LATTICE-THEORY OF ALKALINE EARTH CARBONATES.

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In four recent papers[1] referred to hereafter as I, II, III and IV the lattice-energies and the elasticity constants of the crystals of Calcite and Aragonite were calculated. This note is intended for the correction and modification of some of the results obtained in these papers.

The summations involved in I (2, 18) and III (1, 20) have been revised and extended till the denominators are equal to 200. With the revised values we obtain instead of I (2, 21) and III (1, 23)

$$\phi_0 = -e^2/b\ 149{\cdot}94, \quad \text{for Aragonite,} \quad (1)$$

$$\phi_0 = -e^2/b\ 217{\cdot}52, \quad \text{for Calcite,} \quad (2)$$

respectively.

Further results obtained from these values are given in Table I.

Table I.

Substance	M	ρ	a	$\frac{10^{-12}}{\chi}$	n	U
Calcite	100·07	2·71	90·26	0·658	8·59	610·7
				·719	9·30	616·9
				·746	9·61	619·1
Aragonite	100·07	2·93	56·81	·446	5·24	622·8
				·653	7·21	662·2
Strontianite	146·6	3·7	57·16	·574	7·63	633·5
Witherite	197·3	4·43	58·64	·495	7·50	612·6

The values of U are given in kilo-calories per gram molecule.

1. B. Y. Oke, *Proc. Ind. Acad. Sci.*, 1936, **4**, 1, 514, 525 and 667.

In the thermo-chemical cycle described in I, § 4, since CO_2 decomposes into carbon and molecular oxygen the multiplying factor 3/2 of D_0 is unnecessary ; hence instead of I (4, 2) we have the equation

$$Q_{MCO_3} - U_{MCO_3} + X + I_M - E_0 - Q_{CO_2} + S_M + D_0 = 0 \qquad (3)$$

X is the energy change of the reaction

$$(CO_3)^{--} = CO_2 + O^{--} \qquad (4)$$

Taking the lattice-energy values corresponding to the compressibility measurements of Madelung and Fuchs the values of X are calculated from (3) in Table II.

TABLE II.

	Calcite	Aragonite	Strontianite	Witherite
Q_{MCO_3}	231·8	270·8	279·2	283·0
I_M	413·0	413·0	383·9	349·1
$-E_0$	168·0	168·0	168·0	168·0
S_M	47·5	47·5	39·7	49·1
D_0	59·2	59·2	59·2	59·2
	919·5	958·5	930·6	908·4
U_{MCO_3}	619·7	662·8	634·3	613·4
Q_{CO_2}	97·0	97·0	97·0	97·0
	716·1	759·8	731·3	710·4
$-X$	203·4	198·7	198·7	198·0

All the values are given in kilo-calories.

The agreement between the different values is quite satisfactory ; though, of course, the closeness of the agreement, considering the inaccuracies in the compressibility measurements and the long summations involved is more a matter of chance.

The elasticity constants are determined with the revised values of a and for a series of values of n in the cases both of Calcite and Aragonite. The results obtained are given in Tables III and IV.

TABLE III. *Calcite.*

n	k	c_{33}^{θ}
8·5	0·608	$1·132 \times 10^{12}$
9·0	0·008	$1·156 \times 10^{12}$
9·5	−1·117	$1·179 \times 10^{12}$

These values agree well with the observed values given in IV (4, 10).

TABLE IV. *Aragonite.*

n	k	c_{33}^{θ}
5·0	1·89	$1·007 \times 10^{12}$
6·0	2·29	$1·021 \times 10^{12}$
7·0	2·59	$1·006 \times 10^{12}$

These values agree well with the observed values given in II (5, 2).

k which is defined in II (3, 2) as the the ratio of b_{kk} to $-b_{kk}'$ turns out to be different not only for the crystals of Calcite and Aragonite but in either case it varies with the value of the index of the repulsive potential. This is not surprising in view of the very simplified expression taken for the repulsive potential. In fact, as shown by Wasastjerna,[2] the attracting force between geometrically equivalent ions in the lattice deduced from the crystal properties is merely fictive, appearing in the calculations as a consequence in part of an incorrect assumption regarding the analytic form of the potential of repulsion and in part of the dependence on temperature of the elastic-constants having been disregarded. It cannot be claimed, therefore, that k has any physical bearing. It is of some interest, however, that with such a simple expression for repulsive potential, the calculated values of the elasticity-constants agree well with the observed values.

I wish to record how immensely I have benefited from the guidance and advice of Prof. Max Born during his stay at Bangalore, and I have to express my sincere thanks to the authorities of the Indian Institute of Science for the opportunity afforded me to carry out this work.

2. J. A. Wasastjerna, *Comm. Phy.-Math.*, (*Soc. Sci. Fennica*), **8**, No. 20.