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The Potential Energies of the Alkali Halides: Errata and Extension of the Semi-Empirical Formula

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A correction is first made of the author's previous calculations for CsCl, in which an incorrect empirical value was used. By extending the method of Born and Mayer, six constants in the potential energy expression for CsCl are evaluated from available measurements on the lattice and vapor. The results so obtained are then applied to other alkali halides, and permit the determination of the interionic distances in the gas, the lattice energies and heats of sublimation. The agreement with empirical data is satisfactory for the interionic distances, but is otherwise poor.

INTRODUCTION

SEVERAL attempts have been made to approximate the potential energy curves of the alkali halides by the method of Born and Mayer[1] in which constants in the energy expression for the crystal are evaluated from experimental data. Born and Mayer, and Huggins and Mayer[2] evaluated two such constants but their expressions for the potential energy failed to show why CsCl, CsBr and CsI crystallize normally in the body-centered CsCl-type lattice, and not in a simple lattice of the NaCl type, the form assumed by most of the alkali halides.

The author obtained[3] the proper stability for CsCl by inserting two additional constants in the energy expression and evaluating these from experimental data. The four empirical constants required for this evaluation were the heat of transition of CsCl in passing from the body-centered type, which is stable below 445°C, to the simple lattice type, stable at higher temperatures; the compressibility β and other P-V-T data for the normally stable body-centered type; the lattice constant r_0, i.e., the distance between nearest ions, for the body-centered type at 273°K and for the simple lattice at absolute zero.

The lattice energy U was assumed to be of the form

$$U=\alpha e^2/r_0+cC/r_0^6+cD/r_0^8-B(r_0). \qquad (1)$$

The components of energy are respectively, the electrostatic energy, the energies of the dipole-dipole and dipole-quadrupole van der Waals interactions and the repulsion components. α is Madelung's constant; e, the electronic charge; and C and D, the van der Waals constants as computed theoretically by Mayer.[4] The repulsion components were taken as

$$B(r_0)=b_1M\exp(-r_0/\rho)+b_2M'\exp(-ar_0/\rho). \qquad (2)$$

M and M' are the numbers of nearest and next nearest neighbors of an ion, and a is the ratio of the distances of these second and first neighbors. The four constants to be evaluated are c and the three repulsion constants, b_1, b_2, and ρ. The values of α, M, M' and a, which depend only on the lattice type, are given in Table I.

The four equations necessary for the evaluation of the constants are obtained as follows. The experimental heat of transition was equated equal to the difference of the lattice energies for the body-centered and simple lattice types as given by Eq. (1). The other three relations were obtained by forming the first and second derivatives of this equation with respect to r_0

$$-r_0\frac{\partial U}{\partial r_0}=\frac{\alpha e^2}{r_0}+\frac{6cC}{r_0^6}+\frac{8cD}{r_0^8}+r_0\frac{\partial B}{\partial r_0}=R \qquad (3)$$

and

$$r_0^2\frac{\partial^2 U}{\partial r_0^2}=\frac{2\alpha e^2}{r_0}+\frac{42cC}{r_0^6}+\frac{72cD}{r_0^8}-r_0^2\frac{\partial^2 B}{\partial r_0^2}=-S, \qquad (4)$$

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[1] M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932).

[2] M. L. Huggins and J. E. Mayer, J. Chem. Phys. **1**, 643 (1933).

[3] A. May, Phys. Rev. **52**, 339 (1937).

[4] J. E. Mayer, J. Chem. Phys. **1**, 270 (1933).

Table I. *Constants which depend on lattice type.*

Type of Lattice	α	M	M'	a
CsCl	1.7627	8	6	1.1547
NaCl	1.7476	6	12	1.4142

where R and S are given by

$$R=(3T/N\beta)(\partial V/\partial T)_P \tag{5}$$

and

$$S=\frac{9V}{N\beta}\left[1+\frac{T}{\beta}\left(\frac{\partial\beta}{\partial T}\right)_P +\frac{T}{\beta^2 V}\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial\beta}{\partial P}\right)_T+\frac{2}{3}\frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_P\right]. \tag{6}$$

V is the mole volume; P, the pressure; T, the temperature, and N is Avogadro's number. Eqs. (3) and (4) were applied to the body-centered type lattice at 273°K and Eq. (3) was used for the simple lattice type at 0°K. The lattice constant at 0°K was calculated by extrapolation from values obtained above the transition point.

Errata

In the calculations for CsCl previously reported[3] by the author, $\beta^{-1}(\partial\beta/\partial P)_T$ was inadvertently given a value only one-tenth that experimentally determined.[5] Those calculations have, therefore, been corrected. Most of the P-V-T data used were those recently recomputed by Huggins.[6] They are listed in Table II.

Table III gives the results of the recalculation of the lattice energies of CsCl by this method of four constants. The symbols employed are those of the previous paper except for the addition of a subscript "a," which will be explained later. For the electronic charge, Birge's value[7] 4.803×10^{-10} e.s.u. has been used. A comparison of the values in Table III with those formerly given, shows that while the van der Waals factor, c, is practically the same, 3.5 instead of 3.6, ρ has increased from 0.365 to 0.393 and consequently b_1 has become somewhat less. The ratio b_2/b_1 has dropped from 0.7 to 0.4.

The elastic constants and frequencies, obtained as before, are given in Tables IV and V. They are lower than those previously reported. The optical frequency of 3.16×10^{12} sec.$^{-1}$ for the CsCl-type lattice is 7.5 percent higher than the value of 2.94 obtained by Barnes from the measured infra-red absorption limit of CsCl. Heckmann's correction for the electron polarization results in a value of 2.41×10^{12} sec.$^{-1}$ which is 18 percent lower than Barnes' value.

The determination of the temperature of transition between the two lattice types, by equating the free energies and using the frequencies found for 0°K, yields a value of 741°K, still in substantial agreement with the experimental value of 718°K. As before, an attempt to use, in this computation, the frequencies calculated for the transition temperature fails because of the too rapid decrease of the acoustic frequency limit for the CsCl-type lattice with increasing temperature.

The Molecule

Calculations for the gaseous molecule can be made in a manner entirely similar to that already used for the crystal. Here we are confronted by a source of error, whose magnitude is difficult to estimate. The potential energy expression should contain a polarization term whose size would depend on the number of neighbors of an ion. For CaCl, Neugebauer and Gonbas[8] found the principal part of this term almost identical in form and magnitude with the first van der Waals component. In the method we have used, such a contribution would be indistinguishable from the van der Waals energy and would merely increase the value of c. Since, in the gaseous molecule, each ion has a single companion, this polarization energy should be somewhat greater

Table II. *Data used in calculations for* CsCl *273°K.*

P-V-T Constants	CsCl Type	NaCl Type
$C\times 10^{60}$ erg cm^6	1621	1105
$D\times 10^{76}$ erg cm^8	2630	1751
$r_0\times 10^8$ cm (meas.)	3.553	
$\beta\times 10^{12}$ barye^{-1}	5.95	
$\beta^{-1}(\partial\beta/\partial T)_P\times 10^4$ deg^{-1}	8.8	
$\beta^{-1}(\partial\beta/\partial P)_T\times 10^{11}$ barye^{-1}	−3.40	
$V^{-1}(\partial V/\partial T)_P\times 10^4$ deg^{-1}	1.887	
R $\times 10^{12}$ ergs per molecule	1.79	
S $\times 10^{12}$ ergs per molecule	102.4	
ΔU $\times 10^{12}$ ergs per molecule	0.093	

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[5] P. W. Bridgman, Proc. Am. Acad. **67**, 345 (1932).

[6] M. L. Huggins, J. Chem. Phys. **5**, 143 (1937).

[7] R. T. Birge, Phys. Rev. **52**, 241 (1937).

[8] Th. Neugebauer and P. Gombas, Zeits. f. Physik **89**, 480 (1934).

TABLE III. *Results of calculation of lattice energies of* CsCl.*

	METHOD OF 4 CONSTANTS		METHOD OF 6 CONSTANTS	
	CsCl TYPE	NaCl TYPE	CsCl TYPE	NaCl TYPE
c	3.5	3.5	2.60	2.60
ρ_a } $\times 10^8$ cm	0.393	0.393	0.380	0.380
ρ_b			0.100	0.100
b_2/b_1	0.4	0.4	0.203	0.203
$b_1 \times 10^{12}$ ergs per molecule	3175	3175	3580	3580
$b_{ab} \times 10^{-8}$			3.375	3.375
$\alpha e^2/r_0$	11.44	11.75	11.44	11.67
cC/r_0^6	2.82	2.38	2.09	1.69
cD/r_0^8	0.36	0.32	0.27	0.22
$B_{1a}(r_0)$	3.00	3.08	2.49	2.42
$B_{2a}(r_0)$ } $\times 10^{12}$ ergs per molecule	0.22	0.07	0.09	0.02
$B_{1b}(r_0)$			0.00	0.01
$B_{2b}(r_0)$			0.00	0.00
U	11.40	11.30	11.22	11.13
ΔU	0.10		0.09	
$r_0 \times 10^8$ cm 0°K (calc.)		3.402		3.421
$r_0 \times 10^8$ cm 273°K (estimated)		3.454		3.454
	gas		*gas*	
$r_g \times 10^8$ cm (calc.)	2.94		3.07	
F dynes per cm	5.0		9.0	

* Calculations are for $T=273$°K unless otherwise specified.

than in the crystal, but calculations for the gas were made in the hope that the error might not be important.

The heat of dissociation of molecules into ions, is given by

$$U_D=\frac{e^2}{r_g}+\frac{cc_{+-}}{r_g^{\,6}}+\frac{cd_{+-}}{r_g^{\,8}}-B_g(r_g), \tag{7}$$

where $B_g(r_g)=b_1 \exp(-r_g/\rho)$; c_{+-} and d_{+-} are the van der Waals constants for a pair of unlike ions as computed by Mayer[4] and the subscript, g, denotes the gaseous molecule.

Maxwell, Hendricks, and Mosley[9] have measured the interionic distances of the alkali chlorides, bromides, and iodides in the gaseous state at approximately 1200°C by electron diffraction. Their results furnish an additional test of the correctness of the shape obtained for the potential energy curve of the ions. If it is assumed that at 1200° only a small fraction of the molecules are in excited vibration states, these interionic distances can be calculated for absolute zero by using the equation obtained by differentiating Eq. (7):

$$\frac{e^2}{r_g}+\frac{6cc_{+-}}{r_g^{\,6}}+\frac{8cd_{+-}}{r_g^{\,8}}+r_g\frac{\partial B_g}{\partial r_g}=0. \tag{8}$$

Applying this formula to CsCl, with the constants already obtained from crystal data,

TABLE IV. *Elastic constants* $\times 10^{-11}$ *erg/cm*^{3}.

	c_{11}	c_{12}	c_{44}	ACOUSTIC FREQUENCY LIMIT $\nu_m \times 10^{-12}$
CsCl TYPE AT 273°K				
electrostatic	1.730	−1.694	−1.694	
van der Waals C	−3.357	−1.588	−1.588	
van der Waals D	−0.662	−0.368	−0.368	
repulsion	5.670	4.388	4.388	
$R/6\Delta$	0.043		0.043	
	3.424	0.738	0.781	2.622
NaCl TYPE AT 273°K				
electrostatic	−2.688	0.616	0.616	
van der Waals C	−4.034	−0.337	−0.337	
van der Waals D	−0.982	−0.038	−0.038	
repulsion	11.032	0.113	0.113	
$R/6\Delta$	0.018		0.018	
	3.346	0.354	0.372	2.086
CsCl TYPE AT 0°K	3.787	1.014	1.014	2.890
Nacl TYPE AT 0°K	3.766	0.359	0.359	2.101

TABLE V.* *Optical frequencies at 273° and 0°K. D (Born)* $\times 10^{-26}$ *erg/cm*^{5}.

	CsCl TYPE	NaCl TYPE
at 273°K		
electrostatic	−2.026	−1.484
van der Waals C	−2.055	−1.795
van der Waals D	−0.578	−0.543
repulsion	7.311	6.353
D	2.652	2.531
frequency $\times 10^{-12}$	3.161	3.338
at 0°K		
D	3.213	2.658
frequency $\times 10^{-12}$	3.411	3.379

* For explanation of notation, see reference 3.

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[9] L. R. Maxwell, S. B. Hendricks and V. M. Mosley, Phys. Rev. **52**, 968 (1937).

one finds the interionic equilibrium distance to be 2.94×10^{-8} cm as compared with the measured value of 3.06 ± 0.03. The 4 percent error is rather large.

Still another check of the potential energy expression is available. From spectroscopic absorption measurements of Sommermeyer, Herzfeld has calculated[10] $2\pi^2\omega_e^2\mu$ for a number of the alkali halides. Here ω_e is the classical vibration frequency and μ the reduced mass. This quantity is one-half the force between the gaseous ions for a separation of one cm. The forces so obtained are given in Table VI.

No value is listed for CsCl, but it will apparently be in the neighborhood of 11 dynes/cm and probably less than this, say, 10 dynes/cm.

To calculate the force per unit distance from the potential energy expression we use an equation of the same nature as Eq. (4), namely

$$\frac{2e^2}{r_g^3}+\frac{42cc_{+-}}{r_g^8}+\frac{72cd_{+-}}{r_g^{10}}-\frac{\partial^2 B_g}{\partial r_g^2}=-F. \qquad (9)$$

F is the force at unit distance. Using $r_g=2.94\times 10^{-8}$ cm, we find $F=5.0$ dynes/cm, approximately half the correct value.

METHOD OF SIX CONSTANTS

Since the potential energy form chosen failed to give reasonable agreement for the molecule, the form of the repulsion energy was changed so as to give two additional parameters, making a total of six constants, whose values can then be obtained from six equations, the four previously used, together with Eqs. (8) and (9). The form used for $B(r_0)$ was

$$B(r_0)=b_1M(\exp(-r_0/\rho_a)+b_{ab}\exp(-r_0/\rho_b))$$
$$+b_2M'(\exp(-ar_0/\rho_a)+b_{ab}\exp(-ar_0/\rho_b)) \qquad (10)$$

and consequently

$$B_g(r_g)=b_1(\exp(-r_g/\rho_a)+b_{ab}\exp(-r_g/\rho_b)). \qquad (11)$$

This form assumes that the repulsion energy in the range from r_0 to r_g cannot be adequately expressed by using a single exponential and attempts improvement by including a second exponential and introducing the two additional parameters, ρ_b and b_{ab}. b_{ab} is the ratio of the b-factor for the exponential containing ρ_b to that for the one containing ρ_a. The same shielding factor, b_2/b_1, is assumed for the contributions of the two exponentials.

TABLE VI. *Forces between ions in dynes/cm from spectroscopic measurements.*

	Cl	Br	I
Na			9.0
K		12.4	10.8
Rb	10.2		9.6
Cs		11.0	7.6

The labor involved in the calculations is, of course, tremendously increased. The method employed was first to assume values of ρ_a, ρ_b and c. Next, from data for the CsCl-type lattice, and by use of Eqs. (1), (3) and (4), we solve for b_1, b_2 and b_{ab}. Having, now, values for the six constants, we applied Eq. (3) to the NaCl-type lattice at absolute zero, and determined its equilibrium distance. In general, the distance so found was not a reasonable one. With the same values of ρ_a and ρ_b as before, c was then changed until a suitable result was obtained. Finally the six constants so determined were substituted in Eqs. (8) and (9) for the gas to find what force F and what equilibrium separation r_g result. This whole process was then repeated with new values of ρ_a and ρ_b until all six equations were reasonably satisfied. The results for CsCl are given in Table III. The subscripts 1 and 2 refer to the first and second neighbors of an ion, the subscricripts a and b to the two values of ρ. Thus B_{1a} is the repulsion component containing ρ_a, for the nearest neighbors.

The experimental lattice constant for the NaCl-type lattice has been estimated now at 3.454, while 3.430 was given in the previous paper. This new value appears to be equally justified by the necessary extrapolation and agrees somewhat better with the calculated results.

The question naturally arises as to whether the determinations made for CsCl can be applied to the other alkali halides. A verification of this was attempted by assuming that ρ_a, ρ_b, b_2/b_1 and b_{ab} remain the same throughout the group. The two remaining constants, c and b_1, were then obtained from the lattice constant and com-

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[10] K. F. Herzfeld, *Handbuch der Physik*, Vol. 24/2 (Berlin 1933), p. 102.

TABLE VII. *Constants for various alkali halides.*

CONSTANTS		NaI	Kbr	KI	RbCl	RbI	CsCl	CsBr	CsI
c		0.33	2.28	2.94	2.19	2.82	2.60	2.30	3.78
$b_1\times10^{12}$ ergs per molecule		1110	1980	3800	2000	6800	3580	4800	9780
lattice energy kcal. per mole	(meas.)	166.4[11]		153.8[12]					141.5[12]
	(calc.)	118.2	140.0	159.0	140.5		162.5		184.0
interionic distances $\times10^8$ cm	(meas.)[9]	2.90	2.94	3.23	2.89	3.26	3.06	3.14	3.41
	(calc.)	2.83	2.96	3.13	2.95	3.36	3.07	3.18	3.43
forces between ions dynes per cm	(spect.)[10]	9.0	12.4	10.8	10.2	9.6		11.0	7.6
	(calc.)	20.1	12.4	7.3	13.1	4.8	9.0	6.6	4.8
heat of dissociation $MX_{gas}\rightarrow M^+_{gas}+X^-_{gas}$ kcal. per mole	(calc.)	83.8	92.3	97.0	92.9	96.4	98.9	99.0	100.0
heat of sublimation kcal. per mole	(meas.)	49.1[13]	53.3[14]	47.8[13]	51.3[14]				
	(calc.)	34.4	47.7	62.0	47.6		63.6		84.0

pressibility data of the various salts as given by Huggins.[6] The values of these constants found for some of the alkali halides are listed in Table VII, together with the corresponding lattice energies, heats of dissociation from molecules to ions, equilibrium interionic distances and the interionic forces.

The computed interionic distances check with the measured values to within 1.3 percent for the salts which crystallize in the CsCl type, and within about 3 percent for those of the NaCl type, given in the table. For very small values of r_0, the method fails to give reasonable results, for example, for NaCl the van der Waals factor c is found to be -4. On the whole, the agreement is good for the values of r_g listed. With few exceptions the computed values are too high.

The calculated interionic forces do not check well with those measured, varying from one-half to double these. In general the values found are too low for those cases where the interionic distance is greater than for CsCl, and too high where the distance is less. The large error in a few cases may be due, at least partially, to insufficient accuracy in the experimental compressibility data.

The heats of sublimation have been computed by subtracting the calculated heats of dissociation of molecules into ions, from the lattice energy. The agreement of calculated with measured values of the lattice energies and heats of sublimation is quite poor.

In conclusion the author wishes to express his appreciation to Professor K. F. Herzfeld for helpful discussions during the progress of this work.

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[11] A. N. Tandon, Nat. Acad. Sci., India, Proc. **7**, 102 (1937).

[12] J. E. Mayer, Zeits. f. Physik **61**, 798 (1930).

[13] Landolt-Börnstein, *Physikalisch-Chemische Tabellen* (Berlin 1936) Eg IIIc, p. 2709.

[14] J. E. Mayer and I. H. Wintner, J. Chem. Phys. **6**, 301 (1938).