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The Lattice Energies of the Cuprous Halides

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Following exactly the method employed in the case of the silver halides the lattice energies of the cuprous halides have been calculated. The exponential constant in the empirical repulsion equation expressing the positive repulsive potential between the ions is found to be almost the same as that for the silver halides. The energies of the

salts indicate that, particularly for the iodide there is not purely ionic binding. The lattice energies are calculated to be, for CuCl 216 kcal., CuBr, 208 kcal., CuI 199 kcal. The "experimental" values are, CuCl 221.9 kcal. CuBr 216.0 kcal. and CuI 213.4 kcal.

INTRODUCTION

RECENTLY calculations have been made of the lattice energies of the alkali halides¹ and of the silver and thallous halides² following a method proposed by Born and Mayer.³ In this paper the arithmetical calculations are carried out for the cuprous halides.

The method is exactly the same as that used for the silver halides, and the Table I of this paper follows exactly the contents of Tables I, II, and III of the previous article.²

The compressibilities are taken from an article by Bridgman.⁴ The frequencies assumed for the negative ions are those assumed for the silver salts. The polarizability of the cuprous ion is taken from Pauling.⁵ The experimental lattice constants assumed are those of the *Strukturbericht*.⁶ The energies of reaction are all taken from *International Critical Tables*, with the exception of the heat of sublimation of copper, which is estimated from the boiling point with the aid of Hildebrand's modification of Trouton's rule. The electron affinity of the halides are taken from the calculations on the alkali halides.¹

The disagreement of 2.9, 5.0, and 11.4 kcal. for the chloride, bromide, and iodide, respectively,

between the theoretical lattice energies and the "experimental" values, may in part be due to an uncertainty in the heat of sublimation of copper; however, it is more probable that they

TABLE I.

| | CuCl | CuBr | CuI |
|---|-----------|-----------|-----------|
| 1 Salt | Zincblend | Zincblend | Zincblend |
| 2 Crystal type | | | |
| 3 Q_{00}^2 (neg. ion) $\times 10^{16}$ cm ² | 3.40 | 4.08 | 5.27 |
| 4 ϵ (neg. ion) $\times 10^{12}$ ergs/molecule | 15.6 | 13.9 | 11.0 |
| 5 α (neg. ion) $\times 10^{24}$ cm ³ | 3.45 | 4.47 | 7.29 |
| 6 α (pos. ion) $\times 10^{24}$ cm ³ | 0.43 | 0.43 | 0.43 |
| 7 ϵ (pos. ion) $\times 10^{12}$ ergs/molecule | 29 | 29 | 29 |
| 8 $c_{++} \times 10^{40}$ ergs \times cm ⁵ | 0.41 | 0.41 | 0.41 |
| 9 $c_{--} \times 10^{40}$ " " | 133 | 208 | 437 |
| 10 $c_{+-} \times 10^{40}$ " " | 21.9 | 27.3 | 37.7 |
| 11 $d_{++} \times 10^{14}$ ergs \times cm ⁵ | 0.2 | 0.2 | 0.2 |
| 12 $d_{--} \times 10^{14}$ " " | 270 | 470 | 1230 |
| 13 $d_{+-} \times 10^{14}$ " " | 27 | 38 | 64 |
| 14 S_0 | 4.354 | 4.354 | 4.354 |
| 15 S_0' | 0.762 | 0.762 | 0.762 |
| 16 S_0'' | 4.104 | 4.104 | 4.104 |
| 17 S_0''' | 0.253 | 0.253 | 0.253 |
| 18 $C \times 10^{40}$ ergs \times cm ⁵ | 146 | 198 | 330 |
| 19 $D \times 10^{16}$ ergs \times cm ⁵ | 150 | 220 | 420 |
| 20 $r_0 \times 10^8$ cm | 2.34 | 2.46 | 2.62 |
| 21 $\beta \times 10^6$ (compressibility) bars ⁻¹ | 2.51 | 2.93 | 2.81 |
| 22 $V^{-1}(\partial V/\partial T)_p \times 10^6$ | 65.4 | 62.1 | 73.5 |
| 23 $9V/N\beta \times 10^{12}$ ergs/molecule | 142 | 141 | 177.5 |
| 24 $(3T/N\beta)(\partial V/\partial T)_p \times 10^{12}$ ergs/molecule | 0.94 | 0.88 | 1.32 |
| 25 $\alpha\epsilon^2/r_0 \times 10^{12}$ ergs/molecule | 15.97 | 15.20 | 14.26 |
| 26 $C/r_0^5 \times 10^{12}$ ergs/molecule | 0.89 | 0.89 | 1.01 |
| 27 $D/r_0^5 \times 10^{12}$ " " | 0.16 | 0.16 | 0.19 |
| 28 $\tau \times 10^{12}$ " " | 21.67 | 20.97 | 20.51 |
| 29 $\sigma \times 10^{12}$ " " | 223 | 220 | 262 |
| 30 σ/τ | 10.3 | 10.5 | 12.8 |
| 31 $\rho \times 10^8$ cm (average value = 0.223) | 0.227 | 0.235 | 0.205 |
| 32 r_0/ρ calculated from average | 10.51 | 11.07 | 11.76 |
| 33 $B(r) \times 10^{12}$ ergs/molecule | 2.05 | 1.88 | 1.72 |
| 34 $\frac{1}{2}h\nu \times 10^{12}$ " " | 0.08 | 0.06 | 0.05 |
| 35 $U \times 10^{12}$ " " | 14.89 | 14.32 | 13.69 |
| 36 U (theoretical lattice energy) kcal. | 216 | 208 | 199 |
| 37 $MX_{cr.} 0^\circ K \rightarrow MX_{cr.} 291^\circ K$, ΔH kcal. | 2.8 | 2.9 | 3.0 |
| 38 $MX_{cr.} \rightarrow M_{s.s.} + \frac{1}{2}X_{2 s.s.} 291^\circ K$, ΔH kcal. | 32.5 | 24.6 | 15.8 |
| 39 $\frac{1}{2}X_{2 s.s.} \rightarrow X_g 291^\circ K$, ΔH kcal. | 28.8 | 26.7 | 25.5 |
| 40 $X_g 291^\circ K \rightarrow X_g 0^\circ K$ " " | -1.1 | -1.1 | -1.1 |
| 41 $X_g + e^- \rightarrow X_g^- 0^\circ K$ " " | -86.5 | -81.5 | -74.2 |
| 42 $M_{cr.} 291^\circ K \rightarrow M_{cr.} 0^\circ K$ " " | -1.7 | -1.7 | -1.7 |
| 43 $M_{cr.} 0^\circ K \rightarrow M_g 0^\circ K$ " " | 70.0 | 70.0 | 70.0 |
| 44 $M_g 0^\circ K \rightarrow M_g^+ + e^- 0^\circ K$ " " | 177.0 | 177.0 | 177.0 |
| 45 Sum $MX_{cr.} \rightarrow M_g^+ + X_g^- 0^\circ K$ (lattice energy) ΔH kcal. | 221.9 | 216.0 | 213.4 |
| 46 Difference 36 and 45 $\delta\Delta H$ kcal. | 2.9 | 5.0 | 11.4 |
| 47 Assumed value b_{-} | 77.4 | 105.3 | 189.5 |
| 48 " b_{+} | 202 | 202 | 202 |
| 49 Calculated $r_0 \times 10^8$ cm | 2.34 | 2.49 | 2.59 |
| 50 Experimental $r_0 \times 10^8$ cm | 2.34 | 2.46 | 2.62 |
| 51 Difference $\delta r \times 10^8$ cm | +0.002 | -0.03 | +0.03 |

¹ J. E. Mayer and L. Helmholz, *Zeits. f. Physik* **75**, 16 (1932).

² J. E. Mayer, *J. Chem. Phys.* **1**, 327 (1933).

³ M. Born and J. E. Mayer, *Zeits. f. Physik* **75**, 1 (1932).

⁴ P. W. Bridgman, *Proc. Am. Acad. Arts and Sci.* **67**, 345 (1932).

⁵ L. Pauling, *Proc. Roy. Soc. (London)* **A114**, 181 (1927).

⁶ P. P. Ewald and C. Hermann, *Strukturbericht*, 1913-1928.

show a considerable homopolar binding component. The calculated lattice constants (row 49) show irregular disagreement with the experimental values. This may in part be due to uncertainty in the experimental values but again is probably caused by an error in the assumptions. Table II, however, shows that the purely ionic crystal should be stable in crystal type in which these salts do crystallize, the Zincblend lattice.

Reliable evidence as to whether these crystals are in reality considerably homopolar or very nearly purely ionic can probably only be obtained

TABLE II. *Calculation of the potential energy change with lattice type.*

energies in 10^{-12} ergs/molecule

| Salt | Experimentally stable lattice | Hypo- thetical lattice | Change at constant r_0 of | | | | | $\frac{\partial^2 \Phi}{\partial r^2}$ | $\frac{(\partial r)^2}{2}$ | $\delta \Phi$ |
|------|-------------------------------------|------------------------------|-----------------------------|--------------------|--------------------|----------|-------|--|----------------------------|---------------|
| | | | $-\frac{\alpha_e^2}{r_0}$ | $-\frac{C}{r_0^6}$ | $-\frac{D}{r_0^8}$ | $B(r_0)$ | | | | |
| CuCl | Zincblend | Rocksalt | -1.07 | -0.73 | -0.13 | +2.32 | -0.13 | +0.24 | | |
| CuBr | Zincblend | Rocksalt | -1.02 | -0.76 | -0.14 | +2.38 | -0.13 | +0.33 | | |
| CuI | Zincblend | Rocksalt | -0.95 | -0.95 | -0.18 | +3.36 | -0.13 | +0.14 | | |

by a theoretical calculation of the ionic non-electrostatic (Heitler-London) repulsion from ionic electron wave functions.