

LATTICE-THEORY OF ALKALINE EARTH CARBONATES.

Part I. Lattice-Energy of Crystals of Aragonite Type and Their Thermo-Chemical Applications.

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Introduction.

MEASUREMENTS¹ of the elasticity coefficients of Aragonite show a strong anisotropy. The two elasticity constants in perpendicular directions are in the ratio of 1:2. An attempt is made in this work to explain this anisotropy. According to the suggestion of Prof. M. Born the substance is assumed to be a polar compound composed of Ca^{++} and $(\text{CO}_3)^{-}$. The forces are the electrostatic attractions and repulsions of the charges and some other forces of the form $\frac{b}{r^n}$ which are usually assumed to account for the stability of the crystal.

Before taking up the actual calculations of the elasticity constants, it is necessary to calculate the total lattice-energy and to derive from this, with the help of the compressibility measurements, the value of n . In this paper we restrict ourselves to the evaluation of this n .

The lattice energy of the crystal is not a directly measurable quantity. It is, however, possible to construct chemical cyclic processes; after the manner of Born² and Haber,³ in which this quantity enters along with other chemical quantities such as heat of sublimation, heat of formation, heat of ionisation, etc. The cyclic processes can be used to verify the theoretically calculated value of the lattice-energy, as well as to estimate the heats of certain chemical reactions.

¹ W. Voigt, *Ann. de Phys.*, 1907, **24**, 290.

² M. Born, *Verh. d. Deutsch Phys.*, 1919, **21**, 679.

³ F. Haber, *Verh. d. Deutsch Phys.*, 1919, **21**, 750.

§1. *Lattice-Energy of a Crystal.*

The electrostatic potential of the lattice at a point $\vec{r}_{k'}$ of the lattice is called the "Selbs-potential" of the lattice at the point $\vec{r}_{k'}$ and is given by

$$\phi_{k'}(\vec{r}_{k'}) = \sum_l \sum_k' \frac{e_k}{r_{kk'}} \quad \dots \quad \dots \quad \dots \quad \dots \quad (1, 1)$$

where \sum_l denotes the summation over all the three cell-indices l_1, l_2, l_3 from $-\infty$ to ∞ and the dash over the summation sign \sum denotes that the index combination $l_1 = l_2 = l_3 = 0$ and $k = k'$ does not occur. e_k denotes the charge at the point k and $\vec{r}_{kk'}$ the radius-vector from k to k' .

The electro-static potential ϕ_0 at the points in a unit cell of the crystal is given by

$$\begin{aligned} \phi_0 &= \sum_{k'} e_{k'} \phi_{k'}(\vec{r}_{k'}) \\ &= \sum_l \sum_{kk'} \frac{e_k e_{k'}}{r_{kk'}} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (1, 2) \end{aligned}$$

Let $\vec{a}, \vec{b}, \vec{c}$ be the "Grund-vectors" of the lattice and $\vec{a}', \vec{b}', \vec{c}'$ be the "Grund-vectors" of the reciprocal lattice so that

$$\vec{a}' = \frac{1}{\Delta} [\vec{b} \times \vec{c}]; \vec{b}' = \frac{1}{\Delta} [\vec{c} \times \vec{a}]; \vec{c}' = \frac{1}{\Delta} [\vec{a} \times \vec{b}] \quad \dots \quad (1, 3)$$

where

$$\begin{vmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix} = \delta^3 = \Delta \quad \dots \quad \dots \quad \dots \quad (1, 4)$$

We define a vector \vec{q}^l by

$$\vec{q}^l = 2\pi (l_1 \vec{a}' + l_2 \vec{b}' + l_3 \vec{c}') \quad \dots \quad \dots \quad \dots \quad (1, 5)$$

According to the method of Ewald⁴ $\phi_{k'}(\vec{r}_{k'})$ can be expressed as the sum of two expressions as follows

$$\phi_{k'}(\vec{r}_{k'}) = e_{k'} \bar{\psi}(0) + \sum_k' e_k \psi(\vec{r}_{kk'}) \quad \dots \quad \dots \quad \dots \quad (1, 6)$$

where the dash over the summation sign denotes that the term $k = k'$ does not occur.

$\bar{\psi}(0)$ and $\psi(\vec{r}_{kk'})$ are given by

$$\psi(\vec{r}_{k'}) = \frac{4\pi}{\Delta} \sum_l' \frac{e^{i(\vec{q}^l \cdot \vec{r}_{kk'})}}{|\vec{q}^l|^2} \quad \dots \quad \dots \quad \dots \quad \dots \quad (1, 7)$$

⁴ M. Born, "Ency. der Math. Wissen.," *Physik*, 3, 727.

and $\bar{\psi}(0) = \bar{\psi}_1(0) + \bar{\psi}_2(0) \dots \dots \dots (1, 8)$

where $\left\{ \begin{aligned} \bar{\psi}_1(0) &= \frac{4\pi}{\Delta} \sum_l' e^{-\frac{1}{4\Sigma^2} |q^l|^2} - \frac{2\Sigma}{\sqrt{\pi}} \dots \dots (1, 9) \end{aligned} \right.$

and $\left\{ \begin{aligned} \bar{\psi}_2(0) &= \sum_l' \frac{1 - \frac{2}{\sqrt{\pi}} \int_0^{\Sigma r^l} e^{-\alpha^2} d\alpha}{r^l} - \frac{\pi}{\Delta \Sigma^2} \dots \dots (1, 10) \end{aligned} \right.$

The introduction of this "Partition-factor" (Σ) is the chief advantage of Ewald's method. The final result is independent of the choice of Σ ; which may, therefore, be chosen in any suitable manner.

Substituting from (1, 6) in (1, 2)
 $\phi_0 = \bar{\psi}(0) \sum_{k'} e_{k'}^2 + \sum_{kk'} e_{ke} e_{k'} \psi(r_{kk'}) \dots \dots (1, 11)$

The electro-static energy density U_0 is given by $U_0 = \frac{1}{2\Delta} \phi_0 \dots (1, 12)$

§2. *Electro-Static Energy Density of Aragonite and Similar Crystals.*

The crystals of calcium carbonate in the Aragonite form, as well as the crystals of Strontium and Barium-Carbonates, are ortho-rhombic. The "Grund-vectors" have the components

$a_x = a, \quad b_y = b \quad c_z = c \quad \dots \dots (2, 1)$

all other components being zero.

The values⁵ of a, b, c , as found by X-ray analysis, are tabulated below in Ångström units.

TABLE I.

Substance	a	b	c
CaCO ₃	4.94	7.94	5.72
SrCO ₃	5.13	8.42	6.10
BaCO ₃	5.29	8.38	6.41

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

$a'_x = \frac{1}{a}; \quad b'_y = \frac{1}{b}; \quad c'_z = \frac{1}{c} \quad \dots \dots (2, 2)$

⁵ Wyckoff, *The Structure of Crystals*, 2nd edition, p. 273.

The vector \vec{q}^i will have the components

$$\vec{q}^0 = 2\pi \left(\frac{l_1}{a}, \frac{l_2}{b}, \frac{l_3}{c} \right) \quad \dots \quad \dots \quad \dots \quad \dots$$

(i) "Evaluation of $\bar{\psi}_i(0)$ " —

Substituting the values of the components of \vec{q}^i from (2, 3) in (1), get

$$\bar{\psi}_1(0) = \frac{4\pi}{\Delta} \sum_l e^{-\frac{\pi^2}{\Sigma^2} \left(\frac{l_1^2}{a^2} + \frac{l_2^2}{b^2} + \frac{l_3^2}{c^2} \right)} \quad \dots \quad \dots$$

$$\text{Taking } \Sigma = \frac{\pi}{b} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots$$

$$\bar{\psi}_1(0) = \frac{b^2}{\pi \Delta} \sum_l' e^{-\left(l_1^2 \frac{b^2}{a^2} + l_2^2 + l_3^2 \frac{b^2}{c^2} \right)} \frac{2\sqrt{\pi}}{b} \quad \dots$$

The expression under the sign of summation is rapidly converging we need consider the first few terms only.

We tabulate below the results in detail for the case of Aragonite this we have $\left(\frac{b}{a}\right)^2 = 2.58$ and $\left(\frac{b}{c}\right)^2 = 1.926$. We write $2.58 l_1^2 + 1.926 l_3^2 = \lambda_{l_1, l_2, l_3}$.

TABLE II.

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	2.582	.0757	.0293	2	.0586
0	1	0	1	.3678	.3678	2	.7356
0	0	1	1.926	.1468	.0706	2	.1412
2	0	0	10.328	2
0	2	0	4	.0183	.0046	2	.0092
0	0	2	7.704	2
1	1	0	3.58	.0278	.0078	4	.0312
0	1	1	2.926	.0533	.0182	4	.0728
1	0	1	4.508	.0111	.0024	4	.0096
Sum							1.0582

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:

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

Hence

$$\bar{\psi}_1(0) = \frac{b^2}{\pi abc} 1.0582 - \frac{2\pi}{\sqrt{\pi} b} \quad \dots \quad \dots \quad (2, 7)$$

$$= \frac{.71 \times 1.0582 - 3.544}{b} \quad \dots \quad \dots \quad (2, 8)$$

Now

$$\bar{\psi}_2(0) = S'_l \frac{1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{\pi}{b} r^l} e^{-\alpha^2} d\alpha}{r^l} - \frac{b^2}{\pi abc} \quad \dots \quad \dots \quad (2, 9)$$

The contribution of the first term containing the integral is negligible.

$$\therefore \bar{\psi}_2(0) = - \frac{b|a \times b|c}{\pi b} \quad \dots \quad \dots \quad \dots \quad (2, 10)$$

$$= - \frac{.71}{b}$$

From (2, 8) and (2, 10)

$$\bar{\psi}(0) = \frac{.71 \times .0582 - 3.544}{b} \quad \dots \quad \dots \quad \dots \quad (2, 11)$$

$$= - \frac{3.503}{b} \quad \dots \quad \dots \quad \dots \quad (2, 12)$$

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

A unit cell of the crystal consists of 4 molecules of the carbonate. The calcium atoms are situated at

$$(0, 0, 2); \quad \left(\frac{a}{2}, \frac{b}{2}, 0\right); \quad \left(0, \frac{b}{3}, \frac{c}{2}\right); \quad \left(\frac{a}{2}, \frac{5b}{6}, \frac{c}{2}\right) \quad \dots \quad \dots \quad (2, 13)$$

and the CO₃ radicals at

$$\left(0, \frac{2b}{3}, \frac{c}{6}\right); \quad \left(0, \frac{2b}{3}, \frac{2c}{3}\right); \quad \left(\frac{a}{2}, \frac{b}{6}, \frac{c}{3}\right); \quad \left(\frac{a}{2}, \frac{b}{6}, \frac{5c}{6}\right) \quad \dots \quad \dots \quad (2, 14)$$

From (1, 7) and (2, 3)

$$\psi(r_{kk'}) = \frac{4\pi}{\Delta} S'_l e^{\frac{2\pi i}{\Delta} \left(l_1 \frac{x_{kk'}}{a} + l_2 \frac{y_{kk'}}{b} + l_3 \frac{z_{kk'}}{c} \right)} \frac{1}{4\pi^2 \left(l_1^2 \frac{1}{a^2} + l_2^2 \frac{1}{b^2} + l_3^2 \frac{1}{c^2} \right)} \quad \dots \quad \dots \quad (2, 15)$$

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

Hence

$$\sum_{kk'} e_k e_{k'} \psi(r_{kk'}) = \frac{b^2}{\pi abc} \sum_l' \sum_{kk'} e_k e_{k'} e^{2\pi i \left(l_1 \frac{x_{kk'}}{a} + l_2 \frac{y_{kk'}}{b} + l_3 \frac{z_{kk'}}{c} \right)} \frac{1}{\left(l_1^2 \frac{b^2}{a^2} + l_2^2 + l_3^2 \frac{b^2}{c^2} \right)} \quad \dots (2, 16)$$

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

$$\sum_{kk'} e_k e_{k'} \psi(r_{kk'}) = \frac{b^2}{\pi abc} \sum_l' \sum_{kk'} \frac{2 \cos \left(l_1' \frac{x_{kk'}}{a} + l_2' \frac{y_{kk'}}{b} + l_3' \frac{z_{kk'}}{c} \right)}{\left(l_1'^2 \frac{b^2}{a^2} + l_2'^2 + l_3'^2 \frac{b^2}{c^2} \right)} \quad \dots (2, 17)$$

The dash over the l 's denotes 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 8 points in the cell are given in (2, 11) and (2, 12); from which the values of $x_{kk'}$, etc., are obtained. Substituting these and associating a charge $2e$ with each calcium atom and a charge $-2e$ with each CO_3 group, we obtain

$$\sum_{kk'} e_k e_{k'} \psi(r_{kk'}) = \frac{b/a \ b/c}{\pi \ b} 4e^2 \times 4 \sum_l' \frac{F \{ \cos(l_1', l_2', l_3') \pi \}}{l_1'^2 \frac{b^2}{a^2} + l_2'^2 + l_3'^2 \frac{b^2}{c^2}} \quad \dots (2, 18)$$

where the function F is given by

$$\begin{aligned} F = & 2 \cos(l_1 + l_2) \pi + 2 \cos l_3 \pi + 2 \cos \left(\frac{2}{3} l_2 + l_3 \right) \pi + 2 \cos \left(l_1 - l_2 + \frac{l_3}{3} \right) \pi \\ & + \cos \left(l_1 + \frac{5l_2}{3} + l_3 \right) \pi + \cos \left(l_1 + \frac{l_2}{3} - l_3 \right) \pi + \cos \left(l_1 - l_2 + \frac{4l_3}{3} \right) \pi + \cos \left(l_1 - l_2 - \frac{2}{3} l_3 \right) \pi \\ & - \left\{ 2 \cos \left(\frac{4}{3} l_2 + \frac{l_3}{3} \right) \pi + 2 \cos \left(\frac{2}{3} l_2 - \frac{2}{3} l_3 \right) \pi + \cos \left(\frac{4}{3} l_2 + \frac{4}{3} l_3 \right) \pi + \cos \left(\frac{2}{3} l_2 + \frac{5}{3} l_3 \right) \pi \right. \\ & + 2 \cos \left(l_1 + \frac{l_2}{3} + \frac{2l_3}{3} \right) \pi + 2 \cos \left(l_1 - \frac{l_2}{3} - \frac{l_3}{3} \right) \pi + \cos \left(\frac{2}{3} l_2 + \frac{l_3}{3} \right) \pi + \cos \left(\frac{4}{3} l_2 + \frac{2}{3} l_3 \right) \pi \\ & + \cos \left(l_1 + \frac{l_2}{3} + \frac{5l_3}{2} \right) \pi + \cos \left(l_1 - \frac{l_2}{3} - \frac{4l_3}{3} \right) \pi + \cos \left(l_1 - \frac{l_2}{3} + \frac{2l_3}{3} \right) \pi \\ & \left. + \cos \left(l_1 + \frac{l_2}{3} - \frac{l_3}{3} \right) \pi \right\} \quad \dots (2, 19) \end{aligned}$$

As before we need consider only the first few terms of the series. Carrying out the summation we obtain

$$\sum_{kk'} e_k e_{k'} \psi(r_{kk'}) = - \frac{.71 \times 16e^2}{b} \times 5.598 \quad \dots \quad \dots (2, 20)$$

Substituting the values from (2, 12) and (2, 20) in (1, 11) we get

$$\phi_0 = - \frac{e^2}{b} 173 \cdot 608 \quad \dots \quad \dots \quad \dots \quad \dots \quad (2, 21)$$

From (1, 4) and (2, 1) we get

$$\delta^3 = abc \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (2, 22)$$

Substituting the values for Aragonite from Table (I)

$$\delta = \cdot 765 b \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (2, 23)$$

whence

$$\phi_0 = - \frac{e^2}{\delta} 132 \cdot 8 \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (2, 24)$$

which may be written as

$$\phi_0 = - 2 \frac{e^2}{\delta} a \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (2, 25)$$

where $a = 66 \cdot 4 \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (2, 26)$

The values of a for SrCO_3 and BaCO_3 , by identical calculations, are found to be $66 \cdot 58$ and $66 \cdot 87$ respectively.

§3. The Lattice-Energy.

It has been already remarked that for the stability of the ionic crystals it is necessary to assume other forces besides the electro-static forces. With these forces, of the type $\frac{b}{r^n}$, the function ϕ_0 given in (2, 25) will be of the form

$$\phi_0 = - 2 \left(a \frac{e^2}{\delta} - \frac{\beta}{\delta^n} \right) \quad \dots \quad \dots \quad \dots \quad \dots \quad (3, 1)$$

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

$$\begin{aligned} U &= - \frac{1}{2z} N \phi_0 \\ &= \frac{1}{z} N \left(\frac{a e^2}{\delta} - \frac{\beta}{\delta^n} \right) \end{aligned} \quad \dots \quad \dots \quad (3, 2)$$

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

β and n can be determined from the equation⁶

$$\frac{\partial \phi_0}{\partial \delta} = 0 \quad \text{and} \quad \frac{1}{18\delta} \frac{d^2 \phi}{d\delta^2} = \frac{1}{\chi} \quad \dots \quad \dots \quad \dots \quad \dots \quad (3, 3)$$

where χ is the compressibility.

These equations give

$$\beta = \frac{a e^2}{n} \delta^{n-1} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (3, 4)$$

⁶ M. Born, "Ency der Math. Wissen.," *Physik*, 3, 569, eqn. (90'').

$$\text{and } n = 1 + \frac{9}{ae^2} \frac{\delta^4}{\chi} \quad \dots \quad \dots \quad \dots \quad \dots \quad (3, 5)$$

whence equation (3, 2) can be written as

$$U = \left(1 - \frac{1}{n}\right) N \frac{\alpha}{z} \frac{e^2}{\delta} \quad \dots \quad \dots \quad \dots \quad \dots \quad (3, 6)$$

If ρ is the density and M the molecular weight of the substance

$$\delta^3 N \rho = M_z \quad \dots \quad \dots \quad \dots \quad \dots \quad (3, 7)$$

so that equations (3, 5) and (3, 6) can be written in the more suitable form

$$n = 1 + \frac{9}{ae^2\chi} \left(\frac{M_z}{N\rho}\right)^{\frac{4}{3}} \quad \dots \quad \dots \quad \dots \quad \dots \quad (3, 8)$$

$$\text{and } U = \left(1 - \frac{1}{n}\right) a e^2 \left(\frac{N}{z}\right)^{\frac{4}{3}} \left(\frac{\rho}{M}\right)^{\frac{1}{3}} \quad \dots \quad \dots \quad \dots \quad \dots \quad (3, 9)$$

We tabulate below the results obtained.

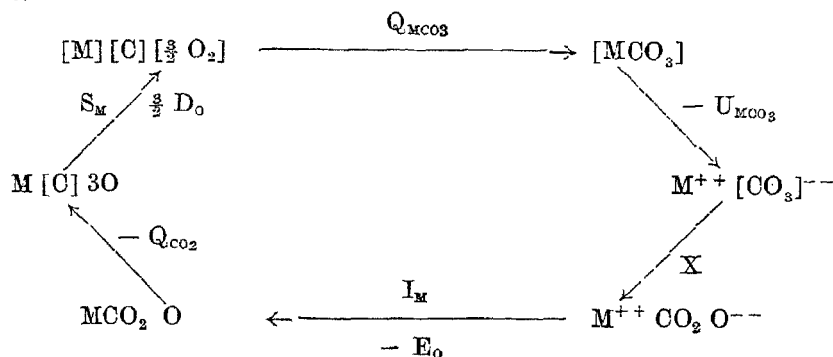
TABLE III.

Substance	α calculated	$\frac{1}{\chi \times 10^{12}}$ dynes/cm. ² experimental	M	ρ	n calculated	U in K.-cal. calculated
CaCO ₃	66.40	.653	100.07	2.93	6.32	755.6
SrCO ₃	66.58	.574	147.62	3.7	6.79	725.6
BaCO ₃	66.87	.495	197.37	4.43	6.64	700.4

The values of χ are taken from Mellor's *Inorganic and Physical Chemistry*.

§4. Thermo-Chemical Cycle.

The "lattice-energy" is not a directly measurable quantity. We shall construct a thermo-chemical cycle, after the manner of Born and Haber so that the lattice-energy can be related to other measurable thermal data. The brackets denote the steady states. M stands for the alkaline earth metal.



where X is the heat of the chemical process



and

Q_{MCO_3} = Heat of formation of the carbonate.

U_{MCO_3} = Lattice-energy of the crystal.

I_{M} = Ionization energy of the metal.

E_{O} = Electronic affinity of oxygen.

Q_{CO_2} = Heat of formation of carbon dioxide.

S_{M} = Heat of sublimation of the metal.

D_{O} = Heat of dissociation of oxygen.

We have

$$Q_{\text{MCO}_3} - U_{\text{MCO}_3} + X + I_{\text{M}} - E_{\text{O}} - Q_{\text{CO}_2} + S_{\text{M}} + \frac{3}{2} D_{\text{O}} = 0 \quad \dots \quad (4, 2)$$

Herein all the quantities except X and U are known. U is calculated in the last article. Hence we can use this equation to determine the value X. The agreement of the values of X from the cases of the 3 carbonates will verify the calculations of the "Lattice-Energy". From (4, 2) we get

$$X = B - A \quad \dots \quad \dots \quad \dots \quad \dots \quad (4, 3)$$

where

$$\begin{cases} B = U_{\text{MCO}_3} + Q_{\text{CO}_2} \\ A = Q_{\text{MCO}} + I_{\text{M}} - E_{\text{O}} + S_{\text{M}} + \frac{3}{2} D_{\text{O}} \end{cases}$$

and

$$\dots \quad \dots \quad (4, 4)$$

TABLE IV.

	CaCO ₃	SrCO ₂	BaCO ₃	Source ⁷
Q_{MCO_3}	270.8	279.2	283.0	1
I_{M}	413.0	383.9	349.1	3
$- E_{\text{O}}$	168.0	168.0	168.0	2
S_{M}	47.5	39.7	49.1	2
$\frac{3}{2} D_{\text{O}}$	88.8	88.8	88.8	1
A	988.1	959.6	938.0	..
U_{MCO_3}	755.6	725.6	700.4	Calculated
Q_{CO_2}	97.0	97.0	97.0	1
B	852.6	822.6	797.4	..
X	135.5	137.0	140.6	..

⁷ ¹ Handbook of Chemistry and Physics, Hodgman-Lange, 5th edition.

² G. Sherman, *Chemical Reviews*, 1932, 9, 136 and 145.

³ G. H. de Boer, *Electron Emission and Adsorption Phenomena*, 30.

The values are expressed in K. calories.

The agreement in the values of X is quite satisfactory. It is intended in the following paper to calculate the values of the elasticity coefficients in perpendicular directions. The knowledge of the value of ' n ' will be found necessary in these calculations.

I wish to thank Prof. M. Born for his guidance in this work.

Summary.

The lattice-energies of crystals of Aragonite, of Strontium carbonate, and of Barium carbonate, which are all of the ortho-rhombic type, are calculated. Further the value of n is calculated with the help of the compressibility measurements. The lattice-energy values are verified by a thermo-chemical cyclic process.