LATTICE-THEORY OF ALKALINE EARTH CARBONATES.

Part III. Lattice-Energy of the Crystals of Calcite and Its Thermo-Chemical Applications.

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Introduction.

In two recent papers by the author,[1] referred to hereafter as I and II, the Lattice-Energy and the elasticity constants of the orthorhombic crystals of Aragonite were calculated. In this and the next part, we deal on exactly similar lines with the crystals of calcite. Thus calcite is assumed to be a polar compound composed of C_a^{++} and CO_3^{--} ions; the forces being the electro-static repulsions and attractions and the "repulsive forces" of the type b/r^n.

On calculating the lattice-energy of the crystal, we obtain the value of 'n' with the help of the compressibility measurements.

§1. *The Electro-Static Energy Density.*

The crystals of calcite[2] belong to the trigonal system, and possess hexagonal symmetry. Taking the z-axis, along the trigonal axis and the x- and y-axes in a plane perpendicular to it, so that the "Grund-vectors" (I §1) will have the components

$$a_x = 4{\cdot}98, \quad b_y = \sqrt{3}\, a_x, \quad c_z = 8{\cdot}55 \qquad .. \qquad .. \qquad .. \quad (1, 1)$$

the other components being zero.

The only surviving components of the "Grund-vectors" of the reciprocal lattice are

$$a'_x = \frac{1}{a_x}, \quad b'_y = \frac{1}{b_y}, \quad c'_z = \frac{1}{c_z} \qquad .. \qquad .. \qquad .. \qquad .. \quad (1, 2)$$

The vector $\vec{q^l}$ [I (1, 15)] will have the components

$$\vec{q^l} = 2\pi \left(\frac{l_1}{a_x}, \frac{l_2}{b_y}, \frac{l_3}{c_z} \right) \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \quad (1, 3)$$

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[1] B. Y. Oke, *Proc. Ind. Acad. Sci.*, 1936, **4**, 1 and 514.

[2] Wycoff, *The Structure of Crystals*, Second Edition, p. 273; or "Zeitschrift fur Kristallographie," *Struktur Bericht*, 1913–26, p. 292.

The electro-static energy density is given by

$$U_\Delta = \frac{1}{2\Delta}\,\phi_0 \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1, 4)$$

where $\phi_0 = \overline{\psi}\,(0) \sum_{k'} e_{k'}{}^2 + \sum_{kk'} e_k\, e_{k'}\, \psi\,(r_{kk'})$ .. .. .. (1, 5)

$\overline{\psi}\,(0)$ and $\psi\,(r_{kk'})$ are defined in I (1, 7) (1, 8) (1, 9) and (1, 10).

(i) Evaluation of $\overline{\psi}\,(0)$.—

From I (2, 6) we have

$$\overline{\psi_1}\,(0) = \frac{b^2}{\pi\, abc} \sum_{l}{}' \frac{e^{-\left(l_1{}^2 \frac{b^2}{a^2} + l_2{}^2 + l_3{}^2 + \frac{b^2}{c^2}\right)}}{\left(l_1{}^2 \frac{b^2}{a^2} + l_2{}^2 + l_3{}^2 \frac{b^2}{c^2}\right)} - \frac{2\sqrt{\pi}}{b} \quad .. \quad (1, 6)$$

As in I, we need consider only the first few terms, since the expression under the sign of summation is rapidly converging.

In this case we have

$$\frac{b^2}{a^2} = 3 \quad \text{and} \quad \frac{b^2}{c^2} = 1{\cdot}018 \quad .. \quad .. \quad .. \quad .. \quad (1, 7)$$

We write

$$3\, l_1{}^2 + l_2{}^2 + 1{\cdot}018\, l_3{}^2 = \lambda_{l_1, l_2, l_3} \quad .. \quad .. \quad .. \quad .. \quad (1, 8)$$

TABLE I.

l_1	l_2	l_3	λ_{l_1, l_2, l_3}	$e^{-\lambda_{l_1, l_2, l_3}}$	$\frac{e^{-\lambda_{l_1, l_2, l_3}}}{\lambda_{l_1, l_2, l_3}}$	$P(l_1, l_2, l_3)$	$P\,\frac{e^{-\lambda}}{\lambda}$
1	0	0	3	·0497	·0166	2	·0322
0	1	0	1	·3676	·3676	2	·7352
0	0	1	1·018	·3614	·3550	2	·7100
2	0	0	12	..	..	..	..
0	2	0	4	·0183	·0046	2	·0092
0	0	2	4·072	·0177	·0043	2	·0086
1	1	0	4	·0183	·0046	4	·0176
0	1	1	2·018	·1326	·0658	4	·2632
1	0	1	4·018	·0179	·0044	4	·0176
0	2	1	5·018	·0066	·0013	4	·0052
0	1	2	5·072	·0062	·0012	4	·0048
1	1	1	5·018	·0066	·0013	8	·0104
						Sum	1·8140

The 7th column gives the number of different combinations for the same numerical values of l_1, l_2, l_3; thus for $|l_1| = 1$, $|l_2| = 1$, and $l_3 = 0$ we have the following 4 combinations:

$$(1, 1, 0);\ (-1, 1, 0);\ (1, -1, 0);\ (-1, -1, 0).$$

Hence

$$\bar{\psi}_1(0) = \frac{b^2}{\pi abc}\,1{\cdot}8140 - \frac{2\sqrt{\pi}}{b} \quad .. \quad .. \quad .. \quad .. \quad (1, 9)$$

$$= \frac{{\cdot}556 \times 1{\cdot}814 - 3{\cdot}544}{b} \quad .. \quad .. \quad .. \quad .. \quad (1, 10)$$

Now

$$\bar{\psi}_2(0) = \sum_{l}{}' \frac{1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{\pi}{b} r^l} e^{-\alpha^2}\, d\alpha}{r^l} - \frac{b^2}{\pi abc} \quad .. \quad .. \quad (1, 11)$$

The contribution from the first term, containing the integral, is negligible.

$$\therefore\ \bar{\psi}_2(0) = -\frac{b/a \times b/c}{\pi b} \quad .. \quad .. \quad .. \quad .. \quad (1, 12)$$

$$= -\frac{{\cdot}556}{b} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1, 13)$$

From (1, 13) and (1, 10)

$$\bar{\psi}(0) = -\frac{3{\cdot}091}{b} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1, 14)$$

(ii) Evaluation of $\sum_{kk'} e_k\, e_{k'}\, \psi(r_{kk'})$.—

A unit cell of the crystal consists of 6 molecules of the carbonates. The calcium ions are situated at

$$(0, 0, 0);\ \left(\frac{a}{2}, \frac{b}{2}, 0\right);\ \left(0, \frac{b}{3}, \frac{c}{3}\right);\ \left(\frac{a}{2}, \frac{5b}{6}, \frac{c}{3}\right)$$

$$\left(0, \frac{2b}{3}, \frac{2}{3}\right) \text{ and } \left(\frac{a}{2}, \frac{b}{6}, \frac{2c}{3}\right) \quad .. \quad .. \quad .. \quad .. \quad (1, 15)$$

$$\left(0, \frac{2b}{3}, \frac{c}{6}\right);\ \left(\frac{a}{2}, \frac{b}{6}, \frac{c}{6}\right);\ \left(0, 0, \frac{c}{2}\right);\ \left(\frac{a}{2}, \frac{b}{2}, \frac{c}{2}\right)$$

$$\left(0, \frac{b}{3}, \frac{5c}{6}\right) \text{ and } \left(\frac{a}{2}, \frac{5b}{6}, \frac{5c}{6}\right) \quad .. \quad .. \quad .. \quad .. \quad (1, 16)$$

From I (2, 15)

$$\psi(r_{kk'}) = \frac{4\pi}{abc} \sum_{l}{}' \frac{e^{2\pi i\left(l_1 \frac{x_{kk'}}{a} + l_2 \frac{y_{kk'}}{b} + l_3 \frac{z_{kk'}}{c}\right)}}{4\pi^2\left(l_1^2 \frac{1}{a^2} + l_2^2 \frac{1}{b^2} + l_3^2 \frac{1}{c^2}\right)} \quad .. \quad .. \quad (1, 17)$$

where $x_{kk'}$, $y_{kk'}$ and $z_{kk'}$ are the projections of $r_{kk'}$ on the three co-ordinate axes.

Hence

$$\sum_{kk'} e_k e_{k'} \psi(r_{kk'}) = \frac{b^2}{\pi abc} \sum_{l}' \sum_{kk'} e_k e_{k'} \frac{e^{2\pi i \left(l_1 \frac{x_{kk'}}{a} + l_2 \frac{y_{kk'}}{b} + l_3 \frac{z_{kk'}}{c}\right)}}{\left(l_1^2 \frac{b^2}{a^2} + l_2^2 + l_3^2 \frac{b^2}{c^2}\right)} \quad .. \quad (1, 18)$$

Expressing the exponential as a cosine function this can be written as

$$\sum_{kk'} e_k e_{k'} \psi(r_{kk'}) = \frac{b^2}{\pi abc} \sum_{l'}' \sum_{kk'} \frac{2\cos\left(l_1' \frac{x_{kk'}}{a} + l_2' \frac{y_{kk'}}{b} + l_3' \frac{z_{kk'}}{c}\right)}{\left(l_1^2 \frac{b^2}{a^2} + l_2^2 + l_3^2 \frac{b^2}{c^2}\right)} \quad .. \quad (1, 19)$$

The dashes over the l's denote that if a certain set of values, say $(\bar{l}_1, \bar{l}_2, \bar{l}_3)$ is taken, we need not consider the set $(-\bar{l}_1, -\bar{l}_2, -\bar{l}_3)$. Any other set like $(\bar{l}_1, -\bar{l}_2, -\bar{l}_3)$ or $(\bar{l}_1, -\bar{l}_2, \bar{l}_3)$ has, however, to be considered.

The co-ordinates of the 12 points in a unit cell are given in (1, 15) and (1, 16) from which the values of $x_{kk'}$ etc., are obtained. Substituting these and associating a change $+2e$ with each calcium ions and a charge $-2e$ with each CO_3 ions, we obtain

$$\sum_{kk'} e_k e_{k'} \psi(r_{kk'}) = \frac{b/a \times b/c}{\pi b} 4e^2 \times 4 \sum_{l'}' \frac{F\{\cos(l_1', l_2', l_3')\pi\}}{\left(l_1^2 \frac{b^2}{a^2} + l_2^2 + l_3 \frac{b^2}{c^2}\right)} \quad .. \quad (1, 20)$$

where the function F is given by

$$\begin{aligned} F = {} & 4\cos(l_1 + l_2)\pi + 2\cos(l_1 - l_2)\pi + 2\cos\left(\frac{4l_2}{3} + \frac{4l_3}{3}\right)\pi \\ & + 6\cos\left(\frac{2l_2}{3} + \frac{2l_3}{3}\right)\pi + 2\cos\left(\frac{4l_2}{3} - \frac{2l_3}{3}\right)\pi + 2\cos\left(\frac{2l_2}{3} - \frac{4l_3}{3}\right)\pi \\ & + 4\cos\left(l_1 + \frac{l_2}{3} - \frac{2l_3}{3}\right)\pi + 2\cos\left(l_1 - \frac{l_2}{3} + \frac{2l_3}{3}\right)\pi + 2\cos\left(l_1 - \frac{l_2}{3} - \frac{4l_3}{3}\right)\pi \\ & + 2\cos\left(l_1 + \frac{l_2}{3} + \frac{4l_3}{3}\right)\pi + 2\cos\left(l_1 + \frac{5l_2}{3} + \frac{2l_3}{3}\right) \\ & - \left\{6\cos l_3\pi + 4\cos\left(\frac{4l_2}{3} + \frac{l_3}{3}\right)\pi + 6\cos\left(\frac{2l_2}{3} - \frac{l_3}{3}\right)\pi\right. \\ & + 2\cos\left(\frac{2l_2}{3} + \frac{5l_3}{3}\right)\pi + 2\cos(l_1 + l_2 + l_3)\pi + 2\cos(l_1 + l_2 - l_3)\pi \\ & + \cos(l_1 - l_2 - l_3)\pi + \cos(l_1 - l_2 + l_3)\pi + 4\cos\left(l_1 - \frac{l_2}{3} - \frac{l_3}{3}\right)\pi \\ & + 5\cos\left(l_1 + \frac{l_2}{3} + \frac{l_3}{3}\right)\pi + \cos\left(l_1 + \frac{5l_2}{3} + \frac{5l_3}{3}\right)\pi \\ & \left. + \cos\left(l_1 + \frac{l_2}{3} - \frac{5l_3}{3}\right)\pi + \cos\left(l_1 + \frac{5l_2}{3} - \frac{l_3}{3}\right)\pi\right\} \quad .. \quad .. \quad (1, 21) \end{aligned}$$

Carrying out the summation until the denominator becomes sufficiently large to neglect the subsequent terms, we obtain

$$\Sigma\, e_k\, e_{k'} \psi\,(r_{kk'}) = -\frac{\cdot 556}{b}\, 16\, e^2 \quad (16 \cdot 18) \qquad \ldots \qquad (1, 22)$$

Substituting the values from (1, 14) and (1, 22) in (1, 5) we get

$$\phi_0 = -\frac{4\, e^2}{b}\,(37 \cdot 09 + 35 \cdot 98) \qquad \ldots \qquad (1, 23)$$

Defining

$$\delta^3 = abc \qquad \ldots \qquad (1, 24)$$

So that from (1, 1)

$$\delta = \frac{1}{1 \cdot 205}\, b \qquad \ldots \qquad (1, 25)$$

(1, 23) can be written as

$$\phi_0 = -\frac{e^2}{\delta}\, 242 \cdot 6 \qquad \ldots \qquad (1, 26)$$

or $$\phi_0 = -2\frac{e^2}{\delta}\, \alpha \qquad \ldots \qquad (1, 27)$$

where $$\alpha = 121 \cdot 3 \qquad \ldots \qquad (1, 28)$$

§2. *The Lattice-Energy.*

For the stability of the crystals, repulsive forces of the type b/r^n, besides the electro-static attractions and repulsions, have to be assumed. With these additional forces the function ϕ_0 given in (1, 27) will be of the form

$$\phi_0 = -2\left(\alpha\, \frac{e^2}{\delta} - \frac{\beta}{\delta^n}\right) \qquad \ldots \qquad (2, 1)$$

The " Lattice-Energy " per one mole of the substance is defined by

$$U = -\frac{1}{2z}\, N\, \phi_0$$

$$= \frac{1}{z}\, N \left(\alpha\, \frac{e^2}{\delta} - \frac{\beta}{\delta^n}\right) \qquad \ldots \qquad (2, 2)$$

where z is the number of molecules per unit cell of the crystal and N is Avogadro's number.

Proceeding as in I [refer equations I (3, 3), (3, 4)....(3, 9)] we get

$$n = 1 + \frac{9}{\alpha e^2 \chi}\left(\frac{Mz}{N\rho}\right)^{\frac{4}{3}} \qquad \ldots \qquad (2, 3)$$

and $$U = \left(1 - \frac{1}{n}\right) \alpha\, e^2 \left(\frac{N}{z}\right)^{\frac{4}{3}} \left(\frac{\rho}{M}\right)^{\frac{1}{3}} \qquad \ldots \qquad (2, 4)$$

where χ is the compressibility, M the molecular weight and ρ the density of calcite.

TABLE II.

$\frac{1}{\chi \times 10^{12}}$ dynes/cm.^{2} experimental	Source[3]	n Calculated	U Calculated
1/1·34	1	7·3	803·3
1/1·39	2	7·1	799·5
1/1·52	3	6·5	782·0

The energy values are expressed in k. cal.

§3. *The Thermo-Chemical Cycle.*

Exactly as in I §4, the calculated value of the "Lattice-Energy" can be verified by a thermo-chemical cycle, quite similar to that in I. The heat of formation of calcite is 231·8 k. cal.[4] With the same notation as in I (4, 2), (4, 3) and (4, 4) we get

$$B = 879{\cdot}0 \text{ k. cal.} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (3, 1)$$

by taking the last value of U from Table II;

$$A = 949{\cdot}1 \text{ k. cal.} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (3, 2)$$

so that $X = 70{\cdot}1$ k. cal. .. .. (3, 3)

The value of X in the case of Aragonite was obtained as 135·5 k. cal. Considering the various infinite summations and the uncertainty in the values of the compressibilities involved in the evaluation of X, this much agreement in the two values is not quite unsatisfactory.

Summary.

The lattice-energy of the crystals of calcite is calculated; and the value of n the index of the repulsive forces is determined with the help of the compressibility measurements. The value of the lattice-energy is applied to a thermo-chemical cyclic process.

[3] 1. Madelung and Fuchs. 2. Adams and Williamson. 3. W. Voigt.
All the values are given together in Mellor's *Inorganic and Physical Chemistry*. There are similar discrepancies in the compressibility measurements of Aragonite also.

[4] *Handbook of Chemistry and Physics*, Hodgman-Lange, Fifth Edition.