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# *Letters to the Editor*

## Lattice energies and thermal expansions of some heavier halides.

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In the classical theory of ionic crystals (Born 1927, Born & Mayer 1932) it is assumed that the ions of an ionic crystal are spherically symmetrical and their interaction with each other consists of (1) an electrostatic term, (2) a repulsive interaction term, (3) multipole interactions i. e. (a) dipole-dipole interaction and (b) dipole-quadrupole interaction and (4) the zero point energy.

Taking into account all the above interactions, the energy of the the crystal per unit cell may be expressed as

$$\phi(r) = -\frac{\alpha e^2}{r} + \frac{\lambda}{r^n} - \frac{C}{r^6} - \frac{D}{r^8} + \epsilon_0 \quad . \qquad (1)$$

where $\alpha$ is the Madelung's constant, $\lambda$ is the repulsive parameter, $C$ is the dipole-dipole interaction parameter, $D$ is the dipole-quadrupole interaction parameter, $\epsilon_0$ is the zero point energy, $e$ is the electronic charge and $r$ is the interionic distance.

We have taken the inverse power form of repulsive term because of its simplicity and also because it is justified by the fact that interionic distance between two ions remains nearly constant being near the value at the potential minimum.

The potential parameters $\lambda$ and $n$ and thence the lattice energies for some heavier halides have been calculated (table 1) using the well-known equilibrium conditions given by Hildebrand (1931).

It can be seen from table 1, that the results obtained in the present work are in as good an agreement with the experimental results as obtained by other authors employing the more cumbersome repulsive forms (Born & Mayer 1932, Huggins 1937, Cubicciotti 1959, 1961, Bleick 1934, Mayer & Levy 1933). Chatterjee (1963) using the same potential form as used here has calculated the compressibility ($\beta$) for lighter halides. However, the procedure used by him does not seem to be justified. He has used the exprimental value of $\beta$ to find free index $n$ and then used value of $n$ to find $\beta$ again and

TABLE 1. COMPARISON OF THEORETICAL AND EXPERIMENTAL VALUES OF LATTICE ENERGIES AND THERMAL EXPANSIONS OF HEAVIER HALIDES.

| Crystal | Structure | Lattice Energy in K Cal/mole. | | | $\alpha_v \times 10^6$ per deg. | | |
|---|---|---|---|---|---|---|---|
| | | Expt. | Present work Equation(1) | Theor | Expt. | Present work (Equation(2)) | Theor |
| $NH_4Cl$ | CsCl | | 160.0 | 161.6*** | 142.00*** | 141.66 | |
| $NH_4Cl$ | CsCl | | 152.4 | 154.0*** | 161.00*** | 161.57 | |
| CuCl | Zincblend | 221.9* | 213.5 | 216.0* | 65.40* | 65.76 | |
| CuBr | Zincblend | 216.0* | 204.4 | 208.0* | 62.10* | 62.30 | |
| CuI | Zincblend | 213.4* | 199 6 | 199.0* | 73 50* | 73.46 | |
| AgCl | NaCl | 205.7** | 200.4 | 203.0** | 98.90** 98.70+ | 98.73 | 94.44+++ |
| AgBr | NaCl | 201.8** | 193.8 | 197.0** | 104.0** 102.30+ | 104.38 | 95.53+++ |
| AgI | Zincblend | 199.0** | 188.0 | 190.0** | | 113.48 | |
| TlCl | CsCl | 170.1** | 164.7 | 167 0** | 168.00++ | 152.83 | 155.54+++ |
| TlBr | CsCl | 165.6** | 161.2 | 164.0** | | 159.80 | |

* Mayer & Levy (1933)
** Mayer (1933)
*** Bleick (1934)

\+ Hummel (1950)
++ International Critical Tables (1928)
+++Kumar (1959)

has called it $\beta_{calc}$. This is objectionable because the two equations used by him are not independent of each other and hence his procedure is of little significance.

In a crystal lattice, the ions oscillate about their equilibrium positions and their amplitudes increase with temperature. Hummel (1950), on this basis, has explained thermal expansion as being due to shifts in equilibrium positions of oscillating ions when their amplitudes become sufficiently large. In view of the effect of the ionic vibrations on thermal expansion of solids, many workers have correlated this property with vibration characteristics of ions.

In the present work, the values of the coefficient of thermal expansion ($\alpha_v$) on the basis of equation (1) have been calculated by the formula

$$\alpha_v = \frac{3F_{T,P}}{T}\left\{\frac{\frac{\alpha e^2}{r} + \frac{6c}{r^6} + \frac{8D}{r^8} - \frac{n\lambda}{r^n}}{-\frac{2\alpha e^2}{r} + n(n+1)\frac{\lambda}{r^n} - 42\frac{c}{r^6} - 72\frac{D}{r^8}}\right\} \tag{2}$$

where $F_{T,P} = 1 + \frac{T}{\beta}\left(\frac{\partial\beta}{\partial T}\right)_P + \frac{T}{\beta^2 V}\left(\frac{\partial\beta}{\partial p}\right)_T\left(\frac{\partial V}{\partial p}\right)T + \frac{2T}{3V}\left(\frac{\partial V}{\partial T}\right)_P.$

Calculated values of ($\alpha_v$) are presented in table 1 along with the experimental values obtained by Kumar (1959) theoretically using a different potential and procedure. For salts other than $NH_4Cl$ and $NH_4Br$ as the data for the calculation $F_P$ is not available we are justified in assuming $F_{T,P}=1$. Very good agreement is obtained. The calculated values of the thermal expansion seem to be in good agreement with the experimental values compared to those calculated by Kumar (1959). The cohesive energy values are, however, slightly inferior in comparison with the other values but this inferiority too does not exceed by more than 4.5% on the average. Therefore, in view of this simple procedure, which gives sufficiently satisfactory results, this simple inverse power of potential energy function may also be used for the computation of other lattice properties for heavier halides. The author anticipates that, if an accurate value of $F_{T,P}$ be used in calculating lattice energy and thermal expansion, still better agreement with experiment may be obtained.

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# Normal coordinate analysis of tungsten hexachloride ($WCl_6$)

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On the basis of available molecular dimensions and spectroscopic data, several molecules and ions of octahedral symmetry ($O_h$) have been subjected to normal coordinate analysis using various types of potential functions, enabling the evaluation of molecular constants like force constans, thermodynamic function, mean amplitudes of vibration etc. In continuation of the same type of work Nagarajan (1964) calculated the valence force field constants and mean amplitudes of vibration of tungsten hexachloride ($WCl_6$) from the estimated frequencies used in the calculation of thermodynamic functions by Stull and his associates (1962). Recently Evans & Lo (1968) have reported the assignments of all the six fundamentals frequencies of tungsten hexachloride with the help of two infrared active fundamental modes and six combination bonds. The fundamental frequencies differ appreciably from the estimated frequencies used by Nagarajan (1964) in his calculations. Since we have been interested in similar work on octahedral molecules and ions (Pandey, Singh & Sanyal 1969), it was considered worthwhile to recalculate the molecular constants like force constants mean amplitudes of vibration and shrinkage effect for this molecule with the recent spectroscopic data (Evans & Lo 1968)