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# The lattice energies of the alkali halides.

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Now that the magnitude of the dissociation energy of fluorine seems to be fairly generally accepted as being about 37 kcal. and values for the electron affinities of the halogens can be obtained by a number of independent experimental methods (Pritchard, 1953), it seems worthwhile to recalculate the lattice energies of the alkali halides from up-to-date experimental thermodynamic data, using the Born–Haber cycle.

The values of the lattice energies $U$ and the relevant thermodynamic data from which they are calculated are shown in Table 1. In addition, theoretical values for the lattice energies $U_0$ calculated by Huggins (1937), assuming ionic crystals with a van der Waals potential, are shown; these are here accepted as the best available theoretical data. The thermodynamic data employed for calculating $U$ values has been taken from the following sources. Values for the heats of formation of the alkali halides $\Delta Hf$ at 298·16° K. have been taken from the National Bureau of Standards Circular (Rossini, Wagman, Evans, Levine & Jaffe, 1952). The heats of atomization $D$ at 298·16° K. of chlorine, bromine and iodine have also been taken from this compilation, while the data for fluorine are from Barrow & Caunt (1953). The electron affinities $E$ are the most probable values given by Pritchard (1953). The heats of atomization $L_0$ at 0° K. for the alkali metals are the quantities adopted by Baughan (1954), while the ionization potentials $I$ of the metals at 0° K. are taken from Finkelnburg & Humbach (1955).

The $U$ values refer to 0° K. and are equal to the sum of the thermodynamic terms, corrected to 0° K. where necessary. The small energy changes between 0° K. and 298·16° K. have been estimated, and are included in the calculation of the lattice energies although they are not given explicitly in the table.

It is evident from Table 1 that there is good agreement between $U$ and $U_0$ figures for the alkali halides. In comparing the data it should be borne in mind that errors in the $U$ values may be of the order of ±2–3 kcal., and errors in the $U_0$ values may be of a similar order of magnitude even if the assumptions under which they are calculated hold exactly.

An alternative method which can be employed for calculating the lattice energies of some of the alkali halides is to combine the known heats of sublimation with the measured heats of ionic dissociation of the gas molecules and other thermodynamic data. Lattice energies $U_e$ obtained in this way are shown in Table 2 together with values of the heats of sublimation $\lambda_0$ at 0° K. and the heats of ionic dissociation $Q_0$ at the same temperature. It is seen that the $U_e$ values agree well with the $U$ and $U_0$ values of Table 1.

The good agreement between the lattice-energy values obtained by the different independent methods provides strong evidence of their reliability. Also, the agreement tends to confirm the validity of the $D$ and $E$ values for the halogens which have been employed in the calculations described above; these values should be satisfactory for use in the calculation of the lattice energies of other inorganic halides by means of the Born–Haber cycle.

The lattice energies of the alkali halides exhibit a remarkable regularity. Thus the lattice energies of the sodium salts are equal to the mean of the lattice energies of the corresponding lithium and potassium salts to

Table 1. *Lattice energies of alkali halides*

(Values in kcal./mole)

| | $-\Delta Hf$ | $D$ | $-E$ | $L_0$ | $I$ | $U$ | $U_0$ |
|---|---|---|---|---|---|---|---|
| LiF | 143·6 | 18·8 | −83·5 | 37 | 124·3 | 244 | 243·6 |
| LiCl | 97·7 | 29·0 | −88·2 | 37 | 124·3 | 201 | 200·2 |
| LiBr | 83·7 | 26·7 | −81·6 | 37 | 124·3 | 193 | 189·5 |
| LiI | 64·8 | 25·5 | −74·6 | 37 | 124·3 | 180 | 176·1 |
| NaF | 136·0 | 18·8 | −83·5 | 26 | 118·4 | 217 | 215·4 |
| NaCl | 98·2 | 29·0 | −88·2 | 26 | 118·4 | 185 | 183·5 |
| NaBr | 86·0 | 26·7 | −81·6 | 26 | 118·4 | 178 | 175·5 |
| NaI | 68·8 | 25·5 | −74·6 | 26 | 118·4 | 167 | 164·3 |
| KF | 134·5 | 18·8 | −83·5 | 21·6 | 102·0 | 195 | 192·5 |
| KCl | 104·2 | 29·0 | −88·2 | 21·6 | 102·0 | 171 | 167·9 |
| KBr | 93·7 | 26·7 | −81·6 | 21·6 | 102·0 | 165 | 161·3 |
| KI | 78·3 | 25·5 | −74·6 | 21·6 | 102·0 | 156 | 152·4 |
| RbF | 131·3 | 18·8 | −83·5 | 20·1 | 96·2 | 185 | 183·0 |
| RbCl | 102·9 | 29·0 | −88·2 | 20·1 | 96·2 | 162 | 162·0 |
| RbBr | 93·0 | 26·7 | −81·6 | 20·1 | 96·2 | 157 | 156·1 |
| RbI | 78·5 | 25·5 | −74·6 | 20·1 | 96·2 | 149 | 148·0 |
| CsF | 126·9 | 18·8 | −83·5 | 18·8 | 89·7 | 173 | 175·7 |
| CsCl | 103·5 | 29·0 | −88·2 | 18·8 | 89·7 | 155 | 153·1 |
| CsBr | 94·3 | 26·7 | −81·6 | 18·8 | 89·7 | 151 | 149·6 |
| CsI | 80·5 | 25·5 | −74·6 | 18·8 | 89·7 | 143 | 142·5 |

Table 2. *Lattice energies of the alkali halides from heats of sublimation and vapour phase ionic dissociation*

(Values in kcal./mole; probable error of $U_e$ values c. ±3 kcal.)

| | $\lambda_0$ | $Q_0$ | $U_e$ |
|---|---|---|---|
| LiCl | 50·6(a) | 150·7(d) | 201·3 |
| LiI | 48·8(c) | 129·1(f) | 177·9 |
| NaCl | 55·0(a, b) | 129·7(d) | 184·7 |
| NaBr | 53·0(a, b) | 124·7(e) | 177·7 |
| NaI | 47·9(c) | 118·8(g) | 166·7 |
| KCl | 52·9(a, b) | 113·5(d) | 166·4 |
| KBr | 51·9(a, b) | 109·3(e) | 161·2 |
| KI | 49·0(a) | 102·4(g) | 151·4 |
| | 49·0(a) | 104·6(h) | 153·6 |
| RbI | 46·1(a) | 99·1(f) | 145·2 |
| CsI | (48) | 94·8(h) | 142·8 |

Data from (*a*) Niwa, 1938; (*b*) Mayer & Winter, 1938; (*c*) Rossini *et al.*, 1952; (*d*) Saha & Tandon, 1937; (*e*) Tandon, 1937*a*; (*f*) Srivistava, 1938; (*g*) Tandon, 1937*b*; (*h*) Mayer, 1930.

within ±1·5 kcal. Similarly, the lattice energies of the rubidium salts approximate to the mean of the lattice energies of the corresponding potassium and caesium salts, even though CsCl, CsBr and CsI have a different crystal structure from the other alkali halides. In addition, the difference between the lattice energies of the chloride and bromide of a given alkali metal is practically constant (6±2 kcal.), as also is the difference between the lattice energies of the bromide and iodide (10±3 kcal.).

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## The unit cell and space group of barium tetratitanate, BaO . 4 $TiO_2$.*

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The compound BaO . 4$TiO_2$ has been prepared by Rase & Roy (1955) during phase investigations in the system BaO–$TiO_2$. It grows as small needle-shaped crystals several millimetres in length from mixtures of 80 molar % $TiO_2$ reacting in the solid phase below 1400° C.

Rotation and Weissenberg photographs of an untwinned crystal have shown the unit cell to be orthorhombic with dimensions

$$a = 3{\cdot}79 \pm 0{\cdot}01,\ b = 14{\cdot}51 \pm 0{\cdot}04,\ c = 6{\cdot}30 \pm 0{\cdot}02\ \text{Å}\,,$$

where $a$ is parallel to the length of the needle, and $b$ and $c$ are parallel to the edges of its rectangular cross-section.

The only systematic absences observed are $hk0$ when $h+k$ is odd, suggesting that the space group is either $P{-}mn$, $Pm{-}n$, or $Pmmn$.

The observed density of 4·6 g.cm.$^{-3}$, measured by pycnometer, agrees well with a value of 4·54 g.cm.$^{-3}$ calculated on the basis of 2 formula units per unit cell.

The short axial distance of 3·79 Å corresponds approximately with the distance between opposite apices of $TiO_6$ octahedra found in other compounds, suggesting that strings of such octahedra are linked corner to corner parallel to the $a$ axis.

A structure determination on this compound is not contemplated.

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