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Joseph E. Mayer

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The Lattice Energies of the Silver and Thallium Halides*

JOSEPH E. MAYER, *Chemical Laboratory, Johns Hopkins University*

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The lattice energies and lattice constants of the silver and thallium halides are calculated assuming ionic crystals with a van der Waals potential. The latter term, which is large, accounts for the low solubilities (high lattice energies) of the salts. The calculations appear to be quantitatively satisfactory for the thallium halides, TlCl, TlBr and TlI, and for the three silver halides AgF, AgCl and AgBr. Definite evidence is found for assuming the existence of a homopolar potential in AgI of about 10 percent of the total

lattice energy. One reason for believing this, is the stability of the zincblend instead of the rocksalt lattice, which latter should be stable were the compound purely ionic. There is presumably some homopolar binding in AgBr but it cannot be large. The thallium salts probably are entirely ionic. The theoretically calculated and experimental (chemical) lattice energies are, respectively, in K cal., AgF, 219, 217.7; AgCl, 203, 205.7; AgBr, 197, 201.8; AgI, 190, 199.2; TlCl, 167, 170.1; TlBr, 164, 165.6; TlI, 159, 160.8.

INTRODUCTION

THE lattice energy of a uni-univalent ionic crystalline salt, namely the energy change at 0°K of the reaction $MX_{cryst.} \rightarrow M_{gas}^{+} + X_{gas}^{-}$, can be calculated as the sum of the heats of a number of reactions. A series of reactions which may be used is shown in Table II. The energy so obtained might be termed the experimental lattice energy. If, for the silver and thallium halides, these experimental lattice energies are compared with the electrostatic energies, it is found that the former are almost as large as, or even larger than the latter. The electrostatic potential is purely attractive, and in addition to it there must exist in a crystal another potential whose first and second derivatives with respect to the lattice constant r (for a uniform increase in all crystal dimensions) at the experimental equilibrium value of $r=r_0$ may be obtained from the value of r_0 and the compressibility respectively.

If this potential of known first and second derivatives is assumed to be purely repulsive and simple in form (that is the potential $V(r) \geq 0$ and $\partial V/\partial r \leq 0$ for all values of r , and $\partial V/\partial r$ and $\partial^2 V/\partial r^2$ both vary fairly slowly with r), it is impossible to account for the experimental lattice energy to within 15 or 20°K cal. for these salts. This means that the remaining non-electrostatic

potential is partially attractive, it takes negative values at some r . It is frequently assumed that this behavior is to be accounted for by the existence of homopolar forces in these crystals.

There is an additional calculable attractive potential besides the electrostatic, the van der Waals potential. Its magnitude can be computed from equations developed by London¹ and by Margenau.² The calculation used here will follow closely a discussion by the author for the alkali halides.³ If the van der Waals potential is included with the electrostatic, the remaining potential may be assumed to be purely repulsive and the calculated lattice energies agree well for all but AgI with the experimental values. The method of calculation of the lattice energy follows closely the method of Born and Mayer,⁴ whose paper shall be referred to in the succeeding paragraphs as B.M. The results of this paper, then, show that the homopolar contribution to the lattice energies of AgF, AgCl, AgBr, TlCl, TlBr and TlI is practically insignificant, and that in AgI is small and can be estimated.

CALCULATION OF THE VAN DER WAALS POTENTIAL

The equations used in calculating the potential are the following:

¹ F. London, *Zeits. f. physik. Chemie* **B11**, 222 (1930).

² H. Margenau, *Phys. Rev.* **38**, 747 (1931).

³ J. E. Mayer, *J. Chem. Phys.* **1**, 270 (1933). See April number.

⁴ M. Born and J. E. Mayer, *Zeits. f. Physik* **75**, 1 (1932).

* A preliminary report was presented at the *Congress on The Solid State at Leningrad*, September, 1932.

$$U_v = U_{dd} + U_{qd} = -C/r^6 - D/r^8, \quad (1)$$

$$C = S_6' c_{+-} + S_6'' (c_{++} + c_{--})/2, \quad (2)$$

$$D = S_8' d_{+-} + S_8'' (d_{++} + d_{--})/2,$$

$$c_{ij} = -\frac{2}{3} e^4 \frac{Q_{i00}^2 Q_{j00}^2}{\epsilon_i + \epsilon_j}, \quad d_{ij} = -\frac{3}{2} c_{ij} \left(\frac{Q_{i00}^2}{p_i} + \frac{Q_{j00}^2}{p_j} \right), \quad (3)$$

$$Q_{i00}^2 = -\frac{3}{2} \frac{\alpha_i \epsilon_i}{e^2}. \quad (4)$$

The complete van der Waals potential in the crystal U_v , is additively composed of a dipole-dipole term U_{dd} varying as r^{-6} and a quadrupole-dipole term U_{qd} varying as r^{-8} , with constants respectively C and D . C and D can be calculated from the corresponding c_{ij} 's and d_{ij} 's, the constants for two ions i and j . In order to make the calculations the sums S_6' , S_6'' , S_8' , S_8'' must be known, which are the sums of l^{-6} and l^{-8} over the odd (unlike) and even (like) points of the lattice, respectively, if l is the distance between the lattice points. The sums depend on the lattice type and on the arbitrary choice of r , which here and in the following, is understood to be the shortest geometrical constant of the lattice, the distance between unlike neighboring ions. The sums can be easily computed from a table of similar sums given by Lennard-Jones and Ingham.⁵ The constants c_{ij} and d_{ij} for the potential between two ions i and j can be calculated from the polarizabilities α and the energies ϵ of the ions in the crystal in question. ϵ is an energy corresponding to a weighted average frequency of the absorption of the ion in the crystal.⁸ For the positive ions the polarizability α and the energy ϵ are presumed to be practically constants of the ions independent of the crystal. ϵ is given the value 90 percent of the ionization potential of the gaseous ion (the second ionization potential of the element). For the negative ions α is supposed to be inversely proportional to ϵ , and ϵ is to be obtained from the experimental ultraviolet absorption of the crystal. This assumption sets Q_{00}^2 , the 00 matrix element of the sum of the q^2 for all electrons, a sort of area of the ion, as being independent of the crystal. The

value of Q_{00}^2 for the halide ions has been calculated from the alkali halides.⁸ p , the number of outer electrons, is taken as the geometric mean of the theoretical (Periodic Table) value, and one calculated from the polarizability and frequency.

For the silver halides the values of ϵ for the negative ions have been chosen after an examination of the absorption curves for the chloride, bromide, and iodide. The value of the polarizability α in the crystal has been calculated by the use of Q_{00}^2 and ϵ with Eq. (4). Pauling's⁶ value $\alpha = 1.72 \times 10^{-24}$ cm³ has been used for Ag⁺ and the sums of the negative and positive polarizabilities, row 7, Table I, has been compared with the experimental value, row 8, calculated from the index of refraction n for yellow light. These experimental values of $\sum \alpha$ (yellow) may be expected to be some 5 percent or more higher than those which would be calculated were the index of refraction extrapolated to $\lambda = \infty$. An estimated value of $\sum \alpha(\lambda = \infty)$ is given in row 9. The agreement indicates only that no great error has been made in the choice of constants.

For the thallium halides the value $\alpha = 3.50 \times 10^{-24}$ cm³ for Tl⁺ ion is chosen from an examination of the index of refraction of some complex thallium salts and the corresponding alkali salts. The values of ϵ for the negative ions are chosen to be in agreement with those of the silver salts.

The choice of values for all these constants is subject to considerable uncertainty. For the silver salts the van der Waals potential may be in error by as much as 30 percent of its value. For the thallium salts the error may be even larger. The author has attempted not to err in such a way as to make the potential too large. It is felt that the actual potential is more likely to be greater than to be smaller than the values calculated here. Owing to the use of an empirical repulsive potential, determined from the attractive potential and the constants of the crystal, the magnitude of the error introduced into the computation of the lattice energy by an error in the assumed values of C , and especially of D , is less than that introduced into the van der Waals potential. That is, if the value of $U_{dd} = -C/r^6$ were assumed to be 3 k cal. greater than the values here given, say for AgF, the total

⁵ J. E. Jones and A. E. Ingham, Proc. Roy. Soc. (London) A107, 636 (1925).

⁶ L. Pauling, Proc. Roy. Soc. (London) A114, 181 (1927).

calculated lattice energy would be only 1.5 kcal greater.

THE REPULSIVE POTENTIAL AND THE LATTICE ENERGY

The compressibilities, β , of AgCl, AgBr, AgI, TlCl and TlBr are given in *International Critical Tables*. The thermal expansion for AgCl and AgBr is also given there. The term $(3T/N\beta)(\partial\nu/T)$, in which the thermal expansion is needed, is small, and its value can be estimated for the other salts without introducing any appreciable error. From these data and the lattice constant, r_0 , which is taken from the *Strukturbericht*⁷ the repulsive potential is computed. The method deviates from that of B.M. only in so far that for the silver salts it is not assumed that the exponents for the repulsive potential between two Ag⁺ ions and two halide ions, or an Ag⁺ ion and a halide ion, are the same.

If the repulsive potential energy of the crystal as a function of r is written $B(r)$ it has been shown that, at $r=r_0$, the lattice constant at temperature T , and $P=0$,

$$-r_0 \frac{dB(r_0)}{dr} = \frac{\alpha e^2}{r_0} + \frac{6C}{r_0^6} + \frac{8D}{r_0^8} - \frac{3T}{N\beta} \left(\frac{\partial V}{\partial T} \right) = \tau, \quad (5)$$

$$r_0^2 \frac{dB(r_0)}{dr^2} = \frac{2\alpha e^2}{r_0} + \frac{42C}{r_0^6} + \frac{72D}{r_0^8} + \frac{9V}{N\beta} = \sigma. \quad (6)$$

These equations differ from those in B.M. only in the inclusion of the D -term and the omission of a factor multiplying $9V/N\beta$ in Eq. (6). This factor always has a value very close to 1.

It is now assumed that the repulsive potential between two ions i and j , $b_{ij}(r_{ij})$ is given by the equation,

$$b_{ij} = c_{ij} b_i b_j e^{-r_{ij}/\rho_{ij}}, \quad (7)$$

with

$$\rho_{ij} = \rho_i + \rho_j,$$

$$2\rho_{H^-} = \rho_- = 0.345 \times 10^{-8} \text{ cm}, \quad (8)$$

$$2\rho_{Ag^+} = \rho_+,$$

$$\rho_{H^-} + \rho_{Ag^+} = \rho.$$

Eq. (7) is that used in B.M. and Eq. (8) is introduced to allow for the fact that not all ion pairs show the same value ρ_{ij} , which, however, was the case for the alkali halides. There is some reason to believe that Eq. (8) is justified. It is sufficient here to point out that the same repulsion is assumed between two negative ions that was found in the alkali halides. The repulsion between the positive ion pairs is negligible for all silver salts on this, or any other reasonable assumption, and the value of ρ_+ is in reality never used. The value of ρ , the repulsive exponent between an Ag⁺ and a halide ion, is calculated from the compressibility, and the assumptions used are relatively unimportant in influencing the value obtained. That is, actually Eq. (8) is entirely unimportant, the repulsion between Ag⁺ pairs is probably negligible and is neglected, that between halide pairs is assumed to be the same function of r as in the alkali halides, and that between Ag⁺ and halide ions is calculated from the constants of the crystal.

Defining as M the number of unlike neighbors of any lattice point, as M' the number of like "next-to-neighbors," as a the ratio of the distance between next-to-neighbors to that between neighbors, and with $c_1 = c_{++}/c_{+-}$, $c_2 = c_{--}/c_{+-}$, the relative effect of the charge on the repulsion, so that $c_1 = 1.20$ and $c_2 = 0.81$ and $c_{+-} = 0.929$ is written c_0 , one obtains for the total repulsive potential in the crystal,

$$B(r) = bc_0 [Mb_+b_-e^{-r/\rho} + \frac{1}{2}M'b_+^2c_1e^{-ar/\rho_+} + \frac{1}{2}M'b_-^2c_2e^{-ar/\rho_-}] \quad (9)$$

$$= M_1(1 + M_2^+ + M_2^-),$$

$$M_1 = Mb_+b_-e^{-r/\rho},$$

$$M_2^+ = \frac{M'c_1b_+}{2Mb_-} e^{-(a/\rho_+-1/\rho)r},$$

$$M_2^- = \frac{M'c_2b_-}{2Mb_+} e^{-(a/\rho_-1/\rho)r}.$$

The constant a has the value 1.155, 1.414 and 1.633 for the CsCl, NaCl and Zincblend lattice, respectively. c_0 , c_1 and c_2 , the dependence of the repulsion on the charge are computed from a theoretical equation of Pauling's⁸ assuming 18

⁷ P. P. Ewald and C. Hermann, *Strukturbericht*, 1913-1928.

⁸ L. Pauling, *Zeits. f. Krist.* **67**, 377 (1928).

electron shell positive ions and 8 electron shell negative ions. The values of the b_- 's are calculated from the alkali halides, and those of the b_+ 's are later calculated in this paper. The constant b is arbitrarily chosen to be 10^{-12} erg.

M_2^+ represents the total repulsion due to pairs of Ag^+ ions divided by that due to Ag^+ halide pairs, and M_2^- the total repulsion of halide pairs divided by that of the Ag^+ halide pairs. M_2^+ at $r \geq r_0$ is entirely negligible for all silver salts and will be omitted from the further calculation.

For the thallium salts ρ is found to have very nearly the same value as in the alkali halides and the somewhat simpler equations of B.M. have been used throughout. The equations are equivalent to Eq. (9) setting $\rho = \rho_- = \rho_+$ and adding $M_2^+ + M_2^- = M_2$.

Using Eq. (9) one obtains for the derivatives,

$$\tau = -r_0 \frac{\partial B(r_0)}{\partial r} = \frac{r_0}{\rho} M_1[1 + yM_2^-], \quad (10)$$

$$\sigma = r_0^2 \frac{\partial^2 B(r)}{\partial r^2} = \left(\frac{r_0}{\rho}\right)^2 M_1[1 + y^2 M_2^-], \quad (11)$$

with

$$y = a\rho/\rho_-,$$

when M_1 and M_2^- are understood to be the values of these functions at $r = r_0$. This leads to the equation for r_0/ρ

$$r_0/\rho = (\sigma/\tau)[1 + (y - y^2)M_2^-/(1 + y^2 M_2^-)]. \quad (13)$$

Table I includes many of the numerical steps of the calculations and the value of ρ , row 33. An average value, $\rho = 0.260 \times 10^{-8}$ cm and 0.361×10^{-8} cm for the silver and thallium salts, respectively, is obtained. The further calculations are made with these average values.

$B(r_0)$ the repulsive potential at $r = r_0$ may now be calculated from Eqs. (9) and (10),

$$B(r_0) = (1 - k)\tau(\rho/r_0), \quad (14)$$

$$k = (y - 1)M_2^-/(1 + yM_2^-).$$

TABLE I. Calculation of the theoretical lattice energies.

1 Salt	AgF	AgCl	AgBr	AgI	TlCl	TlBr	TlI
2 Crystal type	NaCl	NaCl	NaCl	Zincblend	CsCl	CsCl	CsCl
3 Q_{00}^2 (neg. ion) $\times 10^{16}$ cm ²	1.44	3.40	4.08	5.27	3.40	4.08	5.27
4 ϵ (neg. ion) $\times 10^{12}$ ergs/molecule	19.0	15.6	13.9	11.0	15.6	13.9	11.0
5 α (neg. ion) $\times 10^{24}$ cm ³	1.15	3.45	4.47	7.29	3.45	4.47	7.29
6 α (pos. ion) $\times 10^{24}$ cm ³	1.72	1.72	1.72	1.72	3.50	3.50	3.50
7 $\Sigma\alpha \times 10^{24}$ (calc.) cm ³	2.87	5.17	6.19	9.01	6.95	7.97	10.79
8 $\Sigma\alpha$ (yellow) $\times 10^{24}$ (exp.) cm ³	—	5.41	6.58	9.54	—	—	—
9 $\Sigma\alpha$ ($\lambda = \infty$) $\times 10^{24}$ (exp.) cm ³	—	5.14	6.20	9.00	—	—	—
10 ϵ (pos. ion) $\times 10^{12}$ ergs/molecule	30.0	—	—	—	30.0	—	—
11 $c_{++} \times 10^{60}$ ergs \times cm ⁶	67	—	—	—	268	—	—
12 $c_{--} \times 10^{60}$ " "	19	133	208	437	133	208	437
13 $c_{+-} \times 10^{60}$ " "	34.5	89	109	151	179	222	307
14 $d_{++} \times 10^{76}$ ergs cm ⁸	91	—	—	—	500	—	—
15 $d_{--} \times 10^{76}$ " "	23	268	475	1228	268	475	1228
16 $d_{+-} \times 10^{76}$ " "	44	150	199	315	346	460	720
17 S_6'	6.595	—	—	4.354	8.709	—	—
18 S_6''	1.807	—	—	0.762	3.545	—	—
19 S_8'	6.146	—	—	4.104	8.208	—	—
20 S_8''	0.800	—	—	0.253	2.147	—	—
21 $C \times 10^{60}$ ergs \times cm ⁶	305	767	967	850	2270	2785	3930
22 $D \times 10^{76}$ ergs \times cm ⁸	316	1065	1410	1467	3665	4820	7760
23 $r_0 \times 10^8$ cm	2.46	2.772	2.884	2.812	3.33	3.44	3.62
24 $\beta \times 10^6$ (compressibility) bars ⁻¹	—	2.40	2.75	4.11	4.9	5.3	—
25 $V^{-1}(\partial V/\partial T)_p \times 10^6$	—	98.9	104	—	—	—	—
26 $9V/N\beta \times 10^{12}$ ergs/molecule	—	159	156	150	104	106	—
27 $(3T/N\beta)(\partial V/\partial T) \times 10^{12}$ ergs/molecule (1.50)	—	1.57	1.63	(1.70)	(1.60)	(1.70)	(1.80)
28 $\alpha\epsilon^2/r_0 \times 10^{12}$ ergs/molecule	16.20	14.39	13.82	13.29	12.04	11.66	11.09
29 $C/r_0^6 \times 10^{12}$ " / "	1.39	1.70	1.60	1.74	1.66	1.67	1.75
30 $D/r_0^8 \times 10^{12}$ " / "	0.24	0.32	0.29	0.38	0.24	0.25	0.34
31 $\tau \times 10^{12}$ " / "	24.9	25.6	24.6	25.1	22.3	22.0	22.5
32 $\sigma \times 10^{12}$ " / "	—	283.	276.	277.	215.	217.	—
33 σ/τ	—	11.3	10.8	11.0	9.64	9.90	—
34 $\rho \times 10^8$ cm	—	0.247	0.271	0.260	0.356	0.366	—
35 r_0/ρ calculated	9.45	10.65	11.09	10.78	9.21	9.51	10.03
36 $B(r) \times 10^{12}$ ergs/molecule	2.63	2.38	2.20	2.28	2.36	2.23	2.14
37 $\frac{1}{2}h\nu$ " / "	0.10	0.08	0.06	0.05	0.06	0.05	0.04
38 $U \times 10^{12}$ ergs/molecule	15.10	13.95	13.53	13.08	11.52	11.30	11.00
39 U k cal.	219	203	197	190	167	164	159

TABLE II. Calculation of the experimental lattice energies. ΔH in kilocalories of the reactions.*

Reaction		AgF	AgCl	AgBr	AgI	TlCl	TlBr	TlI
$\text{MX}_{\text{cr.}} 0^\circ\text{K} \rightarrow \text{MX}_{\text{cr.}} 291^\circ\text{K}$	291°K	2.5	2.8	2.9	3.0	2.9	3.1	3.2
$\text{MX}_{\text{cr.}} \rightarrow \text{M}_{\text{s.s.}} + \frac{1}{2}\text{X}_{2 \text{ s.s.}}$	291°K	48.7	30.6	23.7	14.9	48.7	41.1	30.1
$\frac{1}{2}\text{X}_{2 \text{ s.s.}} \rightarrow \text{X}_{\text{g.}}$	291°K	31.8	28.8	26.7	25.5	28.8	26.7	25.5
$\text{X}_{\text{g.}} 291^\circ\text{K} \rightarrow \text{X}_{\text{g.}} 0^\circ\text{K}$		-1.1	-1.1	-1.1	-1.1	-1.1	-1.1	-1.1
$\text{X}_{\text{g.}} + e^- \rightarrow \text{X}_{\text{g.}}^- 0^\circ\text{K}$		-95.3	-86.5	-81.5	-74.2	-86.5	-81.5	-74.2
$\text{M}_{\text{cr.}} 291^\circ\text{K} \rightarrow \text{M}_{\text{cr.}} 0^\circ\text{K}$		-1.7	-1.7	-1.7	-1.7	-1.7	-1.7	-1.7
$\text{M}_{\text{cr.}} \rightarrow \text{M}_{\text{g.}} 0^\circ\text{K}$		59.0	59.0	59.0	59.0	59.0	59.0	59.0
$\text{M}_{\text{g.}} \rightarrow \text{M}_{\text{g.}}^+ + e^- 0^\circ\text{K}$		173.8	173.8	173.8	173.8	140.0	140.0	140.0
$\text{Sum} = \text{MX}_{\text{cr.}} \rightarrow \text{M}_{\text{g.}}^+ + \text{X}_{\text{g.}}^- 0^\circ\text{K}$		217.7	205.7	201.8	199.2	170.1	165.6	160.8
Theoretical lattice energy		219	203	197	190	167.	164.	159.
Difference		-1.3	2.7	4.8	9.2	2.9	1.6	1.3

* Subscripts, cr. indicate crystal; s.s., standard state; and g, gas.

The complete lattice energy U is given by

$$-U = \Phi_0 = -\frac{\alpha e^2}{r_0} - \frac{C}{r_0^6} - \frac{D}{r_0^8} + B(r_0) + \frac{1}{2}h\nu_0, \quad (15)$$

the small value of $h\nu_0/2$ can be easily estimated. The values of the lattice energy in ergs per molecule and in k cal. are tabulated in the last two rows of Table I.

In Table II are given the energies of the reactions used to calculate what is called the experimental lattice energies. The heats of formation of the crystals are taken from *International Critical Tables*, as are also the heats of formation of the halogen gaseous atoms. The small energy changes between 291°K and 0°K are all estimated. The electron affinity of the halogen atoms is taken from a paper by Mayer and Helmholtz⁹ where they were calculated from the lattice energies of the alkali halides. The heat of sublimation of the metals has been estimated by the use of the Hildebrand¹⁰ modification of Trouton's rule. The sum of the ΔH 's of all of the first eight reactions give the ΔH , which at 0°K is the ΔE , of the dissociation of the crystal into gaseous ions, the lattice energy. The theoretical lattice energy and the difference between the two values is also tabulated.

The uncertainties in the lattice constants and in the compressibilities may account for 1 k cal. uncertainty in the theoretical lattice energies. The van der Waals potentials of about 20 k cal. may be in error by as much as 6 k cal., which would contribute about 3 k cal. error to the lattice energy calculations. In all the values of the

theoretical lattice energy may be in error by about 4 k cal. as an upper limit, even if the assumptions under which they are calculated hold exactly. The experimental lattice energies may also be in error by as much as 3 or 4 k cal., but the difference between the values for different halides of the same positive ion are not likely to be in error by more than 2 k cal. The trend of 6 k cal. in the difference between the theoretical and experimental energies from fluoride to bromide of the silver salts is probably real, and represents a deviation from a purely ionic character. The trend could be diminished by assuming a greater polarizability for the Ag^+ ion, or in general by changes in the assumptions tending to increase the van der Waals potential; but it seems probable that this trend shows an increasing homopolar contribution to the lattice energy which is zero for the fluoride and about 2 or 3 percent of the total energy in the bromide.

This view is strengthened by the marked difference between the theoretical and experimental energies in the silver iodide. It seems that there is no doubt that this difference cannot be explained by errors in the choice of the van der Waals potential. Further evidence will be deduced later in this paper to show that the homopolar bond contributes approximately 10 percent of the total experimental lattice energy.

The thallium halides on the other hand, are seen to be all, within the accuracy of these calculations, purely ionic.

THE LATTICE CONSTANT

The Eqs. (7) and (8) assume that the repulsive potential between any two ions i, j , can be calculated from constants of the ions, $b_i, b_j, \rho_i,$

⁹ J. E. Mayer and L. Helmholtz, *Zeits. f. Physik* **75**, 16 (1932).

¹⁰ J. H. Hildebrand, *J. Am. Chem. Soc.* **37**, 970 (1915).

TABLE III. *Values of theoretical lattice constants.*

	AgF	AgCl	AgBr	AgI	TlCl	TlBr	TlI
Value of b_-	26.80	77.4	105.3	189.5	77.4	105.3	189.5
Value of b_+	187.8	187.8	187.8	187.8	33.78	33.78	33.78
Calculated $r_0 \times 10^8$ cm	2.45	2.78	2.89	2.952	3.30	3.42	3.69
Experimental $r_0 \times 10^8$ cm	2.46	2.772	2.884	2.812	3.33	3.44	3.62
Difference, $\delta r \times 10^8$ cm	-0.01	0.01	0.01	0.14	-0.03	-0.02	+0.07

ρ_j , and c_{ij} the dependence on charge and outer electron configuration. Actually the method used here and in B.M. does not do this. The constant ρ is indeed calculated from several crystals and an average value chosen for the repulsive potential, but the product $b_i b_j$ is implicitly determined for each crystal by the use of the lattice constant. The ratio b_i/b_j does enter the equations used, but in such an unimportant way (in the computation of the small M_2^+ and M_2^-) that in the calculation of the lattice energies of the alkali halides the Goldschmidt radii were used to estimate the ratio, and no attempt was made, or needed, to justify this, except in a most qualitative way.

Huggins and Mayer¹¹ have shown that 9 values of b for the 9 ions of the alkalis and halides can be so chosen that one can calculate the 20 lattice constants of the 20 alkali halides to within about 0.01A, probably within the experimental error of their determination.

That is, Eq. (7) is justified experimentally for the purely ionic alkali halides. With the values of b_- for the halides found from the alkali halides, the values of b_+ for Ag^+ and Tl^+ may be calculated. One will obtain 4 values from the 4 halides for Ag^+ , and 3 values from the 3 halides for Tl^+ . The values of b for Tl^+ are found to have a slight trend, which is probably of significance but will be ignored, and the average of all used to obtain b for Tl^+ . The values of the b for Ag^+ decrease noticeably with increasing atomic number of the negative ion. Assuming that the salts AgF and AgCl are essentially ionic, the true b_+ for Ag^+ may be taken as an average of that determined from these two salts. (The lattice constant of AgF is sufficiently uncertain to warrant the use of AgCl although it may be somewhat homopolar.)

With these average values of b for Ag^+ and Tl^+ the lattice constants of the salts may be calcu-

lated. The results are tabulated in Table III. For the thallium salts although the calculated lattice constants do not agree well with the experimental values, the differences are probably not much greater than the experimental uncertainty in the lattice constants, which are not well known. A trend is apparent in the differences. For the silver salts the trend is decided and large. The calculated theoretical lattice constant for AgI is considerably higher than the experimental.

This small experimental lattice constant is in good agreement with the observations on the lattice energy for AgI . A homopolar bonding potential is probably pulling the ions closer together and simultaneously lowering the energy. We may regard the calculated lattice constant as the lattice constant of a purely ionic crystal. The lower experimental lattice constant is due to an actual existent homopolar binding in addition to the ionic.

One may now compute more exactly the homopolar part of the potential in AgI . The repulsive potential in Table I has been calculated from the empirical lattice constant of the crystal. Using instead the value of b for Ag^+ found from the fluoride and chloride one may calculate the repulsion in a truly ionic crystal. This truly ionic crystal would have the lattice energy 184 k cal. at its equilibrium lattice constant 2.95A, and 178 k cal. at the experimental lattice constant 2.81A, corresponding to the highly compressed crystal. Subtracting this from the experimental lattice energy one arrives at a value 21 k cal., or 10 percent, which is due to the existence of a homopolar potential.

The actual calculations of the b_+ 's and the lattice constants are not reproduced here in detail. By using Eq. (9) and the value of $B(r)$ at $r=r_0$ given in Table I, b_+ can be calculated if b_- is known. Having an average value of b_+ the value of $B(r)$ at $r=r_0$ can be recalculated. In order to calculate the theoretical lattice constant with the

¹¹ M. L. Huggins and J. E. Mayer, Phys. Rev. **43**, 373A (1933). Abstract of Report at Atlantic City Meeting, December, 1932.

new theoretical value of the repulsion $B(r)$ one seeks a value of r that will satisfy Eq. (5). By using a method of variations the following approximation is obtained. If b_0 is the average b which we have chosen as the correct b of the positive ion, and b_e the experimental value previously determined from the lattice constant of the crystal, one finds for δr , the difference between the theoretical lattice constant and the experimental:

$$\delta r = \rho(\omega - 1)/(9V/N\beta\sigma) \quad (16)$$

with

$$\omega = b_0/b_e.$$

THE STABILITY OF DIFFERENT LATTICE TYPES

In the previous discussion it has been assumed that insofar as the compounds studied are purely ionic and not in such a crystal that the ions are not deformed (which means that one is restricted to regular crystals), the complete potential between any two ions is known as a function of the distance between them. In principle one can then calculate the lattice energy of any regular crystal lattice for these compounds. The actual work of solving for the equilibrium lattice constant r_0 out of Eq. (5) would be somewhat tedious.

It is, however, comparatively simple to obtain the change of energy with change of lattice type at constant r_0 , and the change of energy with r of the new hypothetical lattice, as it adiabatically expands or contracts to its equilibrium r_0 can be easily estimated. The method is that used on the alkali halides in the paper B.M. For each term, except the $h\nu_0/2$, of the expression for the lattice

energy, Eq. (15), one may calculate the change in the value of that term due only to a change in the lattice type, but with r_0 held constant. The sum of these changes will give the complete variation $(\delta\Phi)_{r=r_0}$ in the lattice potential with change of crystal type at constant r_0 . The small term, invariable negative, corresponding to the decrease in lattice potential, $\frac{1}{2}(\partial^2\Phi/\partial r^2)(\delta r)^2$, as the new lattice type changes to its equilibrium density, is then added. Starting always from the experimental type a net positive value for the total $\delta\Phi$ indicates that the calculation shows the hypothetical lattice type to be unstable. A net negative $\delta\Phi$ indicates an error of some sort in the calculation, provided the hypothetical lattice type is not actually experimentally obtained. In Table IV the results of such a calculation are shown.

It is to be seen that AgF, AgCl and AgBr are calculated to be unstable as Zincblend or CsCl lattices, and should, as they do, crystallize in rocksalt lattices. AgI, on the other hand is calculated to be stable in the rocksalt lattice, which is in contradiction to the experimental evidence. The discrepancy of 0.43×10^{-12} erg or 6 k cal. is far too large to be accounted for by anything but a failure of the fundamental assumption that it is ionic. The salts TlCl and TlBr are found to be stable as rocksalt lattices, although they actually crystallize in the CsCl lattice. Here, however, the discrepancy of 0.02 and 0.01×10^{-12} erg is so small that it is easily accounted for by a relatively small error in the van der Waals potential. TlI is found to be stable in the CsCl type lattice.

TABLE IV. *Calculation of potential energy change with change of lattice type.*
Energies in 10^{-12} erg/molecule.

Salt	Experimentally stable lattice	Hypothetical lattice	Change at constant r_0 of				$\frac{\partial^2\Phi}{\partial r^2} \frac{(\delta r)^2}{2}$	$\delta\Phi$
			$-\alpha e^2/r_0$	$-C/r_0^6$	$-D/r_0^8$	$B(r_0)$		
AgF	Rocksalt	Zincblend	+1.02	+0.55	+0.09	-0.95	-0.13	+0.58
AgCl	"	"	+0.90	+0.67	+0.13	-0.96	-0.13	+0.61
AgBr	"	"	+0.87	+0.67	+0.11	-0.93	-0.13	+0.49
AgI	Zincblend	Rocksalt	-0.89	-1.23	-0.26	+2.08	-0.13	-0.43
AgF	Rocksalt	CsCl	-0.14	-0.67	-0.12	+1.16	-0.06	+0.17
AgCl	"	"	-0.12	-0.82	-0.16	+1.72	-0.06	+0.56
AgBr	"	"	-0.12	-0.81	-0.15	+1.99	-0.06	+0.85
TlCl	CsCl	Rocksalt	+0.10	+0.56	+0.09	-0.73	-0.04	-0.02
TlBr	"	"	+0.10	+0.55	+0.08	-0.70	-0.04	-0.01
TlI	"	"	+0.09	+0.57	+0.11	-0.70	-0.04	+0.03

DISCUSSION OF THE RESULTS

The salts here considered all show two distinct variations from the characteristics of the definitely ionic alkali halides. Their lattice energies are markedly high, which is qualitatively evidenced by their low solubilities, and their lattice constants do not increase as rapidly with increasing halide atomic number as do the alkalis. The difference in lattice constant of AgF and AgBr is 0.42A as compared with 0.67A for the difference between NaF and NaBr. The difference $r_0(\text{TlCl}) - r_0(\text{TlI})$ is 0.29A. Compared with 0.39A for CsCl and CsI.

A high attractive van der Waals potential, increasing with the size of the negative ion, and in the case of the silver salts a low repulsive exponent ρ deducible from their low compressibilities, qualitatively explain both of these anomalous characteristics. In the case of the three salts AgF, AgCl and AgBr the explanation is satisfactory quantitatively. There is some evidence that AgBr is not entirely ionic, as one would expect if AgI is supposed to have an appreciable homopolar potential, but it would be possible to account for the deviations from the calculations by assuming a somewhat greater van der Waals potential. AgI, however, cannot be accounted for quantitatively as ionic. Not only are the deviations from the lattice energy and

constant too great to be patched by a small alteration of the assumed polarizabilities and frequencies, but more important, it crystallizes in the wrong type lattice. Were it ionic, and especially if the van der Waals potential were larger, it would be unstable in the zincblend lattice, (and also in the similar Wurtzite lattice). The homopolar potential apparently favors markedly the low coordination number type of lattice, which is probably to be expected.

The quantitative calculation of the TlCl, TlBr and TlI lattice energies is satisfactory. The anomalous lattice constants are not accounted for successfully, although the experimental values are sufficiently uncertain to allow some latitude. The calculated lattice constants would agree better with the experimental, as would also the lattice energies, were the van der Waals potential assumed to be greater, particularly for the iodide. Here the study of the stability of different types corroborates the idea that the van der Waals potential is higher than that used. A higher van der Waals potential is needed to account for the experimental stability of the CsCl type lattice, whereas an existent homopolar potential would be expected to favor the lower coordination number of the rocksalt lattice. The author considers this a strong reason for believing that practically no homopolar binding is present in these salts.