac{Q+M+D\left(\dfrac{Q}{M}+32\right)+\dfrac{6\,D^2}{M}}{Q+2M+42D}\right\}.$$

Again the lattice energy is a larger quantity than for the simple Born–Mayer equation, and the difference ranges from 0.5% for NaCl to 2.5% for CsI.

The object of this part of the paper has been to point out the relations between the lattice energies calculated from various equations. The actual numerical values are collected in Table 3, and also experimental values from the Born–Haber cycle, using data collected by Dasent[6]. As might be expected the calculated values are not very different, and whether they are different enough to make an unambiguous choice of

TABLE 3

COMPARISON OF LATTICE ENERGIES (kJ mole^{-1}) CALCULATED BY VARIOUS EQUATIONS

Compound	*Eqn (1)*	*Eqn (2)*	*Eqn (3)*	*Eqn (4)*	*Observed*
NaCl	−753.1	−765.4	−754.2	−769.3	−783
NaBr	−719.9	−729.7	−721.8	−734.3	−747
NaI	−667.5	−675.9	−669.9	−681.3	−698.5
CsCl	−628.6	−632.9	−637.1	−645.5	−654.5
CsBr	−605.9	−609.9	−616.2	−624.2	−631.5
CsI	−570.6	−574.3	−581.2	−588.6	−597

equation is somewhat a matter of judgement. Probably we should restrict our choice between eqns (3) and (4), since inclusion of the Van der Waals term is certainly valid, and eqn (4) is always somewhat better.

CALCULATION OF HIGHER TERMS IN THE COMPRESSIBILITY

Since the lattice energy itself does not give a very clear basis for choice between these equations, it was thought that calculation of the higher coefficients in the expression for the compressibility, β_1 and β_2 above, might possibly do so. Since

$$\mathrm{d}^2E/\mathrm{d}V^2 = 1/\beta V,$$

it can be shown that, at $r = r_e$

$$\frac{\mathrm{d}^3E}{\mathrm{d}r^3} = \frac{27CN(\beta_0 - Y_1)}{\beta_0^2} = \frac{27CN(\beta_0^2+\beta_1)}{\beta_0^3} \quad \text{and} \quad \mathrm{d}^4E/\mathrm{d}r^4 = 18CNF/\beta_0^3 r_e$$

where $F = \beta_0^2 + 9Y_1^2 - 9\beta_0 Y_1 - 9\beta_0 Y_2 = \beta_0^2 + \dfrac{9\beta_1^2}{2\beta_0^2} + \dfrac{27\beta_1}{2} + \dfrac{9\beta_2}{\beta_0}$.

Hence β_1 and β_2 can be calculated. This assumes that E is given (as above) by some equation containing two adjustable constants, which are fitted to the values of β_0 and r_e.

If we use the same equations as before, we get the following.

(*1*) *Born equation*

$$\beta_1 = -\beta_0^2\left(\frac{Q+8M}{3M}\right) \quad \text{and} \quad \beta_2 = \beta_0^3\left(\frac{Q+16M}{9M}\right).$$

(*2*) *Born equation with Van der Waals term*

$$\beta_1 = -\beta_0^2\left[\frac{Q^2+8QM+6D(18Q-25M)}{3Q(M+6D)}\right] \quad \text{and}$$

$$\beta_2 = \beta_0^3\left[\frac{Q^2M+16QM^2-D(9Q^2-402QM+525M^2)+ + D^2(486Q+3600M-11250M^2/Q)}{9Q(M+6D)^2}\right].$$

(*3*) *Born–Mayer equation*

$$\beta_1 = \beta_0^2\left(\frac{Q^2+7QM-2M^2}{3QM}\right) \quad \text{and}$$

$$\beta_2 = \beta_0^3\left(\frac{Q^3+28Q^2M-6QM^2-4M^3}{18Q^2M}\right).$$

(4) Born–Mayer equation with Van der Waals term

$$\beta_1 = -\beta_0^2 \left[\frac{Q^2 + 7QM - 2M^2 + 102D(Q - 2M) - 252D^2}{3Q(M + 6D)} \right] \quad \text{and}$$

$$\beta_2 = \beta_0^3 \left[\frac{\begin{gathered} Q^3M + 28Q^2M^2 - 6QM^3 - 4M^4 - 6D(4Q^3 - 126Q^2M + \\ + 248QM^2 + 136M^3) + (6D)^2(23Q^2 + 147QM - 1184M^2) + \\ + (6D)^3(14Q - 476M) - (6D)^4 49 \end{gathered}}{18Q^2(M + 6D)^2} \right].$$

If the values of Q, M and D, used earlier, are substituted into these equations, we get the results in Table 4. In general the agreement of observed and calculated values is not good. Over the range of the observations (up to 10^5 atm), the agreement of the calculated $\Delta V/V_0$, or of β, with experiment is poor in all cases. Relatively, eqn (4) above (Born–Mayer with Van der Waals term) is most often the best, but not invariably so. Even this equation gives values of β_1 and β_2 which agree poorly with experiment.

TABLE 4

COMPARISON OF CALCULATED AND OBSERVED VALUES OF β_1 AND β_2

Pressures are in atmospheres.

Compound	*Eqn (1)*	*Eqn (2)*	*Eqn (3)*	*Eqn (4)*	*Observed*
Values of $-10^{12}\beta_1$					
NaCl	84.6	84.2	77.3	77.5	64.5
NaBr	114.7	113.7	105.4	103.3	66.6
NaI	204.4	202.0	188.4	183.7	108.9
CsCl	171.9	164.3	160.8	150.8	80.0
CsBr	217.0	205.1	203.8	188.8	83.9
CsI	344.4	323.9	323.8	298.4	133.5
Values of $10^{18}\beta_2$					
NaCl	179	178	133	128	441
NaBr	271	266	200	192	348
NaI	634	618	465	446	716
CsCl	433	391	310	272	416
CsBr	594	523	422	363	477
CsI	1175	1023	832	709	886

Two minor points may be made. It may be thought that an exponential form for the variation of β with P would be better. This is equivalent to writing $\beta = \beta_0 e^{\beta_1 P/\beta_0}$, and requiring that (to a first approximation) $\beta_2 = \beta_1^2/2\beta_0$. Hence this equation offers no better basis of comparison with experiment. The second minor point is that $\beta=\beta_0+\beta_1 P+\beta_2 P^2$ apparently gives a minimum in β at about 70,000 to 80,000 atm, which is somewhat unexpected. This is in part the result of only taking three adjustable constants, β_0, β_1 and β_2; but, with this number of constants, the quoted values of these constants give the best fit with experiment. In fact the observed values of $\Delta V/V_0$ fit those calculated from $\beta=\beta_0+\beta_1 P+\beta_2 P^2$ very adequately.

EQUATIONS WITH MORE ADJUSTABLE CONSTANTS

A more plausible approach to the problem is to choose a function for the repulsive energy containing four adjustable constants, and to fit these to the observed values of β_0, β_1, β_2 and r_e. This leaves considerable latitude in the choice of the form of this function, and the forms selected below are obviously somewhat arbitrary. What has been done is to derive equations which ensure agreement with the observed β_0, β_1, β_2 and r_e, and thence to calculate the lattice energy. The object of this is to see whether the lattice energies differ appreciably from those calculated earlier, and whether any particular expression gives a generally good agreement with experiment.

The equations for E that were investigated, and the methods of applying them were as follows. They are numbered eqn. (5) onwards, to follow on the four equations used above.

Equation 5

$$E=-\frac{M}{r}-\frac{C'}{r^6}+(B+Gr+Hr^2)\mathrm{e}^{-r/\rho}$$

where C'/r^6 is the Van der Waals term, and the adjustable constants are B, G, H and ρ.

Equation 6

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

where B, G, H and ρ are adjustable constants.

Equation 7

$$E=-\frac{M}{r}-\frac{C'}{r^6}+\frac{B}{r^n}+\frac{Gr}{r^{n+x}}+\frac{H}{r^{n+2x}}$$

where x was some arbitrarily selected small integer, and B, G, H and n are adjustable constants.

Equation 5

If we successively differentiate this equation up to $\mathrm{d}^4E/\mathrm{d}r^4$, and put $r=r_e$, we get

$$\begin{aligned}\mu-\nu-2\pi &= Xe^{u}\\ \mu u-2\nu u-4\pi u+2\pi &= Ye^{u}\\ \mu u^{2}-3\nu u^{2}-6\pi u^{2}+6\pi u &= Ze^{u}\\ \mu u^{3}-4\nu u^{3}-8\pi u^{3}+12\pi u^{2} &= We^{u}\end{aligned}$$

where

$$\begin{aligned}u &= r_e/\rho\\ \mu &= Bu+Gr_e u+Hr_e^2 u\\ \nu &= Gr_e\\ \pi &= Hr_e^2\\ X &= \frac{M+6D}{r_e}\\ Y &= \frac{2M+42D+Q}{r_e}\\ Z &= \frac{6M+336D}{r_e}-\frac{27V_0(\beta_0^2-\beta_1)}{\beta_0^3}\\ W &= \frac{24M+3024D}{r_e}+\frac{9V_0}{\beta_0^5}(2\beta_0^4+9\beta_1^2+27\beta_0^2\beta_1+18\beta_0\beta_2)\end{aligned}$$

X, Y, Z and W can be found from experimental data. If we eliminate μ, ν and π, we get

$$Xu^3-3Yu^2+3Zu-W=0$$

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

$$U=-\frac{(M+D)}{r_e}+\frac{\mu}{u}e^{-u}=-\frac{(M+D)}{r_e}+\frac{(3Xu^2-3Yu+Z)}{u^3}$$

which can be evaluated, once u is known.

Equation 6

Similar treatment of this equation gives

$$\begin{aligned}\mu+\nu+2\pi &= Xe^{u}\\ \mu u+2\nu u+2\nu+4\pi u+6\pi &= Ye^{u}\\ \mu u^{2}+3\nu u^{2}+6\nu u+6\nu+6\pi u^{2}+18\pi u+24\pi &= Ze^{u}\\ \mu u^{3}+4\nu u^{3}+12\nu u^{2}+24\nu u+24\nu+8\pi u^{3}+36\pi u^{2}+96\pi u+120\pi &= We^{u}\end{aligned}$$

where we now define

$$\mu = Bu + Gu/r_e + Hu/r_e^2$$
$$\nu = G/r_e$$
$$\pi = H/r_e^2$$

and u, X, Y, Z and W are defined as before.

Elimination of μ, ν and π gives

$$Xu^6 + (14X - 3Y)u^5 + (78X - 36Y + 3Z)u^4 + (204X - 168Y + 30Z - W)u^3 +$$
$$+ (264X - 360Y + 108Z - 8W)u^2 + (144X - 360Y + 168Z - 18W)u -$$
$$- 144Y + 96Z - 12W = 0.$$

This can be solved numerically for u. The lattice energy is given by

$$U = -\frac{(M+D)}{r_e} + \frac{3X(u^2+4u+2) - 3Y(u+2) + Z}{u(u^2+6u+6)}$$

which can be evaluated as before.

Equation 7

Similar treatment of this equation gives

$$\mu + \nu + \pi = X$$
$$(n+1)\mu + (n+w+1)\nu + (n+2w+1)\pi = Y$$
$$(n+1)(n+2)\mu + (n+w+1)(n+w+2)\nu + (n+2w+1)(n+2w+2)\pi = Z$$
$$(n+1)(n+2)(n+3)\mu + (n+w+1)(n+w+2)(n+w+3)\nu +$$
$$+ (n+2w+1)(n+2w+2)(n+2w+3)\pi = W$$

where we now define

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

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

$$\pi = \frac{(n+2w)H}{r_e^{n+2w}}$$

and X, Y, Z and W are defined as before.

Elimination of μ, ν and π gives

$$Xn^3 + (3wX + 3X - 3Y)n^2 + (2w^2X + 6wX + 3X - 6wY - 9Y + 3Z)n +$$
$$+ 2w^2X + 3wX + X - 2w^2Y - 9wY - 7Y + 3wZ + 6Z - W = 0.$$

This is easily solved numerically for n. The lattice energy is given by

$$U = -\frac{(M+D)}{r_e} + \frac{(3n^2+6nw+3n+2w^2+3w+1)X-(n+w+1)3Y+Z}{n(n+w)(n+2w)}$$

which can be evaluated, once n is known. This was done for several, arbitrarily selected but small, values of w.

The values of X, Y, Z and W, obtained from the experimental data are given in Table 5. The values of u and of the lattice energy calculated from eqns (5) and (6) are given in Table 6; the values of n and the lattice energy calculated from eqn (7) in Table 7.

The first comment on these results is that the values of u or n are larger than from the simpler eqns (1)–(4). This has the effect of making the repulsive energy vary more rapidly with distance; and hence its value at the equilibrium distance, when the forces on the ions are balanced, is less than that calculated from any of the simpler equations. This makes the calculated lattice energies more negative. Secondly there is not much difference between the results of eqns (5), (6) and any of the forms of eqn (7). The calculated lattice energies are now all somewhat too high, and the best fit is with eqn (7) ($w = 4$). In fact this equation gives the smallest deviation between

TABLE 5

VALUES OF X, Y, Z AND W FOR VARIOUS COMPOUNDS (kJ mole^{-1})

Compound	X	Y	Z	W
NaCl	993.8	8565	61865	1513200
NaBr	954.0	8804	50337	1088900
NaI	904.5	8550	45943	904000
CsCl	959.5	10507	59918	1222200
CsBr	945.0	10770	53198	926000
CsI	902.5	10389	52419	947800

TABLE 6

LATTICE ENERGIES CALCULATED FROM EQNS (5) AND (6)

Compound	*Eqn (5)*		*Eqn (6)*	
	u	U (kJ mole^{-1})	u	U (kJ mole^{-1})
NaCl	20.38	−792.9	18.46	−729.5
NaBr	22.96	−759.0	21.05	−760.7
NaI	23.71	−704.7	21.81	−704.4
CsCl	27.76	−668.6	25.84	−667.4
CsBr	29.60	−646.2	27.68	−646.1
CsI	29.88	−609.4	27.96	−611.4

TABLE 7

LATTICE ENERGIES (in kJ mole^{-1}) CALCULATED FROM EQN (7)

Compound	*$w = 1$*		*$w = 2$*		*$w = 4$*	
	n	*U*	*n*	*U*	*n*	*U*
NaCl	19.29	−788.3	18.39	−788.2	16.75	−787.7
NaBr	22.00	−755.7	21.08	−755.6	19.41	−755.3
NaI	22.77	−701.7	21.86	−701.7	20.18	−701.4
CsCl	26.84	−665.3	25.91	−665.3	24.19	−665.1
CsBr	28.70	−644.2	27.79	−644.2	26.00	−644.1
CsI	28.97	−607.5	27.64	−607.1	26.07	−607.1

calculated and observed lattice energies of any equation. Since eqn (7), as w is increased, approximates more and more to eqn (3), it is probable that a value of w could be found which gives good agreement with experiment, though it would be fairly large (at least greater than 10, but varying for different compounds). Since there is some uncertainty in the experimental values, this matter was not pursued in detail. Figure 1 shows the values of E for sodium chloride in the neighbourhood of the minimum, calculated from various equations. All equations necessarily have the same values of d^2E/dr^2 at the minimum, but eqns (5) and (7) have larger values of d^3E/dr^3 and d^4E/dr^4, which gives a faster rise as r decreases.

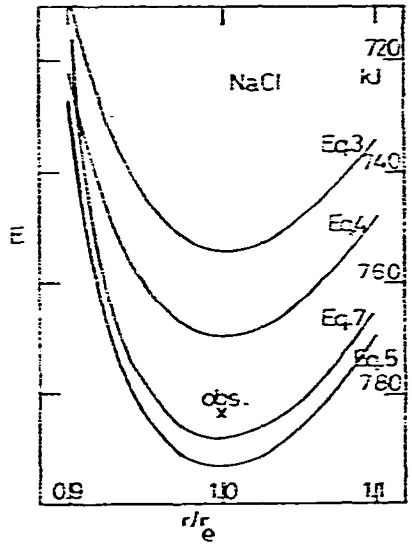

Fig. 1. Energy of sodium chloride at different interionic distances, calculated by various equations.

The conclusions to be drawn from this investigation are that equations which take into account the observed variation of compressibility with pressure give appreciably larger values of the lattice energy for the compounds considered, and on the whole give better agreement with values obtained from the Born–Haber cycle. The exact form of these extended equations makes little difference. Presumably they do reproduce the actual variation of energy with interionic distance more accurately. It would seem that they offer a better, though more complicated, method of calculating lattice energies.

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