

COHESIVE ENERGIES OF ALKALI HALIDES

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The principal interactions in ionic lattices which are Coulomb interaction, van der Waals' interaction and overlap force, are two body forces. In the case of simple ions possessing spherical symmetry and rare gas structures, the cohesive energy can be represented as a function of their distance apart. For the ionic crystals a number of observable properties can be calculated using a bireciprocal Lennard-Jones potential function coupled with a coulombic term. Recently the cohesive energies of ionic crystals have been calculated (Sharma and Madan, 1961) using a (12·6) potential function. It was pointed out that the discrepancy with the experimental data was more pronounced for lighter alkali halides. Hence the authors presently aim to propose an appropriate (9·6) potential function for such alkali halides. This is reasonable in the light of the fact that the values of the repulsion constant 'n' obtained by Pauling's rules (1927, 1928) derived from a theoretical treatment of the interaction of closed shell electronic configurations, lie in the vicinity of 9 (Sherman, 1932).

Hence the energy per cell is represented by

$$\phi_{(r)} = - \frac{\alpha e^2}{r} + \frac{B}{r^9} - \frac{C}{r^6} + \epsilon_0 \quad \dots (1)$$

where α is the Madelung's constant, e is the electron charge, r is the distance between closest ion centres and ϵ_0 is the zero point energy. B and C are the coefficients for repulsive and van der Waals terms.

Here interactions between dipole-quadrupole and other than the nearest neighbours are neglected as their contribution is very small.

By the use of thermodynamic relations it can be easily shown that first and second derivatives of lattice energy can be expressed in terms of directly observable quantities. The equations are :

$$\frac{d\phi_{(r)}}{dr} = \frac{3vT}{r\beta} \left(\frac{1}{V} \cdot \frac{\partial V}{\partial T} \right)_P \quad \dots (2)$$

$$\frac{d^2\phi_{(r)}}{dr^2} = \frac{9v}{r^2\beta} \left[1 + \frac{T}{\beta} \left\{ \left(\frac{\partial \beta}{\partial T} \right)_P + \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \frac{1}{\beta} \left(\frac{\partial \beta}{\partial P} \right)_T \right\} + \frac{2T}{3V} \left(\frac{\partial V}{\partial T} \right)_P \right] \dots (3)$$

TABLE I
Cohesive energy in K. Cal/mole

Compound	Repulsion constant	Experimental	Calculated (present work)	Calculated (12 : 6)	
LiF	6.0	246 ^a	264.6	273.1	246.8
NaF	7.0	218 ^a	227.3	236.6	218.7
LiCl	7.0	201.5 ^b	199.8	212.6	202.0
LiBr	7.5	191.5 ^b	189.0	200.0	190.7
NaCl	8.0	184.0 ^a	182.8	192.8	185.9
KF	8.0	193.0 ^a	195.8	205.8	194.4
LiI	8.5	180.0 ^a	174.8	184.3	176.8
NaBr	8.5	176.0 ^b	172.1	182.1	176.7
RbF	8.5	—	177.9	191.6	185.9
KCl	9.0	167.8 ^a	163.8	174.1	160.4
NaI	9.5	166.0 ^a	159.3	168.8	165.4
KBr	9.5	160.0 ^a	154.8	164.8	162.4
RbCl	9.5	162.0 ^a	155.8	166.8	164.0
RbBr	10.0	157.0 ^a	149.6	159.1	157.5
KI	10.5	152.0 ^a	145.0	155.0	153.0

a. Plondl (1961)

b. Born and Huang (1954)

c. Cubicciotti (1961)

Using Equation (3) the repulsive parameter B can be evaluated and hence the cohesive energy. The experimental data used have been taken from Huggins (1937), Seitz (1940) and Spangenberg (1956), Spangenberg *et al.* (1957). The values of cohesive energy are compared with the observed values and also with other determinations. The values calculated with (12.6) potential function are also given. All values are listed in Table I.

In the case of lighter halides, the ' n ' value is less than the assumed value of 9. Thus for the lightest one, namely LiF, the ' n ' value is around 6 (Sherman, 1932) and hence cohesive energy is higher. Better agreement can be obtained using the value of ' n ' as 7. As we go down the group of alkali halides the agreement becomes better. This is explicable since in all these cases, the ' n ' values are either 9 or very near 9. For heavier crystals, the calculated values are lower and the discrepancy increases as we proceed towards still heavier compounds. Incidentally the ' n ' value increases to 10.5 and (12 : 6) potential function becomes more appropriate.

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